

# **Dried Fruits**

## **Phytochemicals and Health Effects**



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# **Dried Fruits**

## **Phytochemicals and Health Effects**

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# Preface

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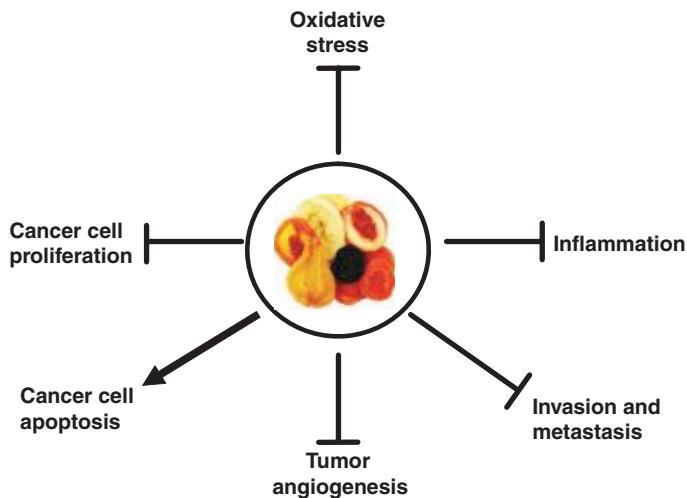
Dried fruits serve as important healthful snacks worldwide. They provide a concentrated form of fresh fruits, prepared by different drying techniques. Dried fruits, with their unique combination of taste/aroma, essential nutrients, fiber, and phytochemicals or bioactive compounds, are convenient for healthy eating and bridge the gap between recommended intake of fruits and actual consumption. Dried fruits are nutritionally equivalent to fresh fruits in smaller serving sizes, ranging from 30 to 43 g depending on the fruit, in current dietary recommendations in different countries. Numerous scientific evidences suggest that individuals who regularly consume generous amounts of dried fruits have lower rates of cardiovascular diseases, obesity, various types of cancer, type 2 diabetes, and other chronic diseases. Therefore, daily consumption of dried fruits is recommended in order to get full benefit of nutrients, health-promoting phytochemicals, and antioxidants that they contain, together with their desirable taste and aroma. Dried fruits also have the advantage of being easy to store and distribute, available around the year, readily incorporated into other foods and recipes, and present a healthy alternative to salty or sugary snacks.

This book examines most popular dried berries (blackberries, blackcurrants, blueberries, cranberries, goji berries, mulberries, raspberries, and strawberries), nontropical dried fruits (apples, apricots, cherries, citrus fruits, figs, nectarines, peaches, pears, prunes, and raisins), and tropical dried fruits (açaí fruits, bananas, dates, guavas, papayas, mangoes, passion fruits, and pineapples). It is divided into three sections preceded by an introductory chapter (Chapter 1) providing an overview of dried fruits: composition, phytochemicals and health effects as well as cancer chemopreventive effects of selected dried fruits (amla fruits or Indian gooseberries, avocados, berries, mangoes, mangosteens, persimmons, prunes, raisins, kiwi fruits, and other dried fruits) (Chapter 2). The first section (Chapters 3–10) covers dried berries; the second section (Chapters 11–20) discusses nontropical dried fruits; and the final section (Chapters 21–26) includes tropical dried fruits.

Contributors to this volume are internationally renowned researchers who have provided a comprehensive account of the global perspectives of the issues of concern to phytochemicals and health effects of dried fruits. The book will serve as a resource for those interested in the potential application of new developments in dried fruits' nutraceuticals and functional foods. Biochemists, chemists, food scientists/technologists, nutritionists, and health professionals, from academia, government laboratories, and industry will benefit from this publication. Although this book is intended primarily as a reference book, it also summarizes the current state of knowledge in key research areas and contains ideas for future work. In addition, it provides easy-to-read text suitable for teaching senior undergraduate and post-graduate students.

We are indebted to the participating authors for their state-of-the-art contributions and dedication in providing authoritative views resulting from their latest investigations on nutritional significance, phytochemical composition, and potential health benefits of dried fruit consumption.

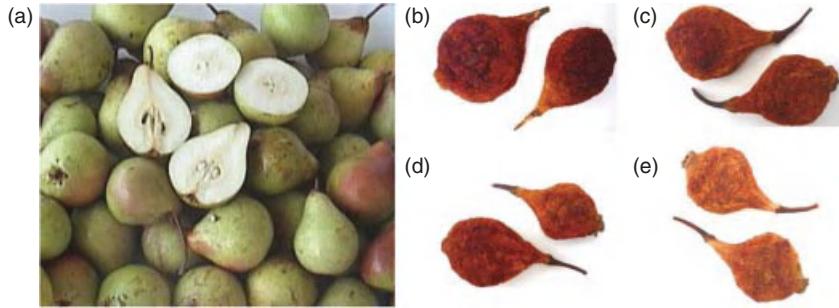
Cesarettin Alasalvar and Fereidoon Shahidi



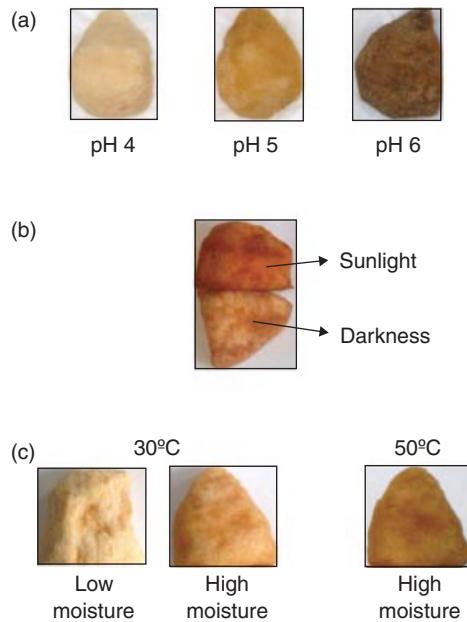
**Figure 2.2** Biochemical mechanisms of chemoprevention with fruit phytochemicals.



**Figure 12.3** Typical images of sun-dried apricots with and without sulfur dioxide treatments.



**Figure 18.1** The S. Bartolomeu pears: (a) fresh pears and pears dried by different technologies, (b) traditional, (c) large glass greenhouse with air convection (GH1), (d) small greenhouse with natural convection (GH2), and (e) hot air tunnel in the absence of light (HAT). (Adapted with permission from Coimbra *et al.* [14]).



**Figure 18.12** Effect of (a) pH variation, (b) sunlight exposure, and (c) moisture and temperature on the development of color of pear tissues. (Adapted from Coimbra *et al.* [14]).

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# **1 Composition, phytochemicals, and beneficial health effects of dried fruits: an overview**

Cesarettin Alasalvar and Fereidoon Shahidi

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## **1.1 Introduction**

Dried fruits serve as a concentrated form of fresh fruits prepared by different drying techniques. In other words, dried fruits possess much lower moisture content as a large proportion of their original water has been removed, either naturally through sun drying or through the use of specialized dryers or dehydrators. Considering the 2011 global production of commercially important dried fruits (Table 1.1), dates rank first on a global basis with a production of 6,598,000 metric tonnes (MT), followed by raisins (1,170,999 MT), prunes (236,500 MT), apricots (198,917 MT), and figs (105,453 MT) [1]. To the best of our knowledge, little information is available about the production of other dried fruits (açai berries, apples, bananas, black currants, blackberries, cherries, citrus fruits, cranberries, gingers, goji berries, guavas, kiwis, mangoes, mulberries, nectarines, papayas, passion fruits, peaches, pears, pineapples, raspberries, star apples, and strawberries, among others).

Dates, figs, prunes, raisins, apricots, peaches, apples, and pears are referred to as “conventional” or “traditional” dried fruits. On the other hand, some fruits such as blueberries, cranberries, cherries, strawberries, and mangoes are infused with sugar solutions (e.g., sucrose syrup) or fruit juice concentrates prior to drying. Some products sold as dried fruit, such as papayas and pineapples, are actually candied fruit [2].

Epidemiologic studies have found an association between dried fruit consumption and diet quality. Raisins may be among the most researched of all dried fruits showing a health benefit [3], followed by dates, prunes, figs, apricots, peaches, apples, pears, and other fruits, which together constitute nearly half of all dried fruits produced in the world each year [2].

This overview chapter summarizes the nutritional significance, phytochemical composition, and potential health benefits of dried fruit consumption and discusses their great potential as medicinal or healthy foods for a number of diseases inflicting human beings.

## **2 Dried Fruits: Phytochemicals and Health Effects**

**Table 1.1** World dried fruits production (metric tonnes)

<b>Production</b>	<b>2007</b>	<b>2008</b>	<b>2009</b>	<b>2010</b>	<b>2011</b>
Apricots	137,100	146,950	164,350	159,100	198,917
Dates	6,400,000	6,323,000	6,599,000	6,708,000	6,598,000
Figs	100,600	92,000	102,000	107,562	105,453
Prunes	199,204	229,942	253,851	245,630	236,500
Raisins	1,053,500	1,042,450	1,061,600	1,083,547	1,170,999

Source: Adapted from INC [1].

## **1.2 Compositional and nutritional characteristics of dried fruits**

Dried fruits come in almost as many varieties as fresh fruits. Although raisins, figs, dates, prunes, and apricots are the most common dried fruits in the marketplace, health food stores and local markets offer many more choices such as dried apples, pineapples, berries, mangoes, papayas, and even the exotic dragon fruit. They are rich sources of essential nutrients and health-promoting bioactive compounds. Table 1.2 summarizes the nutritional composition of some dried fruits (apples, apricots, dates, figs, peaches, pears, prunes, and raisins) [4]. Dried fruits are rich in carbohydrates (61.33–79.18 g/100 g) and devoid of fat (0.32–0.93 g/100 g). The most calorie-rich of these fruits are raisins (299 kcal/100 g), followed by dates (282 kcal/100 g). Dried fruits are excellent sources of sugar ranging from 38.13 g/100 g in prunes to 63.35 g/100 g in dates. Fructose and glucose are the main sugars found in all dried fruits, followed by sucrose. Trace amounts of maltose and galactose are found in some dried fruits. Levels of sugar may differ according to drying methods and regional and varietal factors.

It is important to note that the high content of dietary fiber (3.7–9.8 g/100 g) found in dried fruits is an important source that helps meet our dietary recommendations (14 g of fiber for every 1000 calories of food consumed each day). This becomes 25–38 g of fiber per day depending on age and gender [5]. On a per serving basis (40 g), dried fruits deliver more than 9% of the daily value of fiber, depending on the fruit [4]. It has been reported that dried fruits (40 g/serving) compare favorably in their fiber content with common fresh fruit (one cup or one fruit serving) options [4, 6].

With respect to nutritional aspects, percentage of recommended dietary allowances (RDA) or adequate intake (AI) of minerals for adult males and females (aged 15–50 years) are also given in Table 1.3. Dried fruits, in general, serve as a reasonable source of copper, iron, magnesium, manganese, phosphorus, and potassium. Among the eight dried fruits listed in Table 1.3, peaches possess the highest mineral content, whereas apples contain the lowest. Consuming 40 g (on a per serving basis) of dried fruits (Table 1.3) supplies 0.6–6.5% of calcium, 8.4–16.4% of copper, 2.1–20.3% of iron, 1.6–8.6% of magnesium, 1.6–11.3% of manganese, 2.2–6.8% of phosphorus, and 3.8–9.9% of potassium for RDA or AI for adults [4, 7–9]. Based on RDA and AI values, dried figs are high in calcium, magnesium, and manganese, whereas dried peaches are good sources of iron and phosphorus. Moreover, apricots are an important source of potassium among the eight dried fruits listed in Table 1.3. On a per serving basis (40 g or about one-fourth cup), dried fruits rank among the top potassium sources in diets around the world [6]. Moreover, on a per serving basis, different dried fruits such as apricots, currants, dates, figs, peaches, prunes, and raisins (40 g serving)

**Table 1.2** Compositional and nutritional characteristics of some dried fruits (values in per 100 g edible portion)

Nutrient	Units	Apples	Apricots	Dates <sup>a</sup>	Figs	Peaches	Pears	Prunes	Raisins <sup>b</sup>
<b>Proximate composition</b>									
Water	g	31.76	30.89	20.53	30.05	31.80	26.69	30.92	15.43
Energy	kcal	243	241	282	249	239	262	240	299
Protein	g	0.93	3.39	2.45	3.30	3.61	1.87	2.18	3.07
Lipid	g	0.32	0.51	0.39	0.93	0.76	0.63	0.38	0.46
Ash	g	1.10	2.57	1.60	1.86	2.50	1.11	2.64	1.85
Carbohydrate	g	65.89	62.64	75.03	63.87	61.33	69.70	63.88	79.18
Dietary fiber	g	8.7	7.3	8.0	9.8	8.2	7.5	7.1	3.7
Sugars	g	57.19	53.54	63.35	47.92	41.74	62.20	38.13	59.19
<b>Minerals</b>									
Calcium	mg	14	55	39	162	28	34	43	50
Copper	mg	0.19	0.34	0.21	0.29	0.36	0.37	0.28	0.32
Fluoride	µg	nd	nd	nd	nd	nd	nd	4.0	234
Iron	mg	1.40	2.66	1.02	2.03	4.06	2.10	0.93	1.88
Magnesium	mg	16	32	43	68	42	33	41	32
Manganese	mg	0.09	0.24	0.26	0.51	0.31	0.33	0.30	0.30
Phosphorus	mg	38	71	62	67	119	59	69	101
Potassium	mg	450	1162	656	680	996	533	732	749
Selenium	µg	1.3	2.2	3.0	0.6	0.5	0.2	0.3	0.6
Sodium	mg	87	10	2	10	7	6	2	11
Zinc	mg	0.20	0.39	0.29	0.55	0.57	0.39	0.44	0.22
<b>Vitamins</b>									
Betaine	mg	nd	0.30	0.4	0.7	nd	nd	0.4	0.3
Choline	mg	17.6	13.9	6.3	15.8	12.7	23.0	10.1	11.1
Folate	µg	nd	10.0	19.0	9.0	nd	nd	4.0	5.0
Niacin	mg	0.93	2.59	1.27	0.62	4.38	1.37	1.88	0.77
Pantothenic acid	mg	0.25	0.52	0.59	0.43	0.56	0.15	0.42	0.10
Pyridoxine	mg	0.13	0.14	0.17	0.11	0.07	0.07	0.21	0.17
Riboflavin	mg	0.16	0.07	0.07	0.08	0.15	0.15	0.19	0.13

(continued)

**Table 1.2** (Continued)

Nutrient	Units	Apples	Apricots	Dates <sup>a</sup>	Figs	Peaches	Pears	Prunes	Raisins <sup>b</sup>
<b>Vitamins (cont.)</b>									
Thiamin	mg	nd	0.02	0.05	0.09	tr	0.01	0.05	0.11
Vitamin A (RAE)	µg	nd	180	tr	1.2	4.8	nd	39	nd
Vitamin C	mg	3.9	1.0	0.4	0.19	7.0	0.6	0.6	2.3
Vitamin E (ATE)	mg	0.53	4.33	0.05	0.35	0.06	0.43	0.12	0.12
Vitamin K	µg	3.00	3.10	2.70	15.6	15.7	20.4	59.5	3.5
<b>Amino acids</b>									
Alanine	g	0.033	0.110	0.083	0.134	0.215	0.062	0.066	0.105
Arginine	g	0.029	0.066	0.136	0.077	0.092	0.032	0.037	0.413
Aspartic acid	g	0.162	0.937	0.213	0.645	0.602	0.368	0.801	0.110
Cystine	g	0.012	0.019	0.067	0.036	0.029	0.018	0.011	0.019
Glutamic acid	g	0.097	0.188	0.359	0.295	0.548	0.135	0.114	0.164
Glycine	g	0.037	0.070	0.101	0.108	0.126	0.054	0.047	0.080
Histidine <sup>c</sup>	g	0.015	0.047	0.032	0.037	0.067	0.020	0.027	0.072
Isoleucine <sup>c</sup>	g	0.037	0.063	0.049	0.089	0.104	0.054	0.041	0.057
Leucine <sup>c</sup>	g	0.057	0.105	0.084	0.128	0.204	0.094	0.066	0.096
Lysine <sup>c</sup>	g	0.058	0.083	0.066	0.088	0.116	0.066	0.050	0.084
Methionine <sup>c</sup>	g	0.009	0.015	0.022	0.034	0.087	0.022	0.016	0.021
Phenylalanine <sup>c</sup>	g	0.026	0.062	0.050	0.076	0.114	0.049	0.052	0.065
Proline	g	0.032	0.821	0.130	0.610	0.152	0.051	0.130	0.254
Serine	g	0.038	0.087	0.057	0.128	0.167	0.067	0.059	0.070
Threonine <sup>c</sup>	g	0.033	0.073	0.043	0.085	0.141	0.049	0.049	0.077
Tryptophan <sup>c</sup>	g	0.009	0.016	0.012	0.020	0.010	nd	0.025	0.050
Tyrosine	g	0.017	0.039	0.015	0.041	0.094	0.016	0.021	0.012
Valine <sup>c</sup>	g	0.043	0.078	0.071	0.122	0.197	0.066	0.056	0.083

Source: Adapted from USDA [4].

Note: Some numbers are rounded to the second digit after decimal point.

RAE, retinol activity equivalents; ATE, α-tocopherol equivalents; nd, not detected; tr, trace.

<sup>a</sup>Deglet noor.<sup>b</sup>Seedless.<sup>c</sup>Indispensable amino acids.

**Table 1.3** Percentage of RDA values for adults (aged 19–50) in 40 g of dried fruits (per serving basis)

Mineral	RDA or AI*	Unit	Apples	Apricots	Dates <sup>a</sup>	Figs	Peaches	Pears	Prunes	Raisins <sup>b</sup>	Reference
<b>Males</b>											
Calcium	1000 mg/day*	mg	0.6	2.2	1.6	6.5	1.1	1.4	1.7	2.0	[4, 7]
Copper	0.9 mg/day	mg	8.4	15.1	9.3	12.9	16.0	16.4	12.4	14.2	[4, 8]
Fluoride	4000 µg/day*	µg	nd	nd	nd	nd	nd	nd	tr	2.3	[4, 7]
Iron	8 mg/day	mg	7.0	13.3	5.1	10.2	20.3	10.5	4.7	9.4	[4, 8]
Magnesium	400–420 mg/day	mg	1.6	3.1	4.2	6.6	4.1	3.2	4.0	3.1	[4, 7]
Manganese	2.3 mg/day*	mg	1.6	4.2	4.5	8.9	5.4	5.7	5.2	5.2	[4, 8]
Phosphorus	700 mg/day	mg	2.2	4.1	3.5	3.8	6.8	3.4	3.9	5.8	[4, 7]
Potassium	4700 mg/day	mg	3.8	9.9	5.6	5.8	8.5	4.5	6.2	6.4	[4, 9]
Selenium	55 µg/day	µg	0.9	1.6	2.2	0.4	0.4	0.1	0.2	0.4	[4, 10]
Sodium	1500 mg/day	mg	2.3	0.3	0.1	0.3	0.2	0.2	0.1	0.3	[4, 9]
Zinc	11 mg/day	mg	0.7	1.4	1.1	2.0	2.1	1.4	1.6	0.8	[4, 8]
<b>Females</b>											
Calcium	1000 mg/day*	mg	0.6	2.2	1.6	6.5	1.1	1.4	1.7	2.0	[4, 7]
Copper	0.9 mg/day	mg	8.4	15.1	9.3	12.9	16.0	16.4	12.4	14.2	[4, 8]
Fluoride	3000 µg/day*	µg	nd	nd	nd	nd	nd	nd	tr	3.1	[4, 7]
Iron	18 mg/day	mg	3.1	5.9	2.3	4.5	9.0	4.7	2.1	4.2	[4, 8]
Magnesium	310–320 mg/day	mg	2.0	4.1	5.5	8.6	5.3	4.2	5.2	4.1	[4, 7]
Manganese	1.8 mg/day*	mg	2.0	5.3	5.8	11.3	6.9	7.3	6.7	6.7	[4, 8]
Phosphorus	700 mg/day	mg	2.2	4.1	3.5	3.8	6.8	3.4	3.9	5.8	[4, 7]
Potassium	4700 mg/day	mg	3.8	9.9	5.6	5.8	8.5	4.5	6.2	6.4	[4, 9]
Selenium	55 µg/day	µg	0.9	1.6	2.2	0.4	0.4	0.1	0.2	0.4	[4, 10]
Sodium	1500 mg/day	mg	2.3	0.3	0.1	0.3	0.2	0.2	0.1	0.3	[4, 9]
Zinc	8 mg/day	mg	1.0	2.0	1.5	2.8	2.9	2.0	2.2	1.1	[4, 8]

RDA, recommended dietary allowances; AI\*, adequate intake; nd, not detected; tr, trace.

<sup>a</sup>Deglet noor.  
<sup>b</sup>Seedless.

## **6 Dried Fruits: Phytochemicals and Health Effects**

compare positively in their potassium content with the 10 most common fresh fruit options such as apples, bananas, grapes, mangos, oranges, peaches, pears, pineapples, strawberries, and watermelons (one cup or one fruit serving) [4, 6].

Dried fruits contain both water-soluble (betaine, choline, folate, niacin, pantothenic acid, pyridoxine, riboflavin, thiamine, and vitamin C) and fat-soluble vitamins (A, E, and K) (Table 1.2). Among the eight dried fruits listed, prunes are the richest source of vitamin K (59.5 µg/100 g), whereas apricots are the richest source of vitamin A (180 µg/100 g) and vitamin E (4.33 mg/100 g) [4]. Dried fruits, in general, contain a small amount of vitamin C. With regard to RDA of vitamins, 40 g dried fruits provide up to 1.6–12.5% of niacin, 0.8–4.7% of pantothenic acid, 2.2–6.5% of pyridoxine, 2.2–7.6% of riboflavin, and 0.9–26.4% of vitamin K for RDA or AI for adults [4, 8, 10, 11]. Prunes are particularly high in vitamin K. Among these eight dried fruits, prunes, apricot, and peaches contain higher amounts of vitamins than other dried fruits (Tables 1.2 and 1.4).

Despite the fact that dried fruits contain all indispensable amino acids (except tryptophan in pears), in general, they are not good sources of amino acids due to their low protein content (Table 1.2).

In summary, the following are some nutritional facts about dried fruits [12]:

- Dried fruits are low in their fat and sodium content and, as expected, devoid of trans-fats and cholesterol [4].
- Dried fruits are good sources of dietary fiber and potassium. Among all fruits, they are among the top five contributors of fiber and potassium [5].
- Dried fruits provide essential nutrients that are otherwise low in today's diet, such as vitamin A (apricots and peaches), calcium (figs), vitamin K (prunes), boron (raisins and prunes), iron, and copper [4, 13].
- Traditional dried fruits have no added sugars. Most traditional dried fruits contain low amounts of sucrose; their sugar content is in the form of fructose and glucose [4].

### **1.3 Phytochemicals in dried fruits**

Phytochemicals are defined as nonnutritive, naturally occurring, biologically active, and chemically derived compounds found in the plant kingdom. More than several thousands of individual phytochemicals have been identified in plant-derived foods and their by-products, but a large percentage of phytochemicals still remain unknown and need to be identified before we can fully understand the health benefits of phytochemicals in whole foods. Dried fruits are highly nutritious and provide a range of phytochemicals such as phenolic acids, flavonoids (anthocyanidins, flavan-3-ols, flavones, flavonols, and isoflavones), phytoestrogens, and carotenoids, among others [3, 4, 14–28]. They, in general, contain traces or undetectable amounts of proanthocyanidins [29]. Proanthocyanidins detected in plums and grapes are absent in prunes and raisins, which suggests that these compounds are degraded during the drying process [30].

Dried fruits are excellent sources of phenolic compounds in the diet [31–35]. These make up the largest group of plant phytochemicals in the diet and they appear to be, at least in part, responsible for the health benefits associated with diets abundant in fruits and vegetables. Phenolic compounds contribute most to the antioxidant activity of fruits and vegetables [36] and have a multitude of functional capacities, which may have a beneficial effect on health [6].

**Table 1.4** Percentage of RDA values for adults (aged 19–50 years) in 40 g of dried fruits (per serving basis)

Vitamin	RDA or AI*	Unit	Apples	Apricots	Dates*	Figs	Peaches	Pears	Prunes	Raisins <sup>b</sup>	Reference
<b>Males</b>											
Choline	550 mg/day*	mg	1.3	1.0	0.5	1.1	0.9	1.7	0.7	0.8	[4, 1]
Folate	400 µg/day	µg	nd	1.0	1.9	0.9	nd	0.4	0.5	[4, 1]	
Niacin	16 mg/day	mg	2.3	6.5	3.2	1.6	11.0	3.4	4.7	1.9	[4, 1]
Pantothenic acid	5 mg/day*	mg	2.0	4.2	4.7	3.4	4.5	1.2	3.4	0.8	[4, 1]
Pyridoxine	1.3 mg/day	mg	4.0	4.3	5.2	3.4	2.2	2.2	6.5	5.2	[4, 1]
Riboflavin	1.3 mg/day	mg	4.9	2.2	2.2	2.5	6.5	4.6	5.8	4.0	[4, 1]
Thiamin	1.2 mg/day	mg	nd	0.7	1.7	3.0	tr	0.3	1.7	3.7	[4, 1]
Vitamin A (RAE)	900 µg/day	µg	nd	8.0	tr	4.8	nd	1.7	nd	[4, 8]	
Vitamin C	90 mg/day	mg	1.7	0.4	0.2	0.5	2.1	3.1	0.3	1.0	[4, 10]
Vitamin E (ATE)	15 mg/day	mg	1.4	11.5	0.1	0.9	0.5	0.2	1.1	0.3	[4, 10]
Vitamin K	120 µg/day*	µg	1.0	0.9	5.2	5.2	6.8	19.8	1.2	[4, 8]	
<b>Females</b>											
Choline	425 mg/day*	mg	1.7	1.3	0.6	1.5	1.2	2.2	1.0	1.0	[4, 1]
Folate	400 µg/day	µg	nd	1.0	1.9	0.9	nd	0.4	0.5	[4, 1]	
Niacin	14 mg/day	mg	2.7	7.4	3.6	1.8	12.5	3.9	5.4	2.2	[4, 1]
Pantothenic acid	5 mg/day*	mg	2.0	4.2	4.7	3.4	4.5	1.2	3.4	0.8	[4, 1]
Pyridoxine	1.3 mg/day	mg	4.0	4.3	5.2	3.4	2.2	2.2	6.5	5.2	[4, 1]
Riboflavin	1.1 mg/day	mg	5.8	2.5	2.5	2.9	7.6	5.5	6.9	4.7	[4, 1]
Thiamin	1.1 mg/day	mg	nd	0.7	1.8	3.3	tr	0.4	1.8	4.0	[4, 1]
Vitamin A (RAE)	700 µg/day	µg	nd	10.3	tr	6.2	nd	2.2	nd	[4, 8]	
Vitamin C	75 mg/day	mg	2.1	0.5	0.2	0.6	2.6	3.7	0.3	1.2	[4, 10]
Vitamin E (ATE)	15 mg/day	mg	1.4	11.5	0.1	0.9	0.5	0.2	1.1	0.3	[4, 10]
Vitamin K	90 µg/day*	µg	1.3	1.4	1.2	6.9	7.0	9.1	26.4	1.6	[4, 8]

RDA, recommended dietary allowances; AI\*, adequate intake; RAE, retinol activity equivalents; ATE, α-tocopherol equivalents; nd, not detected; tr, trace.

<sup>a</sup>Deglet noor.  
<sup>b</sup>Seedless.

**Table 1.5** Comparison of total phenolics and ORAC values of some dried fruits (values in per 100 g edible portion)

Dried fruits	Total phenolics (mg of GAE/100 g)	Total ORAC (μmol of TE/100 g)	Reference
Apples <sup>a</sup>	324	6,681	[14, 17]
Apricots <sup>a</sup>	248	3,234	[14, 17]
Dates (Deglet noor)	661	3,895	[14, 21]
Dates (Medjool)	572	2,387	[14, 21]
Figs	960	3,383	[14, 21]
Peaches <sup>a</sup>	283	4,222	[14, 17]
Pears <sup>a</sup>	679	9,496	[14, 17]
Prunes	1195	8,578	[14, 21]
Raisins (golden seedless)	—	10,450	[14, 19]
Raisin (seedless)	1065	3,037	[14, 21]
Raisins (white) <sup>a</sup>	372	4,188	[14, 17]

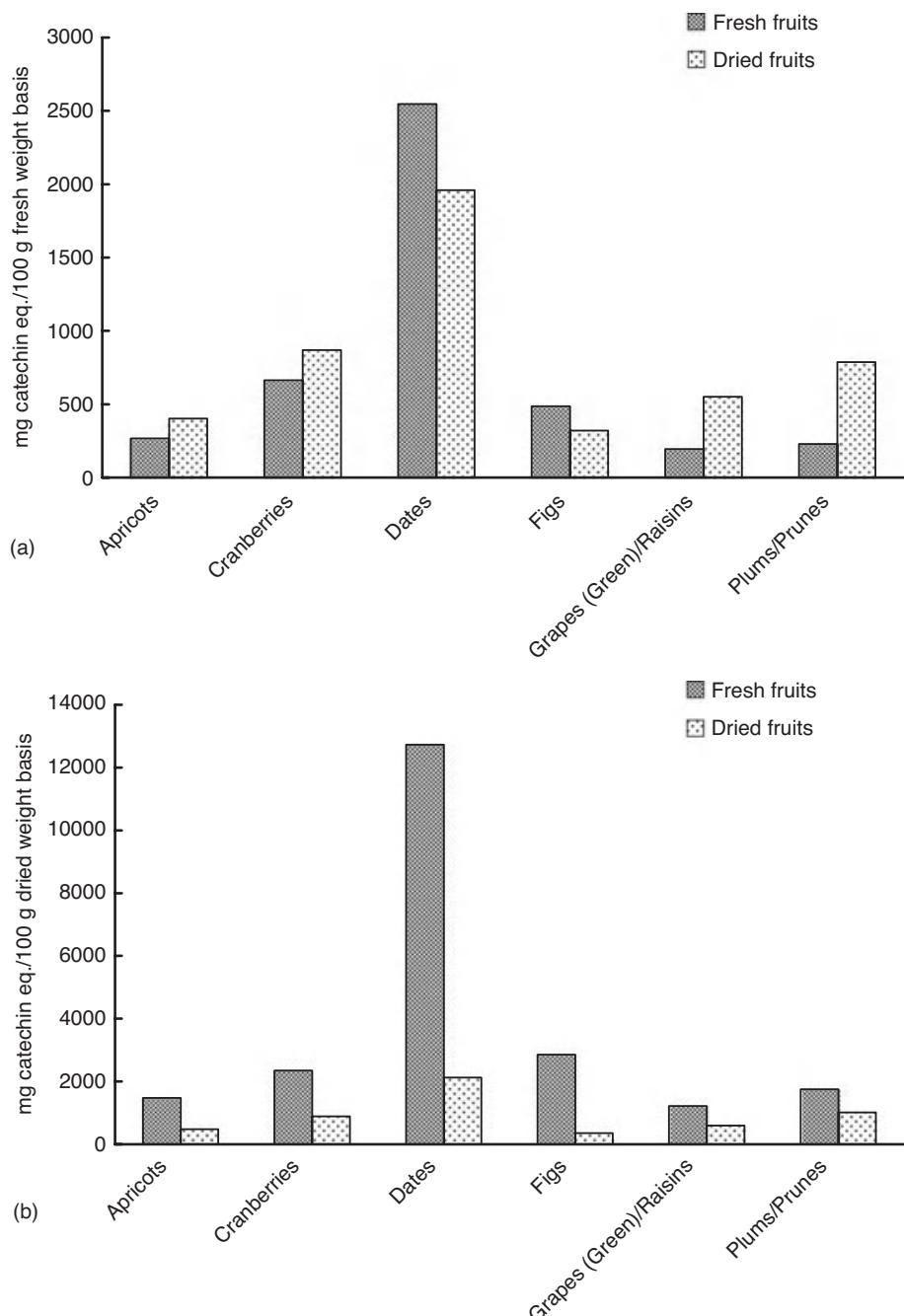
GAE, gallic acid equivalents; TE, trolox equivalents.

<sup>a</sup>Dried to 40% moisture (purchased in Italy).

Values of the total phenolic content and oxygen radical absorbance capacity (ORAC) for a selection of dried fruit are given in Table 1.5. Prunes have the highest total phenolic content (1195 mg of gallic acid equivalents (GAE)/100 g), whereas raisins (golden seedless) have the highest ORAC value (10,450 μmol trolox equivalents (TE)/100 g). Significant differences in the total phenolic content and the ORAC value exist among raisin varieties, being lowest in white raisins and highest in golden seedless raisins [14, 17, 19, 21]. Values are much higher for dried fruits than the corresponding values for their fresh counterparts because antioxidants become concentrated after the drying or dehydration process. While there is a loss or modification of some specific phytochemicals during drying, antioxidant activity and the total phenolic content remain relatively unchanged during the process, implying that many of the phenolic compounds are yet unidentified [37]. This could include oligomeric or polymeric products that are difficult to characterize. Pellergrini *et al.* [38] measured the total antioxidant capacity (using three different *in vitro* assays) of food including four dried fruits (apricots, figs, prunes, and raisins). Among these fruits, prunes exhibited the highest value followed by apricots. Little information is available on the phenolic profiles and antioxidant components of the other dried fruits.

The 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical-scavenging activity and polyphenol content of 22 dried fruits (apples, apricots, bananas, blueberries, cherries, cranberries, figs, raisins, hawthorns, jujube, kiwis, kumquats, mangoes, melons, muscats, papayas, peaches, pears, pineapples, prunes, rakankas, and strawberries) have been evaluated and compared with fresh fruits by Ishiwata *et al.* [39]. Among the dried fruits examined, hawthorns, apricots, and blueberries exhibited the highest DPPH radical-scavenging activity. The polyphenol content of dried fruits and DPPH radical-scavenging activity were highly correlated. On a fresh weight basis, dried fruits, in general, contain higher radical-scavenging activity than fresh fruits. In contrast, the radical-scavenging activity of dried fruits is lower than that of the corresponding fresh fruits on a fresh weight basis [39]. A similar pattern was also reported by Vinson *et al.* [40].

Vinson *et al.* [40] reported the total phenolic content of fresh and dried fruits (apricots, cranberries, dates, figs, grapes/raisins, and plums/prunes) (Figure 1.1a). Dates had the highest



**Figure 1.1** Comparison of quantity of total phenol in fresh and the corresponding dried fruit on a fresh weight basis (a) and dry weight basis (b). (Adapted with permission from Vinson *et al.* [40]).

concentration of total phenolics in both fresh and dried versions (2546 and 1959 mg catechin equivalents (CE)/100 g on a fresh weight basis, respectively). The total phenolic content averaged 731 mg of CE/100 g for fresh fruits and 815 mg of CE/100 g for dried fruits [40]. A comparison of the quantity of total phenolics in fresh and dried fruit pairs on a dry weight basis is illustrated in Figure 1.1b. The average is 3730 mg of CE/100 g for fresh fruits and only 910 mg of CE/100 g for dried varieties [40]. The process of producing dried fruit significantly decreases the total phenol content of the fruits on a dry weight basis. Dried fruits are significantly higher ( $P < 0.005$ ) in total phenols than 20 fresh fruits, 815 versus 173 mg/100 g, respectively [41].

Flavonoids are another group of phenolic compounds that can be classified into seven groups: flavanones, flavones, isoflavones, anthocyanidins, flavonols, flavononols, and flavanols or flavan-3-ols [42]. Flavonoids, which are the most common and widely distributed group of plant phenolics, are increasingly appreciated as an important component of the human diet. Humans consume approximately 1 g of flavonoids per day [43]. Different classes (anthocyanidins, flavan-3-ols, flavones, and flavonols) and amounts of flavonoids have been reported for different dried fruits [15, 18, 23, 24]. Despite the fact that raisins contain the above-mentioned classes of flavonoids, the total content of flavonoids among the four dried fruits listed in Table 1.6 varies between 0.85 mg/100 g in raisins and 7.66 mg/100 g in cranberries. Dried fruits contain traces or undetectable amounts of anthocyanins, which are likely degraded to phenolic acids. Dates contain one anthocyanidin (such as cyanidin) and one flavonol (such as quercetin). Flavan-3-ols are only present in raisins.

The available data show that dried fruits have a unique spectrum of phenols, polyphenols, and tannins. For example, in raisins, the most abundant phenolic compounds are the

**Table 1.6** Comparison of flavonoids (mg/100 g edible portion) of some dried fruits

<b>Flavonoid</b>	<b>Cranberries [15, 23]</b>	<b>Dates<sup>a</sup> [15, 24]</b>	<b>Prunes [15, 23, 24]</b>	<b>Raisins<sup>b</sup> [15, 18, 23, 24]</b>
<b>Anthocyanidins</b>				
Cyanidin	0.60	1.70	0.71	0.03
Delphinidin	0.10	–	0.04	0.01
Pelargonidin	0.02	–	–	0.01
<b>Flavan-3-ols</b>				
(–)-Epicatechin	–	–	–	0.10
(+)-Catechin	–	–	–	0.42
<b>Flavones</b>				
Apigenin	0.01	–	–	–
Luteolin	0.02	–	0.01	0.01
<b>Flavonols</b>				
Kaempferol	0.01	–	0.01	0.01
Myricetin	2.40	–	0.01	0.01
Quercetin	4.50	0.93	1.80	0.25
<b>Total</b>	7.66	2.63	2.58	0.85

<sup>a</sup>Deglet noor.

<sup>b</sup>Seedless.

flavonoids quercetin (Table 1.6) and phenolic acids caftaric and coutaric acids [3]. The predominant phenolic compounds in Greek currants (raisins) are vanillic, caffeic, gallic, syringic, *p*-coumaric, and protocatechuic acids and the flavonoid quercetin [44]. Hydroxycinnamic acids, especially chlorogenic acid isomers, are the major phenolics in prunes, representing more than 94% of the total [45]. Rutin is the predominant flavonol in prunes and prune juice [26]. Prunes also contain quinic acid that is metabolized to hippuric acid, which, as some research suggests, helps prevent urinary tract infections [35, 46]. Four free phenolic acids (protocatechuic, vanillic, syringic, and ferulic) and nine bound phenolic acids (gallic, protocatechuic, *p*-hydroxybenzoic, vanillic, caffeic, syringic, *p*-coumaric, ferulic, and *o*-coumaric) have been reported in fresh and sun-dried Omani dates of three native varieties [47]. Nutritional and functional properties as well as phytochemical characteristics (carotenoids, phytosterols, polyphenols, phenolic acids, flavonoids, anthocyanins, and phytoestrogens) of dates have been extensively reviewed [28, 48].

Phytoestrogens comprise three major classes: isoflavones, lignans, and coumestan. Some dried fruits (such as apricots, currants, dates, prunes, and raisins) have been reported to contain phytoestrogens [such as isoflavones (formononetin, daidzein, genistein, and glycine), lignans (matairesinol, lariciresinol, pinoresinol, and secoisolariciresinol), and coumestan (coumestrol)]. Apricots contain the highest concentration of total phytoestrogens (444.5 µg/100 g) among the five dried fruits listed in Table 1.7, followed by dates (329.5 µg/100 g), prunes (183.5 µg/100 g), currants (34.1 µg/100 g), and raisins (30.2 µg/100 g) [25]. Coumestan, measured as coumestrol, is generally present in low concentrations within dried fruit groups. Dried fruits have higher concentration of lignans (ranging from 20.9 to 400.5 µg/100 g) than isoflavones (ranging from 4.2 to 39.8 µg/100 g) [25].

Five carotenoids (namely, α-carotene, β-carotene, β-cryptoxanthin, lutein, and zeaxanthin) are present in some dried fruits. Of these, β-carotene, which acts as provitamin A, is the

**Table 1.7** Comparison of phytoestrogen content of some dried fruits (µg/100 g edible portion)

Phytoestrogen	Apricots <sup>a</sup>	Currants	Dates <sup>b</sup>	Prunes <sup>c</sup>	Raisins <sup>d</sup>
Formononetin	12.5	0.6	0.4	0.5	0.4
Daidzein	6.4	2.2	1.2	2.6	1.5
Genistein	19.8	10.0	3.4	0.2	5.2
Glycitein	1.1	0.2	0.2	0.9	1.0
<b>Total isoflavones</b>	<b>39.8</b>	<b>13.1</b>	<b>5.1</b>	<b>4.2</b>	<b>8.1</b>
Matairesinol	0.6	1.1	0.3	0.2	0.4
Lariciresinol	62.1	5.8	116.9	2.1	9.2
Pinoresinol	190.1	3.0	100.2	71.5	0.8
Secoisolariciresinol	147.6	10.9	106.2	103.8	11.5
<b>Total lignans</b>	<b>400.5</b>	<b>20.9</b>	<b>323.6</b>	<b>177.5</b>	<b>22.0</b>
Coumestrol	4.2	0.1	0.8	1.8	0.2
<b>Total coumestan</b>	<b>4.2</b>	<b>0.1</b>	<b>0.8</b>	<b>1.8</b>	<b>0.2</b>
<b>Total phytoestrogens</b>	<b>444.5</b>	<b>34.1</b>	<b>329.5</b>	<b>183.5</b>	<b>30.2</b>

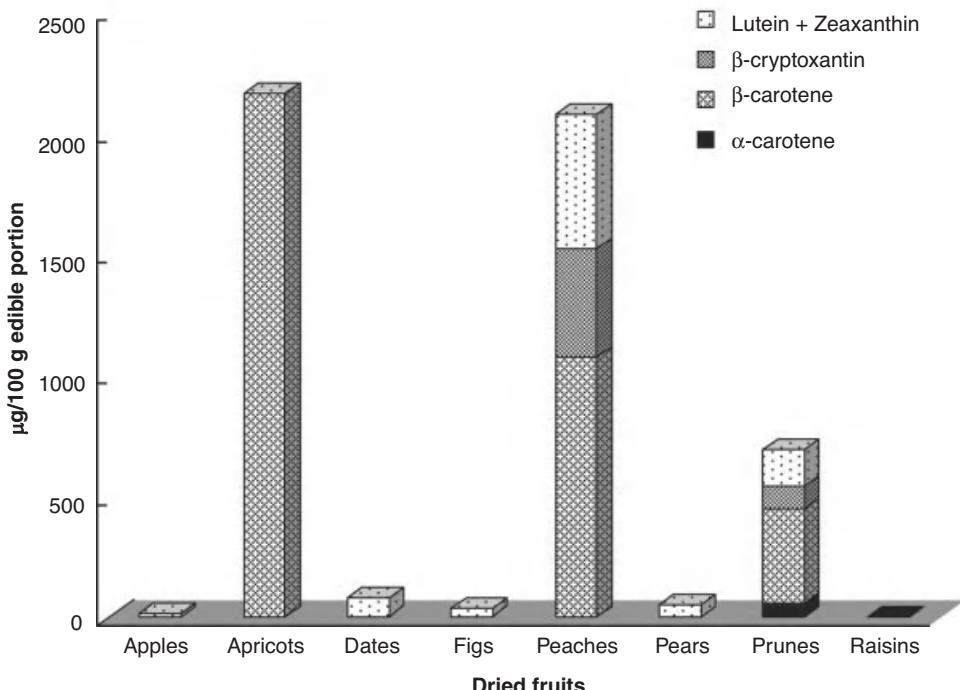
Source: Adapted with permission from Thompson *et al.* [25].

<sup>a</sup>Turkish.

<sup>b</sup>Whole pitted.

<sup>c</sup>Whole pitted.

<sup>d</sup>California seedless.



**Figure 1.2** Carotenoid content of selected dried fruits on a fresh weight basis. (Adapted from USDA [4]).

most abundant in dried apricots (2163  $\mu\text{g}/100 \text{ g}$ ), peaches (1074  $\mu\text{g}/100 \text{ g}$ ), and prunes (394  $\mu\text{g}/100 \text{ g}$ ), followed by lutein + zeaxanthin in peaches (559  $\mu\text{g}/100 \text{ g}$ ), and  $\beta$ -cryptoxanthin in peaches (444  $\mu\text{g}/100 \text{ g}$ ) [4]. No carotenoids are present in raisins and small and/or trace amounts of carotenoids are found in apples, dates, figs, and pears (Figure 1.2).

In summary, the following are some of the health protective components in dried fruits [12]:

- Dried fruits are good sources of phytochemicals [3, 4, 14–28].
- By virtue of their high phytochemical content, dried fruits are an important source of antioxidants in the diet [21, 28, 40]. Dried apricots and peaches are good sources of carotenoids [4].
- Dried fruits, such as prunes, provide pectin, a soluble fiber that may lower blood cholesterol [49].
- Dried fruits, such as raisins, are a source of prebiotic compounds in the diet. They contain fructooligosaccharides such as inulin that contributes to colon health [50, 51].
- Dried fruits contain organic acids such as tartaric acid (raisins) and sugar alcohol such as sorbitol (prunes). These compounds and fiber appear to work synergistically to maintain a healthy digestive system. They may also help increase the bioavailability of minerals in the diet, such as calcium and iron [52].

## 1.4 Beneficial health effects of dried fruits

As shown by multiple epidemiological studies, fruit and vegetable consumption reduces the risk of many chronic diseases such as cancer [53–55], heart disease [56, 57], stroke [58], obesity [59], and type 2 diabetes [59, 60], among others [28]. Additionally, there is an inverse relationship between fruit and vegetable intake and blood pressure [61]. The US National Cancer Institute (NCI) and National Research Council (NRC) recommend at least five servings of fruits and vegetables daily. Similarly, the World Health Organization (WHO) recommends 400 g of fruits and vegetables per day or the equivalent of five servings of 80 g each [62].

Numerous health benefits of dried fruits have been reported [6, 28, 40, 51, 55, 63, 64] and reviewed individually throughout this book. The health benefits of dried fruits mainly originate from their essential nutrients and phytochemicals (such as anthocyanidins, carotenoids, phytoestrogen, flavan-3-ols, flavones, flavonols, and phenolic acids, among others) as well as their antioxidant activities. The intake of flavonoids (major part of phytochemicals) has been associated with a lower incidence of various diseases such as cancer, stroke, cardiovascular disease (CVD), and other chronic disorders [65–67]. The positive health effects of flavonoids are probably related to their strong antioxidant properties, among other mechanisms and effects [68, 69]. There is considerable research supporting the role of dried fruits, particularly, in promoting digestive health [51, 70, 71]. Dried fruits, particularly prunes, play a role in supporting bone health [63, 64, 72]. Finally, dried fruits, such as raisins, may promote healthy teeth and gums [73–75].

Dried fruits are important sources of potassium and dietary fiber. Increasing dietary potassium intake can lower blood pressure [76]. Higher fiber diets are recommended to reduce the risk of developing various conditions including constipation, type 2 diabetes, obesity, diverticulitis, colorectal cancer, and CVD [6]. Dried fruits may contribute to healthy body weights. According to the National Health and Nutrition Examination Survey (1999–2004), data showed that intake of dried fruit was associated with a lower body mass index (BMI), reduced waist circumference, abdominal obesity, and improved diet quality [77]. Emerging data suggest that dried fruit promotes satiety by affecting the levels of hormones such as leptin and regulates appetite [78].

Because of the sweetness of dried fruits, it is expected to exert a high glycemic index (70 and above) and insulin response. Recent studies have shown that dried fruits have a low (55 and under) to moderate (56–69) glycemic and insulin index (Table 1.8) and glycemic and

**Table 1.8** Glycemic index (GI) of some dried fruits

Dried fruits	GI <sup>a</sup>	Reference
Apples	29	[79]
Apricots	30	[79]
Dates	39	[80]
Figs	61	[79]
Peaches	35	[79]
Prunes	29	[79]
Raisins	52	[81]

<sup>a</sup>High GI (70 and above), moderate GI (56–69), and low GI (55 and under).

insulin response comparable to those in fresh fruits [80–83]. This could be due to the presence of fiber, polyphenols, and tannins that can modify the response [84–87]. Foods with a low glycemic index may help decrease the risk of diabetes and are useful in the management of the established condition [6].

As part of a diet study involving 13,292 participants, dried fruit consumers were defined as those who consume at least one-eighth cup-equivalent of fruit per day [88]. Dried fruit consumption is associated with a lower body weight, improved adiposity measures, higher overall diet quality, and higher nutrient intake of vitamins A, E, and K, phosphorus, magnesium, and potassium. These benefits are attributed to a higher fiber content, reduced intake of solid fats, alcohol, and added sugars. However, only 7% of the subjects in the study consumed significant amounts of dried fruits in their diet, which questions the effectiveness of ongoing public health campaigns around the world that encourage an increase in fruit consumption.

Given many of the benefits of dried fruits in terms of health maintenance, what might dried fruits contribute to an increase in fresh and dried fruit consumption while also offering meaningful health benefits beyond their nutritive value? The answer may lie in focusing on foods that offer significant antioxidant and anti-inflammatory benefits.

## **1.5 Commercial products and industrial applications of dried fruits**

Dried fruits are widely used as ingredients in packaged snacks, confectionary products, baked goods, cereals, energy and nutritional bars, ready-to-eat salads, and sweet industries, among many other specialty foods [89].

Fruits can be dried whole (e.g., grapes, apricots, and plums), in halves, as slices, or diced (e.g., mangoes, papayas, and kiwis). Alternatively, they can be chopped after drying (e.g., dates), made into pastes or concentrated juices. Fruits can also be dried in puree form, as leathers, or as a powder, by spray drying. Some fruits can be freeze-dried (e.g., strawberries, raspberries, cherries, apples, and mangoes, among others). The freeze-dried fruits become very light and crispy and retain much of their original flavor (taste and aroma) and phytochemicals [12].

## **1.6 Conclusions**

Dried fruits, with their unique combination of taste and aroma, essential nutrients, fiber, and phytochemicals or bioactive compounds, are a convenient step toward healthier eating and a means to bridge the gap between recommended intake of fruits and actual consumption. They should be included together with fresh fruit recommendations around the world since they help meet dietary guidelines for daily fruit serving (recommended five servings per day) and address barriers to fruit intake. Dried fruits in smaller serving sizes, ranging from 30 to 43 g depending on the fruit, are considered nutritionally equivalent to fresh fruits in current dietary recommendations in different countries [6, 90, 91]. Numerous scientific evidences suggest that individuals who regularly consume generous amounts of dried fruits have a lower rate of CVD, obesity, various types of cancer, type 2 diabetes, and other chronic diseases. Therefore, dried fruits should be consumed daily in order to get full benefit of nutrients,

health-promoting phytochemicals, and antioxidants they contain, together with their unique and desirable taste and aroma.

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## **2 Cancer chemopreventive effects of selected dried fruits**

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### **2.1 Chemoprevention: an overview**

Cancer still imposes a huge health and economic burden throughout the world. The number of new cancer cases, which was recorded as about 3 million in the year 2000, is expected to increase to 7.1 million by the year 2020 [1, 2]. Global cancer mortality is also projected to be doubled in the next 50 years [3]. Such alarming statistics have revitalized our ever-lost war against cancer. Even though the research done over the last few decades failed to generate a magical cure for this dreaded disease, we have learned a lesson that cancer is largely a preventable disease. Since the majority (90–95%) of all cancers are linked to infections, exposure to environmental pollutants, and different lifestyle factors, such as smoking, diet, alcohol consumption, physical inactivity, obesity, and solar exposure, there are ample opportunities for preventing cancer [4].

The cancer prevention research conceptualized by Lee Wattenberg in the 1960s [5] is currently at the forefront in the fight against cancer. “Chemoprevention,” the term coined by Michael B. Sporn in 1976, refers to the use of nontoxic compounds from natural or synthetic sources to inhibit, retard, or reverse carcinogenesis [6]. This definition of chemoprevention has recently been revised to assimilate the clinical status of cancer patients. Thus, chemoprevention now encompasses primary, secondary, or tertiary prevention of cancer. The strategy for primary chemoprevention is to prevent carcinogenesis in healthy individuals, who belong to a low-risk group, while secondary chemoprevention is aimed at intervening in the progression of premalignant lesions into malignancy. Tertiary prevention of cancer refers to the blockade of the recurrence of primary tumors [3, 7, 8].

### **2.2 The promise of dried fruits in cancer prevention**

Convincing results from a wide spectrum of preclinical and epidemiological studies suggest chemoprevention as one of the most practical approaches for reducing the global burden of cancer [9–11]. A report from the World Cancer Research Fund (WCRF) [12] indicates that

about 30–40% of cancers are preventable by proper intake of food and appropriate nutrition and physical activity and by avoiding obesity. An inverse association exists between the regular consumption of fruits and the risk of various organ-specific cancers [13, 14]. For instance, a meta-analysis based on 14 prospective studies and 5838 cases found a significant reduction in the incidence of distal colon cancer that was attributable to frequent consumption of fruits [15]. Pooled analysis of eight cohort studies revealed that the intake of fruits protects against lung cancer as well [16]. The European Prospective Investigation into Cancer and Nutrition (EPIC) study has also shown that adequate consumption of fruits is associated with the reduced risk of colon cancer [17] and lung cancer [18]. The chemopreventive potential of fruits and fruit ingredients has also been documented in a wide range of preclinical studies [19–23].

Common fruits with cancer chemopreventive activity include, but are not limited to, apples, avocados, berries, citrus fruits, kiwi fruits, litchis, mangoes, mangosteens, and persimmons, among others. Many of these fruits are produced on a seasonal basis and are not available in fresh conditions throughout the year. Fresh fruits are, therefore, processed by various techniques to prolong their shelf life. A conventional way of fruit preservation adopted since ancient times is the drying of fruits to reduce moisture content. Fruits can be dried by natural sun drying or by using mechanical devices, such as dryers and a microwave. Freeze drying is another technique to preserve fruits for long-term use. Osmo-convective dewatering of fresh fruits before drying may prevent substantial loss of nutritional ingredients in dried fruits [24]. Appropriate drying methods and temperature are selected depending on the type of fruit. Details of the drying process and its impact on the chemical composition of dried fruits are beyond the scope of this chapter.

Although drying alters the chemical composition to some extent, most of the dried fruits retain the biological properties of their fresh counterparts [25]. For example, vacuum-microwave-dried cranberries retain the antioxidant property of the fresh fruits [26]. Several other studies have reported the antioxidant capacity of dried fruits [27–29]. Among the selected dried fruits, prunes exhibited the highest antioxidant activity followed by dried apricots [27, 29, 30]. Conversely, Halvorsen *et al.* [31] reported the highest antioxidant activity of dried apricots followed by prunes. Such discrepancies are attributable to seasonal variation, and differences in the harvesting stage and the drying process. Raisins exhibited higher oxygen radical scavenging capacity (ORAC) than did fresh grapes [32]. Extracts of different varieties of freeze-dried berries showed antioxidant and cancer chemopreventive activities [23, 33]. Administration of super *CitriMax*, a calcium/potassium salt of (-)-hydroxycitric acid derived from the dried fruit rind of Malabar tamarind (*Garcinia cambogia*), reduced oxidative stress and inflammation in male obese Zucker rats [34]. Heat-treated citrus fruit peel extracts attenuated lipopolysaccharide (LPS)-induced expression of cyclooxygenase-2 (COX-2) and inducible nitric oxide synthase (iNOS), two representative pro-inflammatory enzymes, in murine macrophages [35]. Since oxidative stress and chronic inflammation play key roles in carcinogenesis [36], dried fruits with antioxidative and anti-inflammatory properties hold the promise of cancer chemoprevention. The antioxidant, anti-inflammatory, and chemopreventive activities of dried fruits are largely attributed to their polyphenolic compounds [30, 37]. Vinson *et al.* [28] reported higher polyphenol contents in dried apricots, cranberries, figs, raisins, dates, and prunes as compared with their fresh counterparts. Because of their ready availability and preservation, dried fruits are widely consumed in different societies [38] and can be an excellent natural resource for preventing cancer. The purpose of this chapter is to

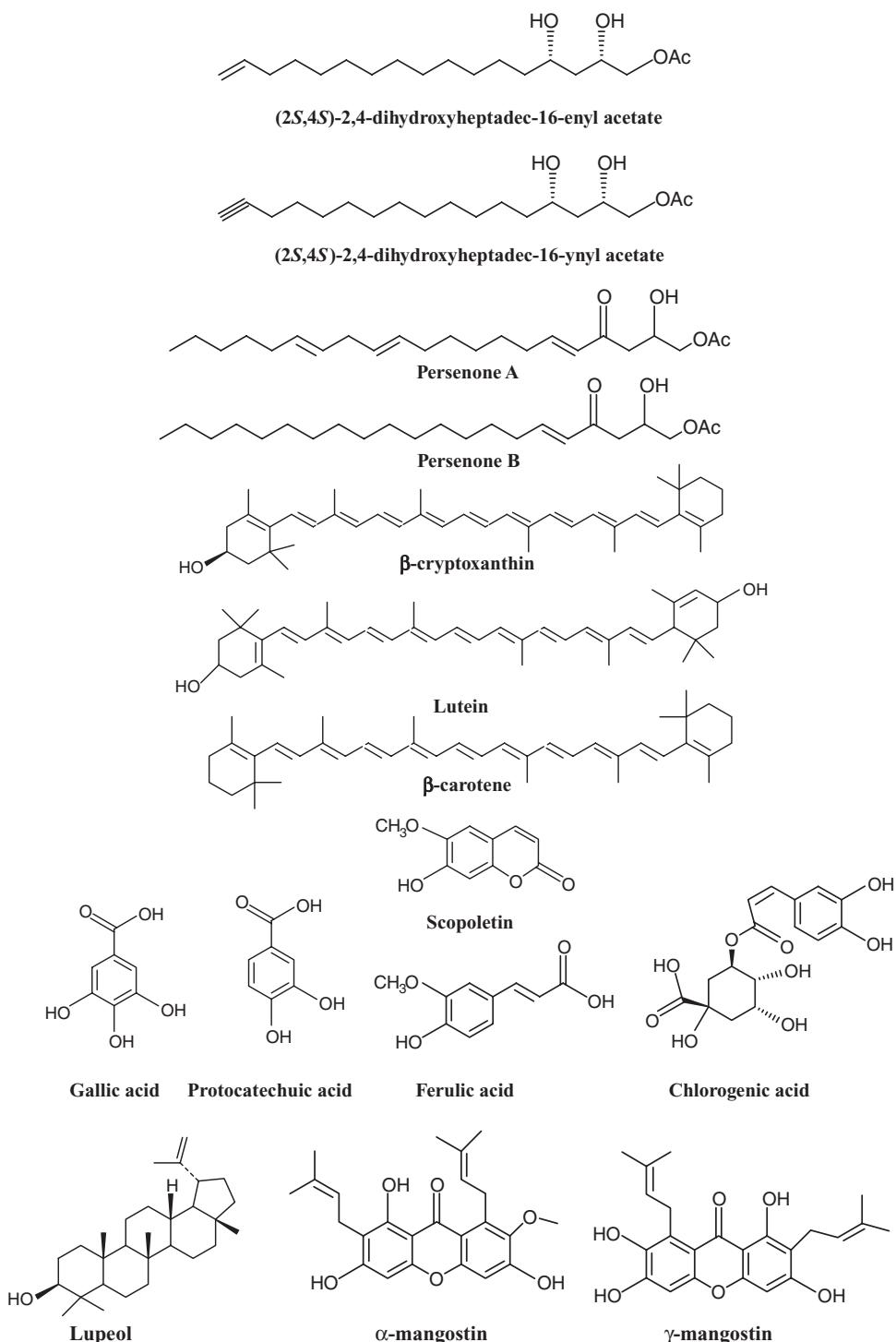
shed light on the cancer chemopreventive potential of selected dried fruits and their active ingredients.

### **2.3 Dried fruits as a potential source of chemopreventive phytochemicals**

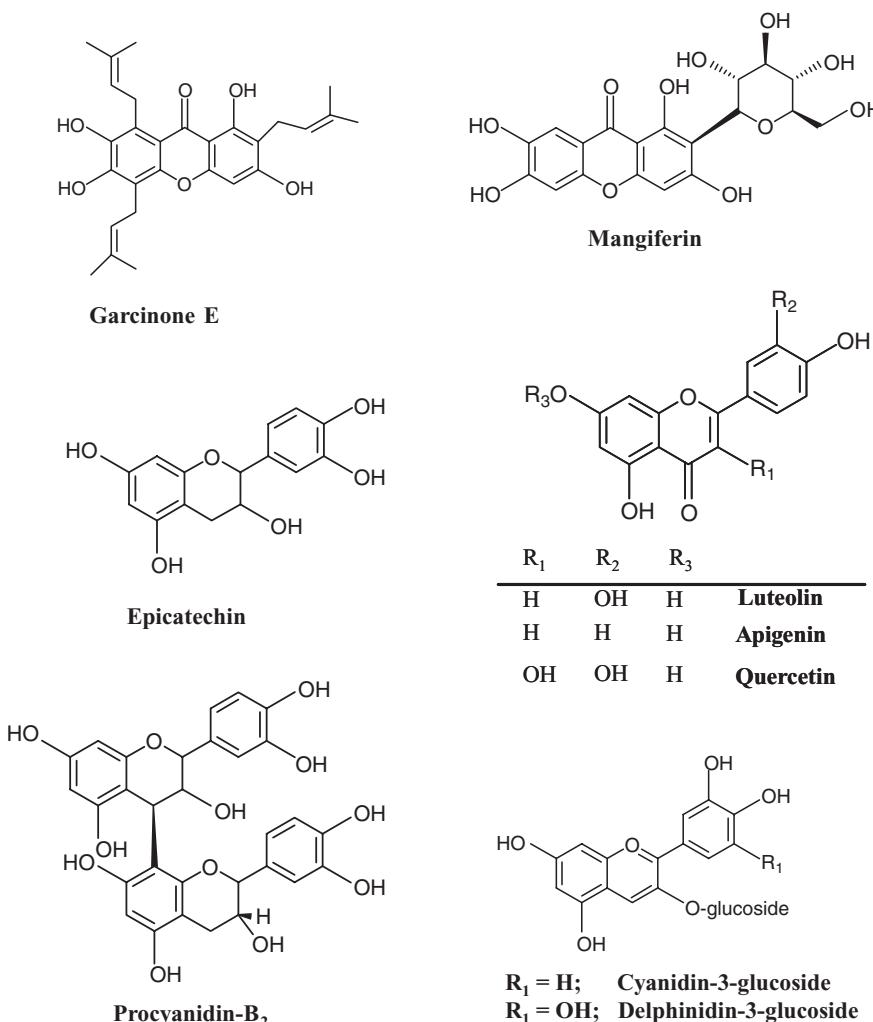
Fruits are rich in antioxidants and anti-inflammatory phytochemicals that help to reduce the incidence of various chronic degenerative diseases including cancer. Vitamins and polyphenols are major chemopreventive phytochemicals present in dried fruits. Drying of fruits by sun exposure or at high temperature in dryers often causes loss of bioactive phytochemicals. For example, fresh grapes contain carotenoids, which are lost in raisins. Certain vitamins are thermolabile and can be degraded during high-temperature drying of fruits. Many volatile compounds present in fresh fruits may be decomposed, while new volatile compounds can be generated during the drying process [39]. Freeze drying is often used to preserve thermolabile components, such as vitamins, carotenoids, and certain phenolics, that are abundant in fresh fruits. Freeze drying extends the shelf life of foods by preventing microbial growth and retarding lipid oxidation [40, 41]. Comparison between *in natura* and freeze-dried pulps of pineapples, cherries, guavas, papayas, and mangoes revealed that freeze drying provides products with higher nutritive value [42]. The effects of freeze drying on the total phenolics and the antioxidant activity of five tropical fruits, namely, starfruits, mangoes, papayas, muskmelons, and watermelons, were investigated [43]. According to this study, freeze drying did not cause any remarkable change in the  $\beta$ -carotene concentration, except for mangoes and watermelons. As compared with fresh fruits, freeze-dried mangoes and starfruits showed a significant decrease in total phenolics and antioxidant activity [43]. Freezing may cause decompartmentalization of polyphenol oxidase, thereby enhancing oxidation of freeze-dried fruit polyphenols. Despite such process-induced loss of active ingredients, dried fruits still contain adequate amount of bioactive compounds, including flavonols, anthocyanins, xanthones, coumarins, phenolic acids, acetogenins, and terpenes, among others (Figure 2.1).

### **2.4 Biochemical basis of chemoprevention with dried fruits**

Because of the presence of antioxidant and anti-inflammatory substances, dried fruits can prevent carcinogenesis. Since oxidative stress and chronic inflammation are the key pathologic events for neoplastic transformation of cells [36, 44], the biochemical basis of cancer chemoprevention with dried fruits might be the maintenance of cellular redox balance and attenuation of inflammatory tissue damage. Though reactive oxygen species (ROS) are physiologic by-products of cellular metabolism and are often essential for many biochemical reactions and cell signaling pathways, excessive generation of ROS can cause oxidative damage to cellular macromolecules, such as proteins, lipids, and nucleic acids [44, 45]. ROS-induced damage of biomolecules perturbs normal cell functions and predisposes cells to acquire a premalignant phenotype. While oxidative stress can cause tissue inflammation,

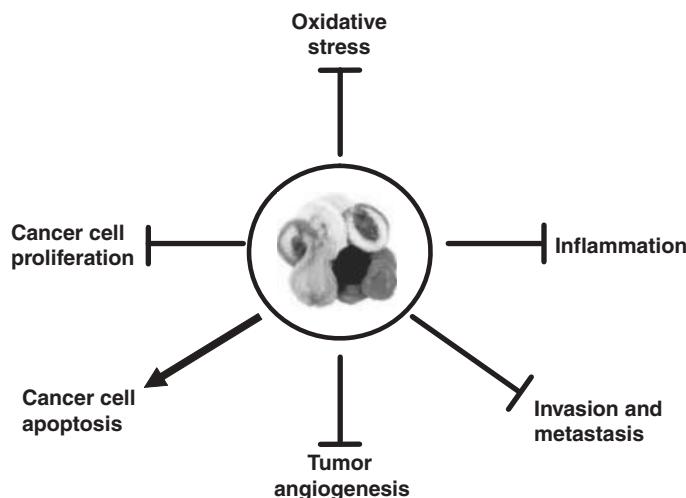


**Figure 2.1** Common chemopreventive phytochemicals present in dry-processed fruits.

**Figure 2.1** (Continued)

persistent inflammation can trigger the generation of ROS [44, 45]. Thus, fruit phytochemicals having both antioxidative and anti-inflammatory properties represent a good choice for cancer chemoprevention.

Carcinogenesis is a heterogenous disease process that consists of several distinct, but closely linked stages of initiation, promotion, and progression. Initiation is a rapid phase of cell transformation often caused by DNA damage. Promotion, the clonal expansion of transformed cells to form a benign tumor, spans several years and involves altered biochemical processes, such as uncontrolled cell proliferation, autonomic growth, lack of differentiation potential, and escape from programmed cell death. Progression is the rapid march of pre-malignant cells toward complete malignancy featuring invasion and metastasis of cancer cells [11, 46]. Although this is oversimplification of the complex cancer biology, such stepwise



**Figure 2.2** Biochemical mechanisms of chemoprevention with fruit phytochemicals. For color detail, see color plate section.

division of carcinogenesis may help to understand the molecular basis of cancer chemoprevention with natural compounds, especially fruit phenolics. Using this simplified model of carcinogenesis, Wattenberg [46] classified chemopreventive agents into two main categories as *blocking* agents and *suppressing* agents. Blocking agents prevent metabolic activation of carcinogens and stimulate cellular detoxification pathways to help eliminate carcinogens, thereby protecting cellular macromolecules, such as DNA, RNA, and proteins, from undesired oxidative or covalent modifications. Suppressing agents, on the other hand, inhibit cell proliferation, induce apoptosis, and block angiogenesis, thereby halting the neoplastic conversion of premalignant cells.

The biochemical basis of cancer chemoprevention with diverse classes of fruit phytochemicals has been extensively investigated. Figure 2.2 represents a general mechanistic aspect of chemoprevention with fruit phytochemicals, which enhance cellular antioxidant capacity and prevent oxidative damage of cellular macromolecules, block the activation of carcinogens, and stimulate carcinogen detoxification, reduce inflammatory responses, inhibit proliferation of cancer cells and induce apoptosis in cancer cells, and block angiogenesis and metastasis.

## 2.5 Chemopreventive properties of bioactive substances derived from selected dried fruits

Fruits processed by drying constitute an important part of our regular diet. Anticancer activity of fresh fruits and various fruit ingredients has been widely investigated. Since numerous health-beneficial fruit phytochemicals are conserved after processing of fruits, regular intake of dried fruits can help prevent cancer. Table 2.1 summarizes the chemopreventive effects of selected dried fruits and their active constituents.

**Table 2.1** Chemopreventive effects of dry-processed fruits and their active ingredients

Treatment	Experimental model	Major findings	Reference
<b>Amla fruits</b>			
Ethanol extract	DMBA-induced genotoxicity	Decreased bone marrow nuclei formation Increased activities of GPx, GR, and GST Reduced the activities of hepatic cytochrome P450 and cytochrome b5 in DMBA-challenged mice Inhibited liver carcinogenesis	[50]
Methanol extract	DEN-initiated and 2-AAF-promoted rat hepatocarcinogenesis	Reduced skin tumor incidence and multiplicity	[54]
Aqueous extract	DMBA-initiated and croton oil-promoted mouse skin carcinogenesis Six human cancer cells: A549, HeLa, MDA-MB-231, SK-OV-3, SW620, chemically induced mouse skin carcinogenesis	Induced DNA fragmentation and apoptosis Activated caspase 3/7 and caspase 8 Increased the expression of Fas Suppressed breast cancer cell invasion Inhibited the average number of skin tumors Reduced the number of ascites and solid tumors Increased life span of tumor-bearing mice	[52]
Polyphenol fraction	Mouse bearing Dalton's lymphoma ascites Dalton's lymphoma ascites NDEA-induced liver carcinogenesis	Decreased Cdc25 phosphatase activity Induced apoptosis in Dalton's lymphoma ascites Reduced hepatic tumor burden Decreased the activities of $\gamma$ -glutamyltranspeptidase, serum alkaline phosphatase, and glutamate pyruvate transaminase Inhibited lipid peroxidation	[51]
<b>Avocados</b>			
Chloroform extract	Premalignant and malignant human oral squamous carcinoma cells	Induced ROS production Activated caspase-8 Induced apoptosis	[59]
Acetone extract (carotenoid-rich fraction)	Human prostate cancer LNCaP and PC3 cells	Attenuated cell proliferation; Induced G2/M cell cycle arrest and p27 expression	[60]
Methanol extract, persenone A or persenone B	LPS plus IFN $\gamma$ -stimulated murine macrophages	Inhibited generation of superoxide and NO; Diminished TPA-induced H <sub>2</sub> O <sub>2</sub> generation in HL60 cells	[61]

{continued}

**Table 2.1** (Continued)

Treatment	Experimental model	Major findings	Reference
Perseone A	IPS plus IFN $\gamma$ -stimulated raw 264.7 cells, and TPA-treated mouse skin	Inhibited the expression of iNOS and COX-2	[62]
Acetogenins	Human oral cancer cells	Inhibited cell proliferation	[21]
Scopolitin	DMBA-initiated and croton oil-promoted mouse skin papillomagenesis	Reduced phosphorylation of EGFR, c-Raf, and ERK Decreased the incidence and multiplicity of mouse skin papillomas	[63]
	Prostate cancer (PC3) cells	Induced apoptosis	[64]
	Multidrug resistant human leukemia cells	Reduced cell proliferation Induced apoptosis	[65]
	Human melanoma A375 cells	Inhibited cell proliferation Decreased expression of survivin, cyclin D1, PCNA, and phosphorylation of STAT3 Induced apoptosis through activation of p53 and caspase-3	[66]
<b>Berries</b>	Human cervical and breast cancer cells	Inhibited cell proliferation	[71]
Ethanol extract of freeze-dried strawberry and blueberry	Breast cancer cells xenograft in nude mice	Reduced the size of xenograft tumor Decreased expression of $\beta$ -catenin Reduced phosphorylation of GSK-3 $\beta$ and APC Inhibited activation of Akt and NF- $\kappa$ B Induced caspase-3 cleavage Decreased MMP-9 activity Inhibited secretion of uPA	[72, 73]
Blueberry extract	Hemangiogenesis formation in nude mice inoculated with transformed murine endothelial cells	Attenuated metastasis of xenografted MDA-MB-231 cells Decreased the incidence and size of hemangioidotheliomas Increased survival Reduced activation of JNK and NF- $\kappa$ B Decreased MCP-1 expression	[75]
Diet rich with 10% extract of freeze-dried bilberry, lingonberry, and cloudberry	APC $^{\text{min+}}$ mice	Inhibited angiogenesis Reduced the development of intestinal adenomas Decreased the expression of $\beta$ -catenin and cyclin D1	[76]

Blueberry polyphenol-rich diet	<i>MMTV-Wnt1</i> -transgenic mice fed with blueberry	Sera from <i>MMTV-Wnt1</i> transgenic mice blocked mammosphere formation in MDA-MB-231 cells in culture	[74]
Dried freeze-dried white currant	$\text{APC}^{\text{min}+}$ mice	Reduced the development of intestinal adenomas	[77]
Aqueous extract of black currant	HepG2 cells	Decreased the expression of $\beta$ -catenin and NF- $\kappa$ B Inhibited cell proliferation	[78]
Anthocyanin-rich black currant in diet	DEN-induced rat hepatocarcinogenesis	Decreased the formation of neoplastic foci	[79]
Freeze-dried black raspberry extract in diet	C57Bl/6 mice challenged with DSS	Reduced hepatic NF- $\kappa$ B activation and COX2 expression Reduced colitis	[86]
Freeze-dried black raspberry extract in diet	NMBA-induced rat oesophageal cancer	Decreased production of TNF $\alpha$ , IL-1 $\beta$ , and expression of COX-2 in mouse colon Decreased esophageal tumors Reduced expression of COX2, iNOS, and VEGF Decreased microvessel density	[87]
<b>Mangoes</b>	Polyphenols of mango fruit	Induced apoptosis	[106]
Supplementation with mango pulp extract or lupeol	Human colon cancer cells Androgen-treated mice Human prostate cancer [LNCaP] cells	Increased expression of p21, Bax, and caspase-8 Inhibited enlargement of the prostate Induced apoptosis Activated caspase-3 Inhibited Bcl-2 and Bcl-xL	[107-109]
Lupeol	Chemically induced mouse skin carcinogenesis	Decreased the incidence and multiplicity of skin papillomas Decreased ODC activity Reduced the expression of COX-2 and iNOS Attenuated activation of Akt and NF- $\kappa$ B Decreased lung tumor formation Increased activities of detoxification enzymes Decreased the incidence and multiplicity of colon tumors Inhibited xanthine oxidase activity Reduced superoxide generation Inhibited expression of iNOS	[110]
Mangiferin in the diet	$\text{B}[{\alpha}]P$ -induced mouse lung tumorigenesis AOOM-treated F344 rats LPS plus IFN $\gamma$ -stimulated rat macrophages		[101]
<b>Mangosteens</b>	Ethanol extract of fruit rind $\alpha$ -Mangostin	<i>In vitro</i> study <i>In vitro</i> study, DMBA-treated mouse mammary organ culture Free radical scavenging effect Antioxidant activity Decreased formation of preneoplastic lesions	[119] [120] (continued)

**Table 2.1** (Continued)

Treatment	Experimental model	Major findings	Reference
<b>γ-Mangostin</b>	Prostate cancer cells	G1 cell cycle arrest Decreased the CDK4 activity Inhibited the growth of prostate cancer cells xenograft in nude mice	[124]
	Mammary cancer cells	G1 and S phase arrest Inhibited Akt phosphorylation Activated caspases Attenuated metastasis of breast cancer cells in tumor-bearing mice	[123]
<b>Garcinone E</b>	C6 rat glioma cells	Attenuated constitutive or LPS-induced expression of COX-2; Inhibited IKK activity, and NF-κB activation	[126]
	Hepatocellular, gastric, and lung cancer cells	Induced apoptosis	[121]
<b>Magostenone (C-E)</b>	Epidermoid carcinoma, breast cancer, lung cancer cells	Induced cytotoxicity	[122]
<b>Persimmons</b>			
Aqueous extract and flavonoids	Human leukemia Molt 4B cells	Inhibited the ODC activity Induced apoptosis	[19]
Ethylacetate extract	Human monocyte [THP-1] cells	Decreased LPS-induced TNFα production	[143]
<b>Prunes</b>			
Ethanol extract	Human colon cancer, Caco-2 and KATO III cells	Decreased the cell viability	[185]
<b>Kiwi fruits</b>			
Hydroalcoholic extract	Human squamous carcinoma (HSC-2) cells	Induced cytotoxicity	[196]
Methanol extract of freeze-dried fruit and quercetin	Rat liver epithelial cells exposed to H <sub>2</sub> O <sub>2</sub>	Restored connexin-43 expression Inhibited ERK phosphorylation Inhibited gap-junction intercellular communication	[199] [199]

2-AFF, 2-acetylaminofluorine; AOM, azoxymethane; APC, adenomatous polyposis coli; B[a]P, benzo[a]pyrene; CDK4, cyclin-dependent kinase-4; COX-2, cyclooxygenase-2; cRAF, the protein product of *raf* oncogene; DEN, diethylnitrosamine; DMBA, 7,12-dimethylbenz[a]anthracene; EGFR, epidermal growth factor receptor; ERK, extracellular signal-regulated kinases; GPx, glutathione peroxidase; GR, glutathione reductase; GST, glutathione-S-transferase; IFNγ, interferon-γ; IKK, IκB kinase; IL-1β, interleukin-1β; iNOS, inducible nitric oxide synthase; JNK, c-Jun N-terminal kinase; LPS, lipopolysaccharide; MCP-1, monocyte chemoattractant protein-1; MMP-9, matrix metalloproteinase-9; NDEA, N-nitroso diethylamine; NF-κB, nuclear factor-κB; NO, nitric oxide; ODC, ornithine decarboxylase; PCNA, proliferating cell nuclear antigen; ROS, reactive oxygen species; STAT3, signal transducer and activator of transcription-3; TNFα, tumor necrosis factor-α; TPA, 12-O-tetradecanoylphorbol-13-acetate; VEGF, vascular endothelial growth factor.

### 2.5.1 Amla (Indian gooseberries) fruits

Fruits of *Phyllanthus emblica* Linn. or *Emblica officinalis* Gaertn. (Eupobiaceae) are commonly known as Indian gooseberry or amla or amlaki, which are consumed in either fresh or in dried form. Sun-dried amla fruits are important components of Ayurvedic medicine. Amla fruits are rich sources of vitamin C, different amino acids, and minerals. Besides these micronutrients, amla fruits contain a wide variety of secondary metabolites, such as alkaloids, flavonoids, terpenoids, and tannins [47–49]. The methanol extract of dried rind of amla fruits has a strong nitric oxide (NO) scavenging activity [48]. Major constituents with the NO scavenging property were identified as gallic acid, methyl gallate, corilagin, furosin, and geranin [48]. Poltanov *et al.* [49] reported that ellagic acid, gallic acid, and corilagin were common antioxidants present in four commercial varieties of dried amla fruits. The ethanol extract of dried amla fruits protected against 7,12-dimethylbenz[a]anthracene (DMBA)-induced genotoxicity in Swiss albino mice [50]. Aqueous extract of dried fruits of *E. officinalis* induced cytotoxicity in L929 cells and reduced the tumor volume in mice implanted with Dalton's lymphoma ascites (DLA). The antitumor effects of amla fruits were associated with the decreased activity of the cell cycle regulating enzyme cell division cycle (Cdc)-25 phosphatase. Moreover, amla fruit extracts increased the life span of DLA tumor-bearing mice [51].

Administration of the aqueous extract of dried amla fruits by gavage significantly inhibited the incidence and the multiplicity of DMBA-initiated and croton oil [52]- or 12-O-tetradecanoylphorbol-13-acetate (TPA)-promoted [53] mouse skin tumorigenesis. Pretreatment with defatted methanolic extract of dried amla fruits attenuated diethylnitrosoamine (DEN)-initiated and 2-acetylaminofluorine (2-AAF)-promoted hepatic carcinogenesis in Wister rats [54]. Incubation with aqueous extract of dried amla fruits induced apoptosis in human cervical cancer (HeLa) cells. According to this study, the amla extracts increased DNA fragmentation, induced the activity of caspase-3, -7, and -8, and elevated the expression of Fas protein [53]. Moreover, the same extracts attenuated the invasiveness of human breast cancer (MDA-MB-231) cells [53]. Arsenic is a ubiquitous environmental carcinogen that causes cancer of the skin, bladder, liver, lung, and kidney [55]. Treatment with the aqueous extract of dried amla fruits inhibited arsenic-induced lipid peroxidation and the activity of serum transaminase in livers of Swiss albino mice [56]. In addition, dried amla fruit extracts restored arsenic-induced depletion of hepatic superoxide dismutase (SOD), catalase, and serum alkaline phosphatase activity in mouse liver [56]. A polyphenolic fraction prepared from dried fruits of *E. officinalis* induced apoptosis in DLA cells and reduced N-nitrosodiethylamine (NDEA)-induced liver tumor formation in rats [57]. Amla fruits contain substantial amounts of tannins and flavonoids. Treatment of human lung cancer (H441 and H520) cells with pyrogallol, a major catechin compound present in amla fruits, induced G2/M phase arrest and apoptosis, which was associated with increased expression of Bax and reduced expression of Bcl-2, cyclin B1, and Cdc25. In addition, dried amla fruit extracts caused the regression of lung cancer cells xenograft in nude mice [58].

### 2.5.2 Avocados

Avocados (*Persea americana* Mill., Lauraceae), also known as alligator pear, are widely consumed throughout the world. They are high in nutrients and low in calories, sodium, and fat. More than 25 chemopreventive phytochemicals have been isolated from avocados [59]. These

include alkanols or aliphatic acetogenins (e.g., persin and persenone A and B), flavonoids (e.g., catechin, epicatechin [EC], luteolin, apigenin, and quercetin), carotenoids (e.g., zeaxanthin, lutein, and  $\beta$ -carotene), terpenoid glycosides, and coumarins [59, 60]. Phytochemicals isolated from avocados induced cell cycle arrest and apoptosis in various cancer cells. Some of the compounds present in avocados, for example, catechin, quercetin, apigenin, and luteolin are well-known cancer chemopreventive agents. Acetone extract of avocados, rich in carotenoids and tocopherols, inhibited the growth of both androgen-dependent (LNCaP) and androgen-independent (PC3) prostate cancer cells. This study also demonstrated that treatment with avocado extracts induced the expression of p27 and arrested the growth of PC3 cells at the G2/M phase of the cell cycle [60]. Kim *et al.* [61] isolated aliphatic acetogenins, persenone A and B, from the methanol extract of fresh avocados. Both persenone A and B showed inhibitory effects on the generation of superoxide and NO in murine macrophage RAW 264.7 cells stimulated with a combination of LPS and interferon- $\gamma$  (IFN $\gamma$ ), and attenuated TPA-induced superoxide generation in human promyelocytic leukemia HL60 cells [61]. Incubation with persenone A caused significant inhibition of iNOS and COX-2 expression in LPS plus IFN $\gamma$ -stimulated RAW 264.7 murine macrophages, and topical application of persenone A attenuated TPA-induced generation of hydrogen peroxide in mouse skin [62]. Chloroform extract of avocados inhibited the growth of premalignant and malignant human oral cancer cells, partly by inducing apoptosis through generation of ROS and FAS (a cysteine-rich transmembrane protein belonging to tumor necrosis factor family of cytokines)-mediated caspase-8 activation [59].

Avocado extracts also inhibited the phosphorylation of epidermal growth factor receptor (EGFR), the protein product of *raf* oncogene (c-RAF), and extracellular signal-regulated kinases (ERK). Bioactivity-guided fractionation of chloroform extract yielded two active constituents, (2S,4S)-2,4-dihydroxyheptadec-16-enyl acetate and (2S,4S)-2,4-dihydroxyheptadec-16-ynyl acetate [21]. Scopoletin (7-hydroxy, 6-methoxy-coumarin) is a bioactive compound present in avocados. Mice fed scopoletin at a daily dose of 50 or 100 mg/kg body weight for 24 weeks reduced the size of skin papillomas induced by DMBA plus croton oil [63]. Moreover, scopoletin induced apoptosis in human prostate cancer (PC3) cells [64] and multidrug-resistant human leukemia (CEM/ADR500) cells [65]. Incubation of human melanoma A375 cells with polylactide-co-glycolide-encapsulated scopoletin inhibited cell proliferation and induced apoptosis, which was associated with downregulation/inactivation of survivin, cyclin D1, proliferating cell nuclear antigen (PCNA), and signal transducer and activator of transcription-3 (STAT3), and also with induction of p53 and caspase-3 activity [66].

Chemical and biological investigations on dried avocados are still limited. Whether the aforementioned chemopreventive phytochemicals reported from fresh avocados are present in dried ones is yet to be confirmed. However, a recent study demonstrated the presence of carotenoids and procyanidins in freeze-dried peels and pulps of avocados. Furthermore, the antioxidant activity of dried avocado parts was correlated with the procyanidin content, but not with the total carotenoids [67]. Considering the presence of anticancer properties in fresh avocados, the chemopreventive activity of dried avocados merits further investigation.

### **2.5.3 Berries**

A wide variety of berry fruits are known to possess diverse health-beneficial effects [68, 69]. Dietary intake of different berry fruits, either fresh or in the processed form, can

prevent multistep carcinogenesis. Commonly consumed berry fruits include blackberries (*Rubus spp.*), black raspberries (*Rubus occidentalis*), blueberries (*Vaccinium corymbosum*), cranberries (*Vaccinium macrocarpon*, *Vaccinium oxycoccus*), red raspberries (*Rubus idaeus*), and strawberries (*Fragaria x ananassa*) [69]. Berries contain a diverse range of phytochemicals with health benefits, such as antioxidant, neuroprotective, anti-inflammatory, and anticancer activities. The major classes of berry phenolics are anthocyanins, flavonols, flavanols, ellagitannins, gallotannins, proanthocyanidins, and phenolic acids [70]. Methanol extract of six popularly consumed berries, including blackberries, black raspberries, blueberries, cranberries, red raspberries, and strawberries, inhibited the growth of human oral, breast, colon, and prostate cancer cells at concentrations ranging from 25 to 200 µg/mL. Ethanol extracts of freeze-dried strawberries and blueberries inhibited the growth of human cervical (Caski and SiHa) and breast (MCF-7 and T47D) cancer cells in culture [71]. Administration of whole blueberry powders in diet significantly decreased the tumor volume in female nude mice implanted with human breast cancer MDA-MB231 cells and reduced the liver metastasis of these cells. Tumors from blueberry-fed mice showed decreased expression of β-catenin, reduced phosphorylation of glycogen synthase kinase-3β (GSK-3β), and elevated expression of adenomatous polyposis coli (APC) [72]. Moreover, tumors from blueberry-fed mice showed decreased activation of Akt and nuclear factor-κB (NF-κB), and induced caspase-3 cleavage [73]. The antimetastatic effect of blueberries was associated with the decreased activity of matrix metalloproteinase (MMP)-9, reduced secretion of urokinase plasminogen activator (uPA), and increased secretion of tissue inhibitor of metalloproteinase-1 and plasminogen activator inhibitor-1 in MDA-MB231 cells [73]. A recent study demonstrated that blueberry polyphenol-containing diet repressed mammosphere formation of human breast cancer cells, suggesting that blueberry extracts may target cancer stem-like cells in preventing breast carcinogenesis [74]. Treatment with blueberry extracts significantly reduced the incidence and the size of hemangioendotheliomas in nude mice subcutaneously inoculated with transformed murine endothelial (EOMA) cells and prolonged the survival of tumor-bearing mice. Blueberry extracts blocked the signaling mediated by c-Jun N-terminal kinase (JNK) and NF-κB, thereby decreasing the expression of monocyte chemoattractant protein-1 (MCP-1) that is required for hemangioendothelioma development. The antiangiogenic effect of blueberry extracts was evident from decreased sprouting on matrigel and transwell migration of EOMA cells [75].

Diets containing 10% freeze-dried bilberries, lingonberries, or cloudberry significantly inhibited the formation of intestinal adenomas in APC<sup>min+</sup> mice with decreased expression of β-catenin and cyclin D1. Affymetrix microarray analysis of adenoma tissues from berry-fed mice revealed the decreased expression of adenosine deaminase, ecto-5'-nucleotidase, and prostaglandin E<sub>2</sub> receptor-4 (EP4), which are involved in intestinal tumorigenesis [76]. Likewise, dietary administration of freeze-dried white currants attenuated the formation of intestinal adenomas in association with decreased β-catenin expression and NF-κB activation in APC<sup>min+</sup> mice [77]. An aqueous extract of black currants' skin, rich in cyanidin-3-O-rutinoside, inhibited proliferation of hepatocellular carcinoma HepG2 cells, and its effect was more pronounced than that of delphinidin and cyanidin, two anthocyanin aglycones present in black currants [78]. Moreover, the same extract inhibited the formation of DEN-induced hepatic gammaglutamyl transpeptidase-positive preneoplastic foci and decreased the expression of COX-2 and activation of NF-κB in rat liver [79].

Seeram *et al.* [70] examined the effects of blackberries, black raspberries, blueberries, cranberries, red raspberries, and strawberries on the growth of various cancer cells and found that extracts of black raspberries and strawberries were most active in arresting

growth and inducing apoptosis in human colon cancer (HT-29) cells. The induction of apoptosis in HT-29 cells with different berry extracts was associated with increased expression of p21 and Bax [80]. The multiplicity and the volume of 17 $\beta$ -estradiol-induced mammary tumors were significantly reduced in female ACI rats given diet supplemented with either blueberry or black raspberry powders or their active constituent ellagic acid [81]. 17 $\beta$ -Estradiol causes oxidative DNA damage via redox cycling of its metabolite 4-hydroxyestradiol. Dietary administration of blueberry extracts or ellagic acid diminished 4-hydroxyestradiol-induced formation of 8-oxo-7,8-dihydroguanine (8-oxodG), a marker of oxidative DNA damage, in rats [81]. Diet containing 5 or 10% freeze-dried strawberries inhibited the multiplicity of *N*-nitrosomethylbenzylamine (NMBA)-induced esophageal cancer in F344 rats, presumably by blocking the metabolic activation of NMBA [82]. A significant decrease in  $O^6$ -methylguanine levels was observed in the esophageal DNA of animals fed strawberries, suggesting that one or more components in strawberries influence(s) the metabolism of NMBA to generate DNA-damaging species. However, according to another study, lyophilized strawberries in the diet failed to inhibit 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK)- and benzo[*a*]pyrene (B[*a*]P)-induced mouse lung tumorigenesis [83].

Administration of lyophilized black raspberries inhibited the formation of the promutagenic adduct  $O^6$ -methylguanine and significantly reduced the multiplicity of NMBA-induced esophageal tumors [84] and inhibited azoxymethane (AOM)-induced aberrant crypt foci (ACF) formation in colon [85] of F344 rats. Treatment of C57BL/6 mice with freeze-dried black raspberry extracts attenuated dextran sulfate sodium (DSS)-induced colitis, which often progress to colon cancer. This study also demonstrated that black raspberry extracts decreased DSS-induced production of tumor necrosis factor- $\alpha$  (TNF $\alpha$ ) and interleukin (IL)-1 $\beta$  and the expression of COX-2 in mouse colon [86]. Black raspberry extracts reduced the mRNA and protein expression of COX-2, iNOS, and c-Jun as well as the level of prostaglandin E<sub>2</sub> (PGE<sub>2</sub>) in preneoplastic lesions of the NMBA-treated rat esophagus [87]. In addition, black raspberry extracts inhibited NMBA-induced expression of vascular endothelial growth factor (VEGF)-C and reduced the microvessel density in NMBA-treated rat esophagus [87], indicative of the antiangiogenic potential of black raspberry. Ethanol extract of freeze-dried black raspberries inhibited the growth of premalignant and malignant, but not normal, human oral epithelial cells. This ethanol fraction reduced the expression of cyclin A and cell division cycle gene 2 (Cdc2) in premalignant cells and that of cyclin B1, cyclin D1, and Cdc2 in the malignant cell lines. Ferulic acid, isolated from ethanol fraction of freeze-dried black raspberries, arrested the growth of premalignant and malignant oral epithelial cells at the G2/M phase of the cell cycle and increased levels of cyclin B1 and Cdc2 in both cell lines [88]. In a subsequent study, dietary administration of an anthocyanin-rich fraction of freeze-dried black raspberries inhibited cell proliferation, inflammation, and angiogenesis and induced apoptosis in rat preneoplastic and papillomatous esophageal tissues [89]. These preclinical chemopreventive effects were supported by significant reduction in the urinary excretion of two oxidative stress markers, 8-epi-prostaglandin F<sub>2alpha</sub> (8-Iso-PGF<sub>2</sub>) and 8-hydroxy-2'-deoxyguanosine (8-OHdG), in patients with Barrett's esophagitis who received lyophilized black raspberry extracts [90]. Incubation of mouse epidermal JB6 cells with different fractions of methanol extract of freeze-dried black raspberries attenuated B[*a*]P-diol-epoxide (BPDE)-induced activation of NF- $\kappa$ B and activator protein-1 (AP-1) through inhibition of phosphorylation of mitogen-activated protein (MAP) kinases and I $\kappa$ B kinase (IKK) [91]. Moreover, treatment with different solvent fractions of freeze-dried black raspberries decreased the expression

of VEGF and iNOS in BPDE-stimulated JB6 cells by blocking phosphatidylinositol-3-kinase/Akt signaling [22]. Major constituents of the most active fractions were identified as cyanidin-3-*O*-glucoside, cyanidin 3-*O*-xylosylrutinoside, and cyanidin 3-*O*-rutinoside, which also attenuated BPDE-induced NF-κB activation in JB6 cells [92]. Topical application of the standardized black raspberry extracts significantly inhibited ultraviolet-B (UVB) radiation-induced inflammation and tumor promotion in mouse skin [93].

### 2.5.4 Mangoes

Mangoes (*Mangifera indica* L., Anacardiaceae) are grown in tropical regions. While green and ripe mangoes are consumed as seasonal fruits, green mangoes are often sun-dried and preserved for off-season use. Mango fruit leathers are made by sun drying a very thin layer of fruit puree to obtain a chewable product [94]. Dried mango peels contain pectin and polyphenols [95]. Several gallotannins have been isolated from both dried peels and pulps of mango [96]. Mangoes also contain high amounts of flavonol-*O*- and xanthone-*C*-glycosides [97, 98]. Moreover, carotenoids constitute a major part of mangoes [99, 100]. Chen *et al.* [100] investigated the effect of different drying conditions on the carotenoid content of Taiwanese mangoes. According to this study, hot-air drying or freeze drying of sliced mangoes reduced the carotenoid content. However mango slices soaked in either NaHSO<sub>3</sub> or ascorbic acid for 30 minutes prior to freeze drying or hot-air drying retained high level of carotenoids. All-*trans*-β-carotene and its *cis* isomers are the major carotenoids isolated from mangoes. Other carotenoids in mango include neochrome, violaxanthin, zeaxanthin, luteoxanthin, neoxanthin, and *cis*-lutein. Since all-*trans*-β-carotene possesses high antioxidant activity, treatment of mango slices with ascorbic acid or NaHSO<sub>3</sub> before drying is important to protect all-*trans*-β-carotene from thermal decomposition.

A major chemopreventive phytochemical present in mangoes is mangiferin (1,3,6,7-tetrahydroxyxanthone-C2-beta-D-glucoside), which is a C-glucosylxanthone. Dietary administration of mangiferin inhibited B[a]P-induced lung carcinogenesis in Swiss albino mice. Mangiferin increased the activities of detoxification enzymes and restored antioxidant enzyme activities in lung and liver of tumor-bearing mice [101]. Diet containing 0.1% mangiferin reduced the incidence and the multiplicity of colon tumors in AOM-treated F344 rats [102]. Mangiferin attenuated the mRNA expression of iNOS, TNFα, and transforming growth factor-β, and diminished the generation of superoxide by blocking xanthine oxidase activity in LPS plus IFNγ-stimulated rat macrophages [103]. Norathyriol (1,3,6,7-tetrahydroxy-9H-xanthen-9-one), an aglycone of mangiferin, has been reported to possess antioxidant and anti-inflammatory properties [104]. Treatment with norathyriol inhibited calcium ionophore-induced COX expression and lipoxygenase activity in rat neutrophils [104]. Topical application of norathyriol suppressed UVB-induced mouse skin papillomagenesis by blocking the activation of NF-κB and AP-1 [105].

Polyphenolic fractions obtained from several varieties of mangoes induced mRNA expression of p21, Bax, and caspase-8, and arrested the growth of human colon cancer (SW480) cells, but did not affect the proliferation of normal colon epithelial cells [106]. Supplementation with mango pulp extracts or their triterpene constituent lupeol inhibited prostate enlargement in androgen-treated male Swiss albino mice [107]. Moreover, incubation with mango pulp extracts or lupeol induced apoptosis in LNCaP cells in culture through activation of caspase-3 and downregulation of B-cell lymphoma-2 (Bcl-2) and B-cell lymphoma-extra

large (Bcl-xL) [108, 109]. Topical application of lupeol inhibited TPA-induced skin inflammation and tumor promotion, which was associated with the decreased expression of ornithine decarboxylase (ODC), COX-2, and iNOS, and the inhibition of NF-κB and Akt [110]. Other polyphenols present in mangoes include ellagitannins and ellagic acid [106, 111], which also exhibited chemopreventive properties [112–114].

### 2.5.5 Mangosteens

Mangosteens (*Garcinia mangostana* L., Guttiferae) also known as the “queen of fruits,” are widely grown in tropical countries. The pericarp of mangosteens has long been used in Ayurvedic medicine for the treatment of infection, pain, inflammation, and gastrointestinal disorders [115]. The fruits contain dark purple or reddish pericarp (peels and rinds) with white, soft, and juicy edible pulps (arils). Mangosteens contain xanthone derivatives [116]. More than 50 xanthone compounds have been isolated from pericarps and pulps of mangosteen. Examples are α-, β-, or γ-mangostin, gartanin, garcimangosone (A–D), tovophyllin (A and B), garcinone (A–E), mangostenone (A and B), caloxanthone-A, macluraxanthone, euxanthone, cudraxanthone, 8-desoxygarnatin, calabaxanthone, demtheylcalabaxanthone, 9-hydroxycalabaxanthone, and 1- or 3-isomangostin [115]. The xanthone content of fruit rinds was significantly reduced during drying at elevated temperatures. However, drying by low-pressure superheated steam has been proposed as an appropriate condition of drying mangosteens for the retention of their xanthone contents and antioxidant property [117]. Phytochemical analysis of freeze-dried mangosteen peels, rinds, and aril parts revealed a high content of phenolic acids, such as hydroxybenzoic acid derivatives (e.g., *m*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, protocatechuic acid, vanillic acid, and veratric acid), hydroxycinnamic acid derivatives (e.g., *p*-coumaric acid, caffeic acid, and ferulic acid), and other phenolic acids (e.g., benzoic acid, cinnamic acid, and *p*-hydroxyphenylacetic acid) [118].

The ethanol extract of mangosteen rinds exhibited free radical scavenging property [119]. Xanthones including 8-hydroxycudraxanthone-G, garcinone D, garcinone E, gartanin, 8-deoxygartanin, garcimangosone B, 1-isomangostin, smeathxanthone A, tovophyllin A, γ-mangostin, and α-mangostin were isolated from dried pericarps of mangosteen. These xanthones showed antioxidant activity, with α-mangostin being the most active [120]. In a mouse mammary organ culture assay, α-mangostin was found to inhibit DMBA-induced formation of preneoplastic lesions with an inhibitory concentration 50% (IC<sub>50</sub>) value of 2.44 μM [120]. Garcinone E elicited cytotoxic effects against human hepatocellular carcinoma, gastric cancer, and lung cancer cells [121]. Suksamrarn *et al.* [122] isolated prenylated xanthones, such as mangostenone (C–E), along with several known xanthones including α-mangostin. Mangostenone-C elicited a potent cytotoxic effect against human epidermoid carcinoma of mouth (KB), breast cancer (BC-1), and lung cancer (NCI-187) cells. The cytotoxic effects of α-mangostin and gartanin were observed against BC-1 and NCI-187 cells with IC<sub>50</sub> values of 0.92 and 2.08 μg/mL, respectively [122]. Treatment with α-mangostin inhibited lymph node metastasis in mice inoculated with metastatic murine mammary adenocarcinoma cells stably transfected with Luc2 gene (BJMC3879luc2) and increased the survival of tumor-bearing mice. This study also demonstrated that α-mangostin induced G1 and S phase cell cycle arrest and induced apoptosis in cultured mammary carcinoma cells, which was associated with increased activation of caspase-9 and -3, and the inhibition of Akt phosphorylation [123]. Likewise, α-mangostin attenuated the proliferation of human prostate cancer cells by inducing G1 cell cycle arrest and inhibiting cyclin-dependent kinase-4 (CDK4) activity.

Moreover, administration of  $\alpha$ -mangostin by gavage significantly reduced the growth of 22Rv1 human prostate cancer cells inoculated to athymic nude mice [124]. Incubation of human melanoma SK-MEL-28 cells with  $\alpha$ -mangostin,  $\gamma$ -mangostin, or 8-deoxygartanin induced apoptosis. The apoptotic effect of  $\alpha$ -mangostin was mediated through the induction of caspase-3 activity and decreased mitochondrial membrane potential [125]. Nakatani *et al.* [126] reported that  $\gamma$ -mangostin attenuated both constitutive and LPS-induced expression and the activity of COX-2 in C6 rat glioma cells by blocking the IKK activity and NF- $\kappa$ B-mediated transcription.

Besides xanthones, phenolic acids and anthocyanins present in mangosteens possess cancer chemopreventive properties. For example, oral administration of either caffeic acid or ferulic acid decreased B[a]P-induced forestomach tumor formation in ICR/Ha mice [127]. Caffeic acid induced apoptosis in human fibrosarcoma HT1080 cells by generating ROS [128]. Ferulic acid, given by gavage, significantly inhibited DMBA-induced formation of rat mammary tumor [129], hamster buccal pouch carcinomas [130], and mouse skin papillomas [131]. Dietary administration of ferulic acid attenuated 4-nitroquinoline-1-oxide (4NQO)-induced rat tongue carcinogenesis [132] and AOM-induced ACF formation in rat colon [133]. Ferulic acid also inhibited proliferation and induced apoptosis in cancer cells in culture [134, 135]. Protocatechuic acid is another chemopreventive phenolic acid present in mangosteens. Lin *et al.* [136] reported that protocatechuic acid inhibited the migration of gastric cancer cells and attenuated the liver metastasis of B16/F10 melanoma xenograft in nude mice. According to this study, protocatechuic acid suppressed the expression and the activity of MMP-2 and downregulated the NF- $\kappa$ B activity by blocking Ras/Akt-mediated signaling [136]. Incubation of human cancer cells with protocatechuic acid induced apoptosis, which was associated with the activation of caspase-3 and -8 [137]. Feeding with protocatechuic acid containing diet significantly decreased the occurrence of advanced tongue squamous cell carcinomas in rats [138]. Dietary administration of protocatechuic acid also suppressed DMBA-induced hamster cheek pouch carcinogenesis [139] and *N*-nitroso-*bis*(2-oxopropyl)amine-induced hamster pancreatic carcinogenesis [140].

## **2.5.6 Persimmons**

Persimmons (*Diospyros kaki* Thunb., Ebenaceae), widely grown in the northeastern part of Asia, are consumed in either a fresh or a dried form. Several varieties of persimmons are commonly known as “kham” in Korea or “kaki” in Japan. Fresh persimmons are available only during autumn and winter. Sun-dried persimmons, known as “kot-kham,” are consumed as a popular snack in Korea. The alcoholic extracts of dried persimmon retained almost equal quantities of dietary fibers, trace elements, and polyphenolic substances as that of fresh fruits [141, 142]. The methanol extracts of dried persimmon exhibited almost an equal antioxidant and free radical scavenging property as that of fresh fruits [141]. Kim *et al.* [143] demonstrated that the ethylacetate fraction of dried persimmons conserved the highest amount of phenolic compounds and elicited the most potent antioxidant activity. The polyphenol-rich ethylacetate extracts of dried persimmon attenuated LPS-induced TNF $\alpha$  production in human monocyte THP-1 cells. Catechins are the major polyphenolic compounds present in persimmons. Treatment of human leukemia Molt 4B cells with persimmon extracts or its flavonoid constituents, such as epicatechin (EC), epicatechin gallate (ECG), epigallocatechin (EGC), or epigallocatechin gallate (EGCG), inhibited ODC expression and induced apoptosis [19]. Among these catechin polyphenols, EGCG has been extensively investigated for its

cancer chemopreventive activity [144]. Topical application of EGCG inhibited UVB-induced DNA damage and mouse skin papillomagenesis [145] and induced apoptosis in mouse skin tumors [146]. Administration of EGCG by gavage attenuated TPA-induced COX-2 expression in mouse skin by blocking the activation of MAP kinases and the DNA binding of NF-κB and cyclic adenosine monophosphate (AMP) response element binding (CREB) protein [147, 148]. Likewise, EGCG diminished TPA-induced NF-κB activation in mouse epidermal JB6 cells [149]. Treatment with EGCG induced apoptosis of various human cancer cells including chondrosarcoma [150], fibrosarcoma [151], human ovarian [152], colon [153], cervical [154], and prostate [155] cancer cells.

Other major chemopreventive phytochemicals present in persimmons are triterpenoids, such as oleanolic acid and ursolic acid [156]. Multiple lines of evidence suggest that these compounds possess cancer chemopreventive potential. Both oleanolic acid and ursolic acid inhibited the proliferation of either parent or multidrug-resistant human colon cancer cells (SW480), and leukemia (HL60), and breast cancer (MCF-7) cells and induced apoptosis by downregulating the expression of Bcl-xL, Bcl-2, and survivin [157]. Treatment of human hepatocellular carcinoma (HuH7) cells with oleanolic acid or ursolic acid induced sub-G1 arrest. According to this study, oleanolic acid- or ursolic acid-induced cell death was associated with induction of caspase-9 and -3 activity, the cleavage of polyadiporibosyl polymerase (PARP), the downregulation of the NF-κB activity, and the expression of X-linked inhibitor of apoptosis (XIAP) [158]. Oleanolic acid and ursolic acid elevated the activity of caspase-3 and -8, and diminished the expression of MMP and VEGF in human liver cancer (HepG2, Hep3B, HuH7, and HA22T) cells [159]. Incubation of human breast cancer (MDA-MB231) cells with ursolic acid resulted in mitochondria-dependent as well as death receptor-mediated apoptosis [160]. Treatment with ursolic acid attenuated the growth of human prostate cancer cell xenograft in nude mice and inhibited the proliferation of prostate cancer (DU-145 and LNCaP) cells by blocking the activation of NF-κB and STAT3 signaling pathways [161]. In a transgenic adenocarcinoma of mouse prostate (TRAMP) model, ursolic acid was found to suppress metastatic progression of prostate cancer, partly by blocking the expression of C-X-C chemokine receptor-4 (CXCR4) and the activation of NF-κB [162].

## 2.5.7 Prunes

Prunes are dried plums of *Prunus domestica* L., Rosaceae). They are produced by dehydrating fresh plums in a hot-air (85–90°C) tunnel dehydrator to reduce the moisture content from 75 to 21% and can be stored at ambient temperature for at least 1 year. Because of their hardness, prunes are subjected to rehydrate before consumption. The total antioxidant capacity of prunes extracts was highest among dried fruits [27, 29]. Despite partial loss of carotenoids present in fresh plums during prune processing, considerable amounts of lutein, β-carotene, and α-carotene were detected in dried prunes [39]. The antioxidative [163] and chemopreventive activity [164–166] of carotenoids, such as β-carotene and lutein, have been well documented. Prunes also contain a trace amount of β-carboline alkaloids [167]. β-Carboline exerts anticancer effects by acting as an inhibitor of the cell cycle regulatory protein CDK4 [168], inducing cancer cell death [169], and blocking DNA synthesis selectively in cancer cells [170].

Prunes also contain large amounts of phenolic compounds, such as chlorogenic acid, neochlorogenic acid, and hydroxycinnamic acids [37]. Kayano *et al.* [171] identified

chlorogenic acid, neochlorogenic acid, and cryptochlorogenic acids as the major antioxidants in prunes. Topical application of chlorogenic acid inhibited TPA-induced ODC activity and chemically induced papillomagenesis in mouse skin [172]. A diet containing chlorogenic acid protected against *N*-methyl-*N*-nitrosourea (MNU)-induced glandular stomach carcinogenesis in rats [173]. Treatment with chlorogenic acid inhibited TPA-induced transformation of mouse epidermal JB6 P+ cells by blocking phosphorylation of MAP kinases and activation of AP-1 and NF-κB [174]. Moreover, chlorogenic acid activated nuclear factor erythroid related factor-2 (Nrf2) and induced the expression and activity of antioxidant enzyme glutathione-S-transferase (GST)-A in JB6 cells [174]. Incubation with chlorogenic acid induced apoptosis in chronic myelogenous leukemia cells by suppressing Bcr-Abl kinase and inducing p38 MAP kinase [175]. Thus prunes, because of their chlorogenic acid content, hold the potential to be a good chemopreventive agent.

Kimura and colleagues isolated oligomeric proanthocyanidins from the methanol extract of prunes. These proanthocyanidins showed a better *in vitro* antioxidative effect than chlorogenic acid [176]. The oligomeric proanthocyanidins comprising of EC and catechin monomers might contribute to the anticancer activity of prunes. Increasing intake of proanthocyanidins reduced the risk of pancreatic [177], gastric [178], and colorectal [179] cancers. Proanthocyanidins inhibited the growth of non-small-cell-lung cancer cells by suppressing PGE<sub>2</sub> production and blocking PGE<sub>2</sub> receptor, subtype-2 (EP2) receptor signaling [180]. The pro-apoptotic and antiangiogenic effects of proanthocyanidins are associated with their ability to activate caspases and to inhibit the activation or expression of NF-κB, MAP kinases, PI3K/Akt, and cell cycle regulatory proteins, and the release of cytokines and growth factors [181].

Prunes contain high dietary fiber, which is known to reduce the risk of colorectal cancer [182]. One of the risk factors for colorectal cancer is the generation of secondary bile acids from primary bile acids by large intestinal microflora [183]. In a pilot human study comprising 41 men, intake of prunes reduced the fecal content of secondary bile acid and lithocholic acid [184], indicating the possible beneficial effects of prunes against colorectal carcinogenesis. The ethanol fraction of concentrated prune juices reduced the viability of human colon cancer cells (Caco-2 and KATO III), but not that of normal colon epithelial (CCD-18Co) cells [185]. In contrast, dietary administration of prune powders did not affect AOM-induced ACF formation in rats. However, this study demonstrated that prune diets reduced total fecal and secondary bile acid concentrations [186].

## 2.5.8 Raisins

Raisins are dried grapes of four different varieties, including Thompson seedless, Muscat, Sultana, and Black Corinth. About 90% of the total raisin supply in the United States is in the form of dark raisins made from Thompson seedless grapes. Other popular varieties of raisins include golden raisins prepared from Muscat grapes, Zante currants made from Black Corinth grapes, and European Sultanas raisins produced from seedless yellow grapes. Due to the loss of moisture during the drying process, the total protein, sugars, and fiber content of fresh grapes become concentrated in raisins [187] and a high sugar, low moisture condition prevents spoilage of raisins during storage. Besides macronutrients, the concentration of minerals is usually 3- to 7-fold higher in raisins than in fresh grapes. However, the drying process leads to the loss of certain vitamins, such as vitamin A, C, and K [188].

Other nonnutritive phytochemicals, especially polyphenols, in raisins are considered to be similar to those present in fresh grapes. However, a remarkable difference in the phenolic contents in raisins and fresh grapes has been noted. Raisins contain higher levels of phenolics than do their fresh counterparts [29, 32]. Major phenolic compounds present in raisins and fresh grapes are phenolic acids and flavonols. As compared with fresh and frozen grapes, sun-dried raisins and golden raisins exhibited better ORAC and a higher content of *trans*-caftaric acid, *trans*-coutaric acid, rutin, quercetin glycosides, and kaempferol glycosides [32]. The increased concentration of total phenolics in raisins may result from the lack of polyphenol oxidase in raisins, and the loss of moisture and modification of certain phenolic compounds during drying processes [29]. In contrast, Karadeniz *et al.* [189] reported that 90% of phenolic acids (e.g., *trans*-caftaric acid and *trans*-coutaric acid) in fresh grapes are lost during processing of grapes into sun-dried raisins. These authors have also demonstrated that procyanidins and flavonols are completely decomposed during the processing of raisins. The reason for such discrepancies may be due to the different grape cultivars, drying temperature, the drying process, and the method of solvent extraction of raisins to obtain phenolic compounds. While stilbenoids, in particular resveratrol, are present in grapes and wine, resveratrol was not detected in raisins [32, 189]. Zhao and Hall [190] reported the presence of catechins and phenolic acids, such as gallic acid, ferulic acid, and chlorogenic acid, in raisins. Thus, more rigorous analysis of the chemical composition of raisins may help to better understand the chemopreventive potential of raisins.

Despite inconsistent data on the phenolic compounds present in raisins as compared to fresh grapes [191], the presence of trace amount of isoflavones, such as daidzein and genistein [192], and chlorogenic acid [190] in raisins suggests the cancer chemopreventive potential of these dried fruits. Moreover, because of the high dietary fiber content, raisins may protect against colon carcinogenesis. Daily consumption of raisins have been shown to decrease urinary excretion of 8-epi-PGF<sub>2α</sub> [193] and 8-hydroxy-2-deoxyguanosine [194], markers of inflammation and oxidative DNA damage, respectively. Thus, the assessment of anticancer effects of raisins merits further investigation.

## 2.5.9 Kiwi fruits

Kiwi (*Actinidia chinensis* L. syn. *Actinidia deliciosa*) fruits are traditionally used for the treatment of many different types of cancers, for example, stomach, lung, and liver cancer in folk medicine. Kiwi fruit extracts inhibit the growth of cancer cells. Kiwi fruits protected against oxidative DNA damage, thereby inhibiting neoplastic cell transformation [195], and the growth of sarcoma 180 in mice [196]. Chemical analysis of kiwi fruit peels and pulps revealed that the fruits are rich in vitamin E, tocopherols, sterols, ursolic acid, chlorogenic acid, and several flavonoids [197]. Freeze-dried pulp extracts of kiwi fruit attenuated H<sub>2</sub>O<sub>2</sub>-induced lymphocyte DNA damage [198]. Hydrophilic fractions of 70% methanol extracts of dried kiwi fruit elicited free radical scavenging activity and inhibited growth of human squamous carcinoma (HSC-2) cells [196]. Moreover, methanol extracts of freeze-dried kiwi fruit powder and their bioactive flavonoid quercetin showed antioxidant activity and inhibited H<sub>2</sub>O<sub>2</sub>-induced disruption of gap-junction intercellular communication in rat liver epithelial (WB-F344) cells by restoring connexin-43 expression and blocking ERK phosphorylation [199].

### 2.5.10 Other dried fruits

Several other dried fruits are commercially available and widely consumed throughout the world. These include apricots, apples, figs, snake fruits, star fruits, guavas, bananas, etc. Apricots are important for their minerals and other nutrients. Sulfurized (sulfur-dried) apricots retain selenium, though to a lesser extent than the fresh fruits [200], which possesses anti-cancer properties [201]. MK615, a formulation developed from Japanese apricots, decreased the viability of MDA-MB231 and MCF-7 cells [202]. Intake of dried Japanese apricots protected against *Helicobacter pylori*-induced chronic atrophic gastritis, a pathological condition often leading to gastric cancer [203]. Moreover, diet containing 15 or 30% sun-dried apricot powders diminished ethanol-induced liver damage in rats by suppressing malondialdehyde production and activating cytoprotective enzymes such as quinone reductase, SOD, GST, and glutathione peroxidase, indicating its potential to prevent liver carcinogenesis [204].

The latex of fresh figs contains polyphenolic compounds. Incubation of human glioblastoma and hepatocellular carcinoma cells with fig's latex reduced proliferation and colony formation, and induced apoptosis in these cells [205]. Significantly higher concentrations of organic acids and phenolic compounds, such as chlorogenic acid, catechin, EC, kaempferol-3-O-glucoside, and luteolin-8-C-glucosides, were detected in sun-dried or oven-dried figs as compared with fresh figs [206]. Thus, dried figs may be utilized for the prevention of cancer. The cancer chemopreventive activity of these dried fruits merits further investigation.

## 2.6 Conclusions

Fruits are nature's gift to mankind both for providing nutrition and for preventing diseases. Although research done until now indicates that consumption of dried fruits can reduce the risk of cancer, more extensive studies are required to examine the chemopreventive potential of diverse classes of dried fruits and to unravel their molecular mechanisms. One of the major safety concerns with regard to dried fruits is the microbial spoilage during storage and the potential health hazard resulting from microbial toxins [207, 208]. Dried fruits can be contaminated with aflatoxins, ochratoxin-A, kojic acid, and, occasionally patulin or zearalenone [209]. Thus, dried fruits must go through routine quality assessment before consumption. Moreover, drying of fresh fruits at high temperature may generate Maillard reaction products, which are potentially genotoxic. Metabolites of 5-(hydroxymethyl)-2-furfural, a Maillard reaction product, have been detected in the urine of human volunteers receiving dried prune juices [210]. The aqueous extract of several commercially available dried fruits induced clastogenic activity as revealed by increased chromosome breaks or exchanges per metaphase plate in cultured Chinese hamster ovary (CHO) cells. Incubation with a liver microsomal S9 mixture reduced this clastogenic effect of dried fruits [211]. To avoid non-enzymatic browning reactions, processing of dried fruits should be carried out at relatively low temperatures. Besides heat-catalyzed Maillard reactions, an enzymatic browning reaction occurs in dried fruits. Appropriate processing can prevent browning of dry-processed fruits. For instance, pretreatment of sliced apples by pineapple juices reduced the rate and extent of enzymatic browning reaction. Other preprocessing techniques include bisulfate and ascorbic acid treatment of fresh fruits prior to hot-air or oven drying. With the advancement in food processing technology, a wide variety of dried fruits and their combinations are now available in the shelves of supermarkets, indicating the increased

popularity of dried fruits. Someday, dried fruits may be exploited to develop functional foods for the prevention of cancer.

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# **Part 1**

## Dried Berries

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### **3 Phytochemicals and health benefits of blackberries and black currants**

Haiming Shi and Liangli (Lucy) Yu

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#### **3.1 Introduction**

Berry fruits are widely consumed not only in fresh and frozen forms but also as processed or derived products including juices, jams, wines, jellies, and canned fruits. Recently, there has been a growing trend toward utilization of berry extracts in functional foods and dietary supplements for health promotion and disease risk reduction [1–3].

Blackberries (genus *Rubus*, Rosaceae) are widely distributed worldwide and their overall consumption has increased rapidly in the past 10 years [4]. Besides vitamins and dietary fiber, blackberries are rich in phenolic compounds including anthocyanins, flavonols, tannins, and phenolic acids [5]. Numerous studies have shown that these phenolic compounds may possess various biological benefits associated with their antioxidant, anticancer, antineurodegenerative, and anti-inflammatory properties [1, 3, 5]. On the other hand, black currants (*Ribes nigrum* L.) are a species of *Ribes* berry native to central and northern Europe and northern Asia. Black currants are one of the richest sources of antioxidants, notably anthocyanins, hydroxycinnamic acids, and vitamin C [6]. Their extracts have been shown to inhibit the development of certain types of cancers, cardiovascular disease (CVD), and chronic inflammation-related diseases [7, 8].

This chapter highlights the compositional and nutritional characteristics, phytochemicals, health effects, and food applications of fresh blackberries and black currants with particular references to their dried counterparts when data are available.

#### **3.2 Compositional and nutritional characteristics of blackberries and black currants**

The nutrient value in fresh blackberries and black currants has been reported by United States Department of Agriculture (USDA) [9] (Table 3.1). The values may vary in fruits growing at different locations and in different years.

**Table 3.1** Compositional and nutritional characteristics of blackberries and black currants (values in per 100 grams edible portion)

<b>Nutrient</b>	<b>Units</b>	<b>Fresh blackberries</b>	<b>Fresh black currants</b>
<b>Proximate composition</b>			
Water	g	88.15	81.96
Energy	kcal	43	63
Protein	g	1.39	1.40
Lipid	g	0.49	0.41
Ash	g	na	na
Carbohydrate	g	9.61	15.38
Dietary fiber	g	5.3	na
Sugars	g	4.88	na
<b>Minerals</b>			
Calcium	mg	29.0	55
Copper	mg	na	na
Iron	mg	0.62	1.54
Magnesium	mg	20.0	24.0
Manganese	mg	na	na
Phosphorus	mg	22.0	59.0
Potassium	mg	162	322
Selenium	μg	na	na
Sodium	mg	1.0	2.0
Zinc	mg	0.53	0.27
<b>Vitamins</b>			
Betaine	mg	na	na
Choline	mg	na	na
Folate (DFE)	μg	25.0	na
Niacin	mg	0.65	0.30
Pantothenic acid	μg	nd	nd
Pyridoxine	mg	0.03	0.07
Riboflavin	mg	0.03	0.05
Thiamin	mg	0.02	0.05
Vitamin A (RAE)	μg	11.0	12.0
Vitamin C	mg	21.0	181
Vitamin E (ATE)	mg	1.17	1.0
Vitamin K	μg	19.8	na

Source: Adapted from USDA database [9].

Note: Some numbers are rounded to the second digit after decimal point.

DFE, dietary folate equivalents; RAE, retinol activity equivalents; ATE, alpha-tocopherol equivalents; na, not available; nd, not detected.

### 3.2.1 Dietary fiber

Blackberries and black currants contain high levels of dietary fiber. The total fiber content of frozen blackberries is 7.1 g/100 g fresh weight, which is higher than other berry species [10]. Forty-two food products, including vegetables and fruits from Belgium, were examined for dietary fiber and the second highest fiber content in fruits was detected in blackberries (4.87 g/100 g) [11]. Chokeberries, bilberries, and black currants collected at maturity were analyzed for acid-detergent fiber [12]. The highest fiber concentration was found in black currants.

### 3.2.2 Vitamin C

Vitamin C is widely distributed in many fruits and vegetables and is well known for its antioxidant activity, as it acts as a reducing agent to reverse oxidation in food and biological systems. Kafkas *et al.* [13] reported the vitamin C content of five blackberry genotypes from Turkey by high-performance liquid chromatographic (HPLC) analysis. Vitamin C was detected in “C. Thornless” (2.5 mg/g extract), “Bursa 2” (4.6 mg/g extract), and “Loch Ness” (14.9 mg/g extract), but not in “Navaho” or “Jumbo” cultivars. In addition, 11 types of blackberries, harvested in different seasons and regions in Mexico and in the United States, were collected and their vitamin C content was determined [14]. Levels of vitamin C ranged from 0.82 mg/g in “Brazos” (from Zitácuaro harvested in spring) to 0.08 mg/g in “Comanche” (from autumn harvest in Zirahuen). Several studies reported the vitamin C content in black currants. Seventeen UK-grown black currant cultivars were analyzed for their vitamin C content [6]. The concentration of vitamin C ranged from 1.92 to 5.41 mg/g fresh weight, which is much higher compared with that in other commonly consumed berry fruits in which the vitamin C content is commonly  $>1$  mg/g fresh weight, confirming that black currants are a good source of vitamin C. In summary, both blackberries and black currants are excellent dietary sources of vitamin C and different cultivars may differ significantly in their vitamin C concentrations.

### 3.2.3 Vitamin E

Vitamin E is found in many fruits including blackberries and black currants. Chun *et al.* [15] determined tocopherol and tocotrienol levels in fruits and vegetables from the United States. The  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -tocopherol levels of blackberries were 1.43, 0.04, 1.42, and 0.85 mg/100 g edible weight, respectively, while tocotrienols were not detected. However, the information on vitamin E composition of black currants is lacking. Overall, blackberries contained much higher levels of vitamin E than some other commonly consumed berries.

### 3.2.4 Sugars

Kafkas *et al.* [13] analyzed the major soluble sugar contents of five blackberry genotypes from Turkey by HPLC. They found that fructose was the most abundant sugar and its level was greatest in the “Navaho.” Sugar was also examined for 52 blackberry samples [16]. Sucrose, glucose, and fructose were found in blackberries. Sucrose levels varied greatly, ranging from 0 to 12.9% of total sugars, with a mean of 4.6%. Glucose and fructose were the dominant sugars present in nearly equal quantities, with the overall glucose to fructose ratio ranging from 0.81 to 1.17. In addition, Bordonaba and Terry [6] reported the sugar composition of 17 UK-grown black currant cultivars. Sucrose, glucose, and fructose were identified in all cultivars, and concentrations ranged between 3.38 and 36.89, 36.86 and 82.78, and 43.43 and 85.73 mg/g fresh weight, respectively. The proportion of each sugar also varied with genotype. Glucose and fructose were the dominant sugars found in all black currant cultivars, making up 40 and 49% of total sugars, respectively. Sucrose, on the other hand, made up 10% of the total sugar concentration but was more variable among cultivars. Impact of latitude and weather conditions on the sugar composition of black currants in Finland was reported [17]. Thus, the level of sugars in blackberries and black currants is

influenced by genetic and environmental factors, including cultivar, maturity, and weather conditions.

### 3.2.5 Minerals

Wu *et al.* [18] determined the content of minerals, including Ca, Fe, K, Mg, Na, Se, and Zn, in five blackberry cultivars (“Navaho,” “Young,” “Brazos,” “Boysen,” and “Triple Crown”) in China. The levels of Ca, K, and Mg were higher than other determined minerals, and K was present in the highest amount and above 1.0 mg/g fresh weight in all tested blackberry samples, except “Boysen.” There was no significant difference ( $P > 0.05$ ) in the mineral contents among the five blackberry cultivars. Furthermore, Ilkay *et al.* [19] reported little change in Ca, K, Mg, and Zn concentrations during ripening of blackberries. In addition, Huo *et al.* [20] reported that black currants contained Ca (0.38 mg/kg), Cu (1.1 mg/kg), Fe (8.7 mg/kg), K (3.04 mg/kg), Mg (0.07 mg/kg), Mn (0.7 mg/kg), Na (0.047 mg/kg), and Zn (23.6 mg/kg).

### 3.2.6 Amino acids

Wu *et al.* [18] reported the amino acid content of five blackberry cultivars collected in China. All samples contained eight essential amino acids and had different total amino acid contents, ranging from 7.91 to 15.21 mg/g fresh weight. According to the review by Huo *et al.* [20], black currants also contained eight essential amino acids, and histidine and lysine concentrations were 108.2 and 64.6 mg/kg fresh weight, respectively.

## 3.3 Phytochemicals in blackberries and black currants

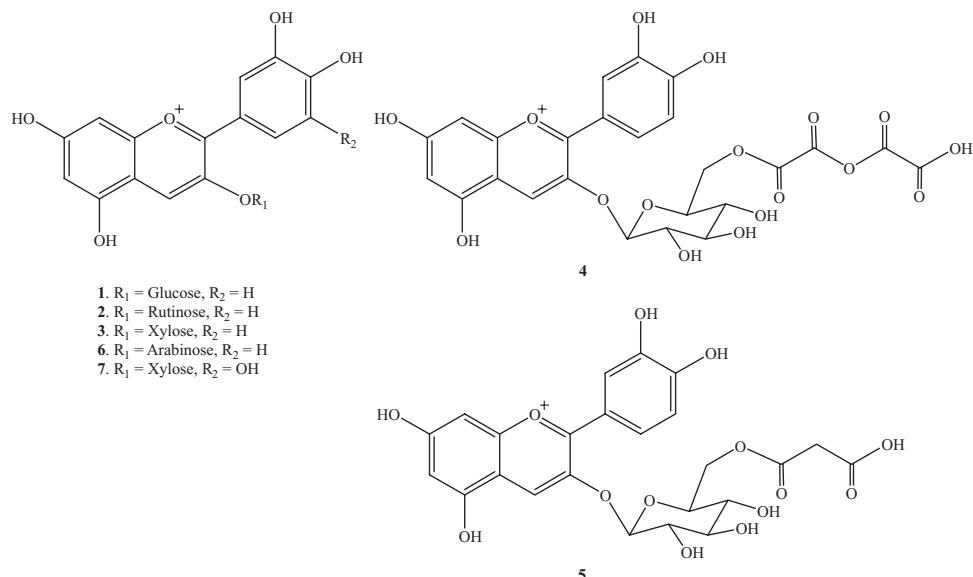
### 3.3.1 Flavonoids

Flavonoids are polyphenolic compounds and represent a large group of secondary plant metabolites. Structurally, flavonoids are usually characterized by a C<sub>6</sub>-C<sub>3</sub>-C<sub>6</sub> carbon skeleton, which may occur as aglycones or glycosides. An inverse association between the intake of flavonoids and the risk of chronic diseases has been shown in epidemiological studies [21]. Flavonoids are found in a wide variety of fruits and vegetables. Blackberries and black currants are good dietary sources of flavonoids.

#### 3.3.1.1 Anthocyanins

Anthocyanins are glycosides of polyhydroxy and polymethoxy derivatives of 2-phenylbenzopyrylium or flavylium salts. They have been extensively studied in fruits and vegetables due to their health benefits and potential as natural food colorants. Blackberries and black currants are rich sources of anthocyanins. There is growing evidence that various biological activities of blackberries and black currants are correlated with their anthocyanins contents.

Cyanidin-3-*O*-glucoside (**1**) and cyanidin-3-*O*-rutinoside (**2**) have long been recognized as the respective major and minor anthocyanins in blackberries [22] (Figure 3.1). Sapers *et al.* [23] reported the presence of cyanidin-3-*O*-xyloside (**3**) along with two cyanidin derivatives

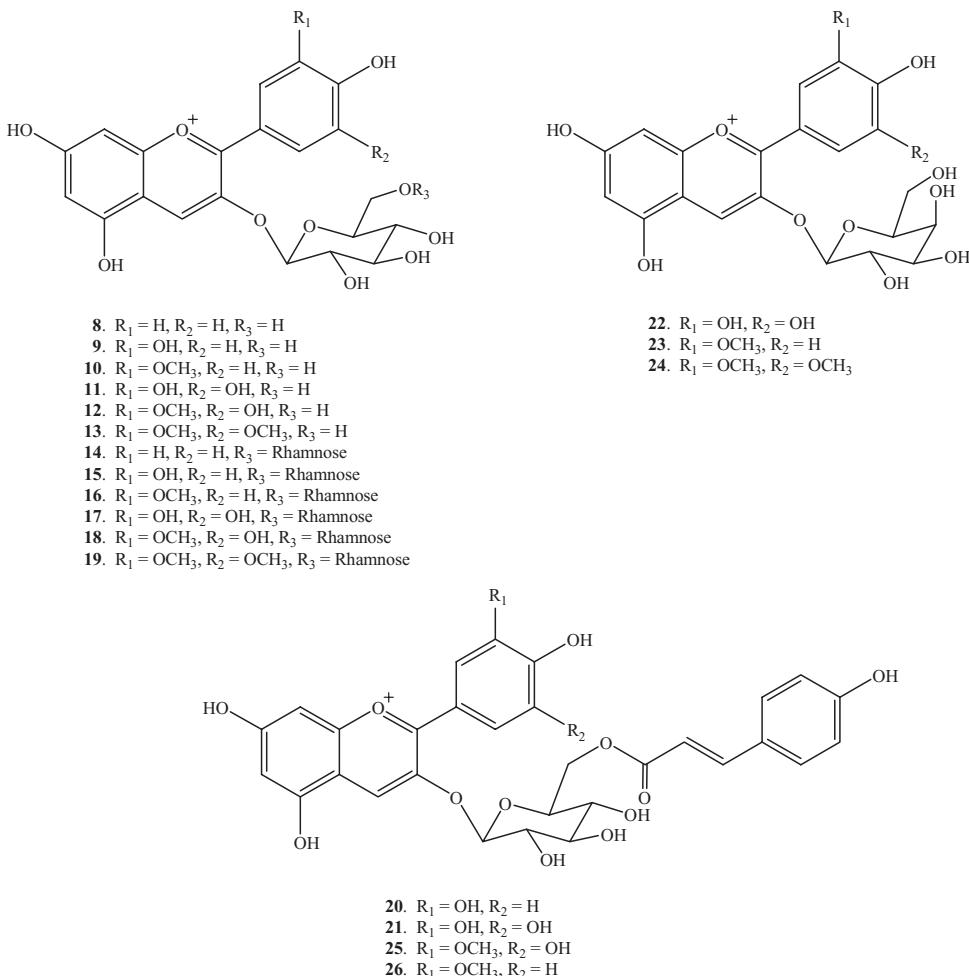


**Figure 3.1** Structures of anthocyanidins isolated from blackberries.

that were vaguely characterized as being substituted with dicarboxylic acids. Later, Fan-Chiang [24] identified one of these anthocyanins as cyanidin 3-*O*-glucoside acylated with malonic acid (**4**) using HPLC–mass spectrometry (HPLC-MS) and chemical reactions. A novel zwitterionic anthocyanin was also isolated from blackberries and structurally characterized as cyanidin 3-*O*-(6''-*O*-dioxalylglicoside) (**5**) [25]. Recently, two minor anthocyanins were also reported in blackberry extracts: one was identified as cyanidin-3-*O*-arabinoside (**6**) and the other one was tentatively deduced as delphinidin-3-*O*-xyloside (**7**) by HPLC-MS analysis [26].

Anthocyanins were also reported in black currants. 3-*O*-glucosides of pelargonidin (**8**), cyanidin (**9**), peonidin (**10**), delphinidin (**11**), petunidin (**12**), and malvidin (**13**); the 3-*O*-rutinosides of pelargonidin (**14**), cyanidin (**15**), peonidin (**16**), delphinidin (**17**), petunidin (**18**), and malvidin (**19**); cyanidin 3-*O*-arabinoside (**6**); and the 3-*O*-(6''-*p*-coumaroylglucoside)s of cyanidin (**20**) and delphinidin (**21**) were found in black currants (Figure 3.2). The four major anthocyanins, the 3-*O*-glucosides and the 3-*O*-rutinosides of delphinidin and cyanidin, made up >97% of the total anthocyanin content [27]. In addition, Borges *et al.* [28] found 11 anthocyanins in a commercial black currant extract including three minor anthocyanins delphinidin-3-*O*-galactoside (**22**), peonidin-3-*O*-galactoside (**23**), and malvidin-3-*O*-galactoside (**24**), which were tentatively identified on the basis of their MS fragmentation profiles. Recently, two anthocyanins petunidin-3-*O*-(6''-coumaroyl) glucoside (**25**) and peonidin-3-*O*-(6''-coumaroyl) glucoside (**26**) were detected in black currants for the first time [29].

The anthocyanin contents in blackberries and black currants might vary with genotype, harvest season, growing location, maturity stage, and other preharvest factors. Bowen-Forbes *et al.* [30] reported that a wild Jamaican-grown blackberry species, *Rubus jamaicensis*,



**Figure 3.2** Structures of anthocyanidins isolated from black currants.

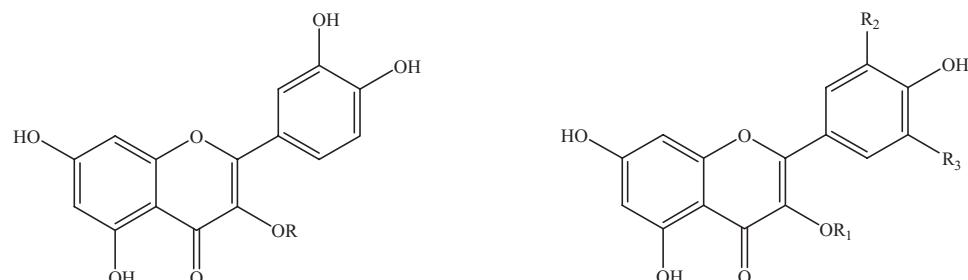
possessed 1673 mg anthocyanins/100 g fresh weight. Fan-Chiang and Wrolstad [31] reported the anthocyanin contents of 51 blackberry samples at 70.3–201 mg of cyanidin-3-O-glucoside equivalents (C3GE)/100 g with a mean value of 137 mg of C3GE/100 g, representing 18 different blackberry varieties and 20 selections from five different geographic locations and three harvest seasons. In addition, Siriwoharn *et al.* [32] observed that the anthocyanin contents in Marion and Evergreen blackberries increased considerably during the course of ripening, which is consistent with previous investigations [23].

The anthocyanin contents of 17 UK-grown black currant cultivars were analyzed [6]. Relative concentrations of cyaniding-3-O-glucoside, cyaniding-3-O-rutinoside, delphinidin-3-O-glucoside, and delphinidin-3-O-rutinoside were 3.1–7.9, 35.4–47.0, 7.6–12.5, and 36.9–50.9%, respectively. In an earlier study, Anttonen and Karjalainen [33] compared the anthocyanin profiles of organically and conventionally grown black currants from commercial

farms within a climatically similar area. Significant differences ( $P < 0.05$ ) were found between farms for all other three compounds but not for cyanidin-3-*O*-rutinoside. The data from these research findings also showed that cultivation technique was not a major factor in determining the anthocyanin contents of black currants.

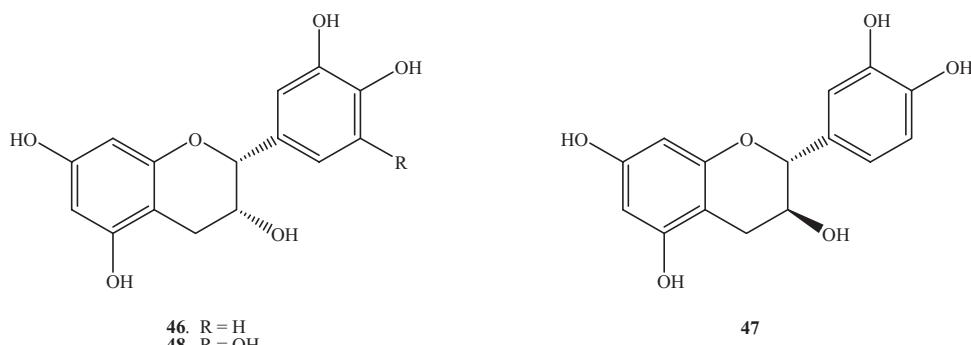
### 3.3.1.2 Flavonols

Flavonols are a class of flavonoids that have the 3-hydroxyflavone backbone. Besides anthocyanins, flavonols from berries are considered as another group of compounds that play an important role against oxidative damage in biological systems due to their potential ability to scavenge free radicals. Cho *et al.* [34] identified eight flavonols of quercetin and quercetin–sugar conjugates in Kiowa blackberries, namely, rutinoside (**27**), galactoside (**28**), methoxyhexoside (**29**), glucoside (**30**), pentoside (**31**), [ $6''$ -(3-hydroxy-3-methylglutaroyl)]- $\beta$ -galactoside (**32**), glucosylpentoside (**33**), and oxalylpentoside (**34**) (Figure 3.3). They also quantified the contents of individual flavonols in six blackberry genotypes. Quercetin 3-*O*-galactoside was the predominant flavonol in the “Apache,” “Arapaho,” “Kiowa,” and “Navaho,” while quercetin 3-*O*-glucoside was the primary flavonol in the “Prime-Jim” and “Chickasaw.” Eight flavonols were identified as myricetin-3-*O*-rutinoside (**35**), myricetin-3-*O*-glucuronide (**36**), myricetin-3-*O*-( $6''$ -malonyl)glucoside (**37**), quercetin-3-*O*-rutinoside (**27**), quercetin-3-*O*-glucoside (**30**), quercetin-3-*O*-( $6''$ -malonyl)glucoside (**38**), kaempferol-3-*O*-rutinoside (**39**), and kaempferol-3-*O*-galactoside (**40**) in black currant extracts by HPLC-MS [28] (Figure 3.3). The HPLC-based quantitative procedure, with improved extraction and hydrolysis, was used to analyze the content of quercetin, myricetin, and kaempferol in 10 black currant cultivars from organic farms and in 5 cultivars from conventional farms [35]. Myricetin was the most abundant flavonol, and its amount varied significantly among cultivars, from 8.9 to 24.5 mg/100 g fresh weight. The quercetin level in black currants



- 27.** R = Rutinose
- 28.** R = Galactose
- 29.** R = Methoxyhexose
- 30.** R = Glucose
- 31.** R = Pentose
- 32.** R = [ $6''$ -(3-hydroxy-3-methylglutaroyl)]-galactose
- 33.** R = Glucosylpentose
- 34.** R = Oxalylpentose
- 38.** R = ( $6''$ -malonyl)-glucose
- 35.** R<sub>1</sub> = Rutinose, R<sub>2</sub> = OH, R<sub>3</sub> = OH
- 36.** R<sub>1</sub> = Glucuronic acid, R<sub>2</sub> = OH, R<sub>3</sub> = OH
- 37.** R<sub>1</sub> = ( $6''$ -malonyl)-glucose, R<sub>2</sub> = OH, R<sub>3</sub> = OH
- 39.** R<sub>1</sub> = Rutinose, R<sub>2</sub> = H, R<sub>3</sub> = H
- 40.** R<sub>1</sub> = Galactose, R<sub>2</sub> = H, R<sub>3</sub> = H
- 41.** R<sub>1</sub> = Glucose, R<sub>2</sub> = OH, R<sub>3</sub> = OH
- 42.** R<sub>1</sub> = Rutinose, R<sub>2</sub> = OCH<sub>3</sub>, R<sub>3</sub> = H
- 43.** R<sub>1</sub> = Glucose, R<sub>2</sub> = H, R<sub>3</sub> = H
- 44.** R<sub>1</sub> = Arabinose, R<sub>2</sub> = OH, R<sub>3</sub> = OH
- 45.** R<sub>1</sub> = Glucose, R<sub>2</sub> = OCH<sub>3</sub>, R<sub>3</sub> = H

**Figure 3.3** Structures of flavonols isolated from blackberries and black currants.



**Figure 3.4** Structures of flavanols isolated from blackberries and black currants.

also varied widely among the cultivars, from 5.2 to 12.2 mg/100 g fresh weight. The levels of kaempferol in black currant cultivars were low, ranging from 0.9 to 2.3 mg/100 g. Koponen *et al.* [36] reported the existence of three flavonols myricetin-3-*O*-glucoside (**41**), isorhamnetin-3-*O*-rutinoside (**42**), and kaempferol-3-*O*- glucoside (**43**), together with two unreported flavonols, myricetin-3-*O*-arabinoside (**44**) and isorhamnetin-3-*O*-glucoside (**45**), in black currants (Figure 3.3).

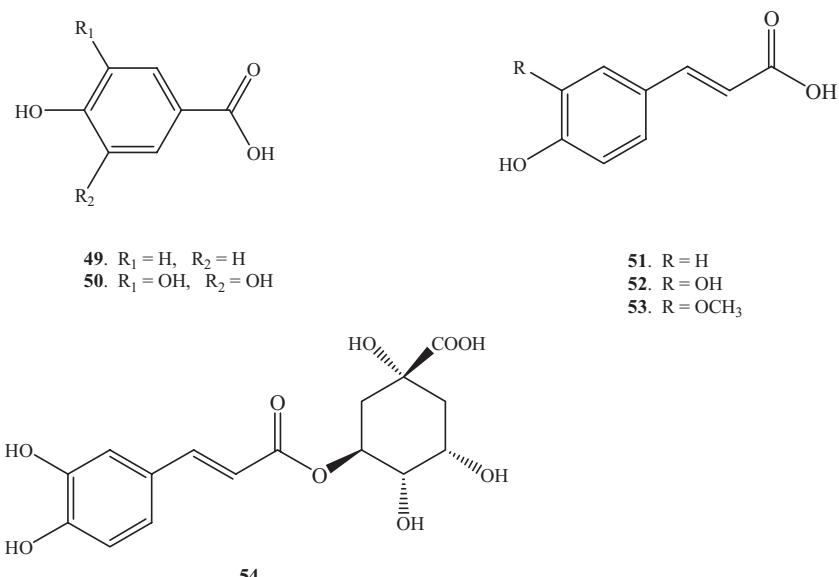
### 3.3.1.3 Flavanols

Unlike the other classes of flavonoids, flavanols are usually found in free rather than glycosylated or esterified form in fruits. Mertz *et al.* [37] identified and quantified (-)-epicatechin (**46**) in two blackberry species (*Rubus glaucus* and *Rubus adenotrichus*) (Figure 3.4). Catechin was detected in two blackberry cultivars: “Choctaw” (313 mg/100 g fresh weight) and “Kiowa” (266 mg/100 g fresh weight) [38]. Black currants contain low levels of the flavanols, (+)-catechin (**47**), (-)-epicatechin (**46**), and (-)-epigallocatechin (**48**) [39], all identified by HPLC-MS analysis [40] (Figure 3.4).

## 3.3.2 Phenolic acids

Phenolic acids constitute about one-third of the dietary phenols, and may occur in plants in the free and bound forms. Bound phenolic acids may be linked to various plant components through ester, ether, and/or acetal bonds [41]. Phenolic acids can be subdivided into two major groups: hydroxybenzoic and hydroxycinnamic acid derivatives. They have various biological activities such as antioxidant and antimutagenic activities [42, 43].

Five phenolic acids such as *p*-hydroxybenzoic (**49**), gallic (**50**), *p*-coumaric (**51**), caffeic (**52**), and ferulic acids (**53**) were quantified in two blackberry cultivars [38] (Figure 3.5). The concentrations were 4.12–6.42, 0.4–2.08, 1.38–3.64, and 2.99–3.51 mg/100 g fresh weight for gallic, *p*-coumaric, caffeic, and ferulic acids, respectively, whereas *p*-hydroxybenzoic acid was not detectable. Later, gallic acid together with gallic acid esters, caffeic acid ester, *p*-coumaric acid esters, and ferulic acid esters were also reported in two blackberry species [37]. In both blackberries, *p*-coumaric acid esters were the most abundant and caffeic acid ester was the second primary one.

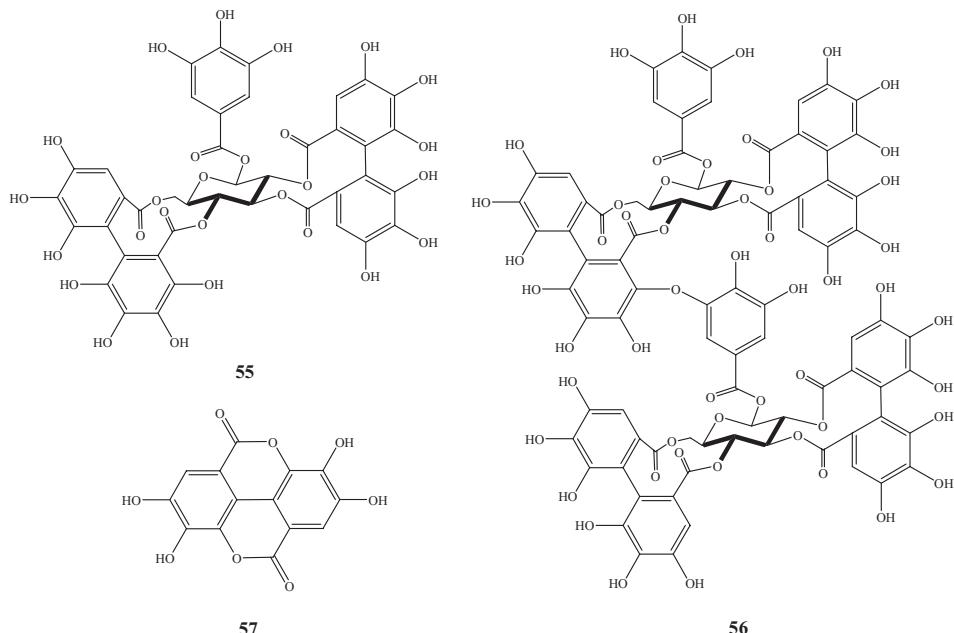


**Figure 3.5** Structures of phenolic acids isolated from blackberries and black currants.

Phenolic acids are also present in black currants. Gavrilova *et al.* [29] reported that a caffeic acid derivative was the major component in black currants; chlorogenic acid (**54**) (Figure 3.5) and derivatives of *p*-coumaric and ferulic acids were also detected, which is in accordance with previous reports [40, 44]. Meanwhile, two minor peaks with *m/z* 421 and 451 in negative ion mode may indicate the presence of *p*-coumaric acid hexose derivative and ferulic acid hexose derivative, respectively. In addition, Zadernowski *et al.* [42] reported the detailed distribution of free, ester-bonded, and glycoside-bonded phenolic acids in blackberries and black currants.

### 3.3.3 Tannins

Tannins are oligomeric and polymeric forms of phenolics and may provide astringency in fruits and vegetables. They are traditionally divided into two classes of condensed and hydrolysable tannins. Hydrolysable tannins contain one or more hexahydroxydiphenic acid moieties, esterified to a polyol, most often to  $\beta$ -D-glucose. Like other berries, blackberries are abundant in hydrolysable tannins. Mertz *et al.* [37] tentatively identified six ellagic acid derivatives and two ellagitannins, sanguin H-6 (**55**) and lambertianin C (**56**), by HPLC-MS in two blackberry species (Figure 3.6). Two isomers of lambertianin A/sanguin H-6, two isomers of lambertianin C, two isomers of pedunculagin, two isomers of castalagin/vescalagin, a isomer of galloyl-hexahydroxydiphenic (galloyl-HHDP) glucose, an isomer of lambertianin D, an isomer of galloyl-*bis*-HHDP glucose, ellagic acid (**57**), and two unknown ellagitannins were detected in blackberry fruits using a combination of HPLC-electrospray ionization-MS (HPLC-ESI-MS) and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) [45]. However, only detailed nuclear magnetic resonance



**Figure 3.6** Structures of representative tannins isolated from blackberries and black currants.

(NMR) analysis allows unambiguous identification due to the diverse and complex nature of tannins. The structural complexity of tannins also makes it difficult to quantify them effectively. Quantitative data on tannins in blackberries have been reported in the last decade by determining acid-hydrolyzed tannins [46, 47].

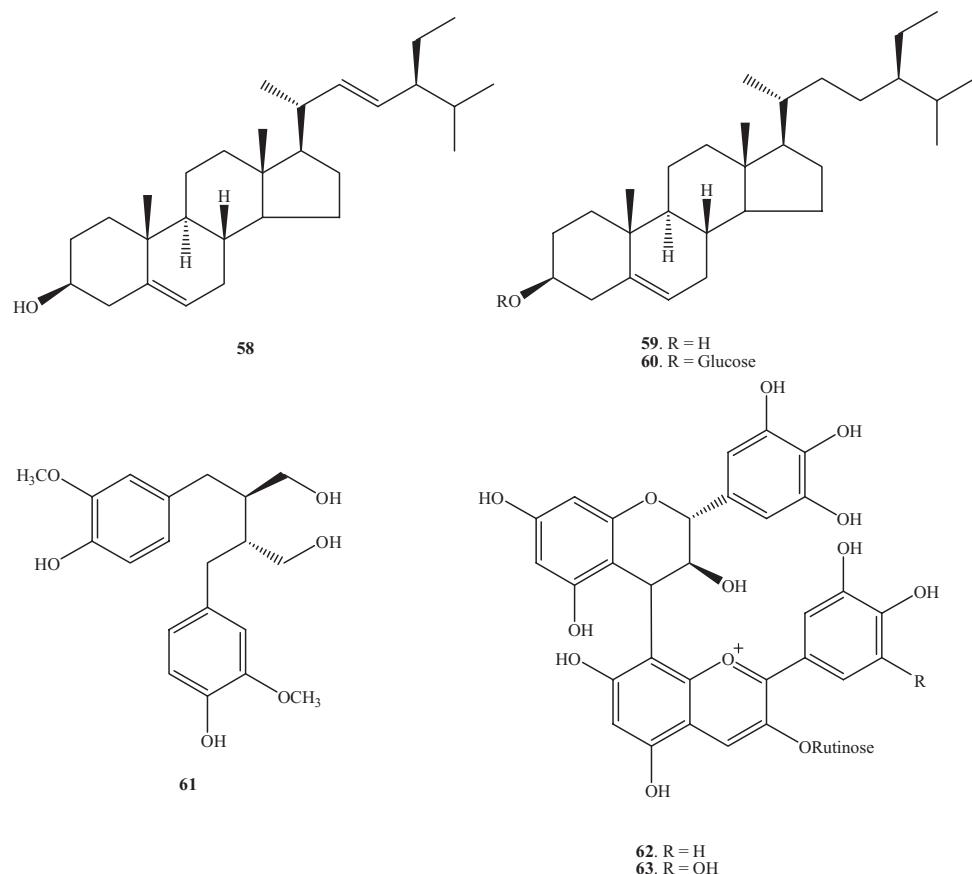
### 3.3.4 Carotenoids

The common carotenoids in blackberries and black currants include lutein, zeaxanthin,  $\beta$ -cryptoxanthin,  $\beta$ -carotene, and  $\alpha$ -carotene [48, 49]. Although carotenoids are a group of effective natural singlet-oxygen quenchers, data on the type and levels of carotenoids in blackberries and black currants are limited, probably due to the difficulties in separating individual carotenoids. Marinova and Ribarova [48] determined the content of lutein, zeaxanthin,  $\beta$ -cryptoxanthin,  $\beta$ -carotene, and  $\alpha$ -carotene in Bulgarian blackberries and black currants. Blackberries had high lutein, zeaxanthin,  $\beta$ -cryptoxanthin,  $\beta$ -carotene, and  $\alpha$ -carotene contents at 270, 29, 30, 9.2, and 100  $\mu\text{g}/100\text{ g}$ , respectively, while only lutein, zeaxanthin, and  $\alpha$ -carotene were detected in black currants at 210, 5.7, and 62  $\mu\text{g}/100\text{ g}$ , respectively. In addition, Heinonen *et al.* [49] reported lutein (440  $\mu\text{g}/100\text{ g}$ ),  $\beta$ -carotene (99  $\mu\text{g}/100\text{ g}$ ), and  $\alpha$ -carotene (trace) in Finnish black currants, whereas Mertz *et al.* [50] detected trace levels of carotenoids in French-grown blackberries. Although berries cannot be considered as good dietary sources of carotenoids, blackberries had a higher level of carotenoids than commonly consumed berries, whereas black currants contained low levels of carotenoids.

### 3.3.5 Other phytochemicals

Besides the above-mentioned compounds, three phytosterols were isolated from freeze-dried blackberries and identified as stigmastera-5,22-dien-3-ol (**58**),  $\beta$ -sitosterol (**59**), and  $\beta$ -sitosterol-3- $\beta$ -D-glucoside (**60**) [51] (Figure 3.7). Blackberries also contained secoisolariciresinol (**61**), which is a lignin resulting from the interactions between two cinnamic acids [52].

McDougall *et al.* [53] reported that black currants might contain a family of flavanol-anthocyanin condensation products (Figure 3.7). Two major condensation products, (E) (+)-allocatechin-cyanidin-3-O-rutinoside (**62**) and (E) (+)-allocatechin-delphinidin-3-O-rutinoside (**63**), could be identified in the fresh black currant extracts. Anttonen and Karjalainen [33] found an aureusidin glucoside in black currants. The fruits of black currant were found to contain cassis polysaccharide (CAPS), consisting of rhamnose, mannose, arabinose, galactose, xylose, and glucose [54]. CAPS might consist of a soluble component and a precipitable component with mean molecular weights of 80 and 600 kDa, respectively, in



**Figure 3.7** Structures of some other compounds isolated from blackberries and black currants.

45% (v/v) ethanol solution. In addition, Hilz *et al.* [55] reported the presence of xyloglucans in black currants, which had a rather simple XXXG-type structure with galactose- and fucose-containing side chains.

## 3.4 Health benefits of blackberries and black currants

### 3.4.1 Antioxidant activities

Blackberries, black currants, and other small fruits are excellent sources of natural antioxidants, which might contribute to their increased popularity in the human diet [5, 9, 56]. Hassimotto *et al.* [57] reported the *in vivo* antioxidant activity of an aqueous extract of blackberries and its two derived fractions, the anthocyanin-enriched fraction (AF) and the ellagitannin-enriched fraction (EF). After 35 days of administration, the AF and EF extracts significantly reduced thiobarbituric acid reactive substance (TBARS) levels and increased glutathione levels in the liver, kidney, and brain of male Wistar rats. The hexane, methanol, and ethanol extracts of blackberries (*R. jamaicensis*) inhibited lipid peroxidation by 74, 53, and 48%, respectively [30]. Antioxidant activity was measured for the low- and high-molecular-weight phenolic fractions (LMWPF and HMWPF) from blackberries by the classical ferric reducing antioxidant potential (FRAP) assay. FRAP values ranged from 2.03 to 3.92 mmol of Fe<sup>2+</sup> equivalents/100 mg of respective fractions [58]. Antioxidant activities of both the crude and anthocyanin-enriched blackberry extracts were determined with oxygen radical absorbance capacity (ORAC) values of 674.2 and 4885 µmol trolox equivalents (TE)/g, respectively [59]. Meanwhile, a cellular antioxidant assay was also determined by the 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH) generated free radicals in INT-407 cells. Similar results indicated that the anthocyanins might contribute a major part of the antioxidant ability to suppress both peroxy radical-induced chemical and intracellular oxidation. The TE antioxidant capacity (TEAC) value of freeze-dried blackberries on 2,2'-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) assay was 406 mmol of TE/g [60]. The antioxidant activities of blackberries ranked fourth and second in the TBARS and ABTS assays in 28 different fruits including cherries, apples, peaches, pears, and grapes, respectively. Results from these studies suggested that anthocyanins were the major contributors to antioxidant capacity in blackberries. Tabart *et al.* [61] reported the antioxidant capacities of different black currant cultivars based on 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging capacity and observed only small differences among the eight tested cultivars. The antioxidant capacity of black currant extracts was also determined using the FRAP assay [28], and it was found that anthocyanins were the major contributors to it. Thus, blackberries and black currants contain antioxidants at a level comparable or greater than that in the commonly consumed fruits such as apples, peaches, pears, and grapes.

### 3.4.2 Anticancer activities

A number of *in vitro* and animal studies have shown that berries might have anticancer properties. The lyophilized and powdered fruits of blackberries (*R. jamaicensis*) were extracted successively with hexane, ethyl acetate and methanol, and the corresponding extracts were evaluated for their tumor cell proliferation inhibitory activities [30]. The hexane extract had the greatest overall capacity to inhibit the progression of tumor cell growth, inhibiting the

proliferation of colon, breast, lung, and gastric human tumor cells by 50, 24, 54, and 37%, respectively. In another study, the blackberry extracts were evaluated for their ability to inhibit the growth of human oral (KB, CAL-27), breast (MCF-7), colon (HT-29, HCT116), and prostate (LNCaP) tumor cell lines with IC<sub>50</sub> values ranging from 49.61 to 122.00 µg/mL. The blackberry extracts were also evaluated for their ability to stimulate apoptosis of the cyclooxygenase-2 (COX-2) expressing HT-29 colon cancer cells and it was found that they induced apoptosis 1.8-fold over untreated controls [5]. In addition, Dai *et al.* [26] reported that blackberry extracts inhibited HT-29 colon cancer cell growth in a concentration-dependent manner with 49.2 µg of total anthocyanins/mL inhibiting HT-29 cell growth up to 66% in 72 hours.

Polysaccharides from black currants showed certain cytotoxicity directly against ehrlich ascite cells, and the IC<sub>50</sub> value was estimated to be about 760 µg/mL. Oral administration of black currant juices and polysaccharide to ehrlich carcinoma-bearing mice retarded the growth of the solid tumor by 45 and 51%, respectively [54]. These research findings suggested that additive and synergistic effects of phytochemicals in blackberries and black currants may also be responsible for their potent anticancer activities.

### **3.4.3 Anti-inflammatory activities**

Chronic inflammation has been associated with the increased risk of several human diseases including cancer and CVD. Consumption of dietary anti-inflammatory components may reduce the risk of these human chronic health problems. The anti-inflammatory activities of LMWPF and HMWPF, isolated from three blackberry cultivars (e.g. Navaho, Kiowa, and Ouachita), were investigated by an *in vivo* mouse ear edema model [58]. All fractions significantly ( $P < 0.05$ ) reduced 12-O-tetradecanoylphorbol-13-acetate (TPA)-induced irritation injury. Furthermore, mouse ear myeloperoxidase (MPO) activity, an indicator of polymorphonuclear leukocyte infiltration, was assessed and found to be significantly reduced after topical application of all blackberry preparations ( $P < 0.05$ ). In another study, the hexane extract of blackberries (*R. jamaicensis*) selectively inhibited COX-2 at 100 µg/mL [30]. Dai *et al.* [26] reported that an anthocyanin-rich extract from Hull blackberries grown in Kentucky inhibited interleukin-12 (IL-12) release from dendritic cells in both background and stimulated levels, which demonstrated the anti-inflammatory properties of the anthocyanin-rich extract of blackberries. Recently, total polyphenolic and anthocyanin- and proanthocyanidin-rich fractions from four wild blackberry genotypes, a domesticated noncommercial breeding line, and a commercial cultivar were reported to inhibit pro-inflammatory responses including nitric oxide (NO) production, inducible nitric oxide synthase (iNOS) expression, COX-2 expression, and prostaglandin E2 (PGE2) in RAW 264.7 macrophages stimulated by lipopolysaccharide (LPS) [62].

Polyphenolic compounds of black currants had the potential to reduce eosinophil recruitment and alleviate eosinophilic-driven airway inflammation [63]. Another study by Balstad *et al.* [64] suggested that high intakes of lyophilized black currants modulated *in vivo* nuclear factor-kappa B (NF-κB) signaling in the liver following LPS-induced stress. In addition, the study by Lyall *et al.* [65] showed that consumption of short-term black currant extracts alleviates exercise-induced oxidative stress and LPS-stimulated inflammatory responses. These research findings suggested the potential of blackberries and black currants in reducing the risk of chronic inflammation and its related health problems.

### 3.4.4 Other bioactivities

A study by Shukitt-Hale *et al.* [66] demonstrated that the polyphenolics in a 2% blackberry-supplemented diet, when fed to rats from 19 to 21 months of age, retarded and even reversed age-related decrements in motor and cognitive performance. The blackcurrant extracts inhibited herpes simplex virus type 1 attachment on the cell membrane completely at a 100-fold dilution, as well as the plaque formation of herpes simplex virus types 1 and 2, and varicella zoster virus by 50% at a 400-fold dilution or lower concentrations [67]. The blackcurrant extracts also showed obvious inhibition activities on influenza virus types A and B [68]. In addition, Takata *et al.* [54] reported the immunostimulatory effects of blackcurrant extracts on the release of IL-2, IL-10, interferon- $\gamma$ , and IL-4 from splenocytes using a phosphate-buffered saline (PBS) control in tumor-bearing mice. Interestingly, black currant extracts could activate endothelial nitric oxide synthase (eNOS) via the Akt/PI3 kinase pathway *in vitro* in human umbilical vein endothelial cells (HUVEC) and the effect was not dependent on vitamin C [69]. Black currant extracts could alleviate physical fatigue with increasing the time of loading swimming, the hepatic glycogen content, and decreasing blood urea nitrogen in mice [70].

## 3.5 Commercial products and industrial applications of blackberries and black currants

Blackberries and black currants, like other berries, are widely distributed as processed products (such as jellies, juices, jams, and wines) because fresh fruits are extremely perishable with a very short shelf life. Many researches have conducted investigations to determine the nutraceutical and health properties of blackberries and black currants and their derived commercial products.

### 3.5.1 Juices

Juices obtained by squeezing fruit without any pasteurization treatments represent an alternative way of consuming fresh fruits. Hager *et al.* [71] reported an approximate 67% loss of total monomeric anthocyanins, 55% loss of ORAC value, as well as a small increase in polymeric color occurred in juice processing of blackberries. Over the storage of six months at room temperature, ORAC value of blackberry juices showed no significant changes ( $P > 0.05$ ), while total monomeric anthocyanins were lost by 69–75% [71]. Later, Hager *et al.* [72] reported that total ellagitannin concentration of juices changed markedly during juice processing steps. The low levels of ellagitannins in juice products were attributed to their loss to the presscake. The anthocyanin pigment profiles of commercial blackberry and black currant juices were characterized by Hong and Wrolstad [73]. They found out that cyanidin 3-*O*-rutinoside, 3-*O*-sophoroside, 3-*O*-glucosylrutinoside, and 3-*O*-glucoside existed in the blackberry samples, while cyanidin and delphinidin 3-*O*-rutinosides and delphinidin 3-*O*-glucoside were present in the black currant samples. Other properties including tintoral strength, total anthocyanin concentration, browning, titratable acidity, and Hunter tristimulus color values were also determined. More recently, Serraino *et al.* [74] showed that blackberry juices containing cyanidin-3-*O*-glucoside scavenged peroxynitrite and exerted a protective effect against endothelial dysfunction and vascular failure induced by peroxynitrite.

### 3.5.2 Jams

Berry jams are an important dietary form of berry fruits [75]. HPLC spectral patterns of blackberry jams showed that the predominant anthocyanin was cyanidin-3-*O*-glucoside, together with traces of cyanidin-3-*O*-rutinoside [76]. The commercial blackcurrant jams contained cyanidin and delphinidin 3-*O*-rutinosides as the major anthocyanins [76]. Blackberry jams had the lowest total phenolic content and total anthocyanins among all processed products including frozen, freeze-dried, hot-air dried, canned-in-water, canned-in-syrup blackberries, and blackberry jams retained only 33% of total phenolic content and 20% of total anthocyanins compared with their frozen controls [77]. This may be explained by the acceleration in condensation and polymerization reactions of phenolic compounds after cellular disruption and the increase in fruit temperature combined with oxygen exposure [78].

### 3.5.3 Wines

Blackberry wines possess stronger superoxide and hydroxyl radical scavenging properties and are more effective in inhibiting calmodulin-promoted phosphodiesterase than red grape wines [79]. Increased antioxidant activity and high total phenolic content were detected in blackberry wines [60%, 1232 mg of gallic acid equivalents (GAE)/L] [80]. Total antioxidant activity, total phenolic content, and mineral contents of black currant wines have been reported [81].

### 3.5.4 Canned fruits

Wu *et al.* [77] reported that canning significantly reduced total monomeric anthocyanins in blackberries. Furthermore, compared with canning in water, canning in sucrose syrup doubled the loss of total monomeric anthocyanins and decreased radical scavenging activities. In addition, 22 and 27% reduction in ORAC and 10.5 and 17.8% reduction in total monomeric anthocyanins accompanied with darkening of polymeric colour were observed in 40° Brix Sweetose syrup and water canned shiny black ‘Apache’ blackberries harvested in Arkansas in 2005, respectively [71]. Additionally, a 6-month postprocessing storage at 25°C led to 60.6 and 65.8% loss in total monomeric anthocyanins, respectively, but no significant changes ( $P > 0.05$ ) in ORAC values were observed. Taken together, these previous studies suggested the potential effects of fruit processing on the components and health properties of blackberries and black currants. This information could be important for better use of blackberries and black currants, as well as other fruits.

## 3.6 Drying effects on antioxidant capacities and phenolics of blackberries and black currants

Drying is a common method to preserve fresh berries by reducing their water activity. Different drying technologies showed different impacts on the bioactive compounds and antioxidant capacities of blackberries (Table 3.2). Freeze drying was recognized as the best technology to make high-quality dried products, resulting in slight changes in bioactive constituents and antioxidant activities. However, obvious decreases in total phenolics, anthocyanins, and antioxidant capacities of blackberries were observed after hot-air drying. Significant decrease

**Table 3.2** Percent change of bioactive compounds and antioxidant activities of two blackberry varieties compared with frozen controls after drying processing

	Total phenolics (mg of GAE/g)	Anthocyanins (mg of C3GE/g)	RSA (mg of AAE/g)	ORAC (μmol of TE/g)	FRAP (μmol of TE/g)
<b>Marion</b>					
Freeze drying	+27%	-25%	nc	nc	nc
Hot-air drying	na	-56%	na	-37%	-27%
<b>Evergreen</b>					
Freeze drying	+21%	+5.5%	+14%	nc	nc
Hot-air drying	-37%	-84%	-13%	na	na

Source: Adapted from Wu *et al.* [77].

RSA, radical scavenging activity; ORAC, oxygen radical absorbance capacity; FRAP, ferric reducing antioxidant potential; GAE, gallic acid equivalents; C3GE, cyanidin-3-glucoside equivalents; AAE, ascorbic acid equivalents; TE, trolox equivalents; na, not available; nc, not changed.

( $P < 0.05$ ) in vitamin C content was observed in freeze-dried and air-dried blackberry samples as compared with their frozen counterparts [82]. The total phenolic levels in air-dried blackberries were 15.6–21.1% lower than those found in frozen fruits [82]. There is limited literature about drying effects on phenolics and antioxidant activities of black currants.

### 3.7 Conclusions

Blackberries and black currants have considerable amounts of nutrients and nutraceutical components as well as potential health benefits. Meanwhile, dried blackberries and black currants retain significant levels of the nutritional value of fresh ones, and are also recommended in daily dietary intake to promote human health. Scientific data suggest that their intake may reduce the risk of several aging-associated human chronic diseases. Additional research is needed to better understand the mechanism behind the health properties of dried blackberries and black currants. Further research is also required to identify and quantify the individual beneficial components in dried blackberries and black currants, as well as the effects of different dehydration procedures and conditions on health components in berry fruits. In addition, the absorption, distribution, metabolism, and excretion of dried blackberries and black currants or their bioactive constituents should be investigated, along with a better understanding of their bioavailability in human.

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## **4 Dried blueberries: the effects of processing on health-promoting compounds**

William L. Kerr

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### **4.1 Introduction**

Blueberries are a sweet, succulent fruit grown in many parts of the world. In 2010, 186,000 metric tonnes (MT) of blueberries were produced in the United States [1]. Maine is the largest grower of wild blueberries, producing some 40,000 MT in 2008. Several other states are major producers of cultivated blueberries including Michigan (49,000 MT), Georgia (28,000 MT), Oregon (24,000 MT), Washington (19,000 MT), North Carolina (18,000 MT), California (13,000 MT), and Florida (8000 MT). Canada is another major producer of blueberries, yielding 42,000 MT in 2010 [2]. It is Canada's largest fruit export, and over half of the fruit-growing area is devoted to blueberries. British Columbia is the main supplier of highbush blueberries, while Nova Scotia and Quebec produce a large number of wild blueberry plants.

South America has more recently developed a major blueberry industry, with some 16,000 hectares devoted to blueberry cultivation. Chile is the largest producer and is a major exporter to North America and Europe, shipping 21,000 MT of fresh fruit and 1000 MT of frozen fruit. Other South American growers include Argentina and Uruguay. Several European countries also produce highbush blueberries, originally in the acidic sandy soils of Germany and the Netherlands, but since spreading to Poland, France, Austria, and Italy [3]. In 2008, an estimated 7300 hectares were planted with blueberries in Europe. Since the 1970s, Australia, New Zealand, and South Africa have also become major blueberry producers.

Recent interest in health-promoting compounds has spurred the production of blueberries. In particular, blueberries have been recognized as a major source of antioxidants and other phytochemicals including anthocyanins, proanthocyanidins, and flavonols that may have potential antidisease effects [4]. In addition, the desire to eat blueberries during off-seasons has encouraged imports from countries such as Chile and Argentina. Worldwide blueberry acreage has nearly doubled from 34,000 to 66,000 hectares from the period 2003 to 2008 [5]. In the United States, production of Maine wild blueberries increased 58%, while cultivated blueberries increased 24,000 hectares in 2008 to 28,000 hectares in 2010 [1].

Blueberries do have a rather short growing season, and this necessitates the development of processes to preserve them. In the United States, approximately 111,000 MT of blueberries

enter the fresh market, while 75,000 MT are processed further [1]. Of processed fruit, about half are individually quick frozen (IQF). Others may be produced into juices, purees, and dried fruit, with the latter often infused with sugars. A wide variety of products may be produced from processed berries including blueberry pies, jams and jellies, baked goods, and snack foods.

This chapter reviews some of the blueberry varieties that are available, the important nutrients and phytochemicals they contain, current research on beneficial health effects, and some of the effects of processing on these components, with particular attention to drying technologies.

## 4.2 Varieties and composition

Blueberries are flowering plants from the family Ericaceae, which contain a variety of shrubs and trees that thrive in acidic soils [6]. They belong to the genus of *Vaccinium*, which consists of over 450 species of deciduous shrubs that thrive in cooler areas. Other *Vaccinium* berries include cranberries, bilberries, cowberries, crowberries, and farkleberries. Blueberries are “false” or epigenous berries and develop from an inferior ovary, and include tissue that develops from parts of the flower. They are perennial plants that live for several years, grow, and develop fruit in spring and summer and die off in the autumn.

Many varieties of blueberries exist, some of which are listed in Table 4.1. Of these, only a few are of major commercial importance in North America. The northern highbush blueberry (*Vaccinium corymbosum* L.) is the most abundant and grows in northeastern United States,

**Table 4.1** Species of blueberries

Species	Common names	Distribution
<i>Vaccinium angustifolium</i>	Wild lowbush	Eastern and Central Canada, and Northeast United States
<i>Vaccinium ashei</i>	Southern rabbiteye	Southeastern United States
<i>Vaccinium boreale</i>	Northern	New England, Newfoundland, and Quebec
<i>Vaccinium caesariense</i>	New Jersey	New Jersey and parts of Eastern United States
<i>Vaccinium corymbosum</i>	Northern highbush	Nova Scotia, Ontario, Southeastern United States, Wisconsin, and Texarkana
<i>Vaccinium cyanococcus</i>	American	North America
<i>Vaccinium darrowii</i>	Southern highbush	Southeastern United States
<i>Vaccinium elliottii</i>	Elliott	Southeastern United States and Texarkana
<i>Vaccinium formosum</i>	Southern	Southeastern United States and coastal plains
<i>Vaccinium fuscatum</i>	Black highbush	New England, Southeastern United States, and Texarkana
<i>Vaccinium hirsutum</i>	Hairy fruited	Georgia, North Carolina, and Tennessee
<i>Vaccinium myrtilloides</i>	Canadian, velvetleaf	Canada, Northeastern, and Northwestern United States
<i>Vaccinium operium</i>	Cyan-fruited	Nova Scotia, Montana to Virginia
<i>Vaccinium pallidum</i>	Dryland, blue ridge	Eastern United States and Ontario
<i>Vaccinium simulatum</i>	Upland highbush	Southeastern United States, Ohio, and Kentucky
<i>Vaccinium tenellum</i>	Small black	Southeastern United States
<i>Vaccinium virgatum</i>	Small flower	Southeastern United States and Texarkana

Quebec, Ontario, parts of the Midwest, southeastern United States, Washington, and British Columbia, and accounts for over half of the world production of blueberries [7]. They can be 1.8 to 3.6 meters in height with two to five stems rising from the base. At least 50 cultivars exist including Bluejay, Bluecrop, Bluetta, Bluerat, Duke, Jersey, and Patriot. These are variations of the basic species selected from the wild, or bred to attain desirable properties, and are maintained by propagation through cuttings.

Another important variety is the Southern Rabbiteye (*Vaccinium ashei*) and includes many cultivars such as Bluebelle, Blue Gem, Brightwell, Climax, Delight, Powderblue, Southland, Tifblue, and Woodard. The Southern Rabbiteye grows primarily in the southern United States in a region stretching from North Carolina down to Florida, and westward to Texas, as it is more adapted to hot, humid summers, and mild winters. Rabbiteyes are also grown in Chile, Brazil, Australia, and South Africa and account for 15% of world production [8]. Plants are typically 1.8–2.4 meters tall, spread 0.9–3.0 meters, and have 5–10 stems developing from the base of the plant. The plants are productive and the berries ship well, but the fruit does tend to ripen a bit late for the fresh market. A little over half of the fruit is destined for further processing.

The lowbush blueberry (*Vaccinium angustifolium*) is a primarily wild-type bush, although a few improved varieties have been developed. It is a low spreading shrub forming dense colonies, and typically less than 0.9 meters in height. It is grown primarily in Maine, Massachusetts, and Canada. While accounting for 40% of the North American production, and 31% of world production, most of the fruit is used for further processing [8].

## **4.3 Compositional and nutritional characteristics of blueberries**

### **4.3.1 Macro- and micronutrients**

As with other berries, blueberries contain a variety of nutrients and related compounds beneficial to health. They are a particularly good source of vitamin C, with a one cup serving providing about one-fourth the recommended dietary allowances (RDA) value needed for an adult (Table 4.2) [9]. Blueberries and similar berries have been touted as a good source for at-risk populations with low vitamin C levels in their diet [10]. While fruits and nuts are not typically rich sources of vitamin K, blueberries (and a few others such as blackberries, grapes, and figs) do provide a significant amount of phylloquinone (vitamin K<sub>1</sub>) [11]. Blueberries can also be a reasonable source of folic acid. Deficiencies of vitamin B have been related to neural tube defect in newborns, so there is concern that expectant mothers have sufficient levels [12]. Some studies have also suggested that folic acid can reduce the risk of heart disease and some types of cancer [13].

Amongst the mineral nutrients, manganese is the most prevalent in blueberries in terms of its contribution to RDA values. A one cup serving provides 0.5 mg or 25% of RDA. Manganese plays a role in forming connective tissue and bones, blood clotting, production of sex hormones, calcium absorption, and blood sugar regulation. It is a component or cofactor of several enzymes, including the antioxidant enzyme superoxide dismutase [14]. There is generally not much concern about adequate amounts of manganese in the diet, although some studies have suggested as many as 37% of Americans may be deficient in manganese, due to an overreliance on cereal grains in the diet in lieu of fruits and vegetables.

**Table 4.2** Compositional and nutritional characteristics of raw blueberries (values in per cup = 148 grams edible portion) and percentage of RDA

	Units	Blueberries	Percent of RDA
<b>Proximate composition</b>			
Water	%	84.2	-
Energy	kcal	84	-
Protein	g	1.1	2
Lipid	g	0.49	1
Starch	g	0.0	-
Carbohydrate	g	21.45	16
Dietary fibre	g	3.6	14
Sugars	g	14.74	-
<b>Minerals</b>			
Calcium	mg	9.0	1
Copper	mg	0.08	4
Iron	mg	0.41	5
Magnesium	mg	9.0	2
Manganese	mg	0.50	22
Phosphorus	mg	18.0	2
Potassium	mg	114	3
Selenium	µg	0.1	0.2
Sodium	mg	1.0	0
Zinc	mg	0.24	2
<b>Vitamins</b>			
Folate	µg	6.0	2
Niacin	mg	0.42	3
Pantothenic acid	mg	0.12	2
Pyridoxine	mg	0.05	4
Riboflavin	mg	0.04	3
Thiamin	mg	0.04	3
Vitamin A (RAE)	µg	3.0	0.3
Vitamin C	mg	9.7	0.5
Vitamin E (ATE)	mg	0.57	4
Vitamin K	µg	19.3	16

Source: Adapted from USDA [9].

Note: Some numbers are rounded to the second digit after decimal point.

RDA, recommended dietary allowances; RAE, retinol activity equivalents; ATE, alpha-tocopherol equivalents.

Blueberries also provide small amounts of copper (4% of RDA), potassium (3% of RDA) magnesium (2% of RDA), and phosphorous (2% of RDA).

### 4.3.2 Dietary fiber

Blueberries are also a good source of dietary fiber. Although an exact definition is lacking, dietary fiber usually refers to plant components that are indigestible in the small intestine. These consist of remnants of the plant cell, lignins, and cell wall polysaccharides that are not digested. In fruits, the parenchymous flesh contains substantial pectin as part of the primary

cell wall. Vascular tissue contains more of the hemicellulose xyloglucan. Epidermal tissue also contains cellulose and lignin along with cutin and other waxy materials [15]. There are two primary types of fiber, which is soluble and insoluble. According to USDA data, one cup of berries supplies 3.6 g of total dietary fiber (TDF), or 14% of RDA. While the database does not specify variety, there seem to be some variations in fiber depending on the cultivar, and indeed on the analytical procedure. Lowbush blueberries from Maine were found to have 4.06–4.39 g/100 g TDF depending on storage time, puree method, and concentration of citric acid used to extract fiber [16]. Pectin content ranged from 0.27 to 0.54 g/100 g. A Canadian study showed that in 100 g fresh blueberries with 2.6 g TDF, there was 0.69 g of soluble fiber and 1.9 g insoluble fiber [17]. In a comparison study of two Rabbiteye varieties (Tifblue and Premier) and two southern highbush varieties (Pearl River and Magnolia), rabbiteyes were found to have significantly higher neutral detergent fiber (NDF) and acid detergent fiber (ADF) than southern highbush varieties [18]. In 2002, the Rabbiteye varieties contained 17.5–23.7% NDF and 8.7–13.6% ADF. In comparison, southern highbush varieties contained 6.9–8.3% NDF and 4.3–4.6% ADF. The NDF fractions were determined to contain cellulose, hemicellulose, and lignin originating from the cell walls. It was also noted that fiber decreased as the fruit changed from a purple to a fully ripe stage.

#### **4.3.3 Sugars and organic acids**

As noted, 148 g of ripe blueberries have on the order of 45 g carbohydrate, with 14.74 g as sugar. In ripe berries, the predominant sugars are fructose [32.9 g/100 g dry weight (DW)], glucose (32.9 g/100 g DW), and sucrose (1.81 g/100 g DW) [19]. During ripening, the total amount of sugars increases from 35 to 63% of dry weight basis, and the ratio of glucose to fructose increases from 0.85 to 1.02. In addition to being sweet, blueberries are tart in nature, but the degree and type of acid vary with the variety. Lowbush varieties have approximately 36 μeq. citric acid, 31 μeq. malic acid, and 20 μeq. quinic acid per gram of dry weight, and also contain 10 μeq./g DW of the phenolic chlorogenic acid [20]. Highbush blueberries have approximately 75% citric acid and 17% succinic acid, while Rabbiteyes have 50% succinic, 37% malic, and 10% citric acids [21].

### **4.4 Phytochemicals**

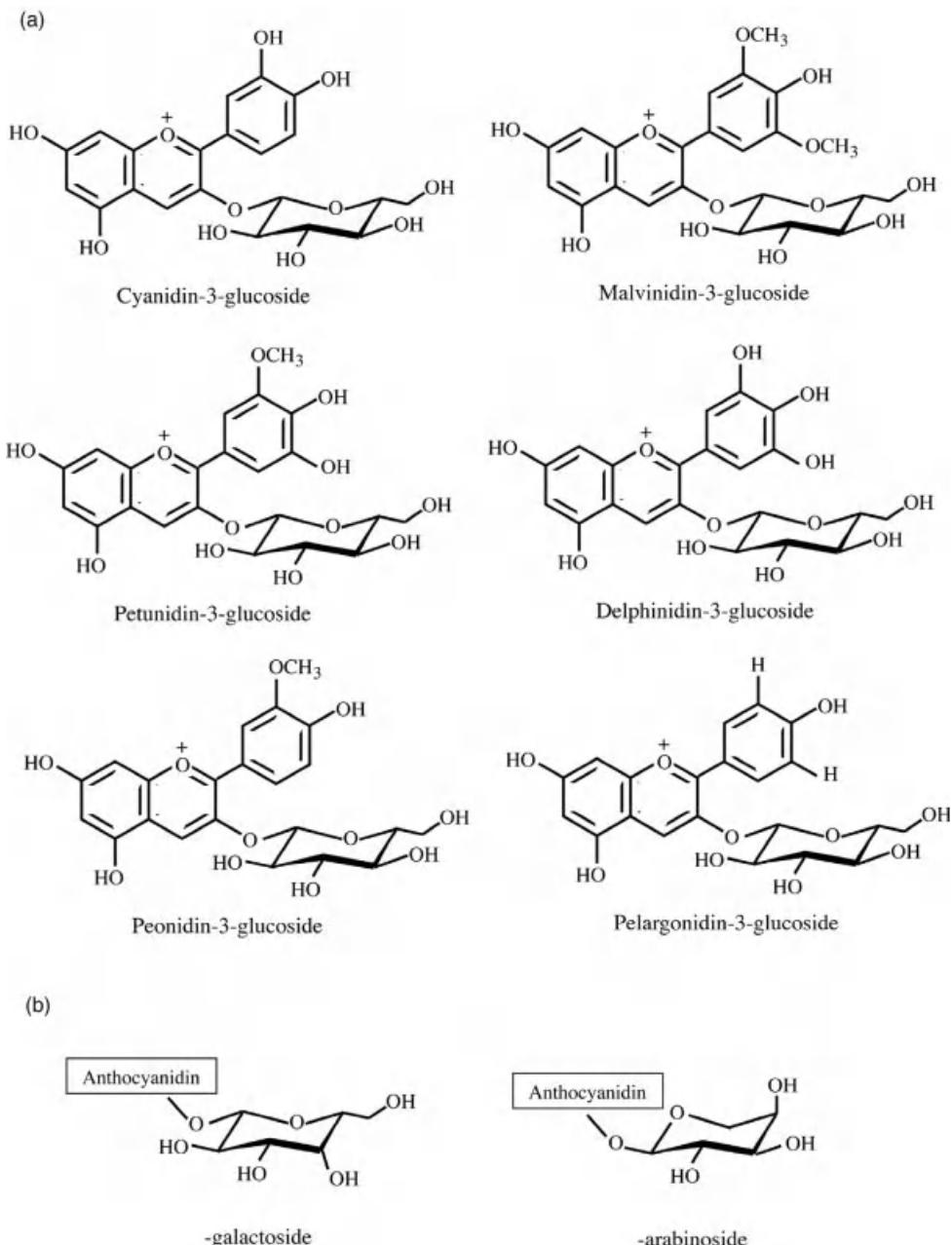
While blueberries are a good source of several nutrients, recent research has focused on the many phytochemicals in blueberries that may positively affect health. Blueberries are a good source of many polyphenolic compounds, including anthocyanins, flavonols, hydroxycinnamic acids, flavon-3-ols, and procyandins. Of these, the class of pigments known as anthocyanins are most well known as they provide the characteristic color to *Vaccinium* spp. and related fruits. Many red, violet, and blue colors in most fruits, vegetables, and cereals arise from anthocyanins [22, 23]. They can occur in various parts of the plant, but are particularly concentrated in fruits and flowers. Anthocyanins are produced by the phenylpropanoid pathway and stored in cell vacuoles, and can occur in fruits, stems, tubers, and leaves. In fruits such as blueberries, the anthocyanins reside mostly in the epidermal layer of the skin. They seem to have several beneficial functions (or consequences) for plants although their exact roles are still debated [23]. In flowers, the color can attract pollinating insects for better pollination, while in the fruit skins the colors attract animals that eat the fruit and

consequently disperse the seed. In leaf tissue, anthocyanins may provide protection against damaging UV radiation. Some research has suggested anthocyanins may modulate reactive oxygen signaling that mediates plant growth and development [24]. While the color of anthocyanidins and anthocyanins are pH dependent, in the low pH environment of fruit, a variety of characteristic colors are possible. Delphinidin typically contributes to blue and blue-red colors; cyanidin, peonidin, and pelargonidin to red-orange and purple colors; petunidin to dark red and purple colors; and malvidin to blue and red colors. In the intact fruit, the colors are modified or enhanced by several copigmentation systems [25].

The separation and identification of anthocyanins from plants can be difficult, particularly due to limited standards and variations caused by different solvent extractions [31]. Thus, many researchers report only on total anthocyanins or total phenolics. In addition, the type, distribution, and glycosylation of anthocyanidins depend upon cultivar, degree of maturity, soil, and weather conditions. This, in turn, determines bioactivity, as, for example, cyanidin-3-glucoside and -rhamnoglucoside have relatively high oxygen radical absorbance capacity (ORAC) values, while pelargonidin-3,5,-diglucoside and malvidin-3-glucoside have relatively low ORAC values [26]. Only five or six anthocyanidins are common in blueberry fruits [27]. Using paper chromatography, researchers isolated 15 anthocyanins from *V. angustifolium* [28] and showed the presence of delphinidin, petunidin, malvidin, peonidin, and cyanidin along with the sugars glucose, galactose, and arabinose (Figure 4.1). More recent studies have been based on high-performance liquid chromatography (HPLC) analysis including identification with standards or mass spectrometry (MS) [29–31]. Table 4.3 shows typical values for a few select lowbush, highbush, and Rabbiteye varieties. Most varieties contain the above aglycones, although varieties of lowbush blueberries do not contain pelargonidin [31, 32]. Most tend to have relatively high levels of delphinidin and malvidin, and lesser amounts of petunidin, cyanidin, and peonidin [32, 33]. Highbush varieties have higher levels of malvidin-3-galactoside, delphinidin-3-galactoside, delphinidin-3-arabinoside, petunidin-3-galactoside, petunidin-3-arabinoside, and malvidin-3-arabinoside than other varieties [34]. Most varieties also contain glucose, galactose, and arabinose, although the disaccharide 6-O-L-rhamnosyl-D-glucose (rutinoside) has been reported, particularly in the form of delphinidin-3-O-rutinoside [35]. Others have shown that many of the glycosyl residues may be acetylated. For example, “Chignecto” cultivars of *V. angustifolium* had 35% of the total anthocyanins in the acetylated form, while other cultivars had lesser amounts [30]. More recent studies have identified 49 different anthocyanins in wild blueberry [31]. Of those, only 19 had been previously identified. The other 30 included compounds such as delphinidin-3-hexose, delphinidin-3-oxaryl-hexose, cyanidin-malyl-pentose, and cyanidin-3-propionyl-galactoside.

Many researchers have preferred to report on the total anthocyanins or total phenolic compounds. Total anthocyanins are often measured by a pH differential method, while total phenolics are determined by reaction with the Folin–Ciocalteu reagent [36]. Table 4.3 shows total anthocyanin and phenolic content for select varieties of blueberries. Some varieties have as low as 33 mg cyanidin-3-glucoside equivalents (C3GE)/100 g (“Bluecrop”) and some as high as 822.7 mg C3GE/100 g. It should be noted that much variation could arise due to the method of extraction. For example, higher levels of anthocyanins are attained with acidified solutions of methanol [37].

As phenolic compounds are concentrated in the skins of most blueberries, it has been hypothesized that smaller berries that have greater surface-to-volume ratios would contain more of these compounds when calculated on a per weight basis. Some research suggests that



**Figure 4.1** Major anthocyanins in blueberries (a) in glucoside forms. Anthocyanidins may also be attached to (b) galactoside or arabinoside groups.

**Table 4.3** Anthocyanins in various blueberry cultivars

	<b>Wild [35]</b>	<b>Fundy</b>	<b>lowbush [30]</b>	<b>Crunchie</b>	<b>highbush [29]</b>	<b>Bluecrop</b>	<b>highbush [35]</b>	<b>highbush [33]</b>	<b>Bluecrop [32]</b>	<b>highbush [32]</b>	<b>Ozarkblue</b>
Delphinidin-3-glucoside	84.4	16.2	7.7	7.9	6.3	12.6	12.6	11.0	18.8	18.8	0.8
Delphinidin-3-galactoside	25.8	15.9	17.5	14.1	11.0	38.9	38.9	11.9	16.3	16.3	18.6
Delphinidin-3-arabinoside	nd	7.1	10.4	14.2	nd	nd	nd	nd	nd	nd	nd
Delphinidin-3-glucoside	17.9	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Petunidin-3-glucoside	30.3	11.5	6.7	5.1	4.3	1.1	1.1	1.1	0.8	0.8	0.8
Petunidin-3-galactoside	25.5	8.0	9.5	7.7	7.4	11.3	11.3	11.3	22.8	22.8	22.8
Petunidin-3-arabinoside	nd	3.3	5.8	5.0	4.9	8.2	8.2	8.2	11.3	11.3	11.3
Malvidin-3-glucoside	139.6	19.9	nd	11.2	15.2	15.3	15.3	15.2	1.8	1.8	1.8
Malvidin-3-galactoside	101.2	17.4	nd	13.7	25.4	15.9	15.9	15.9	19.6	19.6	19.6
Malvidin-3-arabinoside	27.4	nd	8.5	nd	23.5	14.4	14.4	14.4	105.2	105.2	105.2
Peonidin-3-glucoside	17.4	4.9	17.6	0.5	0.9	nd	nd	nd	nd	nd	nd
Peonidin-3-galactoside	16.4	2.5	0.7	0.6	0.8	1.4	1.4	1.4	1.8	1.8	1.8
Peonidin-3-arabinoside	1.1	nd	11.4	nd	nd	nd	nd	nd	0.6	0.6	0.6
Cyanidin-3-glucoside	27.5	9.1	0.9	0.7	1.0	2.0	2.0	2.0	0.4	0.4	0.4
Cyanidin-3-galactoside	nd	9.4	2.1	2.7	1.0	3.6	3.6	3.6	11.3	11.3	11.3
Cyanidin-3-arabinoside	nd	5.8	1.1	2.0	1.0	2.6	2.6	2.6	4.7	4.7	4.7
Pelargonidin-3-glucoside	29.6	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Others	14.3	nd	0.1	1.2	1.2	9.1 (acylated)	9.1 (acylated)	9.1 (acylated)	0.7 (acylated)	0.7 (acylated)	0.7 (acylated)
Total	558.3	131.1	79	101	114.6	143.5	143.5	143.5	144.3	144.3	144.3

Note: Some numbers are rounded to the first digit after decimal point.

nd, not detected.

Values are expressed as mg of cyanidin-3-glucoside per 100 g sample.

lowbush blueberries contain higher levels of anthocyanins, total phenolics, and antioxidant capacity than highbush varieties, but there is no correlation between fruit size and anthocyanin content [37]. Other studies have shown that anthocyanin content is correlated with size in 15 cultivars of *V. corymbosum* ( $r^2 = 0.84$ ), but not in other *Vaccinium* species [38].

It has been shown that total phenolics are highest for unripe green berries and decrease during color break and ripening, particularly at the unripe purple stage [39]. For example, unripe “Bluecrop” cultivars decreased from 60.7 to 33 mg gallic acid equivalents (GAE)/g DW at first harvest. Some varieties stabilized, some increased somewhat.

Often, antioxidant activity, total anthocyanins, and total phenolics content are well correlated. In a study on eight blueberry varieties, the antioxidant activity was correlated with total phenolics ( $r^2 = 0.99$ ) and anthocyanins ( $r^2 = 0.91$ ). Total anthocyanins were also correlated with total phenolics ( $r^2 = 0.87$ ) [40]. However, others have shown modest correlation between ORAC values and total phenolics ( $r^2 = 0.78$ ), but not with total anthocyanins.

## 4.5 Health effects related to blueberries

### 4.5.1 Micronutrients and health

Much of the health-promoting effects of blueberries can be traced to their micronutrient constituents. Many of these are not specific to blueberries and have been reviewed elsewhere. It has been suggested that blueberries can be a good source of vitamin C for at-risk populations [10]. Vitamin C is important for collagen synthesis and plays a role in hormone synthesis, immune system, iron absorption, platelet aggregation, and thrombus formation. It may also play a role in disease prevention by mediating oxidation in the body [41].

Vitamin K is needed as a cofactor for conversion of glutamic acid to  $\gamma$ -carboxyglutamic acid [42] and is important for blood coagulation through prothrombin and related factors, bone metabolism through osteocalcin, MGP, and periostin, and stimulation of vascular cells through growth arrest-specific protein 6. Some evidence suggests vitamin K helps with bone growth and density. Deficiencies of vitamin K are not common, especially as colonic bacteria help produce vitamin K, so this vitamin does not receive much attention. Some have suggested that newborns are at most risk for vitamin K deficiency, and in the United States it is recommended that 0.5–1.0 mg vitamin K<sub>1</sub> be administered to newborns [43], although this practice is not without its critics. Foods containing vitamin K often get a lot of attention due to interactions with “blood-thinning” (anticoagulant) drugs such as warfarin and coumarin, which are used in the treatment of blood clots and embolisms. These drugs are actually vitamin K antagonists, as they decrease blood coagulation by inhibiting vitamin K epoxide reductase [44]. Relatively large amounts of vitamin K can interfere with these drugs, as they promote a secondary pathway for clotting [45]. Patients on anticoagulant medicines are usually monitored to ensure stable clotting times as measured by the international normalized ratio (INR), and there is some concern that eating foods high in vitamin K, particularly at irregular intervals, can interfere with stabilized clotting times.

### 4.5.2 Blueberry phytochemicals and health

In addition to the roles that various vitamins and minerals play in human nutrition, blueberries contain many antioxidants, phytosterols, enzymes, and other phytochemicals that may

benefit human health [46]. These may work independent of, or in concert with, existing nutrients. In blueberries, the anthocyanins have garnered particular attention, but other compounds including pterostilbene, proanthocyanidins, flavonols, tannins, and resveratrol may contribute to bioactivity. In a broad sense, many of these compounds have been related to reduced risk for coronary heart disease (CHD) and cancer, as well as reducing inflammatory processes. There have been many studies linking phytochemicals in blueberries with reduction of risk for different diseases. It should be noted in context, however, that few have reached the state of clinical trials and scientific consensus needed to make a health claim.

#### 4.5.2.1 Role of oxidative stress

Some research suggests that free radicals can damage cells. Aging leads to reduced ability to combat oxidative stress, a state that contributes to cell aging, cancer, cardiovascular disease (CVD), cognitive impairment, cataracts, and macular degeneration [47–49]. Some studies have suggested that blueberries are a leading source of antioxidants, as measured by ORAC values, with values ranging from 13.9 to 44.6 mmol trolox equivalents (TE)/g fresh berries.

#### 4.5.2.2 Role in brain health and cognition

Several research studies have indicated that blueberry phytochemicals can benefit the brain and reduce cognitive impairment from aging and memory loss. One theory is that antioxidants can limit oxidative stresses and inflammation that contribute to cell aging [50]. Polyphenolic antioxidants may also improve communication amongst neurons, mediate neuroprotective shock proteins, aid neuronal plasticity, and inhibit stress producing pathways [51]. Injections of rats with *Vaccinium* extracts showed that it facilitated transport of triiodothyronine (a T3 thyroid hormone that regulates metabolism) into the brain, and into specific areas associated with memory, vision, and sensory input [52]. When aged rats had a diet supplemented with 2% dried blueberry extract, they were able to navigate a maze that tests working memory as well as younger rats, and rats fed blueberry supplement performed better than those supplemented with strawberry or spinach [53]. Other biochemical markers related to neuronal function were also improved, including evoked dopamine uptake by striatal slices, stimulated guanosine triphosphatase (GTPase) activity, and calcium buffering. Related studies tested diet supplementation and its effect on  $\beta$ -adrenergic receptor function, which has been correlated with decline in the ability to learn new motor skills [54, 55]. Researchers reported that after subjecting rats to hyperoxia, a form of oxidative stress, antioxidants in blueberry and spinach improved the ability to navigate mazes and reduced declines in  $\beta$ -adrenergic receptor function in rat Purkinje neurons. They also showed that the diet supplements were able to decrease other age-related deterioration of the brain such as decreases in nerve growth factor [56].

Subsequent studies were conducted on rats predisposed to Alzheimer's disease. Older rats fed a diet chow containing 2% dried blueberry extract were able to learn to navigate a Y maze as well as young rats and better than those without supplementation [57]. In addition, studies on excised brain tissue showed that supplementation enhanced memory-associated neuronal signaling and altered sphingomyelin phospholipase C activity. Related studies showed that rats fed blueberry extracts showed improvement in balance, coordination, working memory, and reference memory [58]. The ability to regenerate hippocampal neurons is associated with memory decline. Studies on aged rats fed 20 g dried blueberry/kg showed

improved biochemical markers for neuronal plasticity including hippocampal neurogenesis and extracellular kinase activity [59]. In addition, rats had fewer memory errors related to spatial tasks.

In other studies, young rats and those supplemented with blueberry extract performed better on tests of object recognition than aged control diet rats [60]. In addition, young rats and blueberry-supplemented aged rats had lower levels of the oxidative stress-responsive protein NF- $\kappa$ B (nuclear factor kappa-light-chain-enhancer of activated B cells) in four brain regions, indicating that these areas were under less oxidative stress. Another study investigated the brain's ability to generate heat shock protein 70 (HSP70), which acts to protect cells from thermal or oxidative stress [51]. Young and old rats were fed diets supplemented with blueberry, then hippocampal tissue was subject to an *in vitro* inflammatory challenge. Old rats with blueberry-supplemented diets had restored HSP70 levels as compared with those without supplementation, again suggesting protection against neurodegenerative processes.

One question of course is whether anthocyanins and related compounds can act directly in brain tissue. In a study on F344 rats fed with 2% blueberry supplementation, liquid chromatography–mass spectrometry (LC-MS) was used to identify anthocyanins in different regions of the brain [61]. Several anthocyanins were found in the cerebellum, cortex, hippocampus, or striatum of supplemented rats, including cyanidin-3-*O*- $\beta$ -galactoside, cyanidin-3-*O*- $\beta$ -glucoside, cyanidin-3-*O*- $\beta$ -arabinose, malvidin-3-*O*- $\beta$ -galactoside, malvidin-3-*O*- $\beta$ -glucoside, malvidin-3-*O*- $\beta$ -arabinose, peonidin-3-*O*- $\beta$ -arabinose, and delphinidin-3-*O*- $\beta$ -galactoside. These compounds were not found in the control groups. In addition, the levels of these compounds in the tissue were correlated with increased spatial learning and memory. This indicates that these anthocyanins can cross the blood–brain barrier and into regions associated with learning and memory. In a related study, in which European greenfinches were fed blackberries or blueberries (one per day for 2 weeks), cyanidin-3-glucoside was measured in homogenized brain tissue [62].

Few trials have been done on human subjects in which cognitive function has been tested after administration of blueberry products. In one medium-term trial, nine older adults with early memory changes drank 2–2.5 cups of *V. angustifolium* blueberry juice for 12 weeks, and were evaluated using the Verbal Paired Associate Learning Test, the California Verbal Learning Test, and the Geriatric Depression Scale [63]. Improvement was noted in paired associate learning and word list recall, and there was a trend toward lower symptoms of depression. Similar positive findings have been found with daily supplementation of Concord grape juice [64].

#### 4.5.2.3 Urinary tract infections

Extensive work has been done on the treatment of urinary tract infections (UTIs) with diet or extracts from the *Vaccinium* family, particularly cranberries, bilberries, and blueberries. By and large, most studies including clinical trials have been carried out with cranberry and suggest that cranberry is beneficial for preventing UTI but less helpful for treating existing UTI [65]. For example, one clinical trial showed that daily consumption of cranberry juice reduced UTIs by nearly half in elderly women [66]. One theory has been that cranberries help reduce the pH of urine from near neutral to 5.5 or lower, which helps prevent bacteria from growing. While urinary pH can be lowered by daily regimens of cranberry juice [67], the role of lower pH in limiting UTI has been questioned [68]. Current hypotheses suggest that particular “A Type” proanthocyanidins in cranberry, blueberry, and peanut skins

inhibit bacterial adhesins that allow bacteria, particularly *Escherichia coli* with fimbriae, from attaching to the mucosal surfaces of the urinary tract, oral cavities, or stomach [69]. One group reported on a compound in blueberry and cranberry juices that inhibits the mannose-resistant (MR) adhesin of *E. coli* [70]. Others studied extracts of wild blueberry that were separated into two fractions: one with a 3.25 and one with a 5.65 average degree of polymerization [71]. The former was able to suppress uropathogenic *E. coli* strains from agglutinating human red blood cells. Evidence also suggests that proanthocyanidins in berries can suppress gene expression that allows *E. coli* to produce fimbriae for attachment [72]. While implications for blueberries in preventing UTI are promising, it should be emphasized that more studies are needed to support their efficacy as a treatment. Indeed, a systematic review of the use of cranberries and blueberries in UTI prevention showed that while several studies indicated that these products significantly reduced the incidence of UTIs, “no trials were identified which evaluated the effectiveness of blueberry products for the prevention or treatment of UTIs” [73].

#### 4.5.2.4 Cancer

A substantial number of studies have investigated whether polyphenolic compounds in fruits and vegetables can reduce cancer risks. In general, epidemiological studies have shown that people with high fruit intake are at reduced risk for cancer mortality [74], and that fruits and vegetables provide significant protective effects against lung, colon, and many other forms of cancer [75]. These effects seem to be related to plant flavonoids. A study on 9959 Finnish men and women reported that persons with higher levels of flavonoids in their diet had a decreased risk of lung cancer [76]. Subsequent work suggested that men with higher intake of quercetin had lower incidence of lung cancer and those with higher intake of myricetin had lower incidence of prostate cancer [77]. Although many studies suggest polyphenolics have chemoprotective activity, some indicate there is no effect or even cancer-inducing effects [78]. The mode of action has been attributed to effects on cellular differentiation, proliferation, and apoptosis, as well as enzymes involved with the cellular processes.

Anthocyanin-rich fractions from several Rabbiteye and highbush blueberries were studied for their ability to regulate apoptosis and phase II enzymes in HT-29 (human colona adenocarcinoma) cell lines [79]. Fractions from Tifblue and Powderblue cultivars at 50–150 µg/mL caused increased DNA fragmentation characteristic of cell apoptosis, suggesting that the cells can then prevent unregulated growth.

Pterostilbene found in blueberries was found to suppress aberrant crypt foci formation in a rat model for colon cancer [80]. These foci are clusters that would eventually form into polyps or colon cancer. Blueberry and other *Vaccinium* species were shown to bind bile acids *in vitro* [81]. The authors suggested this might be beneficial in the prevention of colon cancer by removing toxic substances.

Proanthocyanidin-rich fractions from wild and cultivated blueberries were investigated for their ability to inhibit growth of two prostate cancer cell lines [82]. Two fractions from both types of berries were effective against one cell line but not the other. Nuclear magnetic resonance (NMR) analysis suggested that the active fractions contained a mixture of oligomeric proanthocyanidin molecules. The authors speculated that the proanthocyanidins are most effective against androgen-dependent growth of prostate cancer cells. In another study, fractions prepared from lowbush blueberries were able to inhibit the matrix metalloprotein in

DU145 human prostate cancer cells [83]. This protein is an enzyme that may allow cancer cells to metastasize.

In a comprehensive study on anticancer activity of several berries, extracts were prepared from blackberries, black raspberries, blueberries, cranberries, red raspberries, and strawberries [84]. These extracts were tested for their ability to limit proliferation of human oral, breast, colon, and prostate cancer cell lines. All extracts were able to limit proliferation in the different cell lines and the effect was shown to be dose dependent. Tests were also conducted to see if extracts could stimulate apoptosis in colon cancer (HT-29) cells. Black raspberry and strawberry extracts were the most pro-apoptotic.

#### 4.5.2.5 Cardiovascular disease

Several epidemiological studies have linked diets rich in fruit, vegetable, and whole-grain cereals with reduced risk for CVD [85]. These benefits have been attributed to the dietary fiber and numerous phytochemicals, and of the latter flavonoids have been given particular attention. As berry crops have substantial numbers of polyphenolic compounds, they have been investigated for their health-promoting potential [86]. Several mechanisms have been suggested for the cardioprotective attributes of flavonoids. As they are known antioxidants, they may act *in vivo* to limit the formation of atherogenic oxidized low-density lipoprotein (LDL) [87]. Plaque formation is also related to arterial inflammation and flavonoids may function by reducing this vascular inflammation [88]. Some research also suggests that flavonoids can limit the platelet aggregation and adhesion that accompany arterial plaque formation [89].

Using pigs as a model for human cardiovascular attributes, researchers fed the animals a plant-based diet (70% soy, oats, and barley) supplemented with 1–4% freeze-dried blueberry powder [90]. LDL and high-density lipoprotein (HDL) cholesterol levels were reduced by up to 5% in the diet supplemented with 2% blueberry. The effects of supplementation were reduced when the basal diet contained only 20% plant matter, suggesting a synergistic effect between the blueberry and cereal-based ingredients.

Studies on humans have also been promising. In a feeding trial, 48 obese participants with metabolic syndrome had diets supplemented with 50 g freeze-dried blueberry powder for 8 weeks [91]. Supplemented participants had 6 and 4% lower systolic and diastolic blood pressures than the control group, 28% less oxidized LDL, and 17% lower levels of plasma malondialdehyde.

#### 4.5.2.6 Vision health

A few studies have suggested that extracts from *Vaccinium* spp. can improve eyesight. Most work has been done on bilberry (*Vaccinium myrtillus*), particularly as it relates to improving eyestrain and night vision. For example, rats supplemented with bilberry extract were better able to regenerate the “visual purple” pigment (rhodopsin) in their photoreceptor cells [92]. Human subjects given bilberry extract were also better able to adapt to dark surroundings, with the benefits lasting for 24 hours [93]. Others have suggested that antioxidants including anthocyanins can alleviate underlying causes of macular degeneration [94]. A 2004 review of 30 human trials concluded that while some animal studies and weaker trials showed promising results, more rigorous clinical studies do not support the hypothesis that bilberry anthocyanins improve night vision [95].

## 4.6 Effects of processing on blueberry components

### 4.6.1 Importance of blueberry processing

Blueberries generally have a short harvest season of several weeks. They typically can be stored refrigerated for only 4–6 weeks and those fruit not destined for the fresh market are frozen, processed into juices, and canned products, or dried into intermediate-moisture fruits for hand eating, or into powders for ingredients or supplements.

### 4.6.2 General effects of heat, oxygen, and enzymes

Much food processing relies on the application of heat to destroy microorganisms, inactivate enzymes, or promote the removal of water. Heating is known to be detrimental to anthocyanins, and the temperature and duration of heating determine the degree of degradation. When blueberry juice was heated at 40, 50, 60, 70, and 80°C, the resulting half-life for anthocyanins was 180.5, 42.3, 25.3, 8.6, and 5.1 hours, respectively [96]. Thermal degradation followed a first-order kinetic model. Q10 values were found in the range of 1.6–4.3, which is typical of many chemical reactions. The thermal breakdown of anthocyanins is commodity-specific and depends on solid content, pH and copigment factors. Some anthocyanins may be more susceptible to heat, such as cyanidin-3-glucoside and pelargonidin-3-glucoside in blackberries and strawberries [97]. At pH 3.5, breakdown products include chalcone glycosides with an opening of the flavylium backbone [98]. Phenolic acids and phloroglucinaldehyde were also found as remainders of the B- and A-rings. Acylation and methoxylation improved the stability of anthocyanins to heating [99].

Heating is required, however, to inactivate polyphenol oxidases (PPOs) and catechol oxidases. In plants, the exact function of these enzymes is not fully understood, but they may be related to protection against pests and other stresses [100]. In fruit subject to handling and processing, these enzymes can catalyze the hydroxylation of monophenols to diphenols, with the subsequent formation of *o*-quinones which polymerize to produce brown pigments. PPOs are processed in chloroplasts and cutting, grinding, or bruising actions disrupt compartmentalization, allowing the enzymes to act on phenolic substrates. In addition, catechols and other diphenols are converted to *o*-quinones in the presence of oxygen and cell disruption encourages this exposure. It has been noted that when blueberries and other berries are not blanched, anthocyanin degradation occurs, even when the samples are stored frozen [101].

### 4.6.3 Juices, purees, and canning

Blueberries are processed into several high-moisture products including juices, purees, pie fillings, and concentrates. This requires several operations that may introduce high shear and cell disruption (grinding), heating (blanching and pasteurization), and storage at various temperatures. When frozen highbush blueberries with 99.9 mg C3GE/100 g (total anthocyanins) were processed into juice and concentrate, 33 mg C3GE/100 g were retained in the initial juice, 178 mg C3GE/100 g in the concentrate, and 184 mg C3GE/100 g in the pressed cake, accounting for 18% of the anthocyanins in the original fruit [101]. Interestingly, for juice pasteurized at 90°C for 1 min, anthocyanin levels were higher (38 mg C3GE/100 g). The authors felt that losses were incurred from enzymatic degradation during storage and that these were inactivated during pasteurization. This theory was reinforced as the addition of

blanched blueberry puree to juice resulted in no further loss of anthocyanins, while addition of unblanched puree resulted in a 50% loss. The proportion of malvidin glycosides increased to 80% in the pressed juice and 63% in the pasteurized juice. Delphinidin glycosides were least stable, followed by cyanidin and petunidin glycosides. The authors suggested that malvidin glycosides are stabilized by the two methyl groups on the B-ring, while delphinidin has three ortho phenolic groups. Cinnamic acid is more water soluble, thus more of it is recovered in the juice (13.2 mg/100 g as compared to 27.4 mg/100 g in the fruit), while little was found in the pressed cake (3.2 mg/100 g). Flavonol glycosides totaled 40.1 mg/100 g in the fruit, 24.9 mg/100 g in the juice, 16.7 mg/100 g in the pasteurized juice, and 26.8 mg/100 g in the press cake. The authors noted that these compounds are less susceptible to enzymatic degradation. Procyanidins totaled 9.9 mg/100g in the fruit, 4.5 mg/100g in the initial juice, and 5.0 mg/100g in the pasteurized juice. Little was found in the press cake.

Subsequent studies reported on the effects of pureeing, canning, and juicing on polyphenolics in highbush blueberries [102]. Chlorogenic acid was retained in pasteurized canned berries and nonclarified juice, but not as well in purees and clarified juice. In purees, chlorogenic acid was likely destroyed by PPO prior to blanching. High levels of flavonols were retained in berries canned in water and in purees (>97%). Only 57% remained in clarified juice, which the authors attributed to physical removal or loss of coprotective compounds. After 6 months at 25°C, 75–82% were retained in berries canned in syrup and in nonclarified juice. Anthocyanins were not retained as well during processing (41–72%), with greatest losses in clarified juice followed by purees. All incurred significant losses during six months storage. Related work on procyanidins showed a range of retention levels for nonclarified juice (19%), clarified juice (23%), purees (41%), berries canned in syrup (65%), and berries canned in water (78%) [103]. Larger oligomers were less well extracted during juicing than mono- and dimers. After 6 months storage, only 8–32% of the original levels were present and again mono- and dimers were better retained during storage than oligomers.

Other studies examined the effects of processing on antioxidant and antiproliferation activity [104]. For wild blueberries, IQF had the highest total phenolics followed by fresh, freeze-dried, canned, and juice concentrates. Differences were smaller for cultivated varieties and products that were heat-treated had slightly lower levels. Interestingly, antioxidant assays [ferric reducing antioxidant power full name required (FRAP) and full name required 2,2-diphenyl-1-picrylhydrazyl radical scavenging activity (DPPH)] did not show distinctions between heated and nonheated products. However, heat-treated products had much lower antiproliferation activity against liver cancer cell cultures.

#### 4.6.4 Freezing

Freezing is perhaps one of the best ways to preserve chemical constituents of berries [105]. Studies on *V. corymbosum* L. compared the effects of freezing versus storage of fresh samples at 5°C and drying in a cabinet dryer. For the dried products, anthocyanin content was 41–49% lower than in fresh berries. In contrast, anthocyanin levels in frozen blueberries did not change even after three months storage. Similar studies on *V. corymbosum* L. were conducted in which berries were stored at -18 and -35°C for six months. Derivatives of malvidin and delphinidin accounted for most of the anthocyanins [106]. No significant changes ( $P > 0.05$ ) were found in total anthocyanins, individual anthocyanin components, or chlorogenic acid at either temperature. In addition, antioxidant activity remained unchanged compared to values measured just after freezing. In comparison, studies on raspberries and blackberries

showed some small changes after 12 months storage at  $-24^{\circ}\text{C}$  [107]. For example, for wild blackberries, vitamin C decreased from 25.6 to 16.6 mg/100 g, total phenolics from 978 to 756 mg GAE/100 g, and anthocyanins from 306 to 248 mg C3GE/100 g.

Another study examined the effects of storage temperature on blanched extracts from Tifblue and Powderblue cultivars [108]. At  $-20^{\circ}\text{C}$ , there were no changes on total phenols, anthocyanins, or antioxidant activity after 30 days storage. At  $6^{\circ}\text{C}$ , some changes were noted after 15 days. Greater losses were noted at 23 and  $35^{\circ}\text{C}$ , especially after 15 days storage and anthocyanins were not detected after 60 days storage at  $35^{\circ}\text{C}$ .

#### 4.6.5 Drying

Drying is one of the primary means of preserving fruits and vegetables and functions by lowering the water activity below a point at which microorganisms can proliferate, and hopefully below a point at which chemical degradation occurs. There are several types of drying, however, each utilizing a particular temperature and means of applying heat and removing water. In turn, these result in a variety of products ranging from chewy intermediate-moisture fruits to dried powders, with differing recovery of phytochemicals (Table 4.4).

**Table 4.4** Affects of select drying technologies on blueberry phytochemicals

	<b>Material</b>	<b>Results</b>	<b>Reference</b>
Fresh	Whole highbush (87% moisture)	670 mg GAE/g total phenolics (glycosides)	[113]
Freeze dried	Whole highbush (5% moisture)	342 mg GAE/g total phenolics (glycosides)	[113]
Hot air ( $76^{\circ}\text{C}$ )	Whole highbush (5% moisture)	79 mg GAE/g total phenolics (glycosides)	[113]
Microwave/vacuum	Whole highbush (5% moisture)	234 mg GAE/g total phenolics	[113]
Fresh	Highbush	7.2 mg C3GE/g total anthocyanins	[105]
Hot air ( $90^{\circ}\text{C}$ )	Highbush	4.3 mg C3GE/g total anthocyanins	[105]
Hot air ( $90^{\circ}\text{C}$ ), 60% sugar	Highbush	3.7 mg C3GE/g total anthocyanins	[105]
Extract	Rabbiteye (35% EtOH extract)	9.2 mg C3GE/g total anthocyanins 30 mg GAE/g total phenolics	[120]
Spray dried	Rabbiteye (35% EtOH extract)	3.7 mg C3GE/g total anthocyanins 15 mg GAE/g total phenolics	[120]
Dough	Blueberry concentrate/corn	0.40 mg C3GE/g total anthocyanins	[125]
Extrudate	Blueberry concentrate/corn	0.04 mg C3GE/g total anthocyanins	[125]
Radiant zone	Highbush mix extract	11.7 mg GAE/g total phenolics	[127]
	Highbush mix dried extract	11.2 mg GAE/g total phenolics	
Vacuum belt	Whole rabbiteye (fresh)	16.7 mg C3GE/g total anthocyanins 41.8 mg GAE/g total phenolics	[128]
	Whole rabbiteye (dried)	16.0 mg C3GE/g total anthocyanins 41.7 mg GAE/g total phenolics	[128]

GAE, gallic acid equivalents; C3GE, cyanidin-3-glucoside equivalents; EtOH, ethanol.

#### 4.6.5.1 Freeze drying

Freeze drying occurs at low vacuum and relatively low temperature, and water is removed as vapor from the product directly from the solid state. It is believed to be one of the least detrimental to chemical constituents in foods and pharmaceuticals, although loss of volatiles can occur. Indeed, it is often used as part of the procedure for preparing berries and other food materials for chemical analysis [109]. It has been noted, however, that spray-dried and freeze-dried blueberries can be exceptionally hygroscopic. This is somewhat ameliorated by depectinization, drying with a carrier and the addition of free-flow agents.

When compared to forced air, vacuum oven and microconvection, freeze-dried lowbush blueberries were darker and redder, had higher soluble solids, and higher vitamin C retention [109]. In addition, freeze-dried samples had the lowest bulk density and highest rehydration ratio. In studies on bioactive properties of wild blueberries, it was found that antioxidant activity, galvinoxyl free radical quenching, ability to limit lipid oxidation, and activity against Hepa 1c1c7 cell proliferation were maintained in freeze-dried samples [110].

#### 4.6.5.2 Hot-air drying

Drying berries by subjecting them to a steady stream of hot air is one of the most common technologies in practice in the industry. To improve both heat and mass transfer, various means are used to insure good airflow around individual pieces. In fluidized bed driers, the airflow is sufficient to suspend individual berries. In rotary driers, a drum is used to constantly turn pieces and bring buried pieces to the surface. One impediment to drying is the waxy epidermal layer, which inhibits transfer of moisture in and out of the fruit. Several methods have been investigated for removing this prior to drying. In a research setting, berries have been tumbled with an abrasive sidewall to scuff the surface. In a high-tech variant, researchers have investigated the use of CO<sub>2</sub> lasers to perforate the skin prior to infusion [111]. In commercial practice, berries are usually passed through a scarifier, which consists of a series of blades which score the surface and somewhat flatten the product. In addition, berries destined to be eaten as dried fruits are often pretreated in solutions containing high sugar levels. This osmoconcentration step provides some initial drying and infuses the product, making it more flexible and less dense. The combination of reduced flavor loss, added sugar, and lower tartness often makes for more acceptable dried fruit products.

Hot-air drying was compared with microwave-assisted drying, freeze drying, and vacuum drying of cranberries (*Vaccinium macrocarpon*) infused with 76°C Brix sugar solution [112]. While freeze-dried products had the best rehydration properties and microwave-assisted processes dried the fastest, there were no differences in appearance or taste, save that hot-air-dried berries had the best appearance. In comparative studies on blueberries, the degree of phytochemical and bioactivity retained during freeze, microwave-vacuum (MIVAC), hot-air (76°C), and combined hot-air MIVAC (HAMIVAC) were determined [113]. Hot-air-dried blueberries had highest retention of ellagic acid, quercetin, and kaempferol. Freeze-dried and HAMIVAC drying had best retention of total phenolics and anthocyanins. For example, fresh berries had 66.8 mg GAE/100 g total polyphenols while freeze dried berries had 34.2 g GAE/100 g, HAMIVAC berries had 23.4 mg GAE/100 g, and hot-air-dried berries had 7.99 g GAE/100 g. Corresponding values for total anthocyanins were 113, 291, 147, and 67.9 mg pelargonidin-3-glucoside equivalents (P3GE)/100 g, respectively. Freeze-dried blueberries

had the highest antioxidant capacity. Berries dried only with hot air had the lowest retention of individual polyphenols. A similar study found that a combination of pretreatment in ethyl oleate/NaOH (to make the skin more permeable), osmotic dehydration in sucrose, and microwave-assisted convection drying produced blueberries that were comparable to freeze-dried berries in a relatively short time [114]. The effects of combining microwave with (spouted) fluidized drying (MWSB) of prefrozen blueberries have also been examined [115]. The assisted drying time was reduced up to 1/24th of that for tray drying. MWSB berries had low bulk density, better rehydration properties, and slightly redder color than those produced from noncombined spouted bed or tray drying.

The effects of cabinet drying ( $90^{\circ}\text{C}$  for 90 min) on highbush blueberries, with and without an osmotic pretreatment (60% sucrose and 1% NaCl), were examined [105]. The total anthocyanins was less in dried samples compared to fresh blueberries (7.2 mg C3R/g dry matter). Untreated dried berries had slightly higher values (4.3 mg C3R/g) than osmotically treated berries (3.7 mg C3R/g). It has been noted that dewaxing of the berry cuticle can lead to leaching of anthocyanins when blueberries are placed in osmotic solutions [116].

Several commercially available blueberry products that had been hot-air-dried, spray-dried, or freeze-dried were analyzed for antioxidant and antiproliferation activity [71]. Products that were heat processed generally had slightly lower levels of phenolic compounds and antioxidant activity. However, they had much lower antiproliferation activity against Hepa-1c1c7 cells. Another survey of commercially processed blueberry products found that products that had received less processing had higher antioxidant activity [117]. Compared to fresh fruit with ORAC values of 52.9 mmol TE/100 g dry weight basis, IQF frozen berries had 31.2, intermediate moisture fruit 25.5, low-moisture fruit 15.1, sugar-infused fruit 11.3, and blended powder 7.44 mmol TE/100 g dry weight basis.

The effects of hot air and freeze drying were compared for conventional and organic blueberries [118]. No differences ( $P > 0.05$ ) in phytochemicals were measured between conventional and organic berries. Blanching prior to drying helped to improve the drying rate and the retention of phytochemicals, but air drying resulted in substantial losses in anthocyanins, total phenolic compounds, and antioxidant activity. Freeze drying had lowest losses in phytochemicals.

In an attempt to improve drying properties, Rabbiteye blueberries were subjected to high-frequency ultrasound during osmoconcentration in  $55^{\circ}\text{C}$  Brix sucrose, prior to drying in a cabinet dryer at  $70^{\circ}\text{C}$  for 10 hours [119]. Osmoconcentration decreased titratable acidity and resulted in losses as high as 60% of anthocyanins and phenolics. They attributed this to leakage into the sugar media, facilitated by prior disruption of the skin, and cuticle by freezing. Subsequent air drying decreased levels up to 69% further. The samples treated with ultrasound had even greater losses than those with no treatment. The combination of high temperature, high sugar levels, and oxygen were reported to be most detrimental to color and antioxidant properties.

#### 4.6.5.3 Spray drying

Spray drying is a convenient way to produce dry powders as it allows high production rates and relatively low production costs, particularly as compared to freeze drying. However, spray drying of fruit extracts or purees can be complicated by the presence of high sugar levels. These result in relatively high glass transition temperatures and sticky points. Often, high molecular weight carriers such as maltodextrins are added, which can also help reduce

oxidation by coating the fruit particles [120]. Despite an important processing method, little research has been conducted on spray drying of blueberry products.

Studies showed that for spray drying of several fruit juice concentrates, best results were attained with maltodextrin DE6 at a 65:35 ratio for blackcurrants and 55:45 ratio for raspberries, coupled with relatively low air temperatures (160°C inlet/90°C exit) [121]. Others have noted that spray drying of fruit juices is quite complex, due to the interplay of initial solids, type of carrier, feed flow, and air temperatures [122]. For orange juice, the inlet air temperature and feed flow rate had the greatest effect on dryer yield and wall deposit. In studies on spray-dried acerola pomace extract, the best processing conditions were obtained using an inlet temperature of 194°C, a 4:1 ratio of drying aid (maltodextrin or cashew tree gum) to extract, and replacement of the maltodextrin with up to 80% cashew tree gum [123]. The resulting powders were least hygroscopic and with good flow ability. Follow-up studies showed that there is a trade-off concerning the retention of nutrients and bioactive compounds [124]. Maximum retention of the acerola extract ascorbic acid (93%) and total anthocyanins (90%) were attained at an inlet temperature of 170°C and drying aid-to-extract ratio of 5:1.

As previously noted, spray-dried blueberry products, as well as other products subject to heating, had relatively low antiproliferation activity as compared to fresh, IQF frozen, or freeze-dried products [103]. Total phenolic compounds retained were also lower in spray-dried blueberries as compared to non-heat-treated products, and canned blueberries or juice concentrates.

Response surface methodology was used to optimize a method for producing polyphenolic nutraceuticals from Muscadine grapes and Rabbiteye blueberries [120]. Aqueous 35% ethanol extracts were best obtained at 60°C after depectinization, then fermented with *Saccharomyces cerevisiae* at 25°C. The extract was filtered, then evaporated under vacuum. Concentrated extracts were spray-dried at 150°C (inlet) and 90°C (outlet). Although only 22–52% of the total phenolics and anthocyanins were recovered from the raw material, the authors felt the process was promising for commercial production.

#### 4.6.5.4 Extrusion

Another interesting potential for blueberries, grapes, and other fruit products is as an ingredient for extruded products. Extrusion can technically be considered as a form of dehydration, although the amount of water removal is usually not large. For cooked and puffed snacks and cereals, dough of approximately 15–20% moisture is forced through the extruder barrel by a series of screws that mix, shear, and compress the product. The product exits the die, often with some expansion, at moisture content between 6 and 12%. In one study, white corn meal was extruded with corn syrup, blueberry concentrate, or grape juice concentrate to form a potential breakfast cereal [125]. Extrusion reduced the level of anthocyanins from 40 mg malvidin-3-glucoside equivalents (M3GE)/100 g DW to 4 mg M3GE/100 g DW in the extruded product, but they were stable in subsequent storage for up to three months. Part of the loss was attributed to pigment polymerization and subsequent browning.

In subsequent studies, fruit powders, including blueberries, cranberries, concord grapes, and raspberries, were used to form extruded breakfast cereals [126]. The fruit cereals were slightly denser and redder, and contained higher phenolics and anthocyanins, and blueberry cereals had the highest level of anthocyanins. During 3–6 weeks storage, fruit cereal also had lower levels of hexanal and similar headspace volatiles, which indicated that less lipid oxidation had occurred.

#### 4.6.5.5 Radiant zone and vacuum belt drying

Blueberry powders were prepared from extract, juice, and puree using a novel radiant zone dryer [127]. In this system, liquid product was deposited on a moving polyester belt, and moved through five temperature zones (45–90°C) produced by radiant heaters, allowing for maximum water removal during early drying. No significant changes ( $P > 0.05$ ) in total anthocyanins were noted between liquid and powders. Highest levels were found in the extract and powder made therefrom (11.7 and 11.2 mg C3GE/g dry weight basis). Total phenolics also did not vary between wet and dry materials, with most found in the extract and extract powders (97.1 and 113.1 mg GAE/g dry weight basis). Total antioxidant activity, as determined by a proprietary assay, also did not vary from the wet and dried products.

Continuous vacuum belt drying has been studied in our labs as a means of rapid and low-temperature drying [128]. In this approach, fruit or purees are introduced through an air lock onto a belt held under vacuum. The material is conveyed over several conduction heaters, providing independent temperature during different drying periods. With this approach, Rabbiteye blueberries could be dried to very low moisture levels within 60–90 min. In addition, total monomeric anthocyanins, total phenolics, and ORAC values were not impacted with conduction temperatures 110°C or below.

## 4.7 Conclusions

Several varieties of blueberries exist that contain a combination of traditional nutrients and phytochemicals that are linked to good health promotion. Many studies have examined the phenolic compounds in blueberries, their bioavailability, and their potential for improving brain function, limiting infections, and reducing risk of cancer and CVD. As a significant amount of blueberries are processed, the role of processing in degrading or reducing bioavailability is of considerable interest. Processes that include heating or initiate enzymatic activity are most detrimental. Thus, freezing or freeze drying is least harmful to anthocyanins and related compounds, while juicing, canning, and hot-air drying is most harmful. Amongst drying technologies, freeze drying, radiant zone, and vacuum belt drying cause least changes in blueberry phytochemicals.

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## **5 Functional characteristics of dried cranberries**

K.M. Schaich

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### **5.1 Introduction**

Cranberries (*Vaccinium macrocarpon*) are one of the few fruits native to North America, and are still produced almost exclusively in the northern United States and Canada. At the time the New World was settled, cranberries were extremely important to both indigenous Americans and settling colonists for nutrition and medicine, especially providing a critical source of ascorbic acid (vitamin C) and a natural remedy for urinary tract infections (UTIs). After a very long time of being converted only to juice or reserved for jellied sauce to serve as a condiment with holiday roast meats, these tart little berries have recently returned to the forefront of nutraceuticals with their recognition as one of the “superfruits” that contain very high levels of natural nutrients and phytochemicals unusually protective for health. Today, even mainstream medicine accepts the value of cranberries in treating or preventing a wide range of disorders in addition to the traditional UTI.

Superfruit status [1] has now made dried sweetened cranberries a very popular “healthy” snack, and in addition has focused attention on the use of freeze-dried berries, dried cranberry powder, or other derivatives as supplement additives for a wide range of specialty foods and nutritional support products. All of these dried forms of cranberries offer the advantage of concentrating nutritional components. However, cranberry juice and raisin-like dried cranberry fruits have been criticized by some nutritionists for their high sugar content, while cranberry powder can be mixed with other ingredients using sweetening already present, or can be incorporated into capsules or powder blends for use with no sugar. In addition, cranberry powder is technologically easy to handle, providing a convenient medium for material transfer, portioning, mixing, and control, and is shelf-stable for extended periods [2]. It is not surprising, then, that even a cursory search on the Internet finds a huge number of websites advertising cranberry powders for incorporation in bases for on-the-go drink mixes, health supplements, urinary health products, antioxidant supplements, natural colorant/antioxidant in cosmetics, oral care products, and even pet food and nutrition products. For some years, there were great problems in comparing materials and research results, particularly with medical studies, because of the natural variability in cranberry products from different sources and growth history. To provide a common material of constant

composition that would allow clear delineation of health effects, the US National Institutes of Health National Center for Complementary and Alternative Medicine contracted for development and production of a Standardized Dried Cranberry Powder for use in research on studies of cranberry bioavailability, pharmacokinetics, and physiological effects [3]. Specifications for these products are delineated in the US Code of Federal Regulations 21 CFR parts 110 & 111. Examples of cranberry powders developed under this mandate include the following:

From Ocean Spray Inc. (Lakeville-Middleboro, MA)

- Cranberry 90 MX Powder—spray-dried cranberry concentrate with magnesium hydroxide carrier and tricalcium phosphate anticaking agent, minimum 0.5% proanthocyanidins (PACs) and minimum 30% organic acids.
- Cranberry Extract Powder—freeze-dried liquid extract of cranberries (*Vaccinium macrocarpon*) containing  $\geq 1.5\%$  PACs and  $<10\%$  organic acids.

From Decas Botanical Synergies (Wareham, MA)

- PACran<sup>®</sup>—freeze-dried whole cranberry powder, minimum 1.5% PACs.
- HI-PAC 4.0<sup>®</sup>—spray-dried cranberry juice water extract, minimum 4% PACs.
- HI-PAC POWDER<sup>®</sup>—spray-dried cranberry juice water extract, minimum 10% PACs.
- CystiCran<sup>®</sup>—spray-dried cranberry extract powder standardized to 30% PACs.
- CystiCran 40—spray-dried cranberry extract powder standardized to 40% PACs.

Cranberries and juice products have been reviewed [4, 5], but relatively little detailed consideration has been given to these new dried cranberry powders. To fill this gap, this chapter reviews composition and nutraceutical characteristics of cranberry powder as well as reported therapeutic effects and food applications.

## 5.2 Composition and nutritional characteristics of dried cranberry powder

### 5.2.1 Composition of fresh cranberries and modifications imposed by dehydration

Whole cranberries are well-known as a rich source of many physiological and phytochemical nutrients. Indeed, cranberries had the highest total phenol content of 20 common fruits tested by Vinson [6]. However, they are mostly consumed in some processed form rather than the exceptionally tart fresh raw fruit, so the nutrients that count are those remaining after juicing, gelling, and dehydrating. The number one nutrient loss during processing is ascorbic acid [2, 7] and some of the phytonutrients are damaged as well, by polyphenol oxidase action [8, 9], oxidation [10], hydrolysis [11], phenol condensation and polymerization into brown pigments [12], and thermal degradation [5, 13]. Anthocyanins (such as quercetin, myricetin, and kaempferol) are particularly sensitive, losing sometimes more than half their original content [14]. Nutrients also become diluted in cranberry juice. Overall, then, the nutrient composition of cranberry products actually consumed does not exactly match the composition of fresh whole berries, as was shown in a detailed tabulation of the phytonutrients (classes of compounds, individual components, and amounts) in whole fresh berries versus cranberry products in a recent review [5].

Dried cranberry powders present an interesting and complex paradox. On the one hand, a great concentration of nutrients occurs with dehydration of extracts, cranberry juice, or whole berries except for ascorbic acids (which is destroyed) [2]. Compounds that comprised only 10–20% of fresh berries now become 80–98% of the product, depending on the dehydration method and whether carriers and anticaking agents are added. In addition, dried whole cranberry powders retain the pomace, the skins, seeds, and solids left over after pressing fruit for juice. Cranberry pomace is normally discarded or recycled into sauce after juice extraction. However, it is a good source of dietary fiber and also contains appreciable amounts of polyphenols. White *et al.* [15] found 0.6 g polyphenols/100 g dry weight in lyophilized pomace; about 19% of this was distributed in 6 anthocyanins, 55% was in 13 flavonols, and 26% in 8 procyanidins (Table 5.1). Even if the PACs are bound to the pomace fiber (primarily pectins), they may be released by microbial metabolism in the intestines. Thus, overall, cranberry powders offer distinct advantages when the goal is to provide phytonutrients as an ingredient for food, personal care, and pharmaceutical products.

**Table 5.1** Composition of polyphenols in freeze-dried cranberry pomace (material remaining after removal of juice)

	<b>mg/100 g dry weight</b>
<b>Anthocyanins</b>	
Cyanidin-3-galactoside	13.2
Cyanidin-3-glucoside	4.5
Cyanidin-3-arabinoside	49.6
Peonidin-3-galactoside	20.1
Peonidin-3-glucoside	7.4
Peonidin-3-arabinoside	26.6
<b>Procyanidins</b>	
DP1 cat/epi monomers	5.8
DP2A A-type dimer	82.6
DP2B B-type dimer	4.4
DP3A	30.8
DP3B	1.6
DP4B	22.9
DP5A	7.1
DP6A	12.1
<b>Flavonols</b>	
Myricetin 3-xyloside	1.5
Myricetin 3-arabinoside	1.8
Quercetin 3-galactoside	12.8
Quercetin 3-xyloside	5.5
Quercetin 3-arabinopyranoside	15.2
Quercetin 3-arabinofuranoside	16.7
Quercetin 3-rhamnoside	18.5
Methoxyquercetin 3-xyloside	11.4
Quercetin 3-coumaroyl galactoside	2.3
Quercetin 3-benzoyl galactoside	27.5
Myricetin	55.6
Quercetin	146.2
Unidentified	12.1

Source: Adapted with permission from White *et al.* [15].  
DP, degrees of polymerization.

On the other hand, stresses during dehydration cause the same kinds of damage and loss of nutrients as processing of cranberry juice and sauce [16–19]. Consequently, how the cranberries are dried markedly affects the resulting phytochemical composition. High temperatures, air exposure, and berry disruption are three key factors that must be controlled to maintain nutrients in dried cranberry powder [20]. During heating steps, hydrolysis or thermal degradation of the matrix (cell wall polysaccharides) or polymeric phenols with concomitant release of phenolic acids, monomers, and small polymers are balanced against polymerization or oxidation of phenols. In general, the higher the temperature during drying and the longer the drying time, the greater the loss of phytonutrients [17]. Heat induces oxidation (including phenolic browning), isomerization (e.g., epimerization of catechins), and excision of the gallate group attached to the C-ring of flavonoids [16], and any moisture present during heating (e.g., early stages of dehydration) accelerates hydrolysis and dimerization [17, 21].

Any processing combinations that minimize heat, drying time, or air exposure protect nutrients in dried cranberries. For example, adding vacuum reduces loss of anthocyanins, ellagic acid, flavanols, and ascorbic acid compared to conventional air drying [16], and adding microwave treatments to the vacuum improves protection even further. When cranberries were pretreated by halving and steam blanching to inactivate enzymes, losses of ascorbic acid were 20–40% greater for convection drying than for vacuum microwave drying [19]. Under vacuum, the water boils at temperatures substantially below the atmospheric 100°C; at low microwave power (240 W), microwaves penetrate the center for the product to facilitate heating. The vacuum microwave combination facilitates water evaporation, reduces processing time, and retains acyl coenzyme A oxidase (AOX) activity [16]. At the same time, excessively high vacuums remove large proportions of volatile compounds involved in flavor and aroma. Thus “soft” conditions of vacuum microwave drying (e.g., 72–74 kPa vacuum and 360 W microwave power) have been recommended to retain highest concentrations of volatiles and the best sensory quality [18].

Given these observations, it is not surprising that lyophilization of whole berries under vacuum at 196°C gives dried products with the highest % cranberry solids and greatest retention of color, flavor, and nutrients. Lyophilization of whole or half berries minimizes tissue disruption that accelerates enzyme and oxidation reactions [2], and maintains the lowest temperature during drying, thus maximally immobilizing molecules, removing activation energies, and minimizing chemical and enzymatic reactions.

In spray drying of cranberry juices or extracts, the carriers also affect stability, at least in part due to moisture control. Anthocyanins in spray-dried açai degraded faster as water activity increased. In comparisons of 10 DE and 40 DE maltodextrins, gum Arabic, and tapioca starch as carriers, maltodextrin 10 DE provided the greatest anthocyanin protection.

### **5.2.2 Nutrient and phytonutrient composition of dried cranberry powder**

Nutritionally, cranberries have long been recognized as rich sources of ascorbic acid, vitamin A, thiamine, riboflavin, niacin, dietary fiber, and the essential minerals such as calcium, magnesium, manganese, phosphorus, and potassium that should not be overshadowed by the emphasis on cranberry phytochemicals. Except for ascorbic acid, these are largely retained and concentrated in dried powders, as shown in the nutrient compositions of commercial cranberry powders from two major suppliers of standardized products (Table 5.2). Variations in

**Table 5.2** Nutritional and functional characteristics of commercial dried cranberry powders (values in per 100 grams edible portion)

Units	Spray-dried cranberry juice concentrates					
	Freeze-dried		Spray-dried		Freeze-dried	
	Extract	powder [22, 23] <sup>a</sup>	90 MX	[24, 25] <sup>b</sup>	PACran	90 [28, 29] <sup>c</sup>
Fruit solids	%	98	90	100	90	90
Water	g	5.5	2.5	4.6	3.85	3.85
Energy	kcal	367	360	432	356	356
Protein	g	1.15	<0.10	5.38	0.46	0.46
Fat	g	0.173	0.24	10.99	0.02	0.02
Calories from fat	g	1.56	2.16	99	0.0	0.0
Saturated fat	g	0.038	0.0	0.92	0.0	0.0
Trans fat	g	<0.007	0.0	0.0	0.0	0.0
Cholesterol	g	1.0	0.0	0.0	0.0	0.0
Ash	g	2.9	7.46	1.16	7.22	7.22
Carbohydrate	g	90.3	89.35	77.87	88.45	88.45
Dietary fibre	g	26.1	6.02	45.9	4.1	4.1
Sugars	g	6.4	36.9	13.21	37.91	37.91
<b>Vitamins</b>						
Niacin	mg	1.98	0.8	0.75	1.0	1.0
Riboflavin	mg	0.05	1.14	0.7	0.41	0.41
Thiamin	mg	0.18	0.22	0.24	0.18	0.18
Vitamin A	IU	na	na	892	<40	<40
Vitamin C	mg	<1.0	4.9	19.4	2.8	2.8

(continued)

**Table 5.2** (Continued)

Units	Powder [22, 23] <sup>a</sup>	Freeze-dried		Spray-dried		Freeze-dried		Spray-dried cranberry juice concentrates				
		Extract	[24, 25] <sup>b</sup>	90 MX	[26, 27] <sup>c</sup>	PACran	[28, 29] <sup>d</sup>	NutriCran	90S [30, 31] <sup>e</sup>	Hi-PAC 10	CystiCran	40 [32, 33] <sup>f</sup>
<b>Minerals</b>												
Calcium	mg	185		184		60.4		118.3		118.3		11.3
Copper	mg	0.44		0.5		0.4		0.3		0.3		na
Iron	mg	8.63		4.28		6.61		10		10		na
Magnesium	mg	90.4		2877		49.5		1757		2757		na
Phosphorus	mg	96.9		95		139.4		46.7		46.7		na
Potassium	mg	696		743		444.2		890		890		na
Sodium	mg	406		29		3.7		26.3		26.3		6.0
Zinc	mg	1.12		0.87		1.8		1.5		na		na
<b>Organic acids</b>												
Total phytosterols	%	8–15		30		na		35		35		na
Total phenolics	%	na		na		2.8		na		na		na
Proanthocyanidins	%	na		na		2–5		2–5		2–5		na
Anthocyanins	%	>1.5		0.5		1.5		0.95		1.0		30
Quercetin	mg	na		na		0.15–1.00		0.15		1.00		0.15
						na		3–4.4		3–4.4		na

IU, international unit; na, not available.

<sup>a</sup>Ocean Spray Extract Powder, freeze-dried whole berry powder, 2% tricalcium phosphate added to prevent caking.

<sup>b</sup>Ocean Spray 90 MX, spray-dried with magnesium hydroxide as carrier and tricalcium phosphate as anticaking agent.

<sup>c</sup>Decas PACran, freeze-dried whole berry powder.

<sup>d</sup>Decas NutriCran 90, spray-dried cranberry juice concentrate with magnesium hydroxide, tricalcium phosphate, 1% standardized proanthocyanidins.

<sup>e</sup>Decas NutriCran 90S, spray-dried cranberry juice concentrate with magnesium hydroxide, tricalcium phosphate, 10% proanthocyanidins, with magnesium hydroxide, tricalcium phosphate.

<sup>f</sup>Decas Hi-PAC 10, spray-dried cranberry extract standardized to 30% proanthocyanidins, with magnesium hydroxide, tricalcium phosphate.

<sup>g</sup>Decas CystiCran 40, spray-dried cranberry extract standardized to 30% proanthocyanidins, with magnesium hydroxide, tricalcium phosphate.

**Table 5.3** Classes of phytochemicals in dried cranberry powder

Phytochemicals	Example	Function in cranberry products
<b>Flavonoids</b>		
Anthocyanins	Peonidin-3-O-galactoside	Primary red pigment and AOX
Flavonols	Quercetin-3-O-galactoside	Copigment and AOX stabilizer
Flavanols (catechins)	Epicatechin	Astringent flavors and AOX stabilizer
Proanthocyanidins	Proanthocyanin A2	Astringent flavors and stabilizer
Polymeric colour compounds	Cyanidin-pentoside-flavan-3-ol	Red-brown pigment
<b>Non-flavonoids</b>		
Non-flavonoid	Resveratrol	Astringent flavors and AOX stabilizer
Simple phenolics	Salicylic acid	Odours and AOX stabilizer
<b>Non-phenolics</b>		
Organic acids	Ascorbic acid	Sour flavors
Complex carbohydrates	Pectin	Gelation and edible films
Sugars	Fructose	Sweet flavors

Source: Adapted with permission from Pappas and Schaich [5].

AOX, antioxidant.

composition, particularly in minerals, arise largely from additional ingredients incorporated as carriers and anticaking agents.

Phytochemical composition of dried cranberry powders is not as well documented as for whole berries and cranberry juice, particularly in terms of quantitation. Research is still largely at the stage of identifying total components so an extensive accounting of phytochemicals, as was done by Pappas [5], is not yet possible. The general classes of compounds are, of course, the same as in fresh whole cranberries (Table 5.3), although concentrations and, in some cases also product distribution (particularly PACs), can be quite different in dry powders. PACs are usually the dominant fraction in dry powders.

### 5.2.2.1 Anthocyanins

In one of the earliest studies using HPLC-ESI-MS-MS to determine structure and composition of cranberry anthocyanins, Wu and Prior [36] identified 13 anthocyanins in freeze-dried cranberries in methanol/water/acetic acid (85:15:0.5, v/v/v) extracts (Table 5.4). All were present as glycosides rather than aglycones, with galactose being the major sugar. Importantly, of 18 anthocyanin-rich fruits tested, only cranberries and Concord grapes contained all six anthocyanin backbones.

Instrumentation advances now make it possible to determine both what anthocyanins are present and in what quantities. Brown *et al.* [37] used ultraperformance liquid chromatography (UPLC) with time-of-flight mass spectrometry (MS) to identify and quantitate anthocyanins in five cultivars of freshly harvested and freeze-dried whole cranberries for metabolomic profiling. Peonidins were present in double the cyanidins concentrations, with peonidin-3-galactoside as the dominant anthocyanin in all cultivars tested (Table 5.5). Similar peonidin and peonidin-3-galactoside dominance was observed in anthocyanins of three commercial cranberry powders (Table 5.6) [38], although levels of all anthocyanins detected were considerably lower than in the fresh berry powders. Whether this difference is due to

**Table 5.4** List of anthocyanin glycosides identified in freeze-dried cranberry powder by HPLC-ESI-MS-MS**Anthocyanins**

Cyanidin 3-galactoside  
 Cyanidin 3-glucoside  
 Cyanidin 3-arabinoside  
 Delphinidin 3-arabinoside  
 Malvidin 3-arabinoside  
 Malvidin 3-galactoside  
 Pelargonidin 3-arabinoside  
 Pelargonidin 3-galactoside  
 Peonidin 3,5-digalactoside  
 Peonidin 3-arabinoside  
 Peonidin 3-galactoside  
 Peonidin 3-glucoside  
 Petunidin 3-galactoside

Source: Adapted from Wu and Prior [36].

actual concentrations, cultivars, or analytical methods cannot be ascertained since details were not provided in the Palikova *et al.* [38] study. In contrast, cranberries obtained from a local supermarket and freeze-dried showed 46% cyanidins (39.8 mg/100 g fresh weight) and 43% peonidins (36.8 mg /100 g fresh weight) [39].

These differences show clearly the need for standardization of materials used in medical studies and as food ingredients, as well as for high-level analytical instrumentation to obtain accurate quantitative and qualitative information. They also raise interesting questions about relative postharvest stability of the individual and total anthocyanins that must be considered in preparation of commercial standardized products.

**Table 5.5** Anthocyanin contents (mg/100 g powder in dry weight) in five cultivars of fresh, freeze-dried cranberries ground to a powder

	<b>Cyanidin 3-galactoside</b>	<b>Cyanidin 3-glucoside</b>	<b>Cyanidin 3-arabinoside</b>	<b>Pelargonidin 3-galactoside</b>	<b>Pelargonidin 3-arabinoside</b>
<b>Biological replicates<sup>a</sup></b>					
Ben Lear	149.4	14.6	135.2	367.2	131.9
Bergman	143.1	12.0	131.8	305.9	109.4
GH1	140.6	10.0	118.2	254.1	82.1
Pilgrim	70.0	8.3	61.7	138.5	49.6
Stevens	56.6	9.6	40.9	118.3	55.2
<b>Analytical replicates<sup>b</sup></b>					
Ben Lear	111.2	10.0	85.4	301.3	121.5
Bergman	85.5	8.6	72.5	165.7	79.8
GH1	123.0	10.5	85.5	285.3	108.5
Pilgrim	68.5	8.4	58.2	124.1	58.7
Stevens	49.4	7.9	39.1	108.0	62.3

Source: Adapted with permission from Brown *et al.* [37].

<sup>a</sup>Biological replicates (five individual berries).

<sup>b</sup>Analytical replicates (pooled berries with replicate analyses).

**Table 5.6** Anthocyanin composition of three commercial standardized cranberry powders (mg/100 g powder)

<b>Anthocyanins</b>	<b>NUTRICRAN 90S</b>	<b>HI-PAC 4.0</b>	<b>PACran</b>
Total anthocyanins	440	610	115
Cyanidin-3-arabinoside	24	70	12
Cyanidin-3-galactoside	54	81	21
Cyanidin-3-glucoside	31	10	3
Cyanidin-3-pentoside	13	na	1
Cyanidin-3,5-dihexoside	na	50	na
Delphinidin	8	na	3
Peonidin-3-arabinoside	25	109	16
Peonidin-3-galactoside	135	220	41
Peonidin-3,5-digalactoside	106	50	2
Peonidin-3-glucoside	45	30	6

Source: Adapted with permission from Palikova *et al.* [38].

na, not available.

### 5.2.2.2 Flavonols and flavanols

When product applications are health related, flavonols and flavanols in cranberry powders have attracted even more attention than anthocyanins, flavonols for their role in UTIs and flavanols because they provide building blocks for some PACs. Vvedenskaya *et al.* [40] extracted flavonols from Ocean Spray 90MX cranberry powder (freeze-dried) with acetone followed by ethyl acetate, separated fractions by high-performance liquid chromatography (HPLC), and determined structures of collected fractions by nuclear magnetic resonance (NMR). Twenty-two flavonoid (mostly quercetin) glycosides were identified (Table 5.7), six of them new (previously unidentified). In addition to standard flavonol glycosides,

**Table 5.7** Flavonols of Ocean Spray 90 MX cranberry powder

#### Flavonols of Ocean Spray 90 MX<sup>a</sup>

3'-Methoxyquercetin-3-β-galactoside
Dimethoxymyricetin-hexoside
Methoxymyricetin-pentoside
Methoxyquercetin-pentoside
Myricetin-3-α-arabinofuranoside
Myricetin-3-α-xylopyranoside
Myricetin-3-β-galactoside
Quercetin-3-O-(6"-benzoyl)-β-galactoside
Quercetin-3-O-(6"-p-coumaroyl)-β-galactoside
Quercetin-3-rhamnopyranoside
Quercetin-3-α-arabinofuranoside
Quercetin-3-α-arabinopyranoside
Quercetin-3-α-xylopyranoside
Quercetin-3-β-galactoside
Quercetin-3-β-glucoside

Source: Adapted from Vvedenskaya *et al.* [40].

<sup>a</sup>It is a spray-dried cranberry concentrate with magnesium hydroxide as carrier and tricalcium phosphate as an anticaking agent.

**Table 5.8** Comparison of flavonols reported for three commercial cranberry powders versus cranberries obtained from a local market and freeze-dried (mg/100 g dry weight)

	<b>NUTRICran 90S [38]</b>	<b>HI-PAC 4.0 [38]</b>	<b>PACran [38]</b>	<b>Supermarket<sup>a</sup> [39]</b>
<b>Flavonols</b>				
Quercetin	1352	2179	680	388
Myricetin				332
<b>Flavan-3-ols</b>				
Catechin				16
Catechins gallate				158
Epicatechin				90
Epicatechin gallate				0.0
Epigallocatechin				30
Gallocatechin				0.0
Gallocatechin gallate				8.0

<sup>a</sup>Fresh weight converted to dry wt assuming 95% moisture in whole cranberries.

three unique compounds were identified: two quercetin glycosides conjugated to benzoic or hydroxycinnamic acids and quercetin-3-arabinoside in both furanose and pyranose forms. Galactose and arabinose were the major conjugated sugars.

As with the anthocyanins, quantitation of flavonols by class in the three Decas commercial powders and supermarket cranberries showed large differences (Table 5.8); high levels of quercetin but no myricetin were reported for the Decas berry powders [38], while an order of magnitude lower quercetin and myricetin in about equal quantities were reported in the dried supermarket berries, even after adjusting values from fresh weight to dry weight basis [39]. Reasons for these huge differences were not clear from the papers, but once again argue for standardization of materials to be used in research or as ingredients. Less information is available about the flavanol content of cranberry powders. Flavan-3-ols contents determined in supermarket berries (unspecified variety) that were freeze-dried are also listed in Table 5.8.

### 5.2.2.3 Proanthocyanidins

Probably the most intense interest in composition of cranberry powders has been focused on the PAC fraction due to its reported effects on UTI. PACs (including degree of polymerization two and higher) are the dominant fraction in cranberry powders, accounting for as much as 63% of total phenols [41, 42] (Table 5.9).

The number of individual PAC species possible theoretically is astoundingly large due to the many kinds of linkages that can be formed, degrees of polymerization (DP), and monomer substrates that may be involved. Very few PAC structures have been elucidated fully because dealing with separation and structural analysis of such large molecules is technically quite challenging. However, with improvements in analytical instrumentation this limitation is changing. Until recently, it was assumed that the major (if not exclusive) monomers linked in cranberry PACs were catechin, epicatechin, epigallocatechin, and ellagic acid [43, 44], at least in part because these were the monomers identified in the few PACs whose structure

**Table 5.9** Phenol distributions in Ocean Spray Cranberry OSA7 and freeze-dried whole cranberries

Fraction	OSA7 fraction <sup>a</sup> [41]						Total (mg/g dry weight)
	1 (mg/g solid)	2 (mg/g solid)	3 (mg/g solid)	4 (mg/g solid)	5 (mg/g solid)	6 (mg/g solid)	
Phenolic acids	78						1.3
Flavonols	15	374	294	35	21	26	2.6
Anthocyanins	5	8	23	16	16	31	2.99
Proanthocyanidins	132	61	497	788	743	533	11.73
mDP <sup>c</sup>	1.2	1.6	5.8	6.1	12.7	11.3	2.4–35
% A-type bond	3.3	61.8	21.6	19.3	11.7	12.4	0.1–7.9

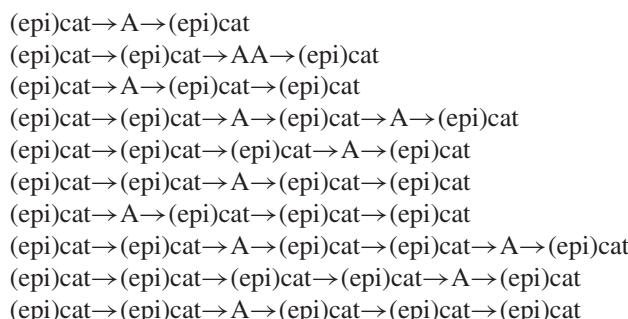
mDP, mean degree of polymerization.

<sup>a</sup>70% acetone fraction of extract from Stevens cranberries lyophilized and fractionated on a diol normal phase HPLC column. Six fractions collected and analyzed by reversed phase LC-MS.

<sup>b</sup>Cranberries purchased in a local supermarket lyophilized and fractions selectively extracted for analysis.

<sup>c</sup>Range over all fractions reported for whole berry powder.

had been determined. For example, Gu *et al.* [43] identified the following monobase PACs with characteristic A-type linkages in freshly harvested and freeze-dried cranberries:



It is extremely interesting, then, that recent application of thiolysis combined with advanced liquid chromatography–mass spectrometry (LC-MS) and UPLC-MS techniques identified mixed polymers with two types of subunits: anthocyanin–ethyl-flavanol (monomer to tetramer) and pyranoanthocyanin–flavanol (monomer to dimer) with DP up to 16 (Table 5.10). Sequential PAC extracts of OSA7 powder identified six fractions increasing in degree of polymerization from 1.2 to 11.3. The novel ethyl bridges were found only in later fractions 4–6 and so were clearly integral to PAC structures. Mixed PACs are not characteristic of fresh berries. Now that advanced methodology is available, it will be interesting to see whether these complex polymers are decomposition products generated during processing, dehydration, or oxidation, and also whether they retain the antioxidant activity associated with native monobase PACs.

#### 5.2.2.4 Simple phenols, phenolic acids, and nonaromatic organic acids

Simple phenols and benzoates are quantitatively minor components of cranberries, but, nevertheless, contribute significantly to physiological effects, chemical reactivity, and innate stability of cranberries. Their effectiveness as antioxidants will be discussed in the next

**Table 5.10** Mixed proanthocyanidins identified in extracts of OSA7 cranberry powder following thiolytic

<b>Proanthocyanidins</b>	<b>Fraction</b>	<b>Proanthocyanidins (Continued)</b>	<b>Fraction</b>
(epi)Cat-ethyl-cyanidin-arabinoside	5	Pyranocyanidin-hexoside-A2	6
Pyranopeonidin-arabinoside-(epi)cat	6	DP2B Pyranocyanidin-hexoside	6
(epi)Cat-ethyl-peonidin-arabinoside	4	A2-ethyl-cyanidin-hexoside	4–6
(epi)Cat-ethyl-cyanidin-hexoside	5, 6	DP2B-ethyl-cyanidin-hexoside	6
Pyranopeonidin-hexoside-(epi)cat	5	Pyranopeonidin-hexoside-A2	6
(epi)Cat-ethyl-peonidin-hexoside	4, 5	DP2B Pyranopeonidin-hexoside	6
Pyranocyanidin-arabinoside-A2	6	A2-ethyl-peonidin-hexoside	4–6
DP2B Pyranocyanidin-arabinoside	6	DP2B-ethyl-peonidin-hexoside	4, 5
A2-ethyl-cyanidin-arabinoside	4–6	DP3 1A-ethyl-peonidin-arabinoside	5, 6
DP2B-ethyl-cyanidin-arabinoside	6	DP3 1A-ethyl-cyanidin-hexoside	6
Pyranopeonidin-arabinoside-A2	6	DP3 1A-ethyl-peonidin-hexoside	5, 6
DP2B Pyranopeonidin-arabinoside	6	DP3B-ethyl-peonidin-hexoside	5
A2-ethyl-peonidin-arabinoside	4–6	DP4 1A-ethyl-cyanidin-hexoside	6
DP2B-ethyl-peonidin-arabinoside	5	DP4 1A-ethyl-peonidin-hexoside	5

Source: Adapted with permission from Tarascon *et al.* [41].

**Table 5.11** Organic and phenolic acids in commercial cranberry powders (mg/100 g powder)

	<b>NUTRICRAN 90S<sup>a</sup> [38, 49]</b>	<b>HI-PAC 4.0<sup>a</sup> [38, 49]</b>	<b>PACran<sup>a</sup> [38, 49]</b>	<b>CCP<sup>b</sup> [38, 49]</b>
<b>Organic acids</b>				
Benzoic	372	311	160	
Citric	1980	1954	nd	
Hippuric				22.20
Malic	1892	1600	263	
Malonic	177	200	nd	
Phenylacetic				<0.2
Quinic	2570	2085	nd	
<b>Phenolic acids</b>				
3,4-Dihydroxyphenylacetic				<0.2
3-Hydroxybenzoic				1.90
3-Hydroxyphenylpropionic				1.53
4-Hydroxybenzoic				3.42
4-Hydroxyphenylacetic				3.21
Caffeic	10	14	6	8.42
Chlorogenic	25	35	nd	10.30
Dihydrocaffeic	121	129	53	
Ferulic				2.96
Gallic				14.50
Gentisic	8	23	nd	1.00
p-Coumaric	79	75	47	25.20
Protocatechuic	65	77	52	51.20
Vanillic	21	52	nd	

CCP, concentrated cranberry powders; nd, not detected.

<sup>a</sup>Products from Decas Botanicals, Inc., Carver, MA.

<sup>b</sup>Concentrated cranberry powder obtained from Decas Botanicals, Inc., Carver, MA.

section. In fresh berries, they are mostly in bound forms, esterified to sugars, cell wall polysaccharides, or other components; usually <10% of benzoates and simple phenols are present in free form (released without hydrolysis) [45]. The three primary nonvolatile organic acids (such as quinic, citric, and malic) of cranberry juice [46–48] are the major organic acids also in cranberry powders (Table 5.11). They contribute to tartness, maintenance of low pH for anthocyanin stabilization, and some metal complexation.

### 5.3 Natural antioxidants in dried cranberry powder

When asked about antioxidants in cranberries, most people immediately mention ascorbic acid first and anthocyanins second. Studies have shown that anthocyanins indeed are key antioxidants in cranberries [50–52], but in some cases flavonoids and PACs are stronger antioxidants than anthocyanins, and ascorbic acid contributes very little to antioxidant content and activity [6, 53]. Attempts to correlate antioxidant activity to total phenols or phenolic profiles in cranberries and other berries have been largely unsuccessful [54, 55]. Even more important is the observation that most of the phenol classes in cranberries have at least some antioxidant activity and they act synergistically with each other to enhance overall antioxidant effects [6, 56, 57], so a more appropriate question may be, what specific action does each of the molecular classes listed below contribute and how do these fractions interact (in parallel, in series, or in concert) to provide the overall effects of cranberry powders and cranberry extracts?

Fraction	Actions
Anthocyanins (dominant fraction)	Scavenge radicals, electron transfer (reducing agents), and recycle ascorbic acid
Flavonoids (flavonols and flavanols)	Inhibit lipid oxidation, chelate metals, scavenge radicals, and complex carbonyls
Tannins Condensed nonhydrolyzable (PACs) Hydrolysable: gallic/ellagic acid esters	Very high radical scavenging activity due to large numbers of phenol group
Phenolic acids	Scavenge radicals and decompose hydroperoxides
Resveratrol	Scavenge radicals

The relative importance of each class varies depending on concentrations and reaction environment. Chemically, this seems quite logical, especially when the phytochemical components exert different and complementary actions (e.g., radical scavenging, metal chelating, recycling other antioxidants, modulation of enzyme activity, and second messenger function) and have different solubilities in lipid versus aqueous phases. It is important to remember also that antioxidant activity is system specific. Many phenols can act predominantly as hydrogen atom transfer agents in one solvent but as an electron transfer agent in another, and which one dominates determines how the antioxidant interacts with target molecules. Reactivity in the common aqueous *in vitro* assays does not always accurately predict antioxidant activity in cell culture, foods, or *in vitro* where multiple phases, catalysts, and targets exist.

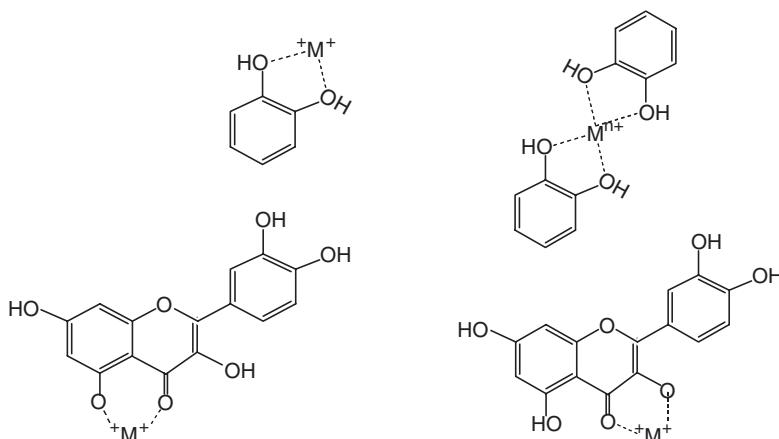
Overall, then, although the question of which fraction is the “most active” remains a controversial issue, it is fair to say that all of the following fractions work both separately and synergistically in contributing to antioxidant activity of cranberries, and that the relative effectiveness and active mechanism is determined by the reaction environment, target radicals active, and phase distribution of catalysts and antioxidants, as well as other factors [55].

How antioxidant activity is expressed makes a great difference in what molecules appear to be most active. Expressing activity on a weight basis (e.g., mmol quenching equivalents/mg dry matter) gives preference to molecules in highest concentration, while expressing activity on a molar basis (e.g., mmol quenching equivalents/mg or mol phenol) identifies which molecules or fractions are inherently more active in a given system. An example of this was shown dramatically in a study of hydrophilic and lipophilic radical scavenging by polar phenols (water-soluble, mostly phenolic acids), apolar phenols (flavonols, flavan-3-ols, and PACs), and anthocyanins [52]. When radical quenching was tested in an aqueous radical system (DPPD) and activity was expressed on a weight basis, anthocyanins were marginally the most active at acid pH but the hydrophilic fraction was twice as active at neutral pH. When expressed on a molar basis, the polar fraction was by far the most active under all conditions and anthocyanins were more active than apolar phenols. This behavior is not surprising considering that the radical test system was also aqueous with polar radicals. In a lipid oxidation test system, the apolar fraction surprisingly did not trade places with the polar fraction. The polar phenols were still the most active, but now only marginally more effective than anthocyanins at both acid and neutral pH. The pH dependence of the response suggests that protonated species are the most active forms. Cranberry anthocyanins are active only in acidic environments; they lose antioxidant activity when neutralized [58].

Structures of cranberry phenols within each class govern radical reactivities. Phenols are excellent radical scavengers because the electron from the phenoxy radical generated when the hydrogen is abstracted becomes delocalized over the ring  $\pi$  system, thus lowering the electron density on the  $-O^\bullet$  and hence the overall reactivity of the radical. As shown in Table 5.11, cranberry powders have appreciable contents of hydroxybenzoic and hydroxycinnamic acids that localize in polar extract fractions and phases of foods. Of these, (di)hydroxycinnamic acids (caffeoic, chlorogenic, ferulic, sinapic, and *p*-coumaric) are more active radical scavengers than the corresponding (di)hydroxybenzoic acid derivatives such as *p*-hydroxybenzoic and vanillic acids [59]. The additional inductive effect of the double bond on the acid side chain in cinnamates pulls electrons away from the phenoxy group, facilitating H release and stabilizing the phenoxy radical.

In terms of flavonols, nine fractions isolated from dried cranberry extracts showed antioxidant activity in 1,1-diphenyl-2-picrylhydrazyl (DPPH) and oxidized low-density lipoprotein (LDL) assays [60]. Nearly all were glycosides: myricetin and its galactoside and arabinoside, quercetin galactoside, arabinoside, rhamnoside, and xyloside; and cyanidin-3 galactosides. In general, myricetin derivatives were less active than quercetin, and (in contrast to other studies), the glycosides were more active than their corresponding aglycones. Cyanidin-3-galactoside was dramatically strongest in its reaction with DPPH and inhibition of LDL oxidation.

Solubility and phase distribution affects how cranberry compounds respond in *in vitro* antioxidant tests and even more in actual applications, whether foods or tissues. Catechin monomers reacted more rapidly than procyandins in quenching stable DPPH radicals, but procyandins more actively inhibited lipid oxidation in emulsions [61]. This is not unexpected; PACs often show high radical scavenging activity because of the large number of phenolic



**Figure 5.1** Examples of metal binding configurations for cranberry phenols.

groups distributed across the molecular surface. However, it is not clear whether these results reflect actual reactivity of the two materials, or just physical properties. PACs are more apolar, so it can be argued that these results stem primarily from their increased solubilization in the lipid. Similarly, the large size of PACs physically limits access to the sterically hindered the DPPH radical, so innate radical reactivity is not being measured. Lipid peroxy radicals in methyl linoleate, on the other hand, are highly accessible. While this study has some interpretation questions, it does provide a good example of how compounds in cranberry powder may act synergistically by distributing differentially in aqueous and lipid phases.

No overview of cranberry antioxidant activity, even cursory ones such as this, can be complete without consideration of metal binding by cranberry phenols. Adjacent phenol groups (vicinal diphenols) and carbonyl-hydroxyl groups (Figure 5.1) are reasonably strong metal binders and mediate a second mechanism of antioxidant action by cranberry phenols. Of the anthocyanins, only delphinidin has the requisite structure (vicinal diphenol in the B-ring), but a number of flavonols and flavan-3-ols have both the B- and C-ring metal binding regions shown in Figure 5.1. Quercetin, the structure shown in Figure 5.1, is the major flavonol in cranberries. It uniquely contains all three metal binding positions [62] and is particularly well-recognized as a metal binder with the potential to inhibit metalloenzymes, inhibit metal-mediated lipid oxidation [63], remove critical metals from growth media, and in general interfere with any process involving or requiring metals [64]. Quercetin was identified as the most active compound in extracts of cranberry powder (Ocean Spray 90 MX) added to washed minced cod muscle to inhibit lipid oxidation; complexation of free iron and iron in heme was proposed as the active mechanism [63]. Metal binding may also contribute to the documented toxicity of quercetin [65].

This section will close with a note on the nonradical quenching antioxidant mechanism recently reported for catechins and procyanidins. Berry extracts were observed to inhibit formation of advanced glycation end-products (AGE) in serum models. Since procyanidins were found in all fractions of berry extracts, they were expected to be a major class of active compounds and a carbonyl complexation mechanism was proposed. Five different catechins–carbonyl adducts were identified in model systems of (+)-catechin and glyoxals

[66], verifying the proposed reaction. Catechins and other phenols can also work on the other side of AGE formation, binding to thiol and amine groups on proteins, thereby blocking carbonyl condensation sites [67, 68, 79]. The two reactions together provide a new antioxidant mechanism by which cranberry phenols may inhibit browning reactions in foods as well as prevent AGE-related chronic diseases *in vivo*.

## 5.4 Health effects of dried cranberry powders

The same antioxidant actions of radical quenching and metal complexation shown by cranberries in model reactions and foods can work in cells and tissues to inhibit progression of diseases that involve oxidative degradation. Cranberry phenols also bind to proteins, altering functionality and enzyme activity [5]. These three basic actions underlie numerous health benefits that have been associated with cranberry consumption and are now being targeted therapeutically with cranberry powders. These basic actions are also responsible for three general categories of cranberry actions in biological systems:

- Pathogen interactions.
- Antioxidant mechanisms or reduction of oxidative stress.
- Enzyme activity, signal transduction, and protein expression and activity.

General health effects of cranberries with specific focus on cranberry powders are covered briefly here. More detailed information is available in several excellent reviews [4, 5, 64, 69, 70].

### 5.4.1 Pathogen interactions

#### 5.4.1.1 Disruption of bacterial adhesion-prevention of UTIs, ulcers, and gum diseases

Cranberries have been used in folk medicine for millennia to prevent UTI, and UTI remains the most-studied health effect of cranberries. Cranberries and cranberry juice have been the carriers in the past, with mixed results because concentrations could not be controlled. Dry cranberry powders offer distinct prophylactic advantages in being able to deliver high concentrations and standardized doses enriched in the most active components. In recent years, this approach has attracted increasing attention as development of antibiotic resistance has increased the rate of ineffective treatment and persistent reoccurrence. Dry cranberry powder has been particularly effective in reducing reoccurrence and severity of symptoms of UTIs.

To provide some examples, cranberry powder containing 200 mg of a concentrated cranberry extract standardized to 30% phenolics given in capsules twice daily for 12 weeks completely prevented UTIs in women who were subject to recurrent infections [71]. In a study of 65 women, 1200 mg cranberry powder/day was required to decrease oxidized proteins in serum (AGP). At that level, samples of subjects' urine inhibited adhesion of *Escherichia coli* strains *in vitro*. Hippuric acid, salicyluric acid and isomers, quercetin glucuronide, and dihydroxybenzoic acid isomers were the main metabolites, but the compounds responsible for antiadhesion activity could not be distinguished. Another study of 60 women aged 18 to 40 with a history of recurrent UTIs and the presence of *E. coli* and mild symptoms of UTI

showed that 500 mg (low) or 1000 mg (high) whole cranberry powder per day reduced the number of *E. coli* detected in urine culture analysis between 25 and 45% after only 10 days of cranberry consumption [72]. This suppression was maintained over the 90 days of the study and, in addition, 40% of women receiving cranberry powder reported complete relief and remission from urological symptoms such as itching and burning sensation during regular and frequent urination. A daily dose of 500 mg or 1000 mg of standardized whole cranberry powder was thus recommended as an adjunct to antibiotic prophylactic therapy against recurrent UTIs. Similarly, in a prospective epidemiological study involving 120 recurrent cystitis patients of 43 urologists, treatment with concentrated cranberry powder reduced severity and prevalence of urinary problems from 98 to 28% after six months [73].

How do cranberries prevent development of UTIs? *E. coli* is the pathogen responsible for the most UTIs, accounting for 75–95% of infections [74, 75]. These bacteria are able to colonize in the urethra by expressing protein-based adhesins or lectins that bind them to glycoproteins and/or glycolipids on epithelial cell surfaces, allowing for subsequent colonization [76] in the urinary tract and finally in the bladder [75]. This binding is critical since free, unbound bacteria are washed out during urination. That cranberry products interfere with bacterial adhesion has been recognized for some time, and it is now generally accepted that the A-type cranberry PACs are the responsible compounds [77–81]. Repeated demonstration that PACs can inhibit adhesion of both resistant and sensitive strains of *E. coli* has led to development of cranberry powders standardized for high concentrations of PACs that are actively being evaluated in clinical tests. Results are still inconsistent due to differences in test systems, for example 50 µg/mL PACs was sufficient to inhibit adhesion of bacteria and hemagglutination of red blood cells *in vitro* [82], but in a study 70 mg PAC/day was required for maximum antiadhesion effects to be observed in the urine in humans [83]. Clearly, validating effects of cranberry powders to prevent UTIs, elucidating potential supporting roles for other cranberry phenols, and determining effective required doses will be a fruitful area for continued research.

Disruption of bacterial adhesion by cranberry compounds is not limited to the urinary tract, but is applicable to other body sites including the mouth and stomach which are constantly exposed to bacteria as well as to general resistance to viral and bacterial infections [see review (5)]. Addition of cranberry PACs to oral care interferes with bacterial adhesion to the tooth enamel, thereby preventing accumulation of the biofilms and plaque that lead to periodontal disease and tooth decay [84, 85]. Similarly, cranberry PACs interfere with the adhesion of *Helicobacter pylori*, a leading cause of stomach ulcers, which in turn are a major cause of stomach cancer. *H. pylori* has many adhesins that facilitate binding to gastric mucus and erythrocytes as well as epithelial cells [86, 87]. Cranberry juice [88] and cranberry juice powder (CJP) [89] have demonstrated generalized inhibition of bacterial cell adherence to surfaces, both glass and tissues, so it is not unreasonable to expect this mechanism to be active in the stomach lining. However, various combinations of blueberry, oregano, and grape seed extract powders with cranberry (dried juice) markedly increased anti-*H. pylori* activity in culture [90], showing apparent synergism between the various polyphenols. It was proposed that combinations of polyphenols can inactivate *H. pylori* by multiple mechanisms rather than a single mechanism of any one alone. Potential mechanisms include hyperacidification of the plasma membrane, disruption of H<sup>+</sup>-ATPase, quenching electron flow in the electron transport cycle, disrupting energy metabolism, and destabilizing membrane structure and stability. Protein binding and metal chelation leading to enzyme inactivation should also be added to this list.

Cranberry compounds active against *H. pylori* have not been clearly identified, although, as with UTI, PACs or some high molecular weight polymers are considered most likely candidates. Much is still to be learned about the role of cranberry components in inhibiting oral diseases and ulcers. Delivering high concentrations of active compounds for prophylaxis or treatment through cranberry powders directly, as in a capsule, or indirectly by incorporation into oral products, foods, or beverages is currently an active area of research.

#### 5.4.1.2 *Antimicrobial actions (metal binding, redox alterations, and protein binding)*

Several classes of cranberry compounds have shown antibacterial activity in broad contexts. Considering that phenol is commonly added to prevent mold growth in laboratory water baths and that polyphenols bind to proteins, this is not a strange observation. The question is, which classes are most active, and what are the mechanisms by which they inactivate microbial cells?

In comparisons of cranberry organic acid, phenolic, and anthocyanin effects on *E. coli* O157:H7, each class of compounds was shown to act by a different mechanism with different pH dependence [91]. Acids and anthocyanins were active only at low pH. Organic acid lowering of environmental and intracellular pH may create an electrical gradient that results in stacking organic acid ions against the cell membrane causing localized intense osmotic stress. Transmission electron microscopy detected completely collapsed cells when exposed to organic acids. In contrast, phenolics mediate redox reactions. Phenolic acids induce localized disruption of outer microbial membranes, and hydrophobic phenols bind to the outer membrane causing changes in membrane fluidity and shape. Once these disruptions occur, small phenolic compounds can enter the cell and disrupt metabolism. PACs bind to the lipopolysaccharide (LPS) on the outer membrane of Gram-negative bacteria by chelating metal ions. This destabilizes the outer membrane, releases LPS, and increases permeability. Metal binding by PACs and quercetin deplete the iron reserves necessary for growth. With these kinds of complementary interactions, it is easy to see why full extracts or combinations of polyphenols are more effective microbial inhibitors than single compounds.

#### 5.4.2 **Antioxidant mechanisms or reduction of oxidative stress and enzyme activity, signal transduction, and protein expression and activity**

There is now substantial evidence that consumption of cranberries leads to increased plasma antioxidant capacity and decreased biomarkers of oxidative stress. What remains unclear is whether phytochemicals directly quench reactive oxygen species (ROS) and free radicals *in vivo* or whether they induce endogenous antioxidant responses through some alternate mechanism(s). It is often difficult to distinguish these two actions in complex systems because seldom is any process cleanly one or the other and production of radicals is difficult to separate from secondary effects of radicals, which include induction of enzymes and other cellular responses, directly or downstream. The brief overview below documents how cranberry phenols intervene in some pathological processes. In most cases, observations are still correlational, that is, feeding cranberry compounds is associated with some

improvement in conditions, and the mechanisms have not yet been completely elucidated. Even so, the case for important positive contributions of cranberries to health continues to build.

#### 5.4.2.1 *Promotion of cardiovascular health*

Since cardiovascular disease (CVD) is largely a condition driven by oxidative challenge and deterioration in blood vessel epithelia, in circulating lipids and proteins, and in circulating leukocytes, it seems logical to expect that the various antioxidant mechanisms of cranberry compounds should be able to reduce the stresses that lead to atherosclerosis and deterioration of heart muscle.

Investigating whether CJP could provide extra benefits when given to prevent UTIs, Valentova *et al.* [92] fed dried cranberry juice (NutriCran90) in capsules to 65 healthy women aged 19–28 at levels of 400 and 1200 mg/day for up to 56 days. Mixed effects were observed at both levels; 400 mg CJP lowered serum levels of LDL but also high-density lipoprotein (HDL) to the same degree ( $\downarrow 0.2$  mM), decreased aspartate aminotransferase (AST) significantly, and increased advanced protein oxidation products. With doses of 1200 mg cranberry powder/day, blood lipids and AST were not affected, but markers of enhanced antioxidant defenses were evident in increased serum uric acid and erythrocyte superoxide dismustase, glutathione peroxidase, and glutathione. Paradoxically, pro-oxidant action was evidenced at the same time in increased erythrocyte malondialdehyde, a lipid oxidation product, and advanced serum protein oxidation products plus decreased protein thiols. These results suggest that radical quenching and signal transduction/enzyme inhibition by cranberries are both active but not working synchronously. Since no polyphenols were detected in the serum but a number of endogenous antioxidants and enzymes were, it is clear that polyphenols in the intestines were triggering signal transduction cascades that activated endogenous antioxidants. The question is, which cranberry components activate antioxidant responses and which active pro-oxidant responses? Thus, while the idea of using cranberry powders for reducing systemic oxidative stress while also treating UTI is intriguing, caution must be advised until more is learned about cell controls that are activated by individual cranberry components.

A recent review of flavonoids also documented multiple pathways by which cranberry flavonoids influence development and progression of CVD, most of which did not involve radical scavenging [62]. While the review was generalized over flavonoids from all sources, the compounds forming the basis of the documentation are the same as those found in cranberries. Thus, it is reasonable to expect that cranberries also influence CVD by the following mechanisms:

(1) Abatement of oxidative stress by:

Direct radical scavenging, for example, inhibition of LDL oxidation

Metal complexation and chelation

Inhibition of ROS producing enzymes such as xanthine oxidase ( $O_2^{-\bullet}$ ), NADH oxidase ( $O_2^{-\bullet}$ ), and lipoxygenase (LOX)

(2) Decreased expression of inflammatory signaling molecules:

Inducible nitric oxide synthase (iNOS) and cyclooxygenase-2 (COX-2) expression

Inhibition of leukocyte activation

## (3) Miscellaneous:

- Inhibition of platelet aggregation
- Stimulation of vasodilation

#### 5.4.2.2 Modulation of inflammatory responses

All of the mechanisms cited above for cranberry effects on CVD are equally applicable to inflammatory responses in general. At the present time, little is understood about the interplay between these mechanisms, and indeed whether individual classes of cranberry phenols act by alternate pathways.

Route of administration has critical effects on actions. For example, direct application to skin does not require absorption and transport to affected sites. Consequently, mouse ear edema induced by 12-*O*-tetradecanoylphorbol-13-acetate was reduced by 34.0 and 55.1% after topical application of 87.5 and 175 µg of quercetin-3-*O*-(6''-benzoyl)-β-galactoside isolated from processed cranberry powder [93]. This may have resulted from direct free radical quenching in the skin cells. Gavaging cranberry concentrate before phorbol challenge also reduced edema, but had to involve downstream signal transduction effects rather than direct radical quenching because no phenols were detected in serum before or during edema formation (unpublished data; Schaich, Singh, and Vorsa, from Rutgers University).

Phenol concentrations are also critical since nearly all antioxidants have multiple reactions that change in dominance with concentration. Of particular concern is the propensity for converting to pro-oxidant action as concentrations increase. For example, feeding rats freeze-dried high-lipid diets supplemented with 5 and 10% cranberry powder raised circulating levels of interleukin-10 (IL-10) and nitric oxide (NO) and decreased C-reactive protein (CRP) and interleukin-1β (IL-1β), but also increased tumor necrosis factor-α (TNF-α), IL-6, and IL-2, especially relative to lipid-injected controls [94]. In most cases, the 10% cranberry powder diet had less effect than the 5% diet, suggesting either saturation of effects or shifts from anti- to pro-oxidant mechanisms.

Clearly, the biochemical effects of cranberry components are complex and more detailed understanding about signal transduction effects, intervention in cytokine cascades, and the balance between various pathways is needed before using high levels of cranberry powder as treatments for any conditions involving inflammatory processes.

#### 5.4.2.3 Prevention and inhibition of cancer

Cranberry phenols prevent initiation of cancer by at least two mechanisms: (1) quenching radicals that react with DNA or proteins to cause irreparable lesions that lead to tumor development [95] and (2) by inhibiting enzymes that metabolize toxicants into carcinogens [96]. Progression is similarly affected by multiple mechanisms, including inhibition of critical enzymes (e.g., ornithine decarboxylase), cell metabolism and proliferation, as well as enhancing unprogrammed cell death (apoptosis).

Doses of 5–30 mg/mL extracts of dried cranberries inhibited human breast cancer MCF-7 cell proliferation in culture by inducing apoptosis [97]. Fifty milligrams per milliliter led to 25% higher apoptosis, while doses of 10–50 mg/mL arrested cells in the G0/G1 phase. These results demonstrate that when cranberry phytochemical extracts come in contact with tumor cells, they have the capability of reducing cell proliferation, and this suppression is at least

partly attributable to initiation of apoptosis and G1 phase arrest. Although the study was conducted with breast cancer cells, for this action to occur *in vivo* requires absorption and transport to breast tissue of sufficient quantities of intact active polyphenols. This is unlikely considering the very low absorption of these compounds. Nevertheless, these results do support a potential role for cranberries in preventing or slowing development of tumors in the gastrointestinal tract, for example, oral, esophageal, and colon cancers.

To determine potential use of cranberry powder in preventing development of esophageal cancer in patients with chronic acid reflux, SEG-1 and BIC-1 human esophageal cells were exposed as monolayers to dried PAC extract in concentrations ranging from 12.5 to 400 µg/mL [98], and cell viability and proliferation as well as acid-induced cell proliferation, cell cycle phase, and apoptosis were monitored for up to 96 hours. Fifty micrograms PACs per milliliter only moderately altered viability but significantly inhibited proliferation of both cell lines. Treatment with PACs before but not after acid challenge to model acid-reflux effects in the esophagus reduced cell proliferation, indicating that cranberry compounds must have been present before the acid challenge. Thus, maximum benefit can be gained by consumption of cranberry powder (in capsule or food) multiple times per day. In addition, PACs improved cell regulation, stopping cells at the G1 checkpoint and inhibiting progression to S phase, and increased apoptosis, unscheduled cell death. Both of these effects are critical in control of esophageal cancer.

Seeram *et al.* [99] fractionated Ocean Spray cranberry extract powder (90% fruit solids) to investigate which fractions contributed to antiproliferation effects of cranberries. Sugars, organic acids, total phenols, anthocyanins, and PACs were tested against human oral, colon, and prostate cancer cell lines in culture. Oral and colon cancer cells showed low responses to individual fractions but marked inhibition of cell proliferation by the total phenol fractions. All cranberry fractions (including phenolic acids) inhibited proliferation of prostate cancer cells by at least 60%, and total phenols almost completely stopped the process. Whether this augmentation was an additive or synergistic effect of multiple phenols could not be determined because doses were so different; total phenols were added at 200 µg/mL and the various fractions were added at their natural proportion of this. Antiproliferative effects toward all tumor cells were enhanced when sugars, organic acids, and phenolic acids were removed. These observations may provide some guidelines for developing cranberry products for cancer prevention, particularly for high-risk populations.

A very interesting series of studies on freeze-dried berries showed that blackberries and black raspberries inhibit both initiation and postinitiation events in rat esophageal and colon carcinogenesis as evidenced by decreases in tumor multiplicity, reduction in adduct formation, reduced proliferative indices, inhibition of preneoplastic lesion formation, and down-regulation of COX-2 and iNOS [2, 96, 100–102]. Other genes in the esophagus associate with multiple cellular processes including apoptosis, angiogenesis, matrix formation, and cell cycle control. The dominant active fraction in these berries was anthocyanins. Cranberries have appreciable levels of anthocyanins (though not as high as in blackberries) [103], as well as flavonoids [39], and among the highest total phenols of all fruits [6]. Concentrating these phytonutrients in dried forms makes it feasible to administer the same levels as are present in other berries. Thus, there is every reason to expect that, as noted above, cranberry powders taken directly or dissolved in foods as carriers may offer significant potential for preventing, slowing, or lessening development of cancers all along the gastrointestinal tract.

#### 5.4.2.4 Protection of pancreatic cells and maintenance of insulin release

Diet, genetics, and environment all play important roles in preserving pancreatic  $\beta$ -cell mass and function during aging. To investigate whether daily consumption of dried whole cranberry powder could prevent decline of pancreatic function and development of type 2 diabetes, rats were fed diets containing 2% whole cranberry from age 6 to 22 months, approximating full life span [104]. Cranberry diets delayed and diminished the decline in insulin production to the extent that after 22 months, the portal insulin concentrations were 7.6 times the control levels. Cranberry diets also improved  $\beta$ -cell glucose responsiveness to oral glucose challenge, dramatically increased  $\beta$ -cell mass and percentage of large islets, raised insulin and glucagon levels in  $\beta$ -cells, and enhanced production of pancreatic and duodenal homeobox-1 or insulin promoter factor-1 (PDX-1), a homeodomain transcription factor in  $\beta$ -cells. Insulin secretion was also increased without changing overall neogenesis patterns of pancreatic islets of leading to insulin resistance. These effects were attributed to flavonoids and proposed to result from a combination of mechanisms, including alteration of  $\text{Ca}^{2+}$  fluxes and cyclic nucleotide metabolism, decreased oxidative stress, and inhibition of  $\alpha$ -amylase and  $\alpha$ -glycosidase, which mediate release of glucose into the bloodstream. Extending this study to humans was recommended, given the positive results. Doses used in this study ( $\sim$ 1000 mg/kg body weight) are equivalent to  $\sim$ 180 mg/kg body weight for humans, which can be achieved by consuming  $\sim$ 12 g cranberry powder daily. This quantity is too great to be administered by conventional capsules, but it might be feasible to deliver this in beverages.

### 5.4.3 Absorption of phenols from cranberry powder

Before closing this section, some note needs to be made regarding absorption and the physiological fate of cranberry phenols. Years of research were focused on free-radical quenching-based antioxidant assays of plant extracts, expecting to identify specific phenols that would be “magic bullets” for treating a broad range of pathologies involving oxidative deterioration. However, documentation of direct absorption of polyphenols, circulation in the blood, and distribution to tissues is skimpy and interpretations are often questionable when low nanomolar concentrations detected are converted to actual absorbed amounts. The issue remains highly controversial, but it is becoming increasingly clear that large polyphenols are very poorly absorbed as such so other mechanisms must be found to explain observed health effects. Two alternatives provide feasible explanations of observed physiological responses to cranberry consumption: (1) cranberry compounds, both monomers and PACs, are metabolized by intestinal flora to smaller compounds that can be absorbed and transported to tissues where chemistry is modified, and (2) cranberry compounds bind to proteins in the intestinal epithelium and thereby initiate a cascade of signal transduction that leads to observed responses.

Prior *et al.* [49] investigated microbial digestion and subsequent metabolite uptake of concentrated cranberry powder (Decas Botanicals) in the intestines of rats by following excretion of phenolic acids in urine. Concentrations of free phenolic acids in urine were rather low, in some cases being only a few percent of total material detected. In contrast, conjugated phenolic acids accounted for 50% (4-hydroxybenzoic acid) to as high as 96% (ferulic acid) of the detected phenolic acids. The major products were hippuric acid, 4-hydroxycinnamic acid, 4-hydroxyphenyl acetic acid, 3-hydroxyphenyl acetic acid, and 3-hydroxyphenylpropionic

acid. 3,4-Dihydroxybenzoic acid was the major phenolic acid in cranberry powder; about 90% of 3,4-dihydroxybenzoic acid in the urine was conjugated. Thus, measuring only free forms of phenolic acids does not provide an accurate measure of phenolic acid excretion. PACs and anthocyanins are metabolized by microbial flora to phenolic acids or other lower weight compounds that are absorbed, conjugated by methylation or sulfonation, and excreted. 3,4-Dihydroxyphenyl acetic acid excretion was not affected by dietary levels of cranberry powder, and so was thought to be absorbed. This metabolite has been shown to have anti-inflammatory action.

## 5.5 Food applications of dried cranberry powders

The intense interest that has fired research in antioxidants for *in vivo* applications has also generated, in the process, a considerable body of information about how antioxidants work. This information, coupled with the current mandate for replacing synthetic antioxidants butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) with natural antioxidants that presumably have no toxicity, is now stimulating interest in using natural materials to stabilize foods, with mixed success. Natural antioxidant applications have been slow to develop due to lack of ability to predict behavior in foods and to strong colors and flavors that accompany antioxidants in extracts. The following brief survey of some recent results using cranberry powder show both the promise and the steep challenges and unpredictability in using natural antioxidants in complex multiphase foods.

### 5.5.1 Meats, poultry, and fish

Turkey and fish products are notoriously difficult to stabilize due to high unsaturation in the lipids and high levels of heme. Chloroform-methanol extracts of CJP mixed with comminuted turkey muscle inhibited lipid oxidation, gaining three weeks in frozen storage when added at 467 µmol/kg turkey. Quercetin and Q-3-*O*-(6'-benzoyl)-β-galactoside were both identified in the active fraction, though nearly all the protective action came from quercetin [105]. If the quercetin was glycosylated, inhibition of lipid oxidation was lost [106], indicating that the aglycone was the active form. Aglycones penetrated into model membranes but their glycosides did not, and ethylenediaminetetraacetic (EDTA) acid had no effect on lipid oxidation in the system. Thus, it was proposed that quercetin inhibits lipid oxidation in turkey meat by becoming embedded in muscle membranes and acting by free radical scavenging or other non-metal-chelating mechanism.

To elucidate actions of individual cranberry fractions in ground turkey, Ocean Spray 90MX powder (spray-dried concentrated juice) was separated into enriched fractions by column chromatography [107]. Fractions were (1) cinnamic acids, (2) anthocyanins, (3) flavonols, (4) flavonols, (5) PACs, and (6) PACs. This sequence parallels molecular size and increasing nonpolarity. Each fraction was mixed with turkey at a concentration of 200 µmol/kg meat. Polar cranberry phenols (e.g., simple phenols and phenolic acids) partitioned into the polar fractions at more than 50:50, but lipid oxidation was barely affected (Table 5.12). In contrast, as the percentage of phenol retained in the fat phase increased, protection correspondingly increased. Fraction 4 with flavonol aglycones was the most effective, while the PACS expected to be strong antioxidants behaved like the small polar compounds. A mechanism was proposed wherein inhibition of lipid oxidation required that the antioxidant

**Table 5.12** Phase partition and inhibition of lipid oxidation in ground turkey by various fractions of cranberry powder prepared from spray-dried concentrated cranberry juice

Fraction	Composition	Percent in aqueous phase	Percent TBARS inhibition
1	Cinnamic acids	51.0	19.0
2	Anthocyanins	49.2	39.5
3	Flavonols (glycosides)	46.7	46.0
4	Flavonols (aglycones and quercetin)	31.7	74.2
5	Proanthocyanidins	44.6	36.2
6	Proanthocyanidins	35.9	21.8

Source: Adapted with permission from Lee *et al.* [107].  
TBARS, thiobarbituric acid reactive substances.

be able to penetrate the lipid regions of membranes to align with acyl chains and be close to release points for heme iron and other catalysts. Small phenols are too polar to do this, while the PACs are too large to enter the membrane. This points out quite clearly how activity in *in vitro* antioxidant assays can be diverted in real systems where phase separations and cell/membrane compartmentalization do not always let the most reactive antioxidants get to their targets.

With green chemistry and the environmental movement, plant refuse, including cranberry press cake, is receiving intense scrutiny as a source of ingredient antioxidants. Press cake was extracted with water, acetone, and ethanol with and without microwave assistance, and these fractions were dissolved in ethanol and mixed with mechanically separated turkey breast [108]. Water extracts were close to inactive, while solvent extraction with acetone or solvent:microwave extraction with ethanol released compounds capable of inhibiting lipid oxidation. Lack of correlation with total phenols and poor correlation with quercetin suggested that other polyphenols in this material must have specific roles in addition to the action of quercetin in stabilizing ground turkey breast. Compounds in each extract were not identified.

Two approaches have been taken in stabilizing meats with natural antioxidants—treating the butchered meats (ground or sectioned) by adding antioxidant solutions as described above to stabilize products during marketing and storage or incorporating natural antioxidants into animal feeds to stabilize the meats endogenously, thus increasing the inherent resistance to oxidation during handling, storage, and cooking. One interesting study tested the second approach, feeding pigs a diet enriched with 15% Ocean Spray 90MX cranberry powder for six months [109]. Meat color was retained better but lipid oxidation [hydroperoxides and thiobarbituric acid reactive substances (TBARS)] was unexpectedly increased with cranberry diets. One explanation proposed was that cranberry compounds stabilize hydroperoxides, slowing their breakdown to reactive alkoxy radicals. However, without measures of uptake and metabolism of cranberry polyphenols, it is not possible to know what compounds were absorbed in what levels and where they were localized. In addition, indirect effects of dietary cranberry compounds on antioxidant and metabolic enzymes have not been determined. Increasing dietary tocopherols has been shown to stabilize beef, but absorption and pharmacokinetics of these natural endogenous antioxidants are well-documented. While the idea of stabilizing meats by increasing levels of natural polyphenol antioxidants in animal

diets is intriguing, phenols have complex actions in living systems, and much more information about microbial metabolism in the intestines; absorption, conjugation, and excretion versus distribution to tissues; binding to proteins; as well as signal transduction and enzyme induction processes is needed to determine whether this approach has promise for stabilizing meats.

Fish is an even greater challenge for stabilization than poultry and pork. Six fractions of OS 90MX cranberry powder (concentrated juice) were added to washed fish (cod) muscle and lipid oxidation was initiated by hemoglobin [63]. Phenolic acids (Fraction 1) and flavonols (Fractions 3 and 4) most effectively inhibited lipid oxidation, extending the lag period several days beyond the control, while the PACs and anthocyanins were relatively inactive, purportedly due to binding to insoluble muscle components. In contrast, reactivity with DPPH increased with fraction number and phenolic acids were the least reactive. Among individual compounds, propyl gallate (Fraction 1) was a stronger inhibitor of lipid oxidation than quercetin (Fraction 4). Propyl gallate is smaller and more lipid-soluble and so it more able to penetrate membranes than quercetin; it is a stronger metal binder so it can block electron transfer from the hemoglobin. Thus, as has been noted before in this chapter, effective antioxidant action in actual products depends most on getting the right antioxidant to the target.

Marinating fish fillets in solutions of cranberry powder appears to be an effective alternative for antioxidant treatment. Herring fillets marinated in a 50 g cranberry powder per liter solution for 24 hours before storage showed significant inhibition of lipid oxidation and production of ammonia as well as prolonged shelf life [110]. This seems to be a simple and cost-effective procedure that could be adapted for stabilizing both refrigerated and frozen commercial fish products.

Cranberry phenols have antimicrobial as well as antioxidant capabilities, as was discussed in Section 5.4. This offers potential for getting double benefits from using them in foods such as meats where microbial spoilage and lipid oxidation are both key problems. To test this possibility, ground beef in 1.5 g balls were autoclaved to sterilize and mimic cooking, soaked first in a 50:50 mixture of water-soluble phenolic extracts from oregano and cranberry extract powder (Decas Botanicals), 750 ppm each with 2% sodium lactate, and then dipped in a solution of *Listeria monocytogenes* and store at 4°C [111]. Log reductions after 20 days were 1.3 for phenols alone, 1.8 for lactate alone, and 2.1 for the total mixture. Proline-induced partial recovery of microbial outgrowth suggested that proline metabolism was being affected by the combination of phenols. Since muscle foods are good sources of proline, providing a ready supply for microbial recovery, meats may not be the optimum food form for application of the dual antioxidant–antimicrobial action.

## 5.5.2 Cereals

The pressure to “go natural,” shifting away from synthetic additives, includes colors as well as antioxidants. Thus, interest in using natural pigments such as anthocyanins to gain a double benefit, antioxidant plus color, is growing. Anthocyanin addition to extruded breakfast cereals at levels ranging from 1 to 84.3% verified that cranberry anthocyanins can indeed serve this dual function [112]. However, there is not yet an experience base to guide formulations. More investigations are needed to determine levels of anthocyanins required to both create desired redness (not just pink) and prevent development of rancidity over desired shelf life.

## 5.6 Conclusions

Dried cranberry powders prepared from whole berries, cranberry juice, or various cranberry extracts deliver high concentrations of cranberry phenols in convenient form that is reasonably stable for long periods in storage. Because of demonstrated effectiveness of cranberries in preventing UTI, some cranberry powder products have been particularly formulated with high PAC concentrations, but fractions enriched in other cranberry classes are also available. Oxidation and heat during cranberry dehydration degrade phenolic compounds, particularly anthocyanins, so great care must be taken to protect sensitive compounds during processing. Lyophilization (freeze drying) is probably the method of choice for cranberry powders intended for nutraceutical applications since the very low temperatures and vacuum impose least stress.

Although studies with dried cranberry powders are still limited since standardized materials have been available commercially for only a few years, results to date show that the powders generally have beneficial health effects similar to those of fresh berries or juice, and in cases where high concentrations are needed, are even more useful. Based on research data, commercial products targeted at prevention of UTIs, prostate cancer, breast cancer, oral health have been developed and are available for use in capsules, beverages, gels, and other delivery modalities.

Although research was initially focused on direct effects of parent polyphenols in cranberry powder, there is increasing recognition that intestinal flora metabolize complex phenols to phenolic acids which may be even more important mediators of physiological effects. Most of these, such as polyphenols, are conjugated and eliminated in the urine, but at least one metabolite, 3-hydroxyphenyl acetic acid, is absorbed and reduces inflammation *in vivo*. Microbial metabolism and other mechanisms by which cranberry phenols can be activated and render their benefits promise to be hot areas of future research.

An interesting and potentially very profitable new direction for use of cranberry powders is inhibition of oxidative degradation in foods. Results have shown that cranberry phenols can limit troublesome lipid oxidation, particularly in muscle foods, but also interact with proteins and carbonyls to limit secondary co-oxidations and browning. For applications where the telltale red cranberry color is not an issue, cranberry powders may thus offer a productive new approach for stabilization of foods with natural compounds.

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## **6 Phytochemicals and health benefits of goji berries**

Ying Zhong, Fereidoon Shahidi, and Marian Naczk

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### **6.1 Introduction**

Goji berries, also known as Lycium fruits or wolfberries, are member of the Solanaceae family. The mature fruits are bright red, ellipsoid berries 1–2 cm long with high juice content. While goji berries are mainly used for decoration of gardens in most parts of the world, they are a well-known tonic food and alternative medicine in Asian countries, especially in China. Among the dozens of *Lycium* species existing around the world, about 90% of commercially available goji berries are *Lycium barbarum*, originating from the north central regions of China. *Lycium chinense* is a species closely related to *L. barbarum*. Both *L. barbarum* and *L. chinense* are medicinal plants native to China, but are also widely found in Korea, Japan, and other Asian countries.

The fruits of Lycium (goji berries), also referred to as *Lycii fructus*, are harvested in the summer and autumn and subjected to a drying process. The fruits are usually dried in the shade followed by exposure to sun for further drying until the skin turns hard, but the pulp remains soft [1]. Goji berries have a long history of application in health promotion in China as a core ingredient in many herbal remedies, especially those for nourishing the blood, enriching the yin, tonifying the kidney and liver, moistening the lungs, improving vision, and promoting longevity [2]. The emenagogue, diuretic, antipyretic, tonic, aphrodisiac, hypnotic, and hepatoprotective effects of goji berries have been well recorded in ancient Chinese Pharmacopoeia 2300 years ago [3]. Goji berries are traditionally consumed as an ingredient in Chinese cuisine (prepared as broth of poultry) or as medicinal elixir (liquor or tea infusion) [1]. Goji berries in formulated Chinese medicine have been used in the treatment of eye diseases, skin rashes, psoriasis, allergies, insomnia, chronic liver disease, diabetes, tuberculosis, and kidney disorders [4]. The *Lycium* species are known for their sedative, diuretic, and digestive actions in Turkish folk medicine [5]. More recently, a trend to use goji berries as a dietary supplement and natural health product in the Western world including the United Kingdom and North America has emerged. This chapter provides a general overview of bioactive components of goji berries and summarizes the research findings on their identification and health effect evaluation, most of which were reported in Chinese or Japanese with a few publications in international journals.

## 6.2 Functional components in goji berries

Goji berries having a significant nutritive value and serve as an excellent source of macronutrient, including carbohydrate (46%), protein (13%), fat (1.5%), and dietary fiber (16%). They also contain micronutrients such as vitamins and minerals. Every 100 g of goji berries contains up to 60 mg of calcium, 5.4 mg of iron, 434 mg of potassium, 1.48 mg of zinc, and 48 mg of vitamin C [6]. Goji berries also contain riboflavin, thiamine, nicotinic acid, and minerals (Cu, Mn, Mg, and Se), among others [7, 8]. In addition to the macro- and micronutrients present, the bioactive components responsible for the health benefits of goji berries have been isolated and evaluated. Functional components such as polysaccharides, carotenoids, and phenolics have been identified and associated with the health effects of goji berries [8, 9].

### 6.2.1 Polysaccharides

Polysaccharides are one of the most valuable functional constituents and active compounds responsible for various health effects of goji berries. High polysaccharide content (5–8% in dried fruits and 40% in many commercial extracts) is a unique compositional characteristic of goji berries. *L. barbarum* polysaccharides (LBP), in particular, have been the focus of much research on bioactives of goji berries. LBP content is considered to be an important indicator of the medicinal efficacy of *Lycium* products [10]. Wang *et al.* [9] reported that the content of crude polysaccharides in *L. barbarum* fruits was 57.2 µg/g, including 25.6 µg/g of neutral polysaccharides and 26.9 µg/g of acidic polysaccharides as well as a small amount of unidentified fractions. Polysaccharides in edible plants in Chinese herbs are generally composed of a minimum number of 100 monosaccharide units with their molecular weights ranging from 10 to 1449 kDa [11]. Several LBP were isolated and purified from their crude extracts by diethylaminoethyl (DEAE) ion-exchange cellulose and gel permeation chromatography, and the LBP fractions had molecular weights of 24–241 kDa [3, 12].

Polysaccharides are usually extracted from goji berries with boiling water and separated by various chromatographic techniques. In some cases, lipids are removed either prior to or after the hot water extraction of polysaccharides. Lipids may be removed by refluxing with chloroform/methanol or ethanol, and/or precipitation with ethanol or acetone [8, 13]. In a study by Wang *et al.* [11], crude polysaccharides were extracted from *L. barbarum* with boiling water, followed by precipitation with ethanol at –20 °C and protein hydrolysis with a proteinase from *Bacillus* L (type III). Subsequent separation of the crude extracts by high-performance size exclusion chromatography yielded five LBP fractions with the two main fractions having a molecular weight of 24 and 79 kDa. Gas chromatographic (GC) analysis revealed the presence of rhamnose, arabinose, xylose, mannose, glucose, and galactose as the major monosaccharides [11]. In another study, the boiling water decoction of *L. barbarum* showed a carbohydrate content of 97.5%, mainly composed of rhamnose, xylose, arabinose, glucose, and fructose [14]. Luo *et al.* [8] separated the crude LBP using a DEAE cellulose column and obtained four pure polysaccharide fractions. The major fraction was analyzed by GC–mass spectrometry (MS) and found to contain six monosaccharides (namely, rhamnose, galactose, glucose, arabinose, mannose, and xylose in a mole ratio of 4.22:2.43:1.38:1.00:0.95:0.38). Similar to other botanical (plant and fungal-derived) polysaccharides, LBP mainly occur as water-soluble glycoconjugates, for example, conjugates of glycan with peptides or proteins [15, 16]. Peng and Tian [3] isolated five glycoconjugates which were composed of 2–6 monosaccharides and 17 amino acids.

Health effects of LBP have been reported by various *in vitro*, cellular, animal, and human clinical studies. LBP were found to possess numerous biological activities and health effects, including antioxidant, antiaging, antitumor, antidiabetic, cytoprotective, neuroprotective, and immunomodulatory effects, among others [16]. Consumption of LBP-standardized goji berry juice for 14 days significantly improved the neurologic/psychologic performance and gastrointestinal function in humans [17]. LBP protected cultured cortical neurons exposed to glutamate by inhibiting glutamate-induced phosphorylation of c-jun N-terminal kinase (JNK) [18]. Neuroprotective effect of LBP against  $\beta$ -amyloid peptide toxicity was also observed [19, 20]. LBP was effective in reducing blood glucose levels and serum total cholesterol (TC) and triacylglycerols (TAG) contents while increasing high-density lipoprotein (HDL) cholesterol levels in alloxan-induced diabetic or hyperlipidemic rabbits [8]. LBP treatment resulted in a significantly decreased level of fasting glucose, TC, and TAG in diabetic mice [21]. Immunomodulatory and antitumor activities of LBP have also been demonstrated. LBP were able to upregulate both innate and adaptive immune responses, increase ConA-triggered proliferation of splenocytes, and cytotoxicity of natural killer cells [22]. The polysaccharide–protein complex in goji berries, which is composed of 6 monosaccharides and 18 amino acid residues, was found to enhance immune function, induce lymphocyte proliferation and cytokine production, activate T lymphocytes, and reduce side effects of chemo- and radiotherapy [23, 24]. LBP have been shown to promote peripheral blood recovery in mice with irradiation or chemotherapy-induced myelosuppression through stimulating the production of granulocyte colony-stimulating factor (G-SF) by peripheral blood mononuclear cells (PBMC) [23]. *In vivo* evidence has shown that LBP can also act against cancer and suppress the growth of malignant tumor [25, 26]. The effects of LBP on cell proliferation and apoptosis in rat and human hepatocellular carcinoma (HCC) cells have been reported [27]. LBP inhibited the growth of transplantable sarcoma S180 and increased macrophage phagocytosis and spleen lymphocyte proliferation, suggesting their potential effect in controlling tumor size and improving immune system [28]. LBP treatment also exerted an inhibitory effect on the growth of human gastric cancer MGC-803 and SGC-7901 cells by inducing cell-cycle arrest at the G0/G1 and S phase, respectively [29]. The antiaging property of LBP has been investigated and found to involve multiple mechanisms [16]. LBP exhibited antidecrepit effect in brain and heart tissues in mice and prolonged the life span of Drosophila [30, 31].

Many of the biological activities of LBP may be directly or indirectly attributed to their antioxidant potential as many chronic diseases are oxidative stress-mediated [32, 33]. LBP can counteract oxidative stress by eliminating reactive oxygen species (ROS) such as free radicals and promoting endogenous antioxidant factors such as superoxide dismutase (SOD), glutathione peroxidase (GSH-Px), and catalase (CAT). *In vitro* assays have supported the antioxidant activities of LBP in scavenging 2,2-diphenyl-1-picrylhydrazyl (DPPH) and superoxide radicals, inhibiting  $\beta$ -carotene-linoleate oxidation, reducing and chelating metal ions [13]. Trolox equivalent antioxidant capacity (TEAC) and oxygen radical absorbance capacity (ORAC) values have also been reported for crude and purified LBP [8]. LBP effectively inhibited peroxyl radical-mediated erythrocyte hemolysis in mice [33]. Administration of LBP decreased malondialdehyde (MDA) levels and increased activities of antioxidant enzymes in mice [34]. LBP were able to restore increased lipid peroxidation and decrease activities of antioxidant enzymes (such as SOD, CAT, and GSH-Px) as well as impaired immune function in aged mice to normal levels [33]. Consumption of a LBP-standardized goji berry juice (1632 mg LBP/120 mL) in a human intervention study significantly enhanced the markers

of serum antioxidant by 8.4% for SOD and 9.9% for GSH-Px, while decreasing the MDA levels by 8.7% [32].

### 6.2.2 Carotenoids

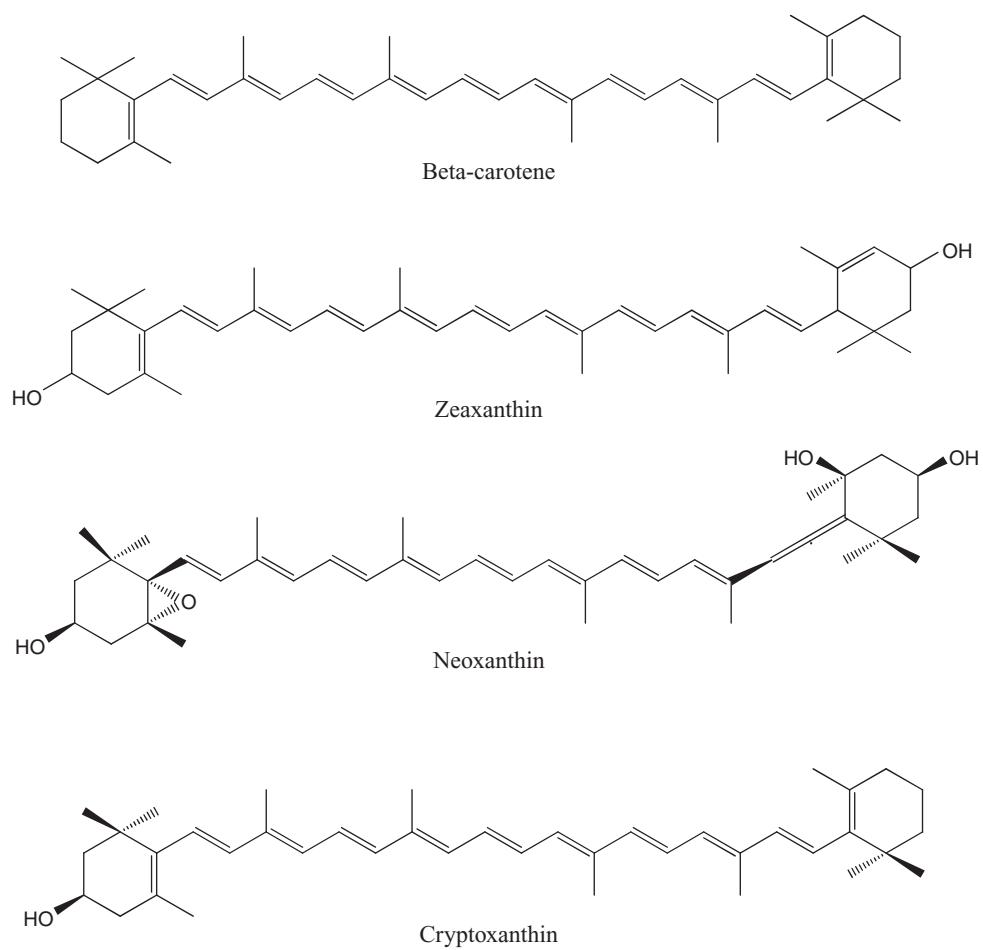
Carotenoids, including carotenes and xanthophylls, are 40-carbon isoprenoids that occur widely in plants, fruits, and vegetables as yellow, orange, and red lipid-soluble pigments. In addition to their use as natural nontoxic colorants in manufactured foods, drinks, and cosmetics, carotenoids possess various biological activities, among which their pro-vitamin A and antioxidant activities are well known. Goji berries are an excellent source of carotenoids both because of their high content and because of their unique profile of carotenoids. Peng *et al.* [35] reported that the total carotenoid content of different goji berries ranged from 0.03 to 0.5%. The carotenoid content varies with season, for example, total carotenoid content is higher in summer fruits than in fall fruits [36]. Carotenoids in goji berries may be in the free, partially esterified, or fully esterified forms. Zeaxanthin and its esters are major contributors to the carotenoids in *L. barbarum* [37, 38]. The content of zeaxanthin esters in ripening goji fruits can reach as high as >77.5% of total carotenoids [37, 39]. Zeaxanthin palmitate (phasalien), in particular, comprises 31–56% of the total carotenoids as detected by high-performance liquid chromatography–diode array detector (HPLC-DAD) [35]. Meanwhile, zeaxanthin dipalmitate, which is the characteristic carotenoid in goji berries, together with zeaxanthin, has been the focus of much research on the protective role of goji berries against atrophic age-related macular degeneration (AMD) [35]. Zeaxanthin as one of the main pigments of retina was found to be effective in preventing and treating AMD [40, 41]. In addition to its contribution to eye health, isolated zeaxanthin and its dipalmitate have been reported to show antihepatotoxic activity, comparable to that of silybin [42]. Zeaxanthin and other carotenoids are also potent antioxidants, which contribute to the health effects of goji berry against oxidative stress-mediated diseases.

Extraction of carotenoids from goji berries is usually carried out by first removing water-soluble components with water or 50% ethanol, followed by extraction with organic solvents, such as acetone, petroleum ether, hexane, toluene, or their mixture. In some cases, a saponification process is employed to obtain free carotenoids. Identification and quantification of goji berry carotenoids by chromatographic and mass spectrometric techniques have been reported. Li *et al.* [37] identified 10 carotenoids, including zeaxanthin,  $\beta$ -cryptoxanthin, violaxanthin, and their esters, using HPLC-DAD analysis. Stephen Inbaraj *et al.* [43] reported the presence of 11 free carotenoids and 7 carotenoid esters by HPLC-MS/GC-flame ionization detector (HPLC-MS/GC-FID). Zeaxanthin dipalmitate (1143.7  $\mu\text{g/g}$ ) was the predominant one among all carotenoids identified, followed by  $\beta$ -cryptoxanthin monopalmitate isomers (32.9–68.5  $\mu\text{g/g}$ ), zeaxanthin monopalmitate isomers (11.3–62.8  $\mu\text{g/g}$ ), all-*trans*- $\beta$ -carotene (23.7  $\mu\text{g/g}$ ), and all-*trans*-zeaxanthin (1.4  $\mu\text{g/g}$ ). In another study,  $\beta$ -carotene, neoxanthin, cryptoxanthin, and zeaxanthin were identified in the saponified extract of goji berry carotenoids [9]. Major carotenoids found in goji berries are presented in Table 6.1 and their structures are given in Figure 6.1.

The content and composition of carotenoids in goji berries may vary depending on the maturation stage of the fruits. For instance, the level of esterified carotenoids increased with maturation of the fruits, while free carotenoids such as zeaxanthin were less abundant in ripe fruits [44]. Goji berries are mostly consumed as dried fruits. The drying process is believed to affect the carotenoid profiles of goji berries. The conventional drying process and

**Table 6.1** Carotenoids identified in goji berries

Carotenoid	Source	Reference
$\beta$ -Carotene	Fruit of <i>Lycium barbarum</i>	[43]
Zeaxanthin	Fruit of <i>Lycium barbarum</i>	[43]
Neoxanthin	Fruit of <i>Lycium barbarum</i>	[9]
Zeaxanthin dipalmitate	Fruit of <i>Lycium barbarum</i>	[35, 43]
Zeaxanthin monopalmitate	Fruit of <i>Lycium barbarum</i>	[43]
$\beta$ -Cryptoxanthin monopalmitate	Fruit of <i>Lycium barbarum</i>	[43]

**Figure 6.1** Structures of major carotenoids in goji berries.

storage usually lead to degradation or transformation of carotenoids. In general, esterified carotenoids undergo enzymatic transformation and oxidative degradation, which release the free form and oxidation products of carotenoids, respectively [36].

### 6.2.3 Phenolics

Phenolics are naturally occurring compounds widely distributed in the plant kingdom and beneficial components of human daily diet. They are important constituents of plants with multiple functions and as dietary phytochemicals for humans display a broad range of functional and biological activities. Phenolic compounds present in goji berries are mainly phenolic acids and flavonoids. Wang *et al.* [9] used 80% ethanol to extract phenolics from *L. barbarum*, followed by a separation with preparative chromatography. Four phenolic acids (chlorogenic, caffeoylquinic, caffeoic, and *p*-coumaric) and three flavonoids (quercetin diglycoside, rutin, and kaempferol-3-*O*-rutinoside) have been identified as the major phenolic compounds. The flavonoid fraction obtained exhibited DPPH and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) scavenging activity, metal ion chelation capacity, and reducing power. In another study, flavonoids were extracted with 95% ethanol from *L. barbarum* and evaluated for their antioxidant potential in terms of ABTS scavenging, metal chelation, and reducing power [1]. The extract contained 1.56 mg quercetin equivalents/g of total flavonoids, among which quercetin, myricetin, and kaempferol were predominant and comprised 43% of total flavonoids [1]. Stephen Inbaraj *et al.* [45] conducted a thorough investigation on the phenolic compounds in *L. barbarum*. The phenolics were extracted with 50% ethanol, isolated using a polymeric solid phase extraction cartridge and identified by HPLC-DAD-electrospray ionization-MS (HPLC-DAD-ESI-MS). The study revealed the presence of 52 phenolic acids and flavonoids. Quercetin-rhamno-di-hexoside (438.6 µg/g) was found to be the most abundant among all, followed by quercetin-3-*O*-rutinoside (281.3 µg/g), dicaffeoylquinic acid isomers (250.1 µg/g), and chlorogenic acid (237.0 µg/g). Caffeic, *p*-coumaric, and vanillic acids were also detected in the extract, although to a lesser extent. Other forms of phenolics, such as phenolic amides, have also been found in goji berries. The root bark of *L. barbarum* was reported to contain four phenolic amides, namely, dihydro-*N*-caffeoyletyramine, *trans*-*N*-feruloyloctopamine, *trans*-*N*-caffeoyletyramine, and *cis*-*N*-caffeoyletyramine [46]. These phenolic amides have been shown to exert antifungal effects at low concentrations (5–40 µg/mL) against dimorphic transition of the pathogen *Candida albicans* [46]. The main phenolic compounds identified in goji berries and their root barks are given in Table 6.2.

### 6.2.4 Other bioactive components

In addition to the major components discussed above, terpenes, alkaloids, cerebrosides, cyclic peptides, phytosterols, betaine, and a number of neutral volatile compounds have also been identified in goji berries [32, 47–50], which also make considerable contribution to the bioactivity and health effects of goji berries. Cerebrosides with hepatoprotective activity have been identified in *L. chinense*. Kim *et al.* [51] isolated a cerebroside from *L. chinense* that was effective in protecting primary cultured rat hepatocytes against galactosamine-induced hepatotoxicity. Kim *et al.* [42] isolated two cerebrosides from *L. chinense* fruits, which significantly suppressed the release of glutamic pyruvic transaminase (GPT) and sorbitol

**Table 6.2** Phenolic compounds identified in goji berries and their root barks

Phenolic compound	Source	Reference
Quercetin	Fruit of <i>Lycium barbarum</i>	[1]
Myricetin	Fruit of <i>Lycium barbarum</i>	[1]
Kaempferol	Fruit of <i>Lycium barbarum</i>	[1]
Rutin	Fruit of <i>Lycium barbarum</i>	[9]
Caffeic acid	Fruit of <i>Lycium barbarum</i>	[9]
p-Coumaric acid	Fruit of <i>Lycium barbarum</i>	[9]
Caffeoylquinic acid	Fruit of <i>Lycium barbarum</i>	[9]
Kaempferol-3-O-rutinoside	Fruit of <i>Lycium barbarum</i>	[9]
Ferulic acid	Fruit of <i>Lycium barbarum</i>	[45]
Vanillic acid	Fruit of <i>Lycium barbarum</i>	[45]
Quercetin-rhamno-di-hexoside	Fruit of <i>Lycium barbarum</i>	[45]
Quercetin-3-O-rutinoside	Fruit of <i>Lycium barbarum</i>	[45]
Chlorogenic acid	Fruit of <i>Lycium barbarum</i>	[45]
dihydro-N-Caffeoyltyramine	Root bark of <i>Lycium barbarum</i>	[46]
trans-N-Feruloyloctopamine	Root bark of <i>Lycium barbarum</i>	[46]
trans-N-Caffeoyltyramine	Root bark of <i>Lycium barbarum</i>	[46]
cis-N-Caffeoyltyramine	Root bark of <i>Lycium barbarum</i>	[46]

dehydrogenase (SDH) by CCl<sub>4</sub>-intoxicated hepatocytes. Other goji berry compounds with hepatoprotective effect have also been identified, such as pyrrole derivatives, betaine, and the arabinogalactan–protein complex [52–55]. Betaine is also a phytochemical that plays an important role in the prevention of cardiovascular disease (CVD) by decreasing homocysteine toxicity and hence reducing the risk of coronary heart disease (CHD) and stroke [56]. Its content was reported to be 1.5% in *L. chinense* leaves and 0.9–1.4% in *L. barbarum* whole plant on a dry weight basis [57, 58]. Lyciumins, a unique cyclic octapeptide in the roots of *L. chinense*, has shown angiotensin converting enzyme (ACE)-inhibitory activity, suggesting its antihypertensive potential [59]. The nonpolar constituents of goji berries have also been studied. The essential oil of goji berries have been reported to be mainly composed of ethyl hexadecanoate, 1-octadecanone, tetrapyrazine, 2-furan-carboxaldehyde, and ethyl linoleate from *L. chinense* and hexadecanoic acid, linoleic acid, β-elemene, myristic acid, and ethyl hexadecanoate from *L. barbarum* [60]. The oil exhibited excellent antioxidant activity in scavenging DPPH radical and inhibiting β-carotene bleaching, and its antioxidant activity was comparable to ascorbic acid and α-tocopherol [61]. In addition, a new analogue of ascorbic acid, 2-O-(β-D-glucopyranosyl) ascorbic acid, has been isolated from goji berries. This provitamin C compound accounts for approximately 0.5% of the dry weight of *L. barbarum*, and was thought to increase the level of blood ascorbic acid in rats and contribute to the antiaging properties of goji berries [62]. Minor bioactive components present in goji berries and their coproducts are summarized in Table 6.3.

### 6.3 Health benefits of goji berries

Goji berries are known for their broad array of biological activities and health effects. *L. barbarum* has been shown by modern studies to possess antioxidant, antiaging, antidiabetic,

**Table 6.3** Other bioactive compounds identified in goji berries and their by-products

Compound	Source	Reference
2-O-(β-D-glucopyranosyl)-ascorbic acid	Fruit of <i>Lycium barbarum</i>	[62]
Hexadecanoic acid	Essential oil of <i>Lycium barbarum</i>	[75]
Linoleic acid	Essential oil of <i>Lycium barbarum</i>	[75]
β-Elemene	Essential oil of <i>Lycium barbarum</i>	[75]
Lyciumin	Root of <i>Lycium chinense</i>	[59]
Betaine	Leaf/stem/root of <i>Lycium barbarum</i>	[58]
Cerebrosides	Fruit of <i>Lycium chinense</i>	[74]
Glycerogalactolipids	Fruit of <i>Lycium chinense</i>	[4]
Pyrole derivatives	Fruit of <i>Lycium chinense</i>	[53]

anticarcinogenic, neuroprotective, and immune enhancing properties [16, 17, 19, 28, 63]. They play a role in the prevention of diabetes, hepatitis, cancer, AMD, thrombosis, and male infertility, among other diseases and health conditions [7, 55]. Goji berry juice has been reported in a randomized double-blinded clinical study to increase subjective feelings of general well-being and improve neurologic/psychologic performance [17]. In addition to the goji berry fruits, the root bark and leaves of goji berries also contain pharmacologically active components with a variety of biological activities. The root bark of goji berries has been shown to possess hypotensive, hypoglycemic, antipyretic, and antiulceration effects in experimental animals and is used in oriental medicine as a tonic to relieve coughing, hypertension, and diabetes mellitus [64–68]. The leaves of *L. chinense* or *Lycii folium* are consumed as herbal tea in the oriental countries as a nourishing and tonic ingredient to reduce the risk of arteriosclerosis and essential arterial hypertension, diabetes, and night blindness [69]. The stamina-improving, tranquilizing, and thirst-quenching properties of goji berry leaf tea have also been well documented [42].

Although the beneficial effects of goji berries on human health have been known and practiced for centuries, only recent modern technology was able to unravel its mechanisms of action at the biochemical level. Many comprehensive studies have attributed the health effects of goji berries to their role as an antioxidant. *L. barbarum* is thought to elicit its protective effects in the body through counteracting free radical-induced oxidative stress [33]. The *L. barbarum* extract exhibited superoxide anion radical scavenging activity and inhibitory effect against oxidation products such as MDA in rat liver homogenates [70]. The aqueous extract of *L. chinense* fruit also inhibited hepatic MDA formation and depletion of reduced glutathione content and CAT activity in CCl<sub>4</sub>-injected rats [55]. The ethanol (70%) extract of *L. chinense* protected liver cells against oxidative stress-induced cell damage by scavenging intracellular ROS, recovering SOD, CAT, and glutathione activity, decreasing lipid oxidation, DNA damage, and protein carbonyl values [71]. In addition to their antioxidant activity, goji berries may also render their hepatoprotective effect through other mechanisms, such as expressional regulation of cytochrome P450 and improving viability of liver cells via inhibition of apoptosis [55, 71]. Other bioactivities of goji berries not directly related to their antioxidant activity have also been reported. For example, the leaves of *L. chinense* have been shown to stimulate the growth of *Lactobacillus acidophilus* and other probiotic cells commonly used in the food industry [72, 73].

## 6.4 Conclusions

Goji berries, an ancient oriental medicinal food, have recently attracted much attention as a functional food and a source of natural health products. Modern research has revealed their multiple biological activities and active components responsible for their health benefits. More research is needed in order to take better advantage of goji berries for promoting human health.

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## **7 Dried mulberries: phytochemicals and health effects**

Mine Gultekin Ozguven and Beraat Ozcelik

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### **7.1 Introduction**

Mulberry (*Morus* sp.) belongs to the family Moraceae which comprises about 40 genera and more than 1000 species [1]. *Morus* consists of 24 species and one subspecies, with more than 100 known varieties [2], with deciduous trees adapted to tropical, subtropical, and temperate zones of Asia, Europe, North and South America, and Africa [1, 3]. The optimum temperature for mulberry trees ranges from 20 to 24°C and the atmospheric humidity from 65 to 80% [4]. Mulberry trees, which are distributed widely, in particular in China and India [5], grow fast when young, but soon start growing slowly until reaching 10–15 meters in height [1]. Generally, mulberries are used for their foliage to feed the silkworm (*Bombyx mori* L.) in most mulberry-growing countries. On the other hand, mulberries are grown by European countries, including Turkey and Greece, for fruit production rather than foliage [2, 6, 7].

Mulberries are white to pale yellow with pink edges at the beginning. They then become red during ripening and dark purple to black when fully ripened [1]. There are three common mulberry species such as *Morus alba* (originated in Western Asia), *Morus rubra* (originated in North and South America), and *Morus nigra* (originated in Southern Russia) [3, 8, 9]. Fruits of white mulberries (*M. alba*) are perishable with a very sweet taste and low acidity and mostly consumed fresh. Purple mulberries (*M. rubra*) have a sweet taste and low acidity with high dry matter. Black mulberries (*M. nigra*) are juicy with extraordinary color and a refreshing acidic flavor [3, 8]. However, the color of mulberries cannot be used to identify the mulberry species since *M. alba* generates several colors of berries, including white, red, and purple [10].

Studies on mulberries have shown that they are rich sources of natural bioactive compounds or phytochemicals that exhibit biological effects on human health. This chapter highlights the compositional and nutritional characteristics, phytochemicals, health effects, and food applications of fresh mulberries with particular reference to their dried counterparts when data are available.

## 7.2 Drying of mulberries

Drying is one of the most important preservation methods of agricultural products since it allows an extended storage period due to reduced moisture content [11]. Reducing water activity inhibits microbial growth, enzymatic reactions, and other deteriorative processes [12]. Since mulberries are highly sensitive to storage and their harvesting seasons are very short, they need to be preserved by drying [7, 9, 13].

Sun drying is traditionally used for mulberry drying. After harvesting mulberries by handpicking or by shaking tree branches, they are spread over a sheet on the ground to be dried [14, 15]. Although solar energy is abundant, cheap, renewable, and environmentally friendly, contamination with dust, soil, and insects may occur. Moreover, exposure to direct sun radiation results in undesirable color changes in the fruits [9, 11, 16, 17]. Due to longer drying time, drying rate should be increased by using pretreatment with ethyl oleate, potassium carbonate, and sodium hydroxide [9]. Therefore, faster, safer, and more controllable drying techniques such as mechanical (artificial) air drying or solar air drying should be used to obtain more uniform, hygienic, and attractive-colored fruits [14, 15, 18]. In a solar dryer, air is heated by the sun in a collector and then passed over the mulberries to be dried. Pangavhane *et al.* [18] reported that sensory qualities of solar dried grape fruits were superior to those of open sun dried ones. Furthermore, the extent of nonenzymatic browning was decreased when using solar drying method [18]. Meanwhile, solar drying needs negligible installation and energy cost. However, due to uncertain environmental conditions in late summer or early fall or climatic variations, inadequate dehydration and long processing periods may cause considerable product loss [19]. For this reason, mechanical air drying in air driers is a good alternative in obtaining a good quality product in a shorter time for the industry [16, 19]. In this method, air dryers are heated by burning a gas (usually propane) or fuel oil, or their combination [19]. The method allows minimizing the composition, texture, and color changes. Despite these advantages, initial investment and additional running costs are high [16, 19].

Freeze and microwave drying techniques for drying berries have also been reported in the literature [20]. Vacuum-assisted microwave drying is effective in preserving the heat- and oxygen-sensitive phenolic components and ascorbic acid, color, and antioxidant activity as well as textural attributes of berries. Moreover, it is a rapid and low-temperature drying process [20, 21]. Meanwhile, freeze-dried berries exhibit the greatest antioxidant effect [20]. Although freeze drying and microwave drying are highly expensive drying methods, they protect the shape of the product with minimal reduction of volume [20, 22].

Drying is completed by controlling the amount of moisture in the final product. Final moisture content must be at least 17% (w/w) for safe storage [9]. Moisture content, texture, uniform size and color, presence of mold, yeast, foreign materials, decay, and insect affect the quality of the final product [9].

## 7.3 Compositional and nutritional characteristics of mulberries

Literature on proximate composition of fresh mulberries indicates a moisture content of 85–88 g/100 g. After the drying process, the moisture content of dehydrated mulberries is

**Table 7.1** Nutrient composition of fresh and freeze-dried mulberries (values in per 100 grams edible portion)

Nutrient	Unit	Fresh mulberries	Freeze-dried mulberries	Reference
<b>Proximate composition</b>				
Water	g	85–88	3.5–17	[24–26]
Energy	kcal	43	na	[24]
Protein	g	0.5–1.4	na	[24, 25]
Lipid	g	0.39–0.5	7.54	[2, 24–26]
Carbohydrate	g	7.8–9.8	na	[2, 24, 25]
Fiber	g	0.9–1.7	24.3	[24–26]
Sugars	g	1.8–16.2	72.7–80.2	[10, 25, 27]
<b>Minerals</b>				
Calcium	mg	39–443	na	[2, 25, 28, 29]
Copper	mg	0.06–0.5	1.18	[2, 24, 26, 29]
Iron	mg	1.85–190	48.1	[2, 24–26, 29]
Magnesium	mg	17–115	na	[2, 25, 28, 29]
Manganese	mg	3.8–4.2	7.45	[2, 26]
Phosphorus	mg	35–247	na	[2, 25, 28, 29]
Potassium	mg	194–1668	na	[2, 24, 25, 28, 29]
Selenium	μg	0.6	65	[24, 26]
Sodium	mg	10–61	na	[2, 25, 28, 29]
Zinc	mg	0.12–3.20	12.1	[2, 24, 26, 29]
Barium	mg	na	4.2	[26]
Molybdenum	mg	na	4.2	[26]
Chromium	mg	na	8.35	[26]

na, not available.

Values are expressed as (minimum–maximum).

decreased to 3.5–17 g/100 g [9, 23–25]. Therefore, nutrient content becomes concentrated, but essentially it is the same in dried mulberries as compared to the fresh ones. The nutrient composition, including proximate composition and minerals of fresh and freeze-dried mulberries, is given in Table 7.1. However, the composition of fruits depends on the species or varieties and the growing conditions, such as soil and geographical conditions [2].

Total sugar content of fresh and freeze-dried mulberries ranges from 1.8 to 16.2 g/100 g [10, 24, 27] and from 72.7 to 80.2 g/100 g [30], respectively (Table 7.1). Individual sugar content of dried mulberries changes from 34.2 to 38.3 g/100 g, from 36.9 to 40.8 g/100 g, and from 0.68 to 2.39 g/100 g for glucose, fructose and sucrose, respectively [30]. Sucrose is hydrolyzed to fructose and glucose during drying, which can participate in Maillard reaction [30]. Since, sugars are the initial precursors in the biosynthesis of anthocyanins, ripe mulberries containing high amounts of sugar include elevated anthocyanin content [10].

Table 7.1 shows the mineral contents in fresh and freeze-dried mulberries. In the literature, 10 minerals were found for fresh mulberries and 9 for freeze-dried ones [2, 24–26, 28, 29]. Mineral composition variation of fruits depends on the species or varieties and the growing conditions, such as soil and geographical conditions; however, it is possible to say that the drying process caused an increase in the mineral contents of mulberries [2, 24–26, 28, 29].

**Table 7.2** Contents of total phenolics, flavonoids, and anthocyanins in fresh and freeze-dried mulberries (mg/g dry weight basis)

Nutrient	Unit	Fresh mulberries	Freeze-dried mulberries	Reference
Total phenolics	mg of GAE	0.96–3.48	23.0	[3, 11, 26, 31, 32]
Total flavonoids	mg of RE	0.18–3.90	3.90	[5, 26]
Total anthocyanins	mg of C3GE	0.01–96.1	0.87	[5, 11, 26, 31]
Resveratrol	mg	na	0.30	[26]
Rutin	mg	na	0.43	[26]
Morin	mg	na	0.15	[26]
Quercetin	mg	na	0.03	[26]
Myricetin	mg	na	0.01	[26]
Vitamin C	mg	11.0–36.4	1.20	[2, 10, 24–26]
Vitamin E	mg of ATE	0.87	0.32	[25, 26]

Note: Some numbers are rounded after decimal point.

GAE, gallic acid equivalents; RE, rutin equivalents; C3GE, cyanidin-3-glucoside equivalents; ATE, alpha-tocopherol equivalents; na; not available.

Values are expressed as (minimum–maximum).

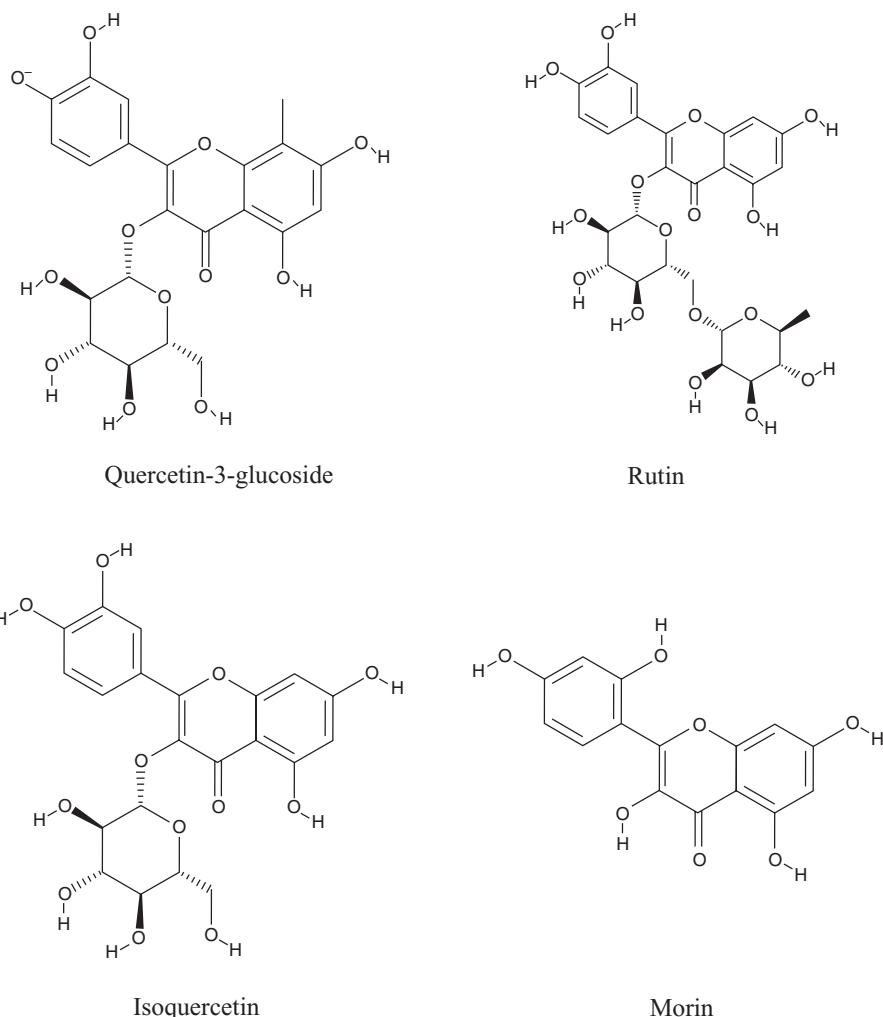
Table 7.2 reports the composition of some vitamins for fresh and freeze-dried mulberries [2, 10, 24–26]. Although fresh mulberries contain the majority of vitamins (such as choline, thiamine, riboflavin, vitamin A, vitamin C, vitamin E, and vitamin K), carotenoids ( $\alpha$ -carotene,  $\beta$ -carotene, and lutein + zeaxanthin), some heat-sensitive vitamins such as vitamin C and vitamin E may be lost during the drying process due to high temperature [33]. Significant loss in vitamin C and vitamin E occurs during the drying process (Table 7.2) [2, 10, 24–26].

## 7.4 Phytochemicals in mulberries and their by-products

Phytochemicals are essential bioactive substances present in plants. However, the human body is not able to produce them [34]. Therefore, plants rich in these bioactive substances should be consumed regularly. According to recent investigations, the fruits and leaves of mulberry plants contain healthful bioactive components such as flavonoids, anthocyanins, polyhydroxylated alkaloids, and hydroxystilbenes [5, 35].

### 7.4.1 Flavonoids

Mulberries are rich sources of flavonoids. The major flavonoids found in mulberries are quercetin-3-glucoside, rutin, isoquercetin, and morin (Figure 7.1) [36, 37], while the main flavonoids in mulberry leaves are quercetin-3-glucoside, kaempferol-3-glucoside (astragalin), and quercetin-3-(6-malonylglucoside) [1, 38]. Recently, Zhang *et al.* [39] isolated four new flavonoids, namely, 8-hydroxyethyl-7,2',4'-trihydroxyflavone, ( $\pm$ )-7-methoxy-8-hydroxyethyl-2',4'dihydroxyflavane, 2R\*,4R\*-8-hydroxyethyl-7,4'-dihydroxy-4,2' epoxyflavane, and 2'E-3'(4"-hydroxyisopentenyl)-2,4,2',4'-tetrahydroxychalcone from the leaves of *Morus mongolica*. Chang *et al.* [40] also identified five phenolics, namely,



**Figure 7.1** Structures of some major flavonoids found in mulberries.

maclurin (49 and 58.4%), rutin (9.3 and 12.5%), isoquercitrin (5.1 and 9.3%), resveratrol (15.5 and not detected), and morin (20.6 and 20.8%) in mulberry twigs and mulberry root bark, respectively. The contents of total phenolics, flavonoids, and anthocyanins in fresh and freeze-dried mulberries are summarized in Table 7.2 [3, 5, 10, 11, 26, 31, 32, 35].

Differences in total phenolic content between *M. nigra* and *M. rubra* are reported [3, 31]. Black mulberry genotypes have a higher phenolic content [1766–3488 µg gallic acid equivalents (GAE)/g] than their purple counterparts (1005–2388 µg GAE/g). However, differences in phenolic composition of the fruits depended on many factors such as growing conditions, genetic differences, and the degree of maturity at harvest [1, 2, 36]. In fact, Zhishen *et al.* [41] reported the total flavonoid content of mulberry leaves varied from 11.7 to 26.6 mg/g in spring and from 9.84 to 23.4 mg/g in autumn for the same mulberry variety;

thus flavonoid content changes depending on the season. The flavonoid content of the spring leaves was higher than that of the autumn leaves [41].

### 7.4.2 Anthocyanins

Anthocyanin profiles of red and black mulberries have been determined by different researchers. Hassimotto *et al.* [42] reported that 79 and 19% of anthocyanins in wild mulberries were cyanidin-3-glucoside and cyanidin-3-*O*-rutinoside, respectively. In contrast, Qin *et al.* [43] showed that most abundant anthocyanins in mulberries were cyanidin-3-*O*-rutinoside (60%) and cyanidin-3-*O*-glucoside (38%). The minor anthocyanins were pelargonidin 3-*O*-glucoside and pelargonidin 3-*O*-rutinoside (2%). These results are in agreement with those reported by others [1, 10, 37, 44]. Du *et al.* [45] also reported the anthocyanins of mulberries as cyanidin-3-*O*-(6"-*O*- $\alpha$ -rhamnopyranosyl- $\beta$ -D-glucopyranoside), cyanidin-3-*O*-(6"-*O*- $\alpha$ -rhamnopyranosyl- $\beta$ -D-galactopyranoside), cyanidin-3-*O*- $\beta$ -D-galactopyranoside, and cyanidin-7-*O*- $\beta$ -D-glucopyranoside. Meanwhile, Wu *et al.* [44] reported delphindin-3-(6"malonyl)-glucoside and peonodin-3-xylosylrhamnoside in mulberries. The total anthocyanin content of fresh and freeze-dried mulberries is summarized in Table 7.2 and the chemical structures of major anthocyanins found in mulberries are given in Figure 7.2.

Total anthocyanin contents of black and purple mulberry genotypes ranged from 693 to 787  $\mu$ g and from 81 to 132  $\mu$ g of cyanidin-3-glucoside equivalents (C3GE)/g, respectively [31]. In addition, Ozgen *et al.* [3] found that the anthocyanin contents in black and red mulberries ranged from 253 to 830 and from 3 to 200  $\mu$ g C3GE/g, respectively. However, drying significantly destroyed the bioactive compounds such as anthocyanins, flavanols, and ascorbic acid [20]. Similarly, Lohachoompol *et al.* [46] found that total anthocyanins in blueberries were lost by 41–49% depending on different treatments.

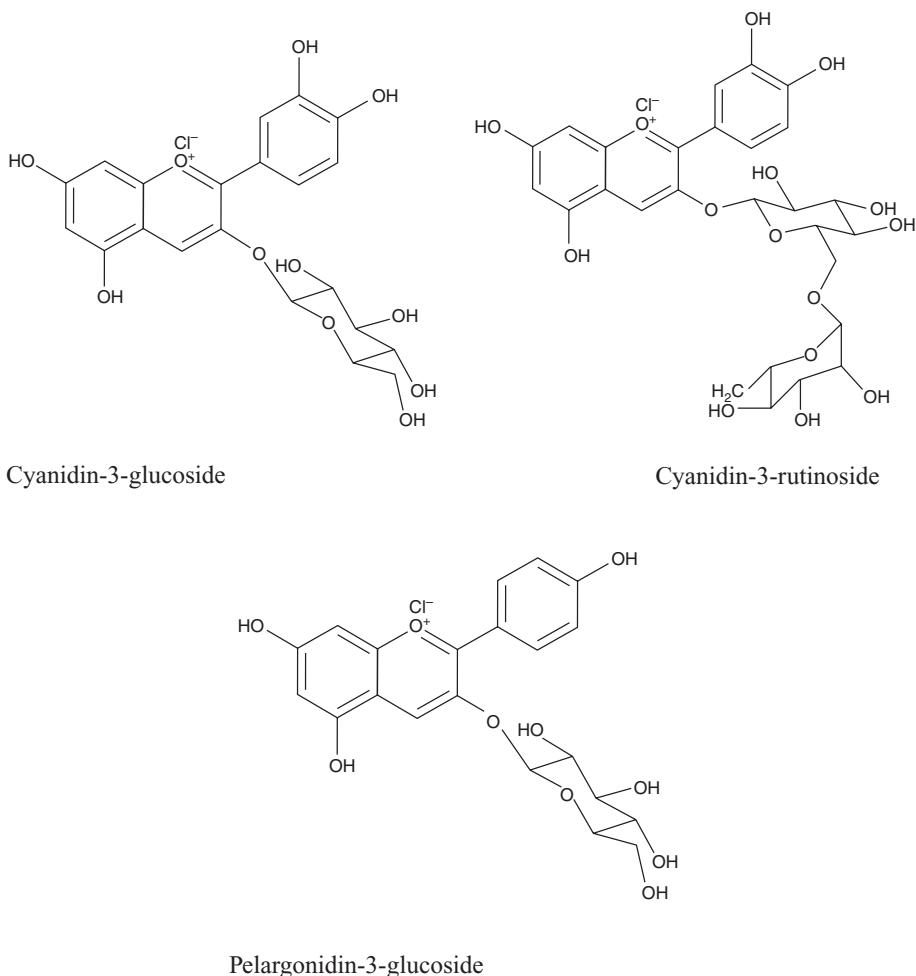
### 7.4.3 Polyhydroxylated alkaloids

Polyhydroxylated alkaloids are widespread and isolated from plants, microbial filtrates, and insects. 1-Deoxynojirimycin was synthesized by removing the anomeric hydroxyl group of nojirimycin, but it was later isolated from bacterial cultures and plant sources [5, 47–49]. In fact, 1-deoxynojirimycin is more stable than nojirimycin; therefore, it has been used as a model glucosidase-inhibiting alkaloid [48]. 1-Deoxynojirimycin was isolated from root bark of the mulberry tree [50]. Nowadays, it can also be isolated from mulberry leaves [5, 48, 49]. The chemical structure of 1-deoxynojirimycin is given in Figure 7.3. Song *et al.* [5] found that the content of 1-deoxynojirimycin varied between 1.389 and 3.483 mg/g in leaves for 33 cultivars. The concentration of 1-deoxynojirimycin in three cultivars of mulberry leaves and their related products (tea leaf, tablet, and powder) was 100–480 mg/100 g in freeze-dried samples [51].

Asano *et al.* [49] described new polyhydroxylated alkaloids such as (2*R*, 3*R*, 4*R*)-2-hydroxymethyl-3,4-dihydroxypyrrolidine-*N*-propionamide isolated from the root bark of *M. alba* L., and 4-*O*- $\alpha$ -D-galactopyranosyl-calystegine B<sub>2</sub> and 3 $\beta$ ,6 $\beta$ -dihydroxynortropane isolated from the fruits.

### 7.4.4 Hydroxystilbenes

Resveratrol (*trans*-3,4,5-trihydroxystilbene) and oxyresveratrol (*trans*-2,3,4,5,50-tetrahydroxystilbene) are hydroxystilbenes found in many plant species including grapes, peanuts,

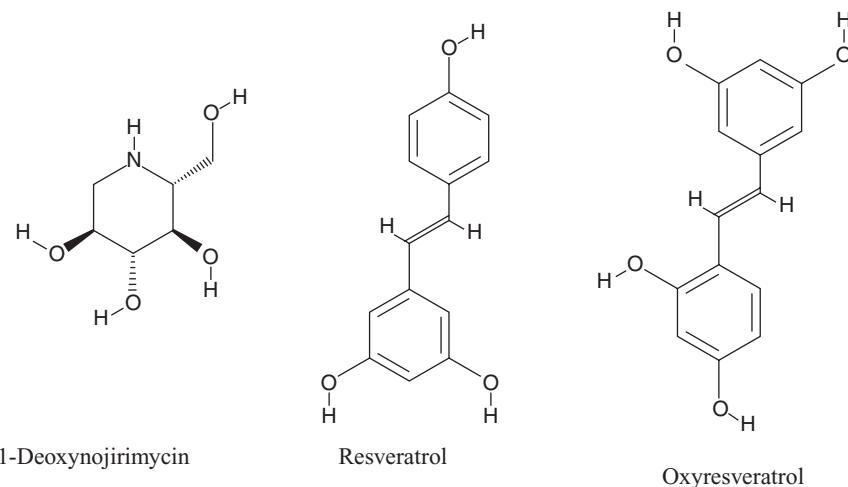


**Figure 7.2** Structures of major anthocyanins found in mulberries.

and mulberries (Figure 7.3). Song *et al.* [5] found oxyresveratrol and resveratrol in 38 cultivars of fresh mulberries, ranging from 2.4 to 29.5 µg/g and from 2.1 to 5.3 µg/g, respectively. In addition, oxyresveratrol varied between 5.3 and 179.9 µg/g in leaves of 33 cultivars [5].

## 7.5 Natural antioxidants in mulberries

Instead of synthetic antioxidants such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA), naturally occurring antioxidants have gained importance in the food industry in recent years since they are considered safe [52, 53]. These natural antioxidants can be phenolic compounds, such as flavonoids and phenolic acids, as well as vitamins A, C, and E. Dark-colored mulberries exhibit strong antioxidant activity due primarily to



**Figure 7.3** Structures of polyhydroxylated alkaloids found in mulberries.

flavonoids in particular anthocyanin pigments [32]. They contain high amounts of water-soluble anthocyanins, which are the most important natural antioxidative compounds in the plant kingdom [54]. Anthocyanins are excellent antioxidant agents due to their ability to inhibit lipid peroxidation via radical scavenging and metal chelating activities [42, 45]. In fact, it is known that *in vitro* antioxidant activities of anthocyanins are superior to vitamin E [32].

Various researchers have studied the antioxidant activities of mulberries. Du *et al.* [45] determined the antioxidant activities of five anthocyanin monomers [cyanidin 3-*O*-(600-*O*- $\alpha$ -rhamnopyranosyl- $\beta$ -D-glucopyranoside), cyanidin-3-*O*-(600-*O*-arhamnopyranosyl- $\beta$ -D-galactopyranoside), cyanidin-3-*O*- $\beta$ -D-glucopyranoside, cyanidin-3-*O*- $\beta$ -D-galactopyranoside, and cyanidin-7-*O*- $\beta$ -D-glucopyranoside] present in *M. alba* and crude mulberry extracts by 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging assay. Compared to vitamin C, crude mulberry extract (95.3%) exhibited the same DPPH radical scavenging activity as that of vitamin C (95.5%) or five anthocyanin monomers (ranging from 95.1 to 96.2%) at a concentration of 0.40 mg/mL, which indicates that mulberry extract is an excellent antioxidant.

Ercisli *et al.* [31] compared the antioxidant activities of black and purple mulberry species grown in Turkey. On the basis of ferric reducing antioxidant power (FRAP) assay, *M. nigra* L. genotypes (black color) had antioxidant activity ranging from 12.26 to 14.11 and *M. rubra* L. genotypes (purple color) ranging from 4.93 to 8.12  $\mu$ mol of trolox equivalent (TE)/g. Similarly, Ozgen *et al.* [3] studied the antioxidant properties of *M. nigra* L. and *M. rubra* L. fruits harvested from Turkey. *M. nigra* L. fruits had the highest total antioxidant activity, within the range of 7.3–16.9  $\mu$ mol TE/g, while that for *M. rubra* L. was 3.7–7.7  $\mu$ mol TE/g by the FRAP method. These results indicate that black mulberries exhibited higher antioxidant activity than purple mulberries. Additionally, the antioxidant activity of fresh mulberries varies from 2.50 to 21.17  $\mu$ mol TE/g on the basis of DPPH assay [31, 55], and from 0.30 and 1.73  $\mu$ mol TE/g on the basis of oxygen radical absorbance capacity (ORAC) assay [35]. No data exist in the literature about antioxidant activity of dried mulberries.

Several studies have also reported the antioxidant activity of mulberry leaves. Antioxidant activity relies on six flavonol glycosides, namely, rutin, isoquercetin, quercetin-3-(6-acetylglucoside), astragalin, kaempferol-3-(6-acetylglucoside), quercetin-3-(6-malonylglucoside), and chlorogenic acid in mulberry leaves [56, 57]. Katsume *et al.* [56] determined the DPPH radical scavenging activity of each polyphenolic compound identified in mulberry leaves and their contributions to this scavenging activity in the extract of freeze-dried mulberry leaves. Chlorogenic acid exhibited 36.2% of the total DPPH radical scavenging activity which makes the largest contribution. Among quercetin glycosides, quercetin-3-(6-malonylglucoside) showed the highest contribution (21.4%), whereas kaempferol glycosides made a slight contribution only (0.2%). Quercetin, as one of the most abundant flavonoids in human diets, has been recovered in rat plasma as sulfate, glucuronide, and sulfoglucuronide conjugates after intragastric administration of quercetin aglycone and these quercetin conjugates protect low-density lipoprotein (LDL) from oxidation induced by copper ion [57]. However, phenolic content and antioxidant activity was not decreased significantly during air drying at 60°C and freeze drying, while both values were decreased during air drying at 70°C. Wanyo *et al.* [58] studied the antioxidant activity of fresh, combined far-infrared radiation with hot-air convection (FIR-HA) dried mulberry leaves and commercial mulberry tea dried by hot-air drying. The fresh leaves exhibited 71% of DPPH radical scavenging. Meanwhile, combined FIR-HA dried leaves provided higher DPPH radical scavenging (76%) than those of commercial tea products (42%). Based on these results, combined FIR-HA technique can be used instead of hot-air drying during commercial tea production.

Arabshahi-Delouee and Urooj [53] investigated the antioxidant properties of mulberry (*Morus indica* L.) leaves. EC<sub>50</sub> value, 50% radical scavenging activity concentration of antioxidants, of methanolic extract of leaves was 79.53 µg/mL compared to values of 61.67 µg/mL for ascorbic acid and 41.07 µg/mL for BHT. Yen *et al.* [59] showed that *M. alba* leaf extracts exhibited strong antioxidant activity (78.2% inhibition on peroxidation of linoleic acid). The antioxidant activity of the extract was slightly less than that of BHA, but was stronger than that of α-tocopherol (72.1% inhibition on peroxidation of linoleic acid). Andallu *et al.* [60] also studied the antioxidant potential of *M. indica* L. leaves. The results indicated that mulberry leaf extract effectively scavenged nitric oxide, superoxide, and DPPH radicals and exhibited tremendous reducing power. Besides, mulberry leaf extract suppressed FeSO<sub>4</sub>-induced lipid peroxidation and conjugated dienes/hydroperoxides in erythrocyte membrane very efficiently.

## 7.6 Health effects of mulberries

Mulberries are used effectively in folk medicines to treat fever, protect liver and kidney from damage, strengthen the joints, facilitate discharge of urine, improve eyesight, treat mouth lesions, lower blood pressure, treat sore throat, hypertension, and anemia, and prevent cardiovascular disease (CVD) [3, 26, 31, 32, 41, 53, 58]. Additionally, mulberry fruits can be used as a warming agent, as a remedy for dysentery, and as a tonic, sedative, laxative, odontalgic, anthelmintic, expectorant, and emetic, among others [1, 61]. Since mulberries are rich in naturally occurring flavonoids and anthocyanins, they exhibit anti-inflammatory, vasoprotective, antioxidant, antiallergic, hepatoprotective, antithrombotic, antiviral, chemoprotective, and anticarcinogenic activities [5, 8, 32, 54, 62]. Therefore, besides anthocyanins are used as

natural sources of food colorants, many consumers and food manufacturers have become interested in phenolic phytochemicals for their medicinal properties, especially their potential role in the prevention of cancers and CVD [32, 43].

In addition to fruits, almost all parts of the mulberry tree (leaves, bark of stems, and roots) are used for pharmacological purposes around the world, especially in Chinese folk medicine [63]. The leaves have been shown to possess diuretic, hypoglycemic, and hypotensive activities, and blood sugar- and blood pressure-reducing effects, whereas the root barks of mulberry trees have long been used for anti-inflammatory, antitussive, and antipyretic purposes [1, 52]. Meanwhile, mulberry leaf extracts were found to prevent amyloid fibril formation and showed neuroprotective effects [64].

### 7.6.1 Anticancer activities

Anthocyanins show greater inhibitory effect on suppressing the growth of tumor cells than other flavonoids [46]. However, biological effects of anthocyanins as well as their appearance depend on pH [65].

Major anthocyanins of colored mulberries, such as cyanidin-3-glucoside and cyanidin-3-rutinoside, are reported to have an inhibitory effect on migration and invasion of lung cancer cells [62]. These compounds help to suppress proliferation and angiogenesis, as well as the induction of cancer cell apoptosis [5, 26, 62]. In fact, effects of anthocyanins on antitumorigenesis in different mechanisms were reported by different researchers. Recently, Huang *et al.* [66] showed that mulberry extracts inhibited the growth of human gastric carcinoma cells. Moreover, they claimed that 0.2% mulberry extracts by both injection and oral gavages exhibited tumor inhibition effect. Therefore, it is suggested that mulberry anthocyanins can be used as potential therapeutic agents in preventing gastric carcinoma formation [66].

Huang *et al.* [8] also reported that mulberry anthocyanins had therapeutic potential on melanoma, a skin cancer type that originates in melanocytes, specialized pigment-producing cells found in both the basal layer of the epidermis and the eye. Mulberry anthocyanins control tumor metastasis based on the observation of its inhibitory effect on the motility of melanoma cancer cell line B16-F1. The researchers suggested that mulberry anthocyanins could suppress melanoma metastasis and may be used as potential candidates for cancer chemoprevention [8].

Resveratrol found in mulberries also exhibits anticancer activities because it acts as an antioxidant, inhibits lipid peroxidation, cyclooxygenases, and protein kinase C and prevents nuclear factor-kappa B (NF- $\kappa$ B) and activator protein-1 (AP-1) transcription factor induction and cytokine release [67].

### 7.6.2 Cardioprotection

Mulberry anthocyanins participate in CVD protection, which is strongly linked to reduction in oxidative stress. Anthocyanins protect from heart attacks since they have the ability of reducing inflammation, enhancing capillary strength and permeability, inhibiting platelet formation, and enhancing nitric oxide release [68]. Both mulberry anthocyanins and leaf extracts can scavenge reactive oxygen species (ROS), LDL cholesterol oxidation, prevent platelet aggregation, and decrease serum lipids, and therefore exert beneficial effects on

blood lipid and atherosclerosis [5, 26, 58, 61, 68]. In particular, quercetin as a major representative of the flavonol group exhibits strong inhibitory effects on oxidative modification of human LDL *in vitro* [38, 56]. Resveratrol component of mulberries also helps cardioprotection [67].

### 7.6.3 Diabetes

The alkaloid component of mulberry leaves, 1-deoxynojirimycin, is known as one of the most potent  $\alpha$ -glycosidase inhibitors that decreases blood sugar levels by establishing glycemic control in type 2 diabetes in humans [5, 49]. Tender mulberry leaves from the top of branches contain the highest amount of 1-deoxynojirimycin in the summer [4]. Hansawasdi and Kawabata [69] reported that hot-water extract of mulberry leaves exhibited inhibitory effect against  $\alpha$ -glucosidases; therefore, mulberry tea can be consumed as an antidiabetic herbal tea. They concluded that infusion of 1 gram mulberry tea in 100 mL hot water (98°C) for 3–5 min exhibits an effective inhibitory activity against  $\alpha$ -glucosidases, sucrase, and maltase enzymes. As an alternative, 1-deoxynojirimycin-enriched dietary supplement can be used for preventing diabetes mellitus [4].

### 7.6.4 Alzheimer's disease

Mulberry extracts help with the treatment of Alzheimer's disease by inhibiting amyloid  $\beta$ -peptide (1–42) fibril formation and showing neuroprotective effects [4, 61, 64], promoting age-dependent antioxidant protection, and reducing oxidative stress-induced damage [4, 64].

### 7.6.5 Hyperpigmentation disorders

The hydroxystilbene component of both mulberry fruits and leaves—oxyresveratrol—is an active compound in dermatology that has an inhibitory effect on tyrosinase to limit melanin biosynthesis [5, 40, 70]. Tyrosinase catalyzes both the hydroxylation reaction that converts tyrosine to 3-(3, 4-dihydroxyphenyl)-L-alanine (DOPA) and the oxidation reaction that converts DOPA into dopaquinone, which causes polymerizing of brown pigments [10]. Therefore, oxyresveratrol is used for whitening skin in cosmetics and treating hyperpigmentation disorders in medicine [5].

## 7.7 Food application of mulberries and their by-products

Food applications of mulberries include not only mulberry fruits themselves, but also their leaves and products.

### 7.7.1 Mulberry fruits and their products

The white, purple, and black mulberry fruits, which have a very pleasant taste, are consumed as fresh fruits. Additionally, black and purple mulberry fruits are consumed in the form of jam, marmalade, frozen desserts, pulp, juice, paste, ice cream, liquor, wine, and canned food,

among others, since there is an increasing interest for mulberries in the food industry due to the presence of anthocyanins in purple and black cultivars [1, 3, 29, 38, 61, 62]. Moreover, mulberry fruits have been used for the production of some traditional Turkish confectionary products such as mulberry pekmez (a concentrated mulberry juice by boiling) and mulberry pestil [71]. Mulberry pekmez is generally consumed with breakfast [72]. It is produced from mulberry fruits by concentration of juices containing up to 70–80% soluble dry matter content [72, 73]. Due to the presence of high amounts of sugar, minerals, and organic acids, pekmez is preferred for babies, children, and sportspersons for supplying rapid energy [72]. Mulberry pestil is a dried fruit snack for consumption in the winter [73]. It is prepared by boiling mulberry juice, starch, and sugar before addition of pistachios and walnuts until a mild, crunchy, tasty, light, and chewable leathery product is obtained [74, 75]. Similar to pekmez, pestil is also a good source of energy containing high amounts of carbohydrates and minerals. Finally, colored mulberries are also used as natural dyes in the cosmetic industry [31, 76].

### 7.7.2 Mulberry leaves

Mulberry leaves are nutritious, palatable, and nontoxic [53]. The leaves have historically been used for feeding silkworms (*Bombyx mori* L.) in China and India [1, 5], the cocoon of which is used to make silk, and has big ecological and economical importance [5]. Fibroin protein solution, gel, and powder obtained from these cocoons have been processed into cosmetics, skin cream, face washing milk, shampoo, and bath agents in Japan [49]. Mulberry leaves are consumed in Thailand in different ways. Mulberry leaf tea has been very popular in Thailand for the last decade [57, 58]. In addition, the leaves are added in spicy soup preparation and the tips are used as a vegetable in light curry [58]. Furthermore, mulberry leaf carbonated beverage and mulberry leaf chrysanthemum beverage are known as functional beverages that are widely consumed in China [77]. The leaves are also used to feed dairy animals to improve milk yield [48]. Liu *et al.* [78] showed that it was possible to use mulberry branch barks to obtain pectin instead of discarding them as agricultural waste. Pectin is used as a gelling agent and stabilizer in the food industry in jams, jellies, and dairy products [78].

## 7.8 Conclusions

Mulberries are valuable horticultural products grown worldwide. They are rich in phytochemicals, in particular anthocyanins, which possess therapeutic and pharmacological benefits such as treating fever, protecting liver and kidney from damage, strengthening the joints and facilitating discharge of urine, among others. Besides fruits, mulberry leaves are used to feed silkworms and are edible.

Although growing conditions and cultural management techniques affect the nutritional value of the *Morus* species, more research is needed in the areas related to dried mulberry phytochemicals as well as their extraction, analyses, and bioavailability. Optimization of various drying techniques is needed to further study to minimize nutritional loss, undesirable texture, flavor, and color changes.

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## **8 Dried raspberries: phytochemicals and health effects**

Esteban I. Mejia-Meza, Jaime A. Yáñez, Neal M. Davies, and Carter D. Clary

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### **8.1 Introduction**

In recent years, consumer demand and awareness for health-promoting food has increased considerably in the United States and around the world. The interest has focused attention on a new group of nutritionally active compounds, principally antioxidants, present in fruits, and being promoted as important components in foods associated with a healthier lifestyle. Therefore, improvement in dietary habits, reducing the impact of sedentary jobs and long commutes, improving physical activity and exercise, and reducing stress are thought to have potential impacts on decreased risk of various degenerative diseases.

Raspberries are a good example of fruits rich in various nutrients and antioxidants [1], and are produced mainly in the Russian Federation [175,000 metric tonnes (MT)], Serbia and Montenegro (90,000 MT), the United States (62,000 MT), Poland (38,000 MT), and Ukraine (25,000 MT) [2]. This chapter provides information about phenolic compounds in fresh, dried, and processed raspberries and the impact of dehydration on their polyphenol constituents.

### **8.2 Dehydration of raspberries**

Dehydration processes are commonly used to preserve fruits by near-complete removal of water. The displacement of water, mainly by evaporation, results in a reduction in moisture content and water activity, as well as inhibits deleterious biochemical reactions such as enzymatic browning, lipid oxidation, and growth of microorganisms [3]. However, traditional hot-air drying results in loss of phytochemicals due to oxidative reactions. Hot-air and drum drying adversely affect sensory and nutritional value of fruits may compromise their functional properties. Dehydration methods such as vacuum and freeze drying are potentially less damaging; however, these methods involve higher production costs [4].

Freeze and vacuum drying are commonly employed techniques that maintain highly desirable nutritional and functional properties of many foods, but the capital and operating costs are high. Microwave-vacuum drying is another technique that may result in the retention

of flavor and color, less cell collapse and loss of tissue structure, and may potentially result in a reduced loss of bioactive components relative to hot-air drying, but it has received little commercial and academic attention until recently. Microwave-vacuum drying [5] takes significantly less drying time than freeze drying and hot-air drying. Nevertheless, the cost of using both techniques (e.g., a combination of freeze and microwave-vacuum drying) is often too high to be justified unless improvements in product quality warrant their use. Therefore, developing and evaluating dehydration technologies that produce high-quality health-promoting fruits at a reasonable cost is a desirable goal. Nevertheless, a combination of conventional drying techniques, such as hot-air drying with microwave-vacuum and/or freeze drying, may provide an opportunity to produce high-quality nutritive dried fruits with a relatively lower cost compared to freeze drying alone.

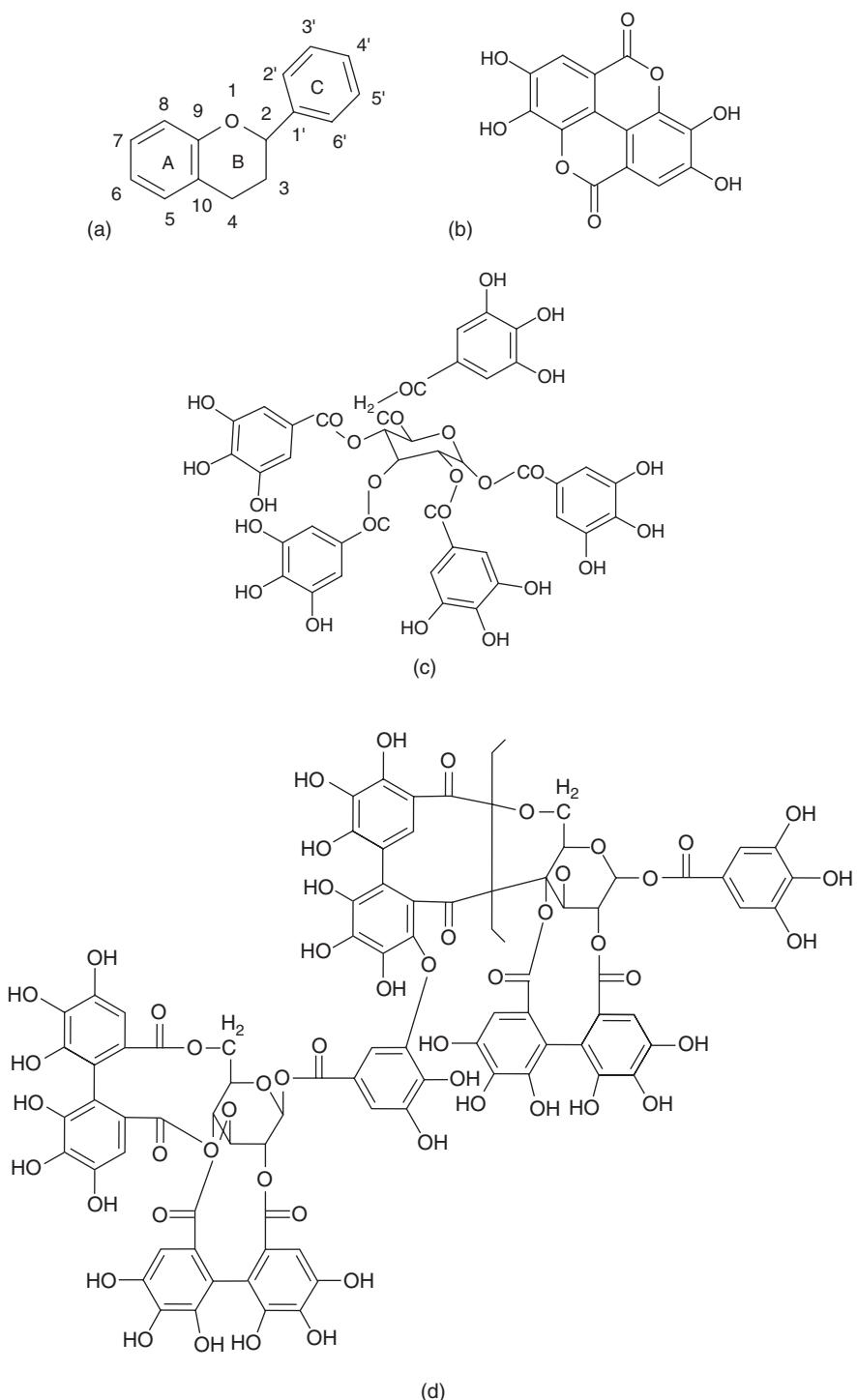
The moisture content of fruits is generally between 80 and 90% or higher [6]. Fruits are metabolically active; therefore, the shelf life of fresh fruits is very limited and makes handling and storage difficult. To extend the shelf life, to increase the availability of fruits over a longer period and to distant markets, and to preserve essential nutritive components, preservation techniques are needed. Dehydration is one technique that has been used since antiquity in the form of solar drying and sun drying (such as raisins), and more recently with industrial driers developed to preserve fruits and produce shelf-stable products with specific functional and sensory characteristics. The main purpose of dehydration is to reduce water activity, which inhibits the growth of microorganisms and retards certain deleterious biochemical reactions in fruits. Hot-air, freeze, and microwave-vacuum dryings are some of the dehydration techniques used to preserve fruits.

Hot-air drying, however, can alter the physical and chemical properties of fruits and may reduce the level of polyphenolic compounds because of their sensitivity to degradation at high temperatures for a relatively long drying time. Although freeze drying reduces the amount of heat damage and produces a dried product with generally better retention of cellular structure, functional, and quality properties, polyphenolics are exposed to oxidative conditions during freeze drying most likely due to the extended drying time. Microwave-vacuum drying is a relatively new dehydration technique that may reduce oxidation of important food components, such as antioxidants, since microwave-vacuum dehydration takes less time and is conducted at a lower temperature compared to hot-air drying. However, operating expenses of microwave-vacuum drying may be higher than for hot-air-dried foods. Therefore, a combination of conventional drying techniques such as hot-air drying with microwave-vacuum and/or freeze drying should reduce dehydration costs while preserving desirable physical and chemical properties of the fruit to a greater extent [5, 7, 8].

### 8.3 Phytochemicals in dried raspberries

Phenolic compounds are well distributed in fruits and their concentrations can vary tremendously between one fruit and another, even in cultivars of the same species [9, 10]. The content of total phenolics in fruits may be influenced by many factors, including genetics, environmental conditions, degree of ripeness, variety, storage, and analytical methods chosen for isolation, detection, and quantification of total phenolics.

Phytochemicals can be divided into different classes including simple phenols, phenolic acids, benzoquinones, phenylpropenes, cumarins, chromones, naphthoquinones, xanthones, stilbenes, flavonoids, tannins, and lignans, among others [11]. In fruits, polyphenols (Figure 8.1) are commonly found as flavonoids, phenolic acids, and tannins. Flavonoids



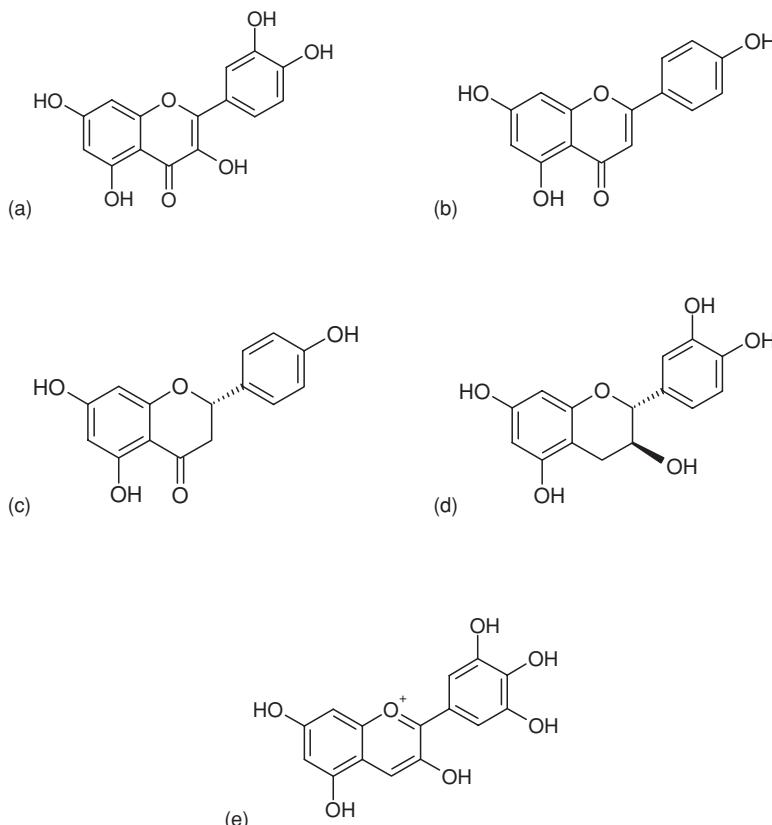
**Figure 8.1** Common polyphenols found in raspberries: (a) generic structure of the flavonoid backbone, (b) ellagic acid, (c) tannic acid, and (d) ellagitannin sanguin H6 [12].

are the most abundant phenolic compounds in fruits and vegetables with more than 5000 compounds identified to date [13, 14].

### 8.3.1 Flavonoids

Flavonoids, which are the largest group of phytochemicals, are classified into 13 subclasses: chalcones, dihydrochalcones, aurones, flavones, flavonols, dihydroflavonol, flavanones, flavonols, flavandiols, anthocyanidins, isoflavonoids, biflavonoids, and proanthocyanidins [11, 15]. They are associated with many physiological properties, including antioxidant, anti-inflammatory, antimicrobial, antihyperlipidemic, anticancer, antiviral, and antiallergenic, all of which are thought to play a role in reducing the risk of degenerative diseases such as cardiovascular disease (CVD).

The most abundant flavonoids in fruits are the flavonols (quercetin, kaempferol, and myricetin), flavones (apigenin and luteolin), flavanones (naringenin, naringin, hesperetin, and hesperidin), flavan-3-ols (catechin, catechin gallate, and proanthocyanidins), and anthocyanidins (cyanidin, delphinidin, pelargonidin, and glucosides anthocyanins) (Figure 8.2)



**Figure 8.2** The most abundant flavonoids in raspberries: (a) quercetin, (b) apigenin, (c) naringenin, (d) (+)-catechin, and (e) cyanidin.

[11, 16, 17]. Flavonols are the most widely distributed flavonoids in fruits and exist mainly in the glycosidic form with a hydroxyl group conjugated most commonly at position 3 of the C-ring and with possible substitutions at 5, 7, 4', 3', and 5' positions (Figure 8.2a) [13, 18]. Quercetin, kaempferol, and myricetin, the most common flavonols, are quantified in apples, berries, plums, tomatoes, peaches, and grapefruits [15, 17, 19]. Quercetin-3-glucoside and kaempferol-3-glucoside and their conjugates have been identified in raspberries [20], while quercetin and kaempferol aglycones and their glycosides have also been reported [21].

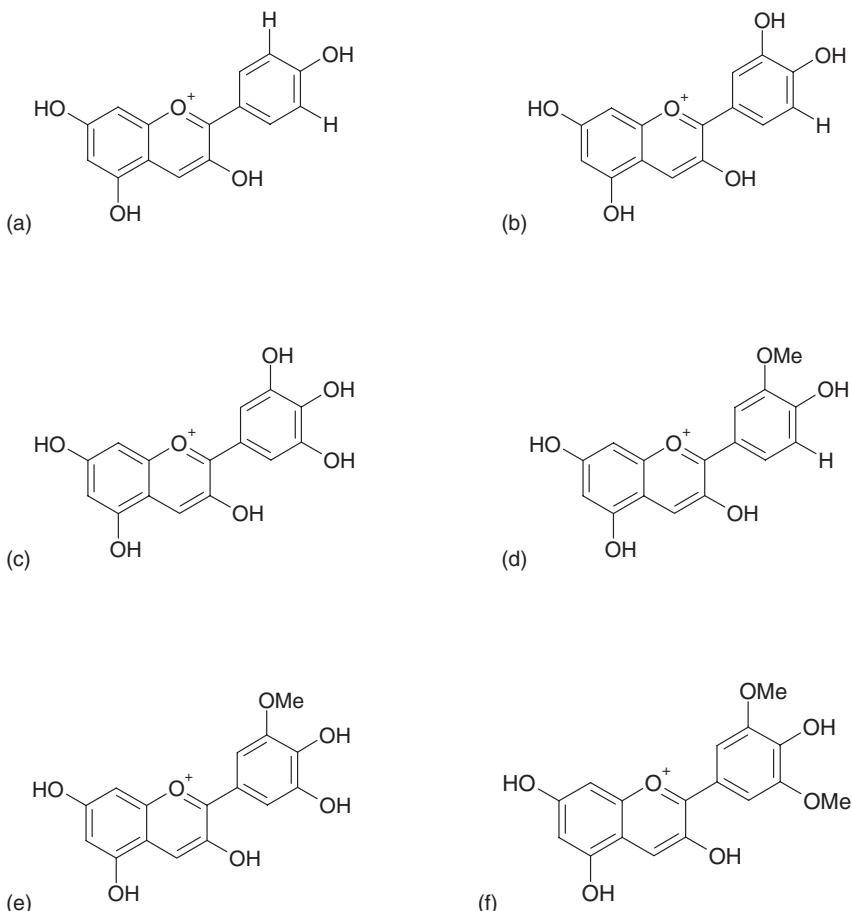
Flavones, another subclass of flavonoids, are common in fruits and exhibit a modified flavonol structure with an extensive range of carbon substitutions. The most common flavone, apigenin, exhibits possible substitutions at the A- and C-rings (Figure 8.2b) and is a constituent of fruits and vegetables including melons, watermelons, grapefruit, and bell peppers [15]. However, flavones have not been fully identified in raspberries [20].

Another subclass of flavonoids with high bioactivity is the flavanones. They occur as hydroxylated, glycosylated, and *o*-methylated derivatives. The most abundant members are naringin and hesperidin (flavanone glycoside), both common in citrus fruits, as naringenin (Figure 8.2c) and hesperetin (flavanone aglycones) [17, 22, 23]. Flavanones are prevalent in citrus fruits, particularly in grapefruits, oranges, and lemons [15, 19, 23]. Flavan-3-ols or flavanols, one of the most complex flavonoids, are characterized by two chiral centers at C2 and C3, in the heterocyclic C-ring for monomeric units such as (+)-catechin (Figure 8.2d) [18, 22, 24]. Flavanols such as (+)-catechin, epicatechin, epigallocatechin, and proanthocyanidins are abundant flavonoids in grapes, cacao, apples, peaches, nectarines, and berries [11, 15, 19, 23]. Flavanols are responsible for the bitterness and astringency of some fruits [17, 18] and raspberries have been reported to contain naringin enantiomers [21].

Anthocyanidins, another subclass of flavonoids, are widely distributed in food plants and are present in the sugar conjugated form, commonly known as anthocyanins [22]. The most common anthocyanidins are cyanidin, pelargonidin, delphinidin, petunidin, peonidin, and malvidin (Figure 8.3), generated from proanthocyanidins under acidic and high-temperature conditions [18]. Anthocyanidins are present in fruits such as red grapes, blueberries, raspberries, cranberries, and strawberries [17, 22].

Limited information is available about the phytochemical composition of dried raspberries. Recently, Mejia-Meza *et al.* [21] studied retention of polyphenol glycoside and aglycone compounds from dried raspberries by different drying techniques (Table 8.1).

Findings included the concentrations of individual polyphenols, namely, ellagic acid, quercetin, phlorizin, *R*-naringin, *S*-naringin, kaempferol, and their aglycones in fresh and dried raspberries (such as freeze drying, microwave-vacuum drying, hot-air drying, and a combination of hot-air drying and microwave-vacuum drying methods). The results demonstrated significantly ( $P \leq 0.05$ ) higher concentrations of glycosides and aglycones compounds in fresh raspberries as compared to that of their dried counterparts. Ellagic acid and quercetin were present at the highest concentration in fresh and dried raspberries. Dehydration led to a reduction in polyphenolic content, but there was a tendency for microwave-vacuum and a combination of hot-air and microwave-vacuum drying to yield products with higher content of polyphenols (Table 8.1). Microwave-vacuum-dried raspberries retained significantly higher ( $P \leq 0.05$ ) concentrations of kaempferol glycoside (0.660 mg/g basis) than other dehydrated samples. The concentration of glycosides and aglycone forms of ellagic acid, quercetin, phloretin, *R*-naringenin, *S*-naringenin, and kaempferol were also measured in dried raspberries. Both ellagic acid and kaempferol aglycones were retained to a greater extend in



**Figure 8.3** Anthocyanidins in raspberries: (a) pelargonidin, (b) cyanidin, (c) delphinidin, (d) peonidin, (e) petunidin, and (f) malvidin.

microwave-vacuum-dried raspberries (0.342 mg/g dry basis), and quercetin aglycone in hot-air-/microwave-vacuum-dried berries compared to other treatments. Raspberries are known to contain relatively high amounts of polyphenols, which are composed of 60% flavonoids, 30% phenolic acids, and 10% tannins [25]. These compounds have been extensively studied for their anticarcinogenic properties [26, 27].

Anthocyanins are responsible for the red and blue coloration of certain fruits, flowers, and leaves [22, 28] and are present in high concentrations in blueberries, raspberries, strawberries, and red grapes (Table 8.2) [19, 29–31]. Raspberries have been reported to contain cyanidin-3-glucoside, cyanidin-3-rutinoside, cyanidin-3-sophoroside, and pelargonidin-3-glucoside [20]. The popularity of anthocyanin-containing foods is increasing tremendously due to recent interest about their multiple health-promoting features including antioxidant, anti-inflammatory, and anticancer activities and more recently due to their chemoprotective, vasoprotective, and antineoplastic properties [29].

**Table 8.1** Retention of polyphenol glycoside and aglycone compounds (mg/g dry basis) from dried raspberries by different drying technologies

Polyphenols	Fresh	Freeze drying	Microwave-vacuum drying	Hot-air drying/ microwave-vacuum drying	
				Hot-air drying	Hot-air drying/ microwave-vacuum drying
<b>Glycosides</b>					
Ellagic Acid	2.53 ± 0.29	0.66 ± 0.01 <sup>a</sup>	2.14 ± 0.02	0.18 ± 0.03 <sup>a</sup>	3.12 ± 0.36
Quercetin	2.18 ± 0.20	0.58 ± 0.03 <sup>a</sup>	1.02 ± 0.06 <sup>a</sup>	0.41 ± 0.06 <sup>a</sup>	1.63 ± 0.22 <sup>a</sup>
Phlorizin	0.02 ± 0.002	0.012 ± 0.007 <sup>a</sup>	0.017 ± 0.001	0.03 ± 0.005 <sup>a</sup>	0.09 ± 0.001 <sup>a</sup>
R-Naringin	0.13 ± 0.01	0.019 ± 0.001 <sup>a</sup>	0.017 ± 0.001 <sup>a</sup>	0.018 ± 0.001 <sup>a</sup>	0.42 ± 0.02 <sup>a</sup>
S-Naringin	0.09 ± 0.01	0.048 ± 0.002 <sup>a</sup>	0.051 ± 0.00 <sup>a</sup>	0.138 ± 0.001 <sup>a</sup>	0.032 ± 0.005 <sup>a</sup>
Kaempferol	0.49 ± 0.04	0.260 ± 0.034 <sup>a</sup>	0.660 ± 0.040 <sup>a</sup>	0.287 ± 0.036 <sup>a</sup>	0.048 ± 0.003 <sup>a</sup>
<b>Aglycones</b>					
Ellagic acid	1.15 ± 0.10	0.142 ± 0.008 <sup>a</sup>	0.342 ± 0.020 <sup>a</sup>	0.152 ± 0.023 <sup>a</sup>	0.068 ± 0.006 <sup>a</sup>
Quercetin	0.188 ± 0.017	0.023 ± 0.001 <sup>a</sup>	0.034 ± 0.001 <sup>a</sup>	0.118 ± 0.023 <sup>a</sup>	0.170 ± 0.018 <sup>a</sup>
Phloretin	0.414 ± 0.041	0.002 ± 0.001 <sup>a</sup>	0.002 ± 0.001 <sup>a</sup>	0.029 ± 0.001 <sup>a</sup>	0.014 ± 0.001 <sup>a</sup>
R-Naringenin	0.05 ± 0.01	0.001 ± 0.000 <sup>a</sup>	—	0.004 ± 0.001 <sup>a</sup>	0.003 ± 0.001 <sup>a</sup>
S-Naringenin	0.041 ± 0.005	0.020 ± 0.008 <sup>a</sup>	0.051 ± 0.001 <sup>a</sup>	0.066 ± 0.005 <sup>a</sup>	0.066 ± 0.005 <sup>a</sup>
Kaempferol	0.101 ± 0.011	0.05 ± 0.01 <sup>a</sup>	0.068 ± 0.003 <sup>a</sup>	0.008 ± 0.002 <sup>a</sup>	0.022 ± 0.001 <sup>a</sup>

Source: Adapted with permission from Mejia-Meza et al. [21].

Values are means ± SEM ( $n = 9$ ).

<sup>a</sup>Significantly different from fresh raspberries ( $P < 0.05$ ).

**Table 8.2** Total anthocyanin content in selected fruits

Fruit	Method	Total anthocyanins	Unit	Reference
Mulberries	Spectrophotometric	137–2057	µg M3GE/g	[29]
Blackberries (raw)	HPLC	81–86	mg/100 g	[19]
Blueberries (raw)	HPLC	157–112	mg/100 g	[19]
Cherries (raw)	HPLC	35–120	mg/100 g	[19]
Cranberries (raw)	HPLC	86.1	mg/100 g	[19]
Raspberries (raw)	HPLC	26–38	mg/100 g	[19]
Strawberries (raw)	HPLC	8–40	mg/100 g	[19]
Plums (raw)	HPLC	12.5	mg/100 g	[19]
Nectarine (raw)	HPLC	3.5	mg/100 g	[19]
Peaches (raw)	HPLC	1.5	mg/100 g	[19]
Raspberries, (raw)	HPLC/colorimetric	1008–1350	mg C3GE/g	[45]
Aksu Kirizisi				
Water extract	Spectrophotometric	49.3	mg C3GE/100 g	[31]
Methanol extract	Spectrophotometric	24.8	mg C3GE/100 g	[31]
Newburgh				
Water extract	Spectrophotometric	69.5	mg C3GE/100 g	[31]
Methanol extract	Spectrophotometric	16.3	mg C3GE/100 g	[31]
Rubin				
Water extract	Spectrophotometric	60.3	mg C3GE/100 g	[31]
Methanol extract	Spectrophotometric	2424.1	mg C3GE/100 g	[31]
Heritage				
Water extract	Spectrophotometric	22.4	mg C3GE/100 g	[31]
Methanol extract	Spectrophotometric	12.4	mg C3GE/100 g	[31]
Hollanda Boduru				
Water extract	Spectrophotometric	45.6	mg C3GE/100 g	[31]
Methanol extract	Spectrophotometric	24.3	mg C3GE/100 g	[31]

HPLC, high performance liquid chromatography; M3GE, malvidin-3-glucoside equivalents; C3GE, cyanidin-3-glucoside equivalents.

Anthocyanins contribute about 25% to the total antioxidant capacity of fresh red raspberries [32], depending on the drying method employed. These phenolic compounds are sensitive to heat and oxidation, and dehydration or other heat preservation processes (e.g., pasteurization) frequently lead to considerable changes in their color and concomitant loss of polyphenols, depending on the drying method used [21, 33–35].

### 8.3.2 Phenolic acids

Another important class of polyphenols present in fruits is the phenolic acids, mainly derived from hydroxybenzoic and/or hydroxycinnamic acids. Phenolic acids are commonly identified as gallic, vanillic, procatechuic, and syringic acids when derived from hydroxybenzoic acid, and as *p*-coumaric, caffeic, and ferulic acids when derived from hydroxycinnamic acid [18, 22]. Fruits, including blueberries, raspberries, cherries, apples, and cacao, contain large concentrations of phenolic acids [15]. Gallic acid is the most common phenolic acid forming the base unit of gallotannins and together with hexahydroxydiphenic acid forms subunits of the ellagitannins. Gallotannins and ellagittannins, also called hydrolysable tannins, release

gallic acid and ellagic acid under dilute acid conditions while condensed tannins do not [22]. Caffeic acid is the most common hydroxycinnamic acid derivative. Dried raspberries have been reported to contain ellagic acid aglycone and glycoside [21], as well as 3'-caffeoylequinic acid, *p*-coumaric glucose, and cinnamoyl glucose [20].

### 8.3.3 Tannins

Tannins are one of the most widespread polyphenolics in fruits and are divided in two main classes of condensed tannins (proanthocyanidins) and hydrolysable tannins [36]. Condensed tannins are high-molecular-weight compounds formed from monomeric units of flavanols or flavan-3-ol, including (+)-catechin, (−)-epicatechin, (+)-gallocatechin, and (−)-epigallocatechin. Oxidative condensation occurs between the heterocyclic carbon C-4 of monomeric units of flavanols and the adjacent positions of carbons C-6 or C-8 of flavanols to create oligomeric and polymeric proanthocyanidins [5, 22, 36]. Condensed tannins are responsible for the astringency of many tannin-rich foods such as red wine and tea, resulting mainly from the precipitation of tannins with salivary proteins. No condensed tannins have been reported in raspberries. Rao *et al.* [12] state that raspberry polyphenols consist primarily of anthocyanins and hydrolyzable tannins. More specifically, raspberries are a particularly rich source of cyanidin glycosides and are unique among all berries for their high ellagitannin content, which when hydrolyzed yield ellagic acid.

## 8.4 Antioxidants in dried raspberries

Fruits are a good source of phenolics with antioxidant activity, specifically flavonoids, phenolic acids, and tannins. Individual analytical methods for the measurement of antioxidant activity can be difficult to interpret and often it is hard to determine what the interaction or synergistic effects are among different antioxidative components in a fruit and the overall antioxidant properties. As a result, numerous antioxidant methods, both *in vitro* and *in vivo*, have been developed to measure the antioxidant properties of food phenolics. There are two classes of *in vitro* assays involving either hydrogen atom transfer or single electron transfer reactions [37]. Single electron transfer assays are more commonly used to measure the antioxidant properties of polyphenolic compounds in fruit and involve redox reactions of an oxidant based indicator as the reaction end point. Types of these assays include the trolox equivalent antioxidant capacity (TEAC) assay, oxygen radical absorbance capacity (ORAC), the 2,2-di(4-*tert*-octylphenyl)-1-picrylhydrazyl (DPPH) assay, and the ferric ion reducing antioxidant parameter (FRAP) assay.

The antioxidant activity of fruits extracts are listed in Table 8.3 [9, 31, 30, 38–41]. Most of the fruits were analyzed in the fresh forms; however, data may be extrapolated to fruits such as raspberries in the dried form depending on the drying method employed. Although some fruits such as apples and berries are known to possess high antioxidant activity, it is difficult to compare the results for antioxidant activity between different methods because different assays can yield different results and may follow different mechanisms. Also, there is often an incomplete description of the fruit sample, how it had been stored and treated, particularly when results for processed food are presented. The wide variety of antioxidant activity methods, different units for reporting data, and other factors already known, such

**Table 8.3** Antioxidant activity of polyphenol for select fruits

Fruit	Method	Antioxidant activity	Unit	Reference
Tomato	TOSC	10.4	µmol VCE/g	[38]
Blueberries				
Wild	FRAP	44	µM CE	[39]
Cultivated	FRAP	96	µM CE	[39]
Wild	FRAP	71	µM CE	[39]
Cultivated	FRAP	78	µM CE	[39]
Highbush blueberries	ORAC	50	µmol TE/g	[40]
Red huckleberries	ORAC	19 to 130	µmol TE/g	[40]
Raspberries	ESR	410	Number of Fremy's radical × 10 <sup>16</sup> reduced	[30]
Raspberries				
Aksu Kirizisi				
Water extract	TEAC	68.0	µmol TE/g	[31]
Methanol extract	TEAC	86.7	µmol TE/g	[31]
Newburgh				
Water extract	TEAC	86.7	µmol TE/g	[31]
Methanol extract	TEAC	98.6	µmol TE/g	[31]
Rubin				
Water extract	TEAC	64.4	µmol TE/g	[31]
Methanol extract	TEAC	72.9	µmol TE/g	[31]
Heritage				
Water extract	TEAC	65.4	µmol TE/g	[31]
Methanol extract	TEAC	74.3	µmol TE/g	[31]
Hollanda Boduru				
Water extract	TEAC	69.7	µmol TE/g	[31]
Methanol extract	TEAC	117	µmol TE/g	[31]
Raspberries				
Aksu Kirizisi				
Water extract	DPPH	76.6	µmol TE/g	[31]
Methanol extract	DPPH	122	µmol TE/g	[31]
Newburgh				
Water extract	DPPH	89.1	µmol TE/g	[31]
Methanol extract	DPPH	122	µmol TE/g	[31]
Rubin				
Water extract	DPPH	64.1	µmol TE/g	[31]
Methanol extract	DPPH	96.7	µmol TE/g	[31]
Heritage				
Water extract	DPPH	66.0	µmol TE/g	[31]
Methanol extract	DPPH	81.2	µmol TE/g	[31]
Hollanda Boduru				
Water extract	DPPH	77.6	µmol TE/g	[31]
Methanol extract	DPPH	142	µmol TE/g	[31]
Apples				
Red delicious (peel)	FRAP	17800	µM CE	[9]
Northern spy (peel)	FRAP	10040	µM CE	[9]
Ida red (peel)	FRAP	12100	µM CE	[9]
Red delicious (flesh)	FRAP	920	µM CE	[9]
Northern spy (flesh)	FRAP	6430	µM CE	[9]
Idared (flesh)	FRAP	2750	µM CE	[9]
Idared (peel)	TOSC	312	µmol VCE/g	[9]

**Table 8.3** (Continued)

Fruit	Method	Antioxidant activity	Unit	Reference
Idared (flesh)	TOSC	47	µmol VCE/g	[9]
Idared (flesh + peel)	TOSC	72	µmol VCE/g	[9]
Rome beauty (peel)	TOSC	228	µmol VCE/g	[9]
Rome beauty (flesh)	TOSC	68	µmol VCE/g	[9]
Rome beauty (peel + flesh)	TOSC	132	µmol VCE/g	[9]
Golden delicious				
Integrated (peel)	DPPH	15.4	mM TE/kg	[41]
Organic (peel)	DPPH	13.2	mM TE/kg	[41]
Integrated (pulp)	DPPH	4.10	mM TE/kg	[41]
Organic (pulp)	DPPH	2.68	mM TE/kg	[41]

TOSC, total oxyradical scavenging capacity; ORAC, oxygen radical absorbance capacity; ESR, electron spin resonance; TEAC, trolox equivalent antioxidant capacity; FRAP, ferric reducing antioxidant power; DPPH, 2,2-diphenyl-1-picrylhydrazyl; VCE, vitamin C equivalents; TE, trolox equivalents; CE, catechin equivalents.

as the conditions of growth, harvest, handling, and storage, make it even more difficult to compare results between different studies.

Fresh raspberries had higher concentrations of individual, total polyphenols, and anthocyanins, and antioxidant activity than dried raspberries [21]. Microwave-vacuum drying and the combination of hot-air/microwave-vacuum drying of raspberries had higher retention of ellagic acid, quercetin, kaempferol, aglycones, and total polyphenols compared to other drying methods including hot-air drying and freeze drying alone. Total anthocyanins were less heat stable than polyphenols. Total aglycone polyphenol compounds may have higher resistance to drying temperatures than glycosides, and may be less affected by the combination of hot-air/microwave-vacuum drying method. Aglycone polyphenols caused a greater reduction in adipogenesis induction than glycoside compounds [21]. These results suggest that consumption of either fresh or dried raspberries can provide an important source of antioxidants and are also foods that could inhibit adipogenesis if these results are extrapolated to the *in vivo* situation after consumption.

## 8.5 Health benefits of dried raspberries

Polyphenolic compounds in fruits, including flavonoids (quercetin and kaempferol), phenolic acids (gallic and ellagic acids), and tannins (red wine polyphenols), exhibit some potential to inhibit the proliferation of certain cancer cell lines (colon and breast) *in vitro* [17]. They have strong antioxidant activities that are believed to inhibit the propagation of free radical reactions [11, 40]. *In vivo* antioxidants may be beneficial for inhibiting free radical-initiated reactions associated with aging, cancer, and CVD [29]. Recently, berries, including raspberries, have been studied to determine their effect in cancer proliferation and the results are summarized in Table 8.4 [42–44]. For instance, it has been reported that a raspberry extract at a concentration of 50 µg/mL gallic acid equivalents (GAE) reduces proliferation (quantified by cell invasion) of HT115 cells by 95% [44].

**Table 8.4** Anticancer activity from berries *in vitro*

Fruit	Method	Proliferation reduction (%)	Concentration	Reference
Black-raspberries	HT-29/HCT116	78	200 µg/mL	[42]
Blueberries	HT-29/HCT116	78	200 µg/mL	[42]
Blackberries	HT-29/HCT116	78	200 µg/mL	[42]
Raspberry-extract	HT115	95 (cell invasion)	50 µg/mL GAE	[43]
Strawberry-extract	HT-29/MCF7	41–63/26–56	0–200 µg/mL	[44]

GAE, gallic acid equivalents.

## 8.6 Conclusions

Raspberries (fresh or dried) are known as a rich source of polyphenolic compounds with flavonoids, phenolic acids, and tannins being the most widely distributed subgroups. Study of these phenolic compounds is popular because of their extensive range of biological properties (antioxidant, anticancer, antimicrobial, antihyperlipidemic, and anti-inflammatory, among others) that may help decrease the risk of chronic health conditions such as obesity, type II diabetes, CVD, and cancer. Therefore, there is a movement among health professionals to encourage consumers to eat more antioxidant-rich foods as a phytopreventative strategy to reduce a variety of diseases. However, we still know very little about the composition and biological activity of polyphenolics in most fruits and how various types of processing may affect either the concentration or biological activity. As reported throughout this chapter, raspberries contain various polyphenols that contribute to their significant antioxidant capacity and observed *in vitro* biological activity. Currently, preservation techniques, including dehydration, as well as some processing techniques are applied to extend the shelf life of fruits but are known to have a negative impact on polyphenol retention depending on the drying method employed. In the case of dehydration, hot-air drying usually results in greater loss of phenolic compounds than other drying methods such as freeze drying or a combination of hot-air and microwave-vacuum drying. If responsible recommendations are to be made for promoting the consumption of fresh, dried, or processed fruits, it will be important to be able to provide a reasonable assessment of both the content and biological activity of these compounds. This conclusion extends to raspberries and any other fruit since the biological matrix and composition of fruits are grossly comparable.

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## **9 Phytochemical antioxidants and health benefits of dried strawberries**

Rong Tsao and Hongyan Li

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### **9.1 Introduction**

Fruits and vegetables are good sources of antioxidant phytochemicals for reducing the incidence of diseases such as cardiovascular disease (CVD), diabetes, and certain types of cancer in humans [1–3]. Compared to other foods, fruits and vegetables are more beneficial to human health due to their safety, low cost, and oral bioavailability [4]. Strawberries contain a large amount of phytochemicals, in both fresh and processed forms [5]. They are widely known for their health-promoting properties such as antioxidant, anticancer, and antiatherosclerotic effects [6, 7]. Research has also shown that dried strawberries can lower the risks of oxidative damage, CVD, and esophageal cancer [8, 9].

Strawberries are available around the world. In the United States, 83% of the strawberries (6.35 million tonnes annually) are grown in California with the most common commercial varieties being *Camarosa*, *Diamond*, *Chandler*, and *Selva*. They have a very short harvesting season (only last 3 to 4 weeks) and relatively short shelf life because of the natural ripening process and their sensitivity to fungal attack [10]. Postharvest storage conditions can also affect the texture, color, flavor, phytochemical content, and antioxidant activity of strawberries [11, 12]. For these reasons, a significant amount of strawberries is consumed in the forms of frozen and dried fruits, jams, yogurt, preserves, and juice concentrates, among others. The color, flavor (odor and taste), and storability of dried strawberry pieces are generally considered to be good. Several drying methods, including microwave drying and vacuum freeze drying, have been widely used to obtain high-quality dehydrated strawberries [13–15].

Strawberries are rich in fiber, potassium, vitamin C, folate, and phytochemicals and are relatively low in calories. The main phytochemicals in dried strawberries have been reported to be hydrolyzable tannins, anthocyanins, flavonols, flavanols, and coumaroyl glycosides [16]. These phytochemicals contribute significantly to the total antioxidant activity of fresh or dried strawberries. Several studies have reported that the high antioxidant activity of strawberries is linked to their phenolic contents [17]. However, the phytochemical contents can be affected by genetics, growing environment, processing and storage conditions, and

by errors caused by different analytical methods [10, 18–20]. The phytochemical compositions of dried strawberries can, therefore, directly affect their antioxidant activity and other bioactivities related to human health.

This chapter reviews the latest research on strawberry phytochemicals and their roles in antioxidant and other human health potentials. Factors effecting the phytochemical composition and antioxidant activity during postharvest storage and drying/processing are also discussed. Readers who are interested in detailed information and in-depth discussions on the specific phytochemicals or functions of strawberries are referred to comprehensive reviews by others [9, 21, 22].

## 9.2 Phytochemicals

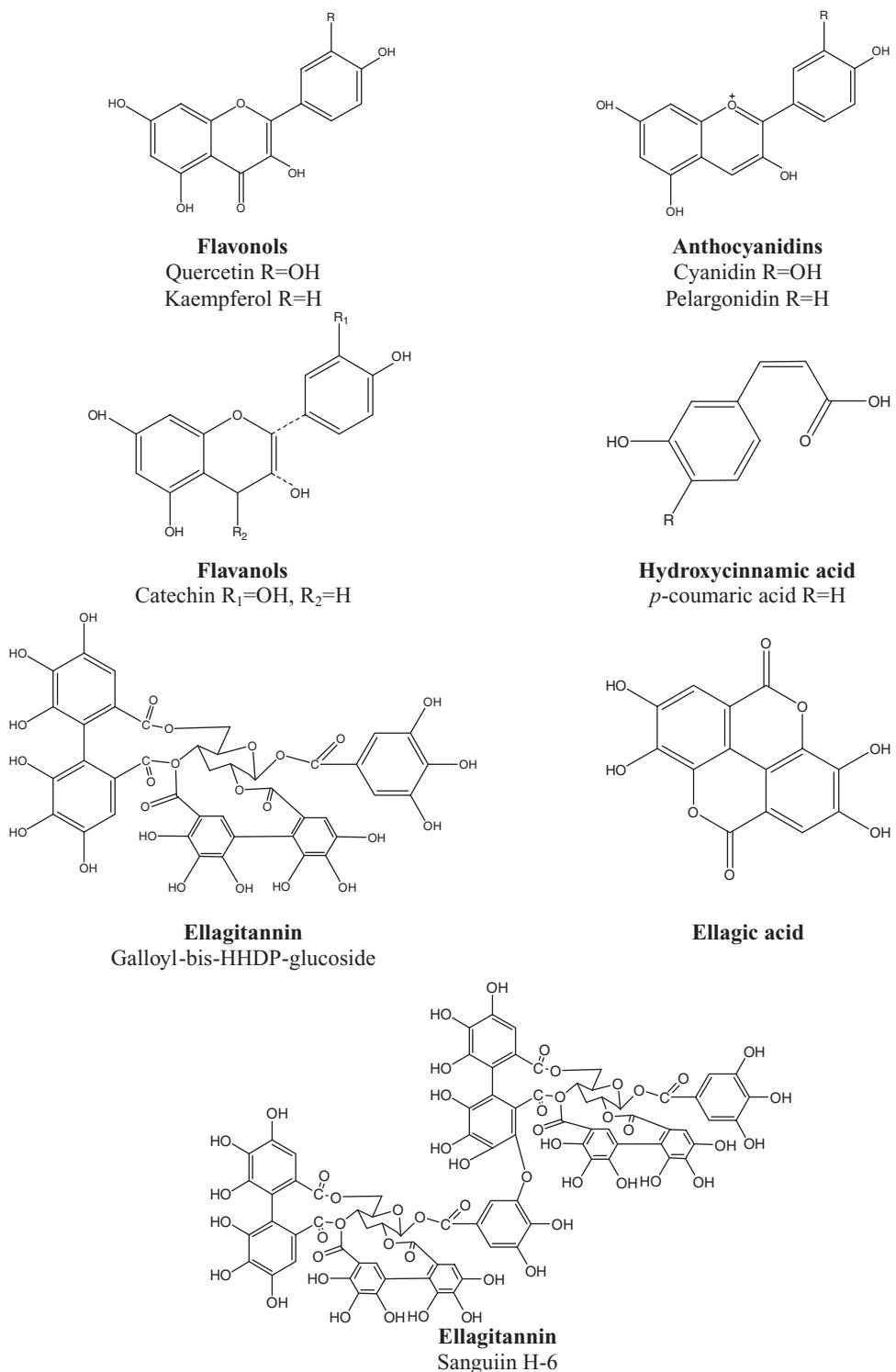
Strawberries are rich in micronutrients and phytochemicals, most of which are phenolic compounds. Extracts of freeze-dried whole strawberry fruit powder and fresh strawberry fruit extracts have been found to contain phenolic acids, hydrolyzable tannins (ellagitannins), coumaroyl glycosides, anthocyanins, flavonols, and flavanols [16]. Gallic, protocatechuic, *p*-hydroxybenzoic, caffeic, *p*-coumaric, *o*-coumaric, ferulic, *trans*-cinnamic, and ellagic acids constitute the phenolic acids in strawberries, with *trans*-cinnamic, *p*-coumaric, and gallic acids in the highest concentrations (566, 213, and 212 mg/kg, respectively) [23]. The major flavonols in dried strawberries are quercetin glycosides and anthocyanins. Pelargonidin and cyanidin glucosides or rutinosides are the main anthocyanins found in strawberries [16, 24, 25]. Major phenolic phytochemicals of strawberries are shown in Figure 9.1. The total phenolic and anthocyanin contents of freeze-dried strawberry powder were 33.74 g ferulic acid equivalents/kg and 3.51 g cyanidin-3-glucoside equivalents/kg, respectively [23]. Changes in major individual and total phytochemical contents before and after drying are listed in Table 9.1. These phytochemicals contributed to the antioxidant activity of strawberries. However, there are considerable differences in reported total and individual phytochemical contents due to the existing differences in genetics, growing environment, processing, handling after harvest, and the analytical methodology [9, 11].

### 9.2.1 Hydrolyzable tannins

Hydrolyzable tannins in strawberries are made up of ellagic acid, ellagic acid glycosides, ellagitannins, and gallotannins. They have been shown to have high antioxidant potential and are effective in preventing many oxidative stress-related chronic diseases [26, 27].

Ellagic acid has been reported to have antioxidant, antiproliferative, and antimalarial properties [28]. There are large differences in the content of ellagic acid in strawberry cultivars [29]. Sharma *et al.* [30] demonstrated that ellagic acid extracts obtained from strawberries were potential anticarcinogenic agents by using human 293T cell line and a luciferase reporter of canonical Wnt pathway-mediated transcriptional activation. Devipriya *et al.* [31] fed female albino Wistar rats (150–170 g) with different concentrations of ellagic acid and found that ellagic acid could inhibit alcohol-induced toxicity by improving body weight, restoring antioxidant status, modulating micronutrients, and attenuating the lipid levels in the circulation of rats.

Ellagitannins are hydrolyzable tannins formed through ester bond between ellagic acid or other phenolic acids and sugar molecules. Ellagitannins in dried strawberries are reported



**Figure 9.1** Major phytochemicals found in strawberries.

**Table 9.1** Phytochemical changes before and after freeze drying of strawberries

Phytochemicals	Fresh strawberries (mg/100 g)	Dried strawberries (mg/100 g)	Changes	Reference
p-Coumaroyl glycoside	9.7	10.0	↑	[13]
Ellagic acid glycoside	13.6	9.0	↓	[13]
Quercetin	12.2	14.4	↑	[13]
Kaempferol	4.3	4.9	↑	[13]
Catechin	47.4	47.8	↑	[13]
Cyanidin-3-glucoside	8.3	9.9	↑	[13]
Pelargonidin-3-glucoside	215.4	218.9	↑	[13]
Pelargonidin-3-rutinoside	11.0	8.5	↓	[13]
Pelargonidin-3-malonyl-glucoside	59.7	64.8	↑	[13]
Total anthocyanins <sup>a</sup>	440	350	↓	[11, 23]
Total polyphenolic content	1906	1802	↓	[13]

All data were based on dried weight basis.

<sup>a</sup>mg cyanidin-3-glucoside equivalents/100 g.

to have antioxidant and cancer chemopreventive activities [26]. *In vitro* studies also indicate that ellagitannins (10–100 μM) have antiatherogenic, antithrombotic, anti-inflammatory, and antiangiogenic effects [26]. Pinto *et al.* [32] evaluated the inhibitory activities of purified ellagitannins from strawberries against α-amylase, α-glucosidase, and angiotensin I-converting enzyme (ACE) and found them to be effective in inhibiting cell proliferation and to have good potential for the management of hyperglycemia and hypertension linked to type 2 diabetes.

However, the bioavailability of the antioxidant ellagic acid and ellagitannins are low due to their poor solubility, permeability, and poor stability at a physiological pH of 7.4. That is why lower *in vivo* activities have been found despite good *in vitro* results [33].

## 9.2.2 Anthocyanins

Anthocyanins are the unique red and pink pigments of strawberries and are considered to be another contributing phytochemical group to the antioxidant activity and health benefits. Anthocyanins play a role in self-protection against biotic and abiotic stresses for the plant itself, and because of the unique pigmentation characteristics, they can also be useful in chemotaxonomy [34]. Although the individual and total anthocyanins contents in dried strawberries are cultivar-dependent, the main aglycones in strawberries are pelargonidin and cyanidin. Strawberry anthocyanins have been shown as strong antioxidants with values of 7156, 4922, and 5514 μM Trolox equivalents/mg for cyanidin-3-glucoside, pelargonidin, and pelargonidin-3-rutinoside, respectively [35].

Anthocyanins of strawberries were the major active components in reducing oxidative stress-induced apoptosis in PC12 cells [17]. Basu *et al.* [36] also reported that whole strawberry (fresh, juice, and freeze-dried) extracts and their purified anthocyanins rendered significant improvements in low-density lipoprotein (LDL) oxidation, lipid peroxidation, total plasma antioxidant activity, dyslipidemia, and glucose metabolism.

Anthocyanins with either a di- or a tri-saccharide were excreted in the urine primarily in the intact form. The urinary recovery of pelargonidin-3-glucoside of strawberries was reported to be 1.8% of intake after a 24-hour post-ingestion period, which is high for anthocyanins in plants [37]. The limited metabolism of anthocyanins that did occur was via methylation. Wu *et al.* [38] investigated the absorption and metabolism of anthocyanins in three different berries (chokeberries, black currants, or elderberries) by feeding weanling pigs, and suggested that the aglycones and the sugar moieties could alter the absorption and metabolism of anthocyanins via methylation and glucuronidation as well as by the formation of both derivatives on the same anthocyanin molecule. Later, Prior *et al.* [39] found that purified anthocyanins from freeze-dried strawberry powders, but not whole strawberry extracts, could prevent the development of dyslipidemia and obesity in mice via drinking with water. They also found that feeding purified anthocyanins from strawberries instead of the whole freeze-dried blueberry powders could reduce obesity in male mice in terms of body weight gain, body fat, and epididymal fat weight, which may have actually reduced obesity [40].

### **9.2.3 Flavonols and flavanols**

Quercetin and kaempferol derivatives in dried strawberries belong to the subclass of flavonoids called flavonols. Flavanols, such as catechin derivatives, are also found in strawberries. Ripening and environmental factors prior to harvest and during food processing can significantly affect the flavanol content [41]. Wojdylo *et al.* [13] showed that the contents of ellagic acid and flavanol in strawberries were also affected by different drying techniques and cultivars.

Epidemiological studies have found a positive link between quercetin or kaempferol consumption and reduced risk of several diseases [42, 43]. Zhang *et al.* [35] evaluated the antioxidant and antiproliferative activities of 10 phenolic compounds from strawberry extracts (cyanidin-3-glucoside, pelargonidin, pelargonidin-3-glucoside, pelargonidin-3-rutinoside, kaempferol, quercetin, kaempferol-3-(6'-coumaroyl)glucoside), 3,4,5-trihydroxyphenyl-acrylic acid, glucose ester of (*E*-*p*-coumaric acid, and ellagic acid) by the Trolox equivalent antioxidant capacity (TEAC) and luminescent adenosine-5'-triphosphate (ATP) cell viability assays. They found that these pure strawberry flavonoids not only had good antioxidant activity at 100 µg/mL but also antiproliferative activity against human oral (CAL-27, KB), colon (HT29, HCT-116), and prostate (LNCaP, DU145) cancer cells. A similar inhibitory activity was found with the crude extracts of strawberry (250 µg/mL) in the same study [35].

Flavanols affect platelet aggregation, vascular inflammation, and endothelial nitric oxide (NO) metabolism and may confer protective effects against neurodegeneration [44]. Nakamura *et al.* [45] found that catechin in green tea could suppress lipopolysaccharide (LPS)-induced bone resorption by inhibiting IL-1β production or osteoclastogenesis. Catechin was also reported to help treatment for men at high risk of prostate cancer and could ameliorate serious obesity and CVD risk factors without raising any safety concerns in Japanese children [46, 47].

The absorbability of flavonols and flavanols depends on the type, chemical binding state (aglycone or glucosides), and food matrix [48]. In general, like other flavonoids, they have a low bioavailability mainly because of the low concentrations detected in plasma and tissues and the instability under digestive conditions.

### 9.2.4 Hydroxycinnamic acid derivatives

Hydroxycinnamic acid derivatives, such as *p*-coumaric acid, are commonly found in dried strawberries. Among major hydroxycinnamic acids, caffeic acid showed the highest antioxidant activities in 2,2-diphenyl-2-picrylhydrazyl (DPPH) radical and oxygen radical absorbance capacity (ORAC) assays whereas *p*-coumaric acid had the least activity [49]. However, *p*-coumaric acid is the most prevalent cinnamic acid, and was shown to protect against oxidative stress and genotoxicity in cultured mammalian cells (HT-29, EMT6, SW620, LOVO, and HCT-8) [50].

*p*-Coumaric acid had good antiplatelet activity and was found to be available through diet, suggesting possible applications for primary prevention of vascular disease [51]. This compound was also found to protect rat hearts against doxorubicin-induced oxidative stress, and thus could potentially be used as adjuvant therapy in cancer management [52]. Garrait *et al.* [53] found that *p*-coumaric acid was absorbed by all digestive organs in rats after oral administration. Moreover, urine excretion of *p*-coumaric acid was 23% after oral administration to rats, which showed less metabolized and better health benefits than trans-cinnamic acid (0.3%) [53].

## 9.3 Factors affecting phytochemicals

Several factors including cultivar, fertilization, mulching, light, temperature, processing, and storage conditions have been reported to affect the contents of phytochemicals in tender fruits such as strawberries [54–56].

### 9.3.1 Genetics and environment

Genetics and environment are two most important factors that have been found to affect the content and composition of phytochemicals in both fresh and dried strawberries. Tulipani *et al.* [19, 57] evaluated the vitamin C, folate, *p*-coumaric acid, ellagic acid derivatives, pelargonidin, and cyanidin contents of different strawberry varieties, and found that there were significant differences ( $P < 0.05$ ) among genotypes. Others have also found significant cultivar differences for similar phytochemical components in different strawberries [58, 59]. Breeding and biotechnological approaches are currently used to increase the content of phytochemicals in fruits, including strawberries [60].

Studies have also shown that the phytochemical content of a particular strawberry cultivar can vary significantly by other factors. Mineral composition, soil type, temperature, light, and water content are among the frequently reported factors that affect the phytochemical contents in strawberries [61–63]. In addition, agronomic practices may also impact the phytochemical compositions; for example, organically grown strawberry fruits were found to have longer shelf life, greater dry matter, higher vitamin C, antioxidant activity, ascorbic acid, and phenolic compounds than their conventional counterparts [64, 65]. This was attributed to the greater microbial functional capability and resilience to stress of the organic soils [64]. Organically grown strawberries had a higher ratio of ascorbate to dehydroascorbate and antiproliferative activity for both HT29 cells and MCF-7 cells than the conventionally produced ones [66]. Shehata *et al.* [67] showed that strawberries grown from compost

fertilized plots exhibited a generally higher total yield, total soluble solid, and anthocyanin content as compared to mineral fertilizer.

### **9.3.2 Postharvest storage**

Postharvest storage may affect the composition of some phytochemicals in strawberries, depending on storage conditions. The main causes of degradation of phytochemicals in fresh strawberries are oxygen, light, and enzymes such as polyphenol oxidase [68]. This is also affected by the biosynthesis of anthocyanins since the synthesis continues in the harvested strawberry (31% increased after 10 days at 5°C) [69]. In addition, strawberries are also dried for an extended storage period for food applications such as breakfast cereal. It is reported that freeze-dried strawberries may be stored in sealed #10 can (with included oxygen absorber packet) for 10 to 15 years under ideal storage conditions (a cool, dry place).

Applications of freeze-dried strawberry pieces in liquid carriers are limited by the high rehydration rate and dissolution of anthocyanins, which lead to collapse of the dried strawberry pieces and loss of color. The rehydration characteristics were influenced by the coating time and different drying conditions [70]. Attempts have been made to tackle this problem by coating the dried strawberry pieces. A unique formula consisting of 10% whey protein, 3% glycerol, and 10% lactose was found to be effective in keeping the integrity of the pieces [70]. By adding 3 mg/mL Na<sup>+</sup> and 0.5 mg/mL β-cyclodextrin in the coating solution, the authors were able to keep the original color of the dried strawberries.

### **9.3.3 Food processing (drying methods)**

Many drying methods such as heated air drying, convective drying, freeze drying, microwave drying, osmotic dehydration, spray drying, and spouted bed drying are commonly used in preserving strawberries. Among them, convective drying is the most popular method for its low cost and easy operation. However, this method is relatively time-consuming, thus it usually results in decrease in the quality of the dried product due to the high temperature and air application [71]. Sublimation drying, for example, freeze drying was reported to be more effective in preserving valuable phytochemicals in food than traditional air drying; however, it is relatively costly [13, 55, 72]. Vacuum-microwave drying has become increasingly popular due to the many advantages such as short drying time, energy saving, and improved product quality in final dried products [73, 74]. All drying methods may reduce the contents of phytochemicals including ascorbic acid, ellagic acid, flavanol, anthocyanins, and antioxidant activity of dried strawberries [13]. However, there are considerable differences in the retention of phytochemical content and antioxidant activity in dried strawberries obtained using different methods.

Yurdugül [75] reported that freeze-dried strawberries had no difference in characteristics such as firmness, sugar content, pH, color, weight loss, dissolved solids, anthocyanin, and vitamin C content when compared with their fresh counterparts. Freeze drying was also found to better preserve total phenolic content than air drying in strawberries [71]. Similarly, freeze-dried strawberries showed greater total phenolic and anthocyanin contents and better antioxidant activity than the air-dried products [72]. Moreover, enzymes such as trehalase have been used and found to be a good drying aid for better aroma retention in freeze-dried strawberry puree [76].

Wojdylo *et al.* [13] found that vacuum-microwave drying (especially at 240 W) could actually produce high-quality strawberries of higher anthocyanins, flavanols, hydroxycinnamic acids, and flavonols contents and greater antioxidant activity, and also reduce processing times compared to freeze drying, convective drying, and vacuum drying. Böhm *et al.* [14] found that the residual phytochemical contents (phenolic compounds and anthocyanins) in vacuum-microwave-dried processing were close to those in freeze-dried products except for ascorbic acid. Attenuation of temperature can increase the stability of ascorbic acid. In the same study, it was found that the soluble phenolic and anthocyanin contents and the antioxidant activity were affected significantly by the pretreatment bath, which could lead to a significant loss during thawing of the materials [14].

Certain drying methods may be more advantageous than others over the quality of dried strawberries. A microwave-assisted hot-air drying method was found to be more effective than hot air drying, although the rehydration parameters and drying rate were dependent on the microwave energy used [55]. Krulis *et al.* [73] found that a low initial moisture content and high microwave power could lead to low density, porous structure, and optimum puffing effects of dried strawberries, but at the expense of slower moisture evaporation rate and higher energy consumption. Osmotic dehydration of strawberries improved dehydration rates than atmospheric pressure operation, resulting in a dried strawberry with intermediate moisture content, which could be used as input material of further processes [77]. A new processing method of sequential infrared and freeze-drying method (SIRFD) has been studied for producing high-quality crispy fruit pieces. Crispy strawberry pieces produced with SIRFD were found to be more desirable in color, crispness, and shrinkage, although lower in rehydration ratio than regular freeze drying [78]. In fact, freeze drying could not produce a high-crispness product as found in the same study [78]. However, more studies are needed to better examine the effects of phytochemical contents on antioxidant activities.

## 9.4 Health benefits of strawberries

Strawberries have been shown to have strong antioxidant activity *in vitro*, and to play important roles in reducing risks of oxidative stress-related chronic diseases *in vivo*. The majority of published literature has been carried out *in vitro* using chemical and cell culture models. However, a growing number of animal and human intervention studies have recently been conducted. The antioxidant activities and the responsible phytochemicals of strawberries are discussed later in this chapter. The focus of this section is on the *in vitro* and *in vivo* biological evidence shown by dried strawberry powder and its phytochemicals.

### 9.4.1 *In vitro* biological activities

The main reported *in vitro* activities of strawberries are listed in Table 9.2. Numerous studies have convincingly established the antioxidant potential of strawberries. The antioxidant activity of freeze-dried strawberry powder can be stronger than that of some of the well-known berry fruits such as Saskatoon berries and wild blueberries [23]. One serving (100 g) of strawberries in a DPPH radical scavenging assay was equivalent to 182 mg vitamin C and 483 mg vitamin E [23]. Other *in vitro* models such as the ferric reducing antioxidant power (FRAP) assay and LDL oxidation model also support the high antioxidant potential of strawberry extracts [79].

**Table 9.2** Reported major *in vitro* activities of strawberries

Activity	Method	Reference
Antioxidant	DPPH radical scavenging activity FRAP assay	[23] [79]
Anti-inflammatory	Inhibition of LDL oxidation	[79]
Antitumor or anti-cancer	Colon cell (HT-29, HCT116, COX-2) Lung cell (A549) Stomach cell (SNU-638) Fibrosarcoma cell (HT-1080) Oral cell (KB, CAL-27) Breast cell (MCF-7) Leukemia cell Prostate cell (LNCaP) Liver cell (HT-29)	[7, 16] [7] [7] [7] [16] [16] [81, 82] [16] [16]
Enzyme inhibitor	Inhibit $\alpha$ -glucosidase Acetylcholinesterase Activation of PI-3-PKB	[29] [84] [85]
Others	LPS-induced iNOS protein Inhibition of copper-induced oxidation of human LDL	[7] [86]

DPPH, 2,2-diphenyl-1-picrylhydrazyl; FRAP, ferric reducing antioxidant power; LDL, low-density lipoprotein; PI-3, phosphatidylinositol-3; PKB, kinase/protein kinase B; LPS, lipopolysaccharide; iNOS, inducible nitric oxide synthase.

Strawberry extracts with good antioxidant activity were found to inhibit the proliferation of several cancer cells including human colon (HCT-116), lung (A549), stomach (SNU-638), and fibrosarcoma (HT-1080) cancer cell lines [7] and of human oral (KB, CAL-27), breast (MCF-7), colon (HT-29, HCT116), and prostate (LNCaP) tumor cell lines in a concentration-dependent manner (25–200 µg fresh weight/mL) [80]. A significant proapoptotic effect was also found in HT-29 [80]. Strawberry extracts at 0.5% (w/v) inhibited the proliferation of HT-29 and MCF-7 cells by 53 and 43%, respectively [66]. Strawberry extracts also inhibited LPS-stimulated NO production and suppressed LPS-induced inducible nitric oxide synthase (iNOS) protein, and mRNA expressions in mouse macrophage RAW 264.7 cells [7]. Phytochemicals in strawberries may also have high potential in the prevention or treatment of high-risk lymphoblastic leukemia and in reducing oxidative stress-induced apoptosis [81]. Induction of apoptotic cell death in the leukemia cells by strawberry powder extracts was also found in studies by Zunino *et al.* [82], who also found that phytochemicals of strawberries (quercetin, kaempferol, and ellagic acid) could induce apoptotic cell death in pre-B high-risk acute lymphoblastic leukemia via loss of nuclear DNA, loss of mitochondrial membrane potential, and activation of caspase-3 [83].

Extracts of strawberries were a good inhibitor of  $\alpha$ -glucosidase but not of  $\alpha$ -amylase, suggesting that strawberries may be a potential dietary source of antihyperglycemic agents [29]. The same strawberry cultivars had no significant ACE inhibitory activity, indicating low anti-hypertensive potential [29]. Screening of the acetylcholinesterase (AChE) inhibitory activity by Ellman's method showed that strawberries (at the concentration of 1.36 g dried powder/L) had strong inhibition, which could be helpful in preventing Alzheimer's disease [84]. Edirisinghe *et al.* [85] demonstrated that extract of freeze-dried strawberries caused

endothelium-dependent relaxation (EDR), which is mediated by NO produced by activation of endothelial nitric oxide synthase (eNOS) in human umbilical vein endothelial cells (HUVECs). The phosphorylation of eNOS was caused by activation of the phosphatidylinositol-3 (PI-3)-kinase/protein kinase B (PKB) signaling pathway [85]. This effect makes strawberries a vasodilator to help lower the risk of CVD. It was also reported that strawberry juice [at the concentration of 0.01% fruit juice dissolved in phosphate buffered saline (PBS)] showed complete inhibition of copper-induced oxidation of human LDL *in vitro* [86].

#### **9.4.2 *In vivo* effects in animals**

The strawberry-fed rats were better able to retain place information (a hippocampally mediated behavior) and offered better protection against spatial deficits in the maze compared to controls [87]. Supplementation with strawberries (745 g/day) could also reduce the oxidative stress by decreasing malondialdehyde formation and protecting mononuclear blood cells against increased DNA damage in a 11 kg (lean body weight) pig model for 22 days [88]. Purified anthocyanins from freeze-dried strawberry powders were found to be key in preventing the development of dyslipidemia and obesity in mice [39]. The alcohol/water-insoluble fraction of strawberries, as well as that of the black raspberries and blueberries, was found to reduce *N*-nitrosomethylbenzylamine (NMBA)-induced tumorigenesis in rat esophagus [89]. Moreover, Stoner *et al.* [90] proved that the serum levels of interleukin-5 (IL-5) and GRO/KC (interleukin-8) might be predictive of the inhibitory effect of chemopreventive agents on rat esophageal carcinogenesis. Three extracts of strawberry cultivars (40 mg/day/kg body weight) prevented exogenous ethanol-induced damage to rats' gastric mucosa, which confirmed that a diet rich in strawberries could exert a beneficial effect in the prevention of gastric diseases [91]. Freeze-dried strawberries could also cause an EDR in rabbit aorta, which could help to lower the risk of CVD [85]. In another study, hamsters received an atherogenic diet and at the same time strawberry juice at a daily dose corresponding to the consumption of 275 mL by a 70 kg human (0.22 g strawberries/mL). After 12 weeks, the group receiving strawberry juice showed 97% reduction in aortic lipid deposition and lowered activity of hepatic antioxidant enzymes, not accompanied by lowered plasma cholesterol, which suggests that moderate consumption of strawberry juice can help prevent the development of early atherosclerosis [92]. Extracts of strawberries having significant antiplatelet and antioxidant effects *in vitro* were further assessed with a laser-induced thrombosis test in mice, and were found to significantly reduce flow-mediated vasodilation. Both the antiplatelet/antioxidant activities and the antithrombotic effect were considered important mechanisms for the potential health benefits of strawberries in reducing the risk of arterial thrombotic disease [93].

#### **9.4.3 *In vivo* effects in humans**

Some *in vivo* studies have shown promising health effects of strawberries in humans. Volunteers (three men and five women) were asked to eat 1 kg of strawberries within a space of 10 min to assess an acute effect of strawberries in healthy subjects, and it was found that antioxidant activity (FRAP values) and the ascorbate concentration in plasma significantly increased after 3 hours [94, 95]. In another study, 12 healthy volunteers were invited to consume 500 g

of strawberries per day, for 16 days. This led to increases in serum antioxidants [96, 97]. The short-term or medium-term intake of strawberries could help to improve plasma antioxidant status, which could further prevent the development of risk of several chronic diseases caused by oxidative stress. A strawberry beverage containing 10 g freeze-dried fruit was shown to lower triacylglycerols (TAG) and oxidized LDL after high-fat meals, in a study involving 24 hyperlipidemic men and women (14 women, 10 men; mean age  $50.9 \pm 15$  years) [98]. In another study, 28 hyperlipidemic subjects who had followed the strawberry-supplemented diet showed reduced oxidative damage to LDL and blood lipids [99]. In a study of 27 males and 13 females of age  $24 \pm 3$  years, the whole strawberry juice (300 g in drinking water) was found to reduce 70% of carcinogen N-nitrosodimethylamine (NDMA) formation caused by nitrate intake (400 mg/day) [100].

Despite the above human trials, there is lack of clear epidemiologic support for direct human health benefits arising from strawberry consumption, particularly for lowering the risk of CVD. Sesso *et al.* [33] examined strawberry intake for its potential effect on CVD risk in 38,176 women and on the cross-sectional association with lipids and C-reactive protein in a subset of 26,966 women. No associations between strawberry intake and the risk of CVD incidence, lipids, or C-reactive protein were found in middle-aged and older women, though higher strawberry consumption at 2 servings/week may slightly reduce the likelihood of having elevated C-reactive protein levels. The authors suggested that further epidemiologic data are needed to better understand the health beneficial effect of strawberries in CVD prevention.

#### 9.4.4 Bioavailability

The bioavailability of phytochemicals is defined as the fraction of an ingested nutrient that becomes available to the body for utilization in physiological functions or for storage [101]. It includes bioaccessibility, absorption, metabolism, tissue distribution, and bioactivity [102]. In a study in which concentrations of strawberry phenolic acids were analyzed 30 min after strawberries (750 g fresh weight) were consumed by four healthy human volunteers ( $32 \pm 6$  years), all cinnamic acids in the plasma were found to be low and only benzoic acid was detected in the plasma. The major free (gentisic, protocatechuic, and *p*-hydroxybenzoic acids) and conjugated (syringic acid) benzoic acids were 26–27% recovered in the urine within 5 hours. Cinnamic acids escaped absorption early in the gastrointestinal tract and went completely undetected in plasma and only trace amounts were found in the urine [103]. In another study comparing the bioavailability of phytonutrients in fresh strawberries and stored strawberries, Azzini *et al.* [104] found that the plasma vitamin C level increased significantly in the plasma after 2, 3, and 5 hours ( $P < 0.05$ ) in subjects consuming both types of strawberries. In the same study, no quercetin or anthocyanins were found in plasma, while coumaric acid, 4-hydroxybenzoic acid (4HBA) (the major human metabolite of pelargonidin-3-glucoside), and protocatechuic acid (the major human metabolite of cyanidin-3-glucoside) were retrieved in the plasma after 8 hours. Among the urinary metabolites, pelargonidin-3-glucoside represented 91 and 95% of the total compounds after fresh and stored strawberry consumption, respectively [104]. Pelargonidin glucuronide, pelargonidin glucoside, and pelargonidin aglycone peaked in urine excreted after 2 and 24 hours and was approximately 0.9% of the pelargonidin glucoside ingested. In general, most of the phenolic compounds were detected in very small amounts both in plasma and in tissues (they are poorly absorbed from the

intestine, highly metabolized, or rapidly eliminated), thereby indicating low bioavailability. The bioavailability of anthocyanins is relatively low compared to that of the other flavonoids [105]. The phytochemicals undergo similar but more complex metabolic degradations *in vivo* as compared to the *in vitro* digestion [106]. During the course of absorption, phenolic compounds are conjugated (usually methylated, sulfated, and glucuronidated) in the small intestine by the colonic microflora and later in the liver by a metabolic detoxification process that facilitates biliary and urinary elimination [6]. The low bioavailability of phytochemicals causes lower *in vivo* activities despite the good *in vitro* results in strawberries [7, 33].

Little information is available on the effects of food matrix on the bioavailability of strawberries. Better knowledge of bioavailability is essential for investigating the health effects of strawberries. Further studies are needed to focus on the absorption and metabolism of the phytochemicals in strawberries *in vivo*, and to gain insight into the mechanisms underlying the interactive effects in complex food matrices.

## 9.5 Conclusions

Strawberries are a rich source of antioxidative phytochemicals, particularly various phenolic acids, flavonoids, and ellagic acids. The composition of these phytochemicals may be affected by different genetics and environmental factors, and more importantly by postharvest storage and processing conditions. Drying methods can particularly alter the quality of dried strawberries, and the quality and quantity of phytochemicals and their potential health benefits. There is sufficient data showing that strawberry extracts are strong antioxidants and can inhibit proliferation of various cancer cells *in vitro*. Biomarkers related to cancer, inflammation, diabetes, and CVD were found to be positively affected by strawberry extracts; however, there seems to be a lack of strong *in vivo* evidence in support of the *in vitro* findings. Further research should focus on the bioavailability and metabolism of strawberry phytochemicals *in vivo*, and on the regulatory effect of these compounds and their metabolites on biomarkers related to chronic diseases. The strong *in vitro* antiproliferative effect suggests that dried strawberry extracts may have chemopreventive potential. Further studies on consumption of dried strawberry products and health benefits are important as dehydration technology advances.

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# **10 Beneficial effects of dried berry fruits in human health and disease prevention**

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## **10.1 Introduction**

An overwhelming body of research confirms that the dietary intake of berry fruits has a beneficial and significant impact on human health, function, and disease. Berry fruits, which are commercially cultivated and commonly consumed as fresh and processed in North America, include blueberry (*Vaccinium corymbosum*), cranberry (*Vaccinium macrocarpon* American cranberry and *Vaccinium oxycoccus* European cranberry), red raspberry (*Rubus idaeus*), blackberry (*Rubus* spp.), black raspberry (*Rubus occidentalis*), and strawberry (*Fragaria ananassa*). Other berry fruits, which are less known but consumed in the traditional diets of North American tribal communities, include chokecherry (*Prunus virginiana*), highbush cranberry (*Viburnum trilobum*), serviceberry (*Amelanchier alnifolia*), and silver buffaloberry (*Shepherdia argentea*). In addition, berry fruits such as arctic bramble (*Rubus arcticus*), and bilberries (*Vaccinium myrtillus*; also known as bog whortleberries), black currant (*Ribes nigrum*), boysenberries (*Rubus* spp.), cloudbERRIES (*Rubus chamaemorus*), crowberries (*Empetrum nigrum*, *Empetrum hermaphroditum*), elderberries (*Sambucus* spp.), gooseberry (*Ribes uva-crispa*), lingonberries (*Vaccinium vitis-idaea*), loganberry (*Rubus loganobaccus*), marionberries (*Rubus* spp.), Rowan berries (*Sorbus* spp.), as well as sea buckthorn (*Hippophae rhamnoides*), are also popularly consumed in other parts of the world. Recently, the nutraceutical market has shown a surge in the promotion of exotic fruits and berries such as the açai berry (*Euterpe oleracea*), mangosteen (*Garcinia mangostana*), pomegranate (*Punica granatum*), goji berries or wolfberry (*Lycium barbarum*), and the maqui berry (*Aristotelia chilensis*).

Berry fruits contain many important dietary components: vitamins, including folate, minerals, and fiber; but it is their polyphenolic content to which their biological action is most often attributed [1]. It is thought that these effects are synergistic as opposed to being due to one constituent alone. Berry phenolics include flavonoids (anthocyanins, flavonols, and flavanols), tannins [condensed tannins (proanthocyanidins) and hydrolyzable tannins (ellagitannins and gallotannins)], stilbenoids, and phenolic acids. Anthocyanins, pigments that account for their attractive colors, are more widely studied and have a broad

range of bioactivities including anti-oxidant, anticancer, and anti-inflammatory properties, among others.

While the majority of research has been carried out on flavonoids and in particular the anthocyanins, there is increasing interest in the tannins as well. The types of tannin molecule vary considerably among different berries. Condensed tannins [also known as oligomeric proanthocyanidin (OPC), pycnogenols, and leukocyanidins] are predominantly found and consumed in blueberries and cranberries. Hydrolyzable tannins or ellagitannins are predominantly found and consumed in blackberries, black raspberries, red raspberries, and strawberries. Thus, the class and specific chemical structures of tannins present in a particular berry type may contribute significantly to its unique biological properties. The OPC found in cranberries hold an A-type structural linkage responsible for its bacterial anti-adhesive properties [2]. Similarly, the biological effects observed in proanthocyanidin-rich blueberries and ellagitannin-rich strawberries on neuronal function and behavior in aging animals may be due to the effects of the individual classes of tannins in different regions of the brain [3]. This chapter highlights the beneficial effects of dried berry fruits in human health and disease risk reduction.

## 10.2 Antioxidant protection

Anthocyanins are novel anti-oxidants and potent inhibitors of lipid peroxidation as compared to other classic anti-oxidants [4–6]. Endothelial dysfunction has been proposed to play an important role in the initiation and development of vascular diseases, and anthocyanins significantly improve endothelial function [7–9]. The enrichment of endothelial cells with elderberry anthocyanins conferred significant protective effects of endothelial cells against diverse oxidative stressors [9, 10]. Vascular endothelial cells can incorporate anthocyanins into the membrane and cytosol, conferring significant protective effects against oxidative insult, which may have important implications on preserving endothelial cell functions and preventing against vascular diseases [9].

Dietary consumption of blueberry polyphenols has demonstrated significant protection against free radicals and oxidative stress within red blood cells *in vivo* [10]. Black raspberry has also been shown to provide significant anti-oxidant protection in the gut epithelium of weanling pigs due to its high anthocyanin content [11]. A comparative assessment was performed on total anti-oxidant status in serum following consumption of strawberries, spinach, red wine, or vitamin C in eight elderly women. It was concluded that the consumption of strawberries, spinach, or red wine, which are rich in anti-oxidant phenolic compounds, can increase the serum anti-oxidant capacity in humans [12]. Extensive studies were conducted on six edible berry extracts including wild blueberry, wild bilberry, cranberry, elderberry, raspberry seed, and strawberry powder, and accordingly a novel synergistic combination of these six berry extracts was developed, OptiBerry, which demonstrated optimal oxygen radical absorbance capacity (ORAC) value in conjunction with high cellular uptake and low cytotoxicity, as shown by lactate dehydrogenase (LDH) leakage [13].

## 10.3 Cardiovascular health and metabolic syndrome

Berries show substantial cardioprotective benefits due to their high polyphenol content. Few studies have investigated their efficacy in improving features of metabolic syndrome and

related cardiovascular risk factors in obesity. Berry anthocyanins act as cardioprotectant by maintaining vascular permeability, reducing inflammatory responses and platelet aggregation, and offer superior vascular protection as compared to other cardioprotective drugs [8, 9]. Hypertension, atherosclerosis, and arteriosclerosis can reduce the flexibility of arterial walls, which contributes to poor blood flow and plaque formation [8, 9]. Rat aortas exposed to anthocyanin-enriched blueberry extract *in vitro* exhibited relaxation caused by endothelium generated nitric oxide [14]. In another study, treatment of rats with bilberry anthocyanosides (*Vaccinium myrtillus*) for 12 days before the induction of hypertension kept the blood–brain barrier permeability normal and limited the increase in vascular permeability in the skin and the aorta wall [15]. Hamsters given oral doses (10 mg per 10 g body weight) of a commercial product containing 36% bilberry anthocyanosides for 2 or 4 weeks exhibited better capillary perfusion and fewer sticking leukocytes in the capillaries as compared to the untreated controls [16].

### 10.3.1 Atherosclerosis

Hypercholesterolemia, an integral constituent of the atherosclerotic index and a significant cardiovascular risk factor, is prevalent in the US population [17]. Atherosclerosis is a disease of the arteries in which fatty plaques develop on the inner arterial wall, which eventually obstructs blood flow [17]. Risk factors for atherosclerosis include genetics, diet, lifestyle, smoking, circulating lipid and cholesterol levels, and molecular and circulating signals of chronic vascular inflammation. The protective ability of anthocyanins against atherosclerosis is based partly on their anti-oxidant properties.

In animal studies, hamsters are used due to the similarities in lipid profile to hypercholesterolemic humans when fed a hypercholesterolemic diet of 0.2% cholesterol and 10% coconut oil [17, 18]. The efficacy of OptiBerry supplementation in hamsters against the incidence of atherosclerosis was assessed in male hamsters. The animals were divided into two groups of nine animals with equal weights (about 80 g each) and given powder chow containing 10% coconut oil and 0.2% cholesterol mixed with water and made into a brownie. Treated group animals were fed with chow containing 1% OptiBerry. The animals were weighed after 12-week of feeding the atherogenic diet. Plasma was obtained by cardiac puncture and analysed for triacylglycerols (TAG). All animals in the experimental group gained significantly less weight than the control group (approximately 8% decrease in weight gain) indicating a weight reduction from appetite loss or increased metabolism. Table 10.1 demonstrates the effect of OptiBerry on body weight, lipid profile, and the percentage of aorta covered with foam cells, a biomarker of atherosclerosis *in vivo*. No significant changes ( $P > 0.05$ ) were observed in TAG levels. The atherosclerotic index (% of aorta covered with foam cells) was significantly reduced by 36.6% following supplementation of OptiBerry as compared to the untreated controls. The low-density lipoprotein (LDL) + very low-density lipoprotein (VLDL) oxidation levels in Table 10.2 show that the control oxidized at the greatest rate and OptiBerry group had a significantly lower rate of oxidation of the atherogenic lipoproteins ( $P < 0.05$ ). Thus, OptiBerry which is high in anthocyanins and has a higher ORAC value demonstrated least oxidation of the lipoproteins. Overall, OptiBerry supplementation resulted in less body weight gain as compared to the controls, which might have happened due to its anti-angiogenic potential. Furthermore, OptiBerry may provide significant health benefits by dramatically ameliorating the incidence of atherosclerosis as demonstrated by

**Table 10.1** Body weight, lipid, and % atherosclerosis data

Group	Body weight (g)	Plasma TAG (mg/dL)	Atherosclerosis (%)
Control	140 ± 4	163 ± 62	20.5 ± 1.7
OptiBerry	129 ± 3 <sup>a</sup>	177 ± 111	13.0 ± 3.1 <sup>a</sup>

Source: Adapted with permission from Zafra-Stone *et al.* [18].

Each value represents the mean ± standard deviation of 4–6 animals.

TAG, triacylglycerol.

<sup>a</sup>Significantly different from control ( $P < 0.05$ ).

reducing the formation of foam cells as well as its reduced ability to oxidize functional lipoproteins [17, 18].

In a randomized controlled trial, the effects of blueberry supplementation were examined on features of metabolic syndrome, lipid peroxidation, and inflammation in obese men and women [19]. Forty-eight participants with metabolic syndrome \*\*\*4 males and 44 females; BMI: 37.8 ± 2.3 kg/m<sup>2</sup>; age: 50.0 ± 3.0 y (mean ± SE)\*\*\*\* consumed freeze-dried blueberry beverage (50 g freeze-dried blueberries, approximately 350 g fresh blueberries) or equivalent amounts of fluids (controls, 960 mL water) daily for 8 weeks. The decreases in systolic and diastolic blood pressures were greater in the blueberry-supplemented group (26 and 24%, respectively) than in controls (21.5 and 21.2%) ( $P < 0.05$ ), whereas the serum glucose concentration and lipid profiles were not affected. The decreases in plasma oxidized LDL, serum malondialdehyde, and hydroxynonenal concentrations were greater in the blueberry group (228 and 217%, respectively) than in the control group (29 and 29%) ( $P < 0.01$ ). This study shows that blueberries may improve selected features of metabolic syndrome and related cardiovascular risk factors at dietary achievable doses [19].

**Table 10.2** LDL + VLDL oxidation time

Time (s)	Conjugate diene formation (234 nm)	
	Control	OptiBerry
0	0	0
600	0.314	0.116 <sup>a</sup>
900	0.459	0.143 <sup>a</sup>
1200	0.518	0.147 <sup>a</sup>
1500	0.547	0.142 <sup>a</sup>
1800	0.566	0.138 <sup>a</sup>
2100	0.569	0.128 <sup>a</sup>
2400	0.570	0.130 <sup>a</sup>
2700	0.563	0.110 <sup>a</sup>
3000	0.560	0.105 <sup>a</sup>
3300	0.554	0.093 <sup>a</sup>
3600	0.546	0.075 <sup>a</sup>

Source: Adapted with permission from Zafra-Stone *et al.* [18].

LDL, low-density lipoprotein; VLDL, very low-density lipoprotein.

<sup>a</sup>Significantly different from control ( $P < 0.05$ ).

## 10.4 Neuroprotection

Brain functions such as balance, coordination, short-term memory, and information retrieval can be impaired with advancing age. Furthermore, the onset of age-related neurodegenerative diseases such as Alzheimer's or Parkinson's disease, superimposed on a declining nervous system, could exacerbate the motor and cognitive behavioral deficits. Although the mechanisms involved in the behavioral deficits during aging remain to be determined, it is clear that oxidative stress [20] and inflammation [21, 22] are involved. Increased exposure to the long-term effects of oxidative stress and inflammatory insults are thought to be contributing factors to the decline in cognitive and/or motor performance seen in aging and other neurodegenerative diseases. Research has shown that discrepancies in brain functions due to oxidative stress may arise because of degeneration in the endogenous anti-oxidant defense mechanisms [23–26] and the susceptibility of the brain to the deleterious effects of oxidative damage [27]. Research also indicates that not only is the central nervous system particularly vulnerable to oxidative stress but also this vulnerability increases during aging and may also enhance central vulnerability to inflammation [28, 29]. With age, there are increases in inflammatory mediators (e.g., cytokines) [30–32], as well as increased mobilization and infiltration of peripheral inflammatory cells, which have been shown to produce deficits in behavior similar to those observed during aging [33]. Furthermore, age-related changes in brain vulnerability to oxidative stress and inflammation may be the result of membrane changes and differential receptor sensitivity [34].

Research suggests that the polyphenolic compounds found in berry fruits, such as blueberries and strawberries, can reverse age-related and oxidative stress-induced decline in brain functions [35–37]. Berry fruits may exert their beneficial effects either through their ability to lower oxidative stress and inflammation or directly by altering the signaling involved in neuronal communication, calcium buffering ability, neuroprotective stress shock proteins, plasticity, and stress signaling pathways. Berries have been shown to enhance dopamine release in the brain, which improves the ability of brain cells to enhance intracellular communication [35–37]. Strawberry supplementation was shown to enhance striatal muscarinic receptor sensitivity, and this appeared to be reflected in the reversal of cognitive behavioral deficits [36, 37]. Strawberries and blueberries have also been shown to reverse age-induced declines in  $\beta$ -adrenergic receptor function in cerebellar Purkinje neurons, while blueberries prevented and/or reversed age-related declines in cerebellar noradrenergic receptor function [38].

In a series of studies conducted by Joseph *et al.* [39], it was demonstrated that dietary supplementation with berry fruits can prevent or reverse decrements in brain and behavioral aging in the rodent model. In their first study, Fischer 344 (F344) rats underwent long-term feeding from adulthood (6 months) to middle age (15 months) with a control diet or diets supplemented with vitamin E (500 IU/kg of diet) or with extracts of strawberry or spinach that contained identical anti-oxidant level to determine if the feeding would prevent age-related decrements in motor and cognitive behavior as well as brain function [39]. A number of different parameters known to be sensitive to oxidative stress were prevented by the anti-oxidant diets including (1) receptor sensitivity, as measured by oxotremorine-enhanced dopamine release in isolated striatal slices and cerebellar Purkinje cell activity; (2) calcium buffering capacity, or the ability of striatal synaptosomes to extrude calcium following depolarization, deficits of which ultimately result in reduced cellular signaling and eventually cell death; (3) changes in signal transduction assessed by carbachol-stimulated

GTPase coupling/uncoupling in striatal membranes; and (4) cognition (spatial learning and memory) as measured by Morris water maze performance [39]. Spinach-fed rats demonstrated the greatest retardation of age-effects on all parameters except GTPase activity, for which strawberry had the greatest effect; strawberry and vitamin E showed significant but equal protection against these age-induced deficits on the other parameters.

In other studies conducted by Bickford *et al.* [38, 40], they found that dietary supplementations (for 8 weeks) with spinach, strawberry, or blueberry extracts in a control diet were also effective in reversing age-related deficits in brain and behavioral function in aged (19 months) F344 rats. While all of the supplemented diets showed positive effects on cognitive behavior, rats on the blueberry diet showed the greatest increase in motor performance, carbachol-stimulated GTPase activity, and oxotremorine-enhanced dopamine release [36]. In addition, the blueberry-fed group showed no decrements in calcium recovery following exposure to an oxidative stressor [36]. However, though blueberries exhibit the highest anti-oxidant capacity of all fruits and vegetables tested, they were not equally effective in preventing/reversing age-related changes. Therefore, anti-oxidant activity alone was not predictive in assessing the potency of these compounds against certain disorders affected by aging. In fact, oxidative stress markers were only modestly reduced by the diets [36], suggesting that these fruit and vegetable polyphenolics possess a multiplicity of actions, aside from anti-oxidative, and that differences in the polyphenolic composition of these extracts could account for the positive effects observed.

A more recent study has suggested that, in addition to Morris water maze performance, cognitive declines in object recognition were effectively reversed by blueberry supplementation [41]. Furthermore, the beneficial effects of blueberries were seen even when superimposed on an already well-balanced, healthy rodent diet, which was more representative of a balanced human diet [42].

In a separate investigation, rats given intraperitoneal injections of bilberry anthocyanins (200 mg/kg/day) for 5 days had significantly more triiodothyronine (T3) in their brains than rats given only the solvent (26% alcohol). T3 enters the brain by a specific transport in the capillaries; therefore, anthocyanins may mediate T3 transport at the capillary level. Bilberry-treated animals exhibited superior memory, better vision, and better control of sensory input [37].

## 10.5 Anticancer activity

A large body of evidence suggests that berry fruits may have beneficial effects against several types of human cancers. The anticancer activity of berries has been related to a multitude of bioactive phytochemicals, stilbenoids, lignans, and triterpenoids and shown to reduce and repair damage resulting from oxidative stress and inflammation. In addition, berry bioactives also regulate carcinogen and xenobiotic metabolizing enzymes, various transcription and growth factors, inflammatory cytokines, and subcellular signaling pathways of cancer cell proliferation, apoptosis, and tumor angiogenesis [43]. Berry phytochemicals may also sensitize tumor cells to chemotherapeutic agents by inhibiting pathways that lead to treatment resistance and provide protection from therapy-associated toxicities.

Chemopreventive agents present in berries include vitamins A, C, and E, folic acid,  $\beta$ -carotene,  $\alpha$ -carotene, calcium, selenium, lutein,  $\beta$ -sitosterol, stigmasterol, triterpene esters, as well as phenolics—anthocyanins, proanthocyanidins, flavonols, flavanols, ellagitannins, and

phenolic acids, among others. As described earlier, the chemistry of berry phenolics directly influences their bioavailability, metabolism, and biological effects *in vivo* [44, 45]. The structural diversity of berry phenolics is observed in several ways including—their measure of oxidation and hydroxylation, their abilities to exist as stereoisomers, glycosylation by sugar moieties, and other substituents, and conjugation to form polymeric molecules, such as tannins and other derived molecules [46].

Blueberry, bilberry, cranberry, strawberry, lingonberry, tart cherry, black raspberry, and red raspberry as such, and their extracts, in either juice or dried form, exhibited potential cancer chemopreventive properties [47–49]. Freeze-dried extracts of strawberries or black raspberries along with ellagic acid displayed potent chemopreventive activity which appears to involve cellular transformation and interference of uptake, activation, detoxification, and/or intervention of DNA binding and DNA repair [47]. Research on black raspberries has shown that they inhibit azoxymethane-induced colon cancer, esophageal tumorigenesis as well as shows antiproliferative effect in liver cancer cells [47–51], while freeze-dried strawberries have been shown to be potent inhibitors of esophageal cancer [48]. An ethanolic extract of black raspberry has been demonstrated to suppress cell proliferation and nitric oxide synthase activity as well as induce both apoptosis and terminal differentiation in human oral squamous cell carcinoma cells [52].

### 10.5.1 Anti-angiogenic properties

“Angiogenesis” defines the growth of new blood vessels, an important natural process which takes place in the animal or human body contributing to both health and diseased conditions [53]. Angiogenesis occurs in the healthy body for healing wounds and for restoring blood flow to tissues after ischemic injury or insult, while unwanted growth of blood vessels may lead to varicose veins, tumor formation, and cancer metastases, while an anti-angiogenic approach can serve as a form of therapeutic intervention [53, 54]. The healthy body controls angiogenesis through angiogenesis-stimulating growth factors or angiogenesis inhibitors. Black raspberry extract was demonstrated to be anti-angiogenic in human tissue based on *in vitro* angiogenesis assays and can be promising for cancer therapy [55].

Vascular endothelial growth factor (VEGF) is a biomarker of angiogenesis, and plays a crucial role for the vascularization of tumors [56]. The effects of multiple berry extracts on inducible VEGF expression by human HaCaT keratinocytes were evaluated in our laboratory. Six individual berry extracts (wild blueberry, bilberry, cranberry, elderberry, raspberry seed, and strawberry) and OptiBerry a combination of berry extracts were investigated. All of the six berry extracts and OptiBerry demonstrated significant inhibition of both H<sub>2</sub>O<sub>2</sub>- as well as tumor necrosis factor  $\alpha$  (TNF $\alpha$ )-induced VEGF expression by human keratinocytes, while OptiBerry exhibited the greatest effect [57]. In the same experimental setting, anti-oxidants such as grape seed proanthocyanidin extract (GSPE) or  $\alpha$ -tocopherol did not influence inducible VEGF expression, while pure flavonoids such as ferulic acid, catechin, and rutin suppressed oxidant-inducible VEGF expression. OptiBerry was also shown to impair angiogenesis in a matrigel assay model [57]. Thus, structural characteristics of berry anthocyanins are responsible for their inhibitory potential on inducible VEGF expression and release [13].

The efficacy of OptiBerry was tested in a model of proliferating hemangioma, a unique model to assess *in vivo* angiogenesis. Macrophages are commonly involved in proliferating hemangiomas. The chemokine monocyte chemotactic protein-1 (MCP-1), a major accessory facilitating angiogenesis, has been shown to be responsible for recruiting macrophages to

the infection or inflammation sites, and antagonists to MCP-1 are considered to be anti-angiogenic [58]. MCP-1 transcription in angiogenesis is mediated by several transcription factors among which nuclear factor- $\kappa$ B (NF- $\kappa$ B) is a key player. The endothelioma (EOMA) cells derived from spontaneously arising hemangioma were activated with TNF $\alpha$  (400 IU/mL) for 12 hours and elevated levels of basal MCP-1 transcription in these EOMA cells were observed. Pretreatment of these EOMA cells with OptiBerry significantly inhibited basal MCP-1 transcription as well as NF- $\kappa$ B activity [56]. Subsequently, 8-week-old 129P3/J mice were injected (s.c.) 100  $\mu$ L of EOMA cell suspension (56,106 cells) with or without OptiBerry pretreatment. OptiBerry pretreatment did not result in hemangioma formation in all the mice and significantly reduced the average mass of tumor growth below 50% [57]. Histological analysis demonstrated that OptiBerry markedly decreased infiltration of macrophages in hemangiomas [57]. Thus, both anti-oxidant and anti-angiogenic properties of edible berry anthocyanins may act synergistically to promote significant health benefits.

### 10.5.2 Antiproliferative cellular activities and viability

Numerous studies have demonstrated that different berry fruits might act through different mechanisms in their cancer preventive ability. Certain berry extracts and their phenolic constituents inhibit cell proliferation, modulate cell cycle arrest, and induce apoptosis in cancer cells with little or no cytotoxic effects in normal cells. Blackberry, black raspberry, blueberry, cranberry, red raspberry, and strawberry extracts have been shown to inhibit the growth of human oral, breast, colon, and prostate cancer cell lines in a dose-dependent manner [59, 60]. Strongest inhibition of cell growth was observed for the raspberry, lowbush blueberry, and cranberry. Researchers have shown that the inhibition of proliferation by the berry was independent of caspase-dependent apoptosis but appeared to involve cell-cycle arrest, as evidenced by downregulation of the expression of cyclin kinases, cdk 4, cdk 6, cyclin D1, and cyclin D3. Some of the berries also significantly inhibited the TNF-induced activation of the cyclooxygenase-2 (COX-2) enzyme expression and activation of the transcription factor NF- $\kappa$ B.

Researchers have also demonstrated that the berry extracts stimulated apoptosis of a human colon cancer cell line, HT29, which expresses COX-2 [61]. Several berry extracts, including strawberry and raspberry, were recently evaluated for their effects on cell viability and expression of markers of cell proliferation and apoptosis *in vitro* [62]. Researchers concluded that the berry extracts inhibited cancer cell proliferation mainly *via* the p21WAF1 (a member of the cyclin kinase inhibitors) pathway. The pro-apoptosis marker, Bax, was found to be increased in cells treated with the berry extracts in the apoptosis experiments. In addition, researchers demonstrated that in addition to anthocyanins, other phenolic compounds, such as ellagitannins and nonphenolic compounds, might also contribute greatly toward the antiproliferative activity of berries [62].

Red raspberry extract was shown to decrease the population of human HT29 colon cancer cells in the G1 phase of the cell cycle [63]. In addition, the raspberry extract imparted significant protective effects against DNA damage induced by hydrogen peroxide in the colon cancer cells. Researchers also reported that the raspberry extract significantly inhibited the invasion of HT115 colon cancer cells in a matrigel invasion assay [63].

Isolated cell lines from human oral squamous cell carcinoma tumors were recently used to investigate the effects of a freeze-dried black raspberry ethanol extract on cellular growth [52]. The study showed that the black raspberry extract suppressed cell proliferation without

perturbing viability, inhibited translation of the complete angiogenic cytokine VEGF, suppressed nitric oxide synthase activity, and induced both apoptosis and terminal differentiation [52]. In another study, red raspberries showed potential in the inhibition of absorption of environmental carcinogens such as polycyclic aromatic hydrocarbons (PAHs) using a Calu-3 cell monolayer model [64]. Researchers demonstrated that the phytochemicals present in red raspberries inhibited PAH absorption across the Calu-3 cell monolayers and are likely to influence the exposure of lung epithelial cells to PAH-induced DNA damage [64].

Three cultivars of blueberries were extracted and assessed for their antiproliferative and pro-apoptotic effects on liver HepG2 cancer cells [65]. The greatest inhibitory effects were observed for the blueberry anthocyanin fractions (ranging from 70 to 150 µg/mL concentrations) with 50% inhibition of cancer cell population growth. Induction of apoptosis was assessed by DNA fragmentation, and the blueberry anthocyanin fraction showed a 2–4-fold increase in apoptosis compared to control [65]. In another study, lowbush blueberries have also been shown to inhibit the activities of enzymes, which play a significant role in cancer metastasis, such as matrix metalloproteinases (MMP) [43]. Researchers investigated the ability of flavonoid-enriched fractions from lowbush blueberry to downregulate MMP activity in DU145 human prostate cancer cells [66]. Differential downregulation of MMP was observed in cells exposed to both anthocyanin- and proanthocyanidin-enriched blueberry fractions. The possible involvement of protein kinase-C and mitogen-activated protein kinase pathways in the flavonoid mediated decreases in MMP activity was observed. Researchers concluded that the downregulation of MMP activities by the blueberry flavonoids might occur through multiple mechanisms [66].

Cranberry extracts were shown to significantly inhibit the growth of human breast cancer MCF7 cells, which was attributed to the ability of the extracts to initiate apoptosis and induce G1 phase arrest in the cell cycle [67]. Researchers isolated and identified 20 pure compounds from cranberries, including ursolic acid, quercetin, and 3,5,7,3',4'-pentahydroxyflavonol-3-O-β-D-glucopyranoside and showed that these compounds have potent antiproliferative activities against liver HepG2 and breast MCF7 cancer cell growth [68]. Cranberry fruits have also demonstrated the potential for negating drug resistance in cancer cells. Recently, cranberry proanthocyanidin fractions have been reported to show cytotoxicity toward platinum-resistant human ovarian cancer cell lines, neuroblastoma, and prostate cancer cell lines [69]. The cranberry fractions sensitized human ovarian SKOV3 cancer cells to the platinum drug, paraplatin. A significant synergistic effect between cranberry proanthocyanidins and the chemotherapy drug was suggested as being operative [69].

Berry-derived products such as their seed flours have also been evaluated for anticancer properties. Black raspberry, red raspberry, blueberry, and cranberry seed flours were shown to inhibit the proliferation of human HT29 colon cancer cell line [70]. Researchers suggested that berry fruit seed flours might have the potential for the development of value-added products for cancer prevention and optimal health.

### 10.5.3 *In vivo anticancer studies*

#### 10.5.3.1 *Animal studies*

A rodent model of human esophageal squamous cell carcinoma was used to evaluate the chemopreventive effects of freeze-dried black raspberry powder for this disease and to determine potential mechanisms of action [71]. Researchers showed that dietary freeze-dried black

raspberry powder inhibited N-nitrosomethylbenzylamine (NMBA)-induced tumor development in the rat esophagus by inhibiting the formation of DNA adducts and reducing the proliferation rate of preneoplastic cells. On a molecular level, the freeze-dried black raspberry powder downregulated the expression of c-Jun, COX-2, and inducible nitric oxide synthase (iNOS). Researchers also analyzed the effect of freeze-dried black raspberry powder on angiogenesis. Freeze-dried black raspberry powder significantly suppressed VEGF expression from a  $(2.38 \pm 0.34)$ -fold increase in animals treated with NMBA alone to a  $(1.08 \pm 0.22)$ -fold increase in animals treated with NMBA plus freeze-dried black raspberry powder ( $P < 0.005$ ). In addition, the microvessel density of the esophagus was decreased from  $53.7 \pm 5.6$  vessels/cm in animals treated with NMBA alone to  $22.6 \pm 2.6$  vessels/cm in animals treated with NMBA plus freeze-dried black raspberry powder ( $P < 0.0001$ ). This study also showed that the downregulation of VEGF was correlated with suppression of COX-2 and iNOS. It was concluded that because high vascularity is a risk factor for metastasis and tumor recurrence, freeze-dried black raspberry powder might have cancer therapeutic effects in human esophageal cancer [71].

In an earlier study, the same researchers treated F344 rats with NMBA, three times per week for 5 weeks [72]. After one week, the animals were fed a diet containing 5% freeze-dried black raspberry powder for the duration of the bioassay (25 weeks) and were sacrificed at weeks 9, 15, and 25. The expression and enzymatic activities of COX-2 and iNOS, as well as the expression of c-Jun in the esophagi, were evaluated to investigate the potential mechanism(s) by which freeze-dried black raspberry powder modulate tumorigenesis. At week 25, freeze-dried black raspberry powder inhibited tumor multiplicity, from  $3.78 \pm 0.41$  tumors per rat in NMBA-treated animals to  $2.23 \pm 0.21$  tumors per rat in animals treated with NMBA plus freeze-dried black raspberry powder ( $P < 0.005$ ). The black raspberry powder reduced mRNA and protein expression levels of COX-2, iNOS, and c-Jun as well as the level of prostaglandin E2 in preneoplastic lesions of the esophagus at week 25. The black raspberry powder inhibited mRNA expression of iNOS and c-Jun, but not COX-2, in papillomatous lesions of the esophagus. Prostaglandin E2 and total nitrite levels were also decreased by black raspberry powder in papillomas. Thus, black raspberry powder was suggested to render a novel tumor suppressive role through the inhibition of COX-2, iNOS, and c-Jun [72].

The mechanistic basis of the cancer anti-initiating effects of freeze-dried black raspberry powder by studying NMBA metabolism in esophageal explant cultures, and in liver microsomes taken from rats fed a control diet versus a control diet containing freeze-dried black raspberry powder (at 5 or 10% concentrations), were investigated [73]. At both test concentrations, dietary black raspberry powder inhibited NMBA metabolism in explants (26 and 20%, respectively) and in microsomes (22 and 28%, respectively). Researchers identified individual active components of black raspberry powder as ellagic acid, and the anthocyanins, cyanidin-3-glucoside and cyanidin-3-rutinoside. NMBA metabolism in explants was inhibited maximally by cyanidin-3-rutinoside (47%) followed by ellagic acid (33%), cyanidin-3-glucoside (23%), and then the black raspberry powder extract (11%). Similarly, in liver microsomes, the inhibition was maximal with cyanidin-3-rutinoside (47%), followed by ellagic acid (33%) and cyanidin-3-glucoside (32%). Dietary freeze-dried black raspberry powder was shown to induce glutathione-S-transferase activity in the liver [73].

In another recent study, diets containing freeze-dried black raspberries suppressed the development of NMBA-induced tumors in the rat esophagus. Using bioassay-directed

fractionation, the anthocyanins in freeze-dried black raspberry powder were found to be the most active constituents for downregulation of carcinogen-induced NF- $\kappa$ B and activator protein-1 expression in mouse epidermal cells *in vitro*. The present study was therefore undertaken to determine if the anthocyanins contributed to the chemopreventive activity of freeze-dried black raspberry powder *in vivo*. F344 rats consumed diets containing either (a) 5% whole black raspberry powder, (b) an anthocyanin-rich fraction, (c) an organic solvent-soluble extract (a–c each contained approximately 3.8  $\mu$ mol anthocyanins/g diet), (d) an organic-insoluble (residue) fraction (containing 0.02  $\mu$ mol anthocyanins/g diet), (e) a hexane extract, and (f) a sugar fraction (e and f had only trace quantities of anthocyanins), all derived from BRB. Animals were fed diets two weeks before treatment with NMBA and throughout the bioassay. Control rats were treated with NMBA only. Animals were killed at week 30, and esophageal tumors were enumerated. The anthocyanin treatments (diet group a–c) were about equally effective in reducing NMBA tumorigenesis in the esophagus, indicating that the anthocyanins in black raspberry have chemopreventive potential. The organic-insoluble (residue) fraction (d) was also effective, suggesting that components other than berry anthocyanins may be chemopreventive. The hexane and sugar diets were inactive. Diet groups a, b, and d all inhibited cell proliferation, inflammation, and angiogenesis and induced apoptosis in both preneoplastic and papillomatous esophageal tissues, suggesting similar mechanisms of action by the different berry components.

#### 10.5.3.2 Human studies

Increased fruit and vegetable consumption has been associated with the decreased risk of a number of cancers of epithelial origin, including esophageal cancer. As discussed above, dietary administration of lyophilized freeze-dried black raspberry powder has been shown to significantly inhibit chemically induced oral, esophageal, and colon carcinogenesis in animal models. A 6-month chemopreventive pilot study conducted by administering 32 or 45 g (female and male, respectively) of black raspberry powder to patients with Barrett's esophagus (BE), a premalignant esophageal condition in which the normal stratified squamous epithelium changes to a metaplastic columnar-lined epithelium, has been reported [74]. BE's importance lies in the fact that it confers a 30–40-fold increased risk for the development of esophageal adenocarcinoma, a rapidly increasing and extremely deadly malignancy. At the time of the publication, interim findings from 10 patients with BE supported the finding that daily consumption of black raspberry powder promoted reductions in the urinary excretion of two markers of oxidative stress, 8-epi-prostaglandin F2R and, to a lesser more variable extent, 8-hydroxy-2'-deoxy-guanosine [74].

It is noteworthy that this group of researchers has also investigated the formulation and characterization of a novel gel formulation for local delivery of the freeze-dried black raspberry powder chemopreventive compounds to human oral mucosal tissues [75]. Anthocyanins contained in mucoadhesive berry gel formulations were readily absorbed into human oral mucosa tissue as evidenced by detectable blood levels within five minutes after gel application. There was a trend for greater penetration of berry anthocyanins into tissue explants for berry gels with a final pH of 6.5 *versus* 3.5. The results from this study showed that the berry anthocyanin stability was dependent upon gel pH and storage temperature and also demonstrated that the gel composition was well suited for absorption and penetration into the target oral mucosal tissue site [75].

## 10.6 *Helicobacter pylori* and inflammatory response

Approximately 50% of the world's population is infected with *Helicobacter pylori*, which has been demonstrated as a causative factor for diverse gastrointestinal diseases including duodenal ulcer and gastric cancer [76]. *H. pylori* is slowly developing resistance to clarithromycin, a proven antibiotic agent against *H. pylori* infection. In our laboratory, we evaluated the *in vitro* bactericidal activities of various berry extracts including blueberry, bilberry, elderberry, cranberry, strawberry and raspberry seeds, and OptiBerry, with or without clarithromycin on *H. pylori* [76]. All samples tested, at all concentrations, inhibited the growth of *H. pylori*, compared with controls, with maximum inhibition with OptiBerry. At the lowest concentration of 0.25%, significant inhibition of *H. pylori* was observed with elderberry (30%), bilberry (50%), blueberry (50.5%), and OptiBerry (62%). A concentration-dependent increase in inhibition of *H. pylori* with the higher concentrations of 0.5 and 1% of all the berry extracts was observed. Modest increases in bactericidal effect were seen with the 0.5% concentration of strawberry, raspberry, and cranberry extracts, compared with the increases noted for elderberry, bilberry, blueberry, and OptiBerry. At the 1% concentration, all extracts showed >70% inhibition, with cranberry, elderberry, bilberry, and blueberry extracts showing >90% inhibition, and OptiBerry exhibiting 100% inhibition. The addition of clarithromycin to the 0.25% berry concentrations led to a significant increase in the bactericidal effects of the elderberry, bilberry, blueberry, and OptiBerry extracts against *H. pylori* compared with other berry extracts alone [76]. When clarithromycin was added to the 0.5% berry concentrations, a significant increase in the inhibition of *H. pylori* was observed with all the extracts tested. Finally, when clarithromycin was added to the 1% berry concentrations, >90% inhibition was noted for all the extracts, with elderberry, bilberry, blueberry, and OptiBerry exhibiting 100% inhibition [76].

### 10.6.1 Inhibitory effect of berry anthocyanins on *Helicobacter pylori*-induced IL-8 production in gastric MKN45 cells

In a pilot study, we assessed the effect of OptiBerry on IL-8 (one of the major mediators of the inflammatory response and also a potent angiogenic factor) inhibition in *H. pylori*-treated cultured human gastric cancer cells MKN45, and this is being reported for the first time [76]. *H. pylori* ATCC 49503 cells were used in this study. OptiBerry dramatically inhibited *H. pylori*-induced IL-8 production in MKN45 gastric cells.

Cultured human gastric MKN45 cells (16,106 cells) were grown in Roswell Park Memorial Institute (RPMI) media commonly used in human lymphoid cells culture, and treated with or without 0.5% OptiBerry, 10 ng of TNF $\alpha$ . Supernatants were collected at 6, 12, and 24 hours of treatment, centrifuged and IL-8 levels measured using assay kits.

A significant increase in IL-8 production was observed in cultured MKN45 following treatment with *H. pylori* cells. Approximately, 20, 22, and 25% increases in IL-8 production were observed at 6, 12, and 24 hours of treatment, respectively. Addition of OptiBerry completely inhibited IL-8 production in the *H. pylori*-treated cultured MKN45 cells at all time points. Table 10.3 demonstrates the effect of *H. pylori* on IL-8 production in cultured MKN45 cells and the time-dependent inhibition by OptiBerry [76].

**Table 10.3** Effect of *Helicobacter pylori* on IL-8 production in cultured MKN45 cells and the time-dependent inhibition by OptiBerry

	IL-8 (pg/mL) at time points (h)		
	6 h	12 h	24 h
Control	413.0 ± 21.6	546.0 ± 42.0	600.0 ± 81.0
TNF $\alpha$	895.3 ± 68.4 <sup>a</sup>	1156.3 ± 170.3 <sup>a</sup>	1296.0 ± 184.0 <sup>a</sup>
TNF $\alpha$ + OptiBerry	546.0 ± 69.0	593.0 ± 74.0	546.0 ± 70.0
TNF $\alpha$ + <i>H. pylori</i>	1031.3 ± 126.2 <sup>a</sup>	1406.3 ± 218.3 <sup>a</sup>	1625.0 ± 195.4 <sup>a</sup>
TNF $\alpha$ + <i>H. pylori</i> + OptiBerry	546.0 ± 28.5	562.0 ± 67.0	578.0 ± 80.3

Source: Adapted from Chatterjee *et al.* [76] and Zafra-Stone *et al.* [18].

TNF $\alpha$ , tumor necrosis factor  $\alpha$ .

<sup>a</sup>Significantly different from control ( $P < 0.05$ ).

## 10.7 Diabetes and vision

The leaves and fruits of *Vaccinium myrtillus* (containing 25% anthocyanidins) have been used for centuries in Europe to ameliorate the symptoms of diabetes [77]. Consumption of *V. myrtillus* with breakfast cereals and other whole grain foods could add another level of protection against the onset of diabetes [77]. An aqueous alcoholic extract of *V. myrtillus* leaves produced a 26% reduction in plasma glucose levels in streptozotocin-induced diabetic rats. Plasma TAG decreased in proportion with the amount of bilberry leaf extract given to rats (1.2 or 3.0 g/kg body weight) fed a hyperlipidemic diet [77]. Antihyperglycemic potential of anthocyanins has also been demonstrated by Matsui *et al.* [78].

The berry anthocyanins appear to benefit vision in several ways, including improving night vision by enhanced generation of retinal pigments, increasing circulation within the capillaries of the retina, decreasing macular degeneration and diabetic retinopathy, and improving or preventing glaucoma, retinitis pigmentosa, and cataracts [79]. Bilberry has been demonstrated to improve eyesight particularly night vision. It is worthwhile to mention that bilberry jam was extensively used by British Air Force Pilots during World War I and II before their bombing mission. Since carotenoids with vitamin A activity are found in *Vaccinium* species, some of the benefits pertaining to vision are attributable to these compounds. A double-blind, placebo-controlled study showed that oral doses of anthocyanins are important for generation of visual purple, which helps to convert light into electrical signals for the brain. Adapto-electroretinograms of two sets of six subjects were made before treatment at 1 and 3 hours post administration. Subjects given the bilberry adapted to the light within 6.5 minutes, compared with 9 minutes for the control group. In another study, 50 patients with senile cataracts were given a combination of bilberry extract standardized to contain 25% anthocyanosides (180 mg twice daily) and vitamin E in the form of dl-tocopheryl acetate (100 mg twice daily) administered for 4 months. The progression of cataracts was stopped in 96% of the subjects treated ( $n = 25$ ) compared to 76% in the control group ( $n = 25$ ) [80].

In a double-blind study, 14 diabetic and/or hypertensive outpatients with vascular retinopathy underwent therapy with vanillylmandelic acid (VMA) (160 mg b.i.d.) or placebo ( $n = 20$ ) for 1 month. At the end of the month, placebo-treated patients received the active drug for one additional month. Ophthalmoscopic and fluoroangiographic findings recovered before and after treatments showed an improvement ranging from 77 to 90% of

anthocyanosides-treated patients. In another randomized, double-blind, placebo-controlled trial, 50 patients, 21 men and 29 women (mean age 67 year, range 48–81) suffering from mild senile cortical cataract underwent therapy with vitamin E plus VMA (2 tabs b.i.d.) for 4 months. VMA was able to stop lens opacity progress in 97% of the cataracts. No adverse-drug reactions were recorded [81].

Long-term administration of berry supplements including anthocyanins is safe and can inhibit the development of the early stages of diabetic retinopathy, and this finding warrants further investigation to unveil the mechanism [82, 83].

In another study, Tsuda *et al.* [84] explored the gene expression profiles in human adipocytes treated with anthocyanins and demonstrated that anthocyanins can regulate adipocytokine gene expression to positively modulate adipocyte function to control obesity and diabetes.

## 10.8 Conclusions

There are numerous research studies demonstrating consumption of anthocyanin-rich fruit and vegetables might slow or prevent the onset of chronic diseases. Edible anthocyanin and anthocyanidin phytopharmaceuticals exhibit complementary, pharmacologic and diverse overlapping mechanisms of action, including anti-oxidative, antibacterial, antiviral, induction of detoxification enzymes, stimulation of the immune system, reduction of platelet aggregation, modulation of cholesterol synthesis, antihypertensive, and anti-angiogenic effects [85]. Edible berry anthocyanins have been shown to inhibit cellular transformation and our study exhibited the potent inhibitory effect on inducible VEGF expression [13, 57]. It is worthwhile to mention that the number of novel anti-oxidants did not exhibit anti-angiogenic effect such as berry anthocyanins [13, 56, 57]. Thus, anti-oxidant property alone may not account for the total observed anti-angiogenic effect. OptiBerry, a novel combination of six berry anthocyanins, significantly inhibited basal MCP-1 and inducible NF- $\kappa$ B transcriptions, and that EOMA cells pretreated with OptiBerry showed a diminished ability to form hemangioma [13]. Histological analysis exhibited markedly decreased infiltration of macrophages in hemangioma of berry formulation-treated mice compared to the control animals [13]. Thus, berry anthocyanins may exert novel chemoprevention, as well as anti-oxidant and anti-angiogenic properties by several mechanistic pathways. These broad spectrum beneficial and mechanistic effects have been examined primarily in *in vivo* models, experimental dietary studies in humans have also demonstrated the capacity of anthocyanin-rich fruit and vegetables and their constituents to modulate some significant benefits and disease-preventive actions. Furthermore, anthocyanins can offer an achievable, safe, and inexpensive adjunct therapy to inhibit the development of several degenerative diseases including obesity, diabetes, cardiovascular dysfunctions, cancer, and retinopathy, among others.

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## **Part 2**

### Nontropical Dried Fruits

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# **11 Phytochemicals and health benefits of dried apple snacks**

H.P. Vasantha Rupasinghe and Ajit P.K. Joshi

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## **11.1 Introduction**

Snack foods such as dehydrated chips made from fruits and vegetables make up an important part of consumer's diet in North America who are becoming more concerned about the nutritional value of foods [1]. Recently, with increasing public awareness about dietary antioxidants and biologically active phytochemicals and their associated health benefits, there is a growing demand for convenience snacks with nutritional and health benefits [2, 3]. Hence, the innovative drying processes for producing non-fried snacks could provide the consumers with nutritional benefit, convenience, and taste [3].

Preservation of phytochemicals in fruits during dehydration is important for obtaining their optimum health benefits. Furthermore, fortification of dried fruits with additional nutrients, antioxidants, and flavors can become attractive value-added food products and serve as a source of minerals, vitamins, and indispensable amino acids to meet daily dietary requirement of the public [4–9]. The appropriate use of these technologies can result in the enhancement of both quality and nutritional benefits in fruit-based snacks [4, 10–13]. In this chapter, food industry applications, phytochemicals, potential health benefits, and compositional and nutritional characteristics of dried apple snacks are discussed. Comparison is made with fresh and dried apples where it is needed.

## **11.2 Food applications of dried apple snacks**

The total retail sale of snack foods in Canada was estimated at \$981.4 million for the year 2004 and it is predicted that the domestic snack food market will increase in the coming years [14]. Revenues from Canada's snack food industry have increased from \$1.2 billion in 1999 to \$2.1 billion in 2008 [15]. In 2009, snack food sale in Canada was \$1.4 billion [16]. A 20-year study from 1977 to 1996 on snack consumption trends in the United States showed that snacks consumed by most of the children and young people in 1996 were high

in energy density and low in calcium density as compared to those consumed during 1977 and 1988 [17]. In another study, it was determined that some of the available snacks made from potatoes, corn, and wheat had a total fat content in the range of 9–46% [18]. High energy and high fat containing foods are considered as the leading cause of obesity among children [17], and this may further lead to several other adult onset of chronic diseases such as hypertension, diabetes, and cardiovascular disease (CVD) [19]. An increasing incidence of obesity at all age levels of North American population has encouraged introduction of non-traditional chips and snacks containing low amount of oil [14].

The snack food industry is now focusing more on manufacturing fruit- and vegetable-based products because of the associated health benefits and consumer preferences for low caloric healthy snack foods [2, 3]. Some of the health benefits associated with the intake of fruits and vegetables rich in phytochemicals, dietary fiber, and minerals, are the reduced risk of obesity, CVD, diabetes, and other chronic diseases [20]. In addition, the consumption of fruit has been found to inversely correlate with cancers in the esophagus, oral cavity, pancreas, and stomach [21]. Considering the health benefits of apples and their suitability for snack production [3], the promotion of apple-based snack products such as non-fried apple snacks could also be an alternative marketing option for the apple producing and processing industries.

## 11.3 Effects of drying methods and vacuum impregnation (VI) on apple phytochemicals

### 11.3.1 Drying methods

Most of the fruit- and vegetable-based snacks currently available in the market are processed by frying in oil. Investigations are in process to develop alternative processing methods to reduce the oil content in these fried snacks. A study was conducted on making non-fried carrot slices by vacuum frying at different temperatures (70, 90, 100, and 110°C) and times (5, 10, 15, 20, 25, and 30 min). The resultant snacks with higher oil content (22.5%) were observed to have more crispiness than other snacks with lower oil content [22]. Another study focused on vacuum frying of apple slices and to achieve the desired crispiness, high-temperature frying and a longer time (110°C for 25 min) was required which not only resulted in an increased oil gain of 39%, but also resulted in non-enzymatic browning in the fried apple slices [23]. The health concerns associated with consumption of high fat foods further emphasizes the need for exploration of non-frying methods for the development of low- or no-fat snack foods with desired crispiness and maximum retention of nutrients [19]. Thus, drying could be a promising alternative process for producing healthy snacks as it does not cause uptake of oil into the food and does allow much of the nutritional value to be maintained.

Drying of fruits is an important method of preservation and production of a wide variety of snack products. To have a desirable shelf-life of fruit products, it is necessary to reduce the moisture content to appropriate levels [24]. In turn, drying has a direct effect on the fruit's quality including nutritional and nutraceutical value, texture, taste, and shelf-life stability [24, 25]. Some of the drying methods that can be used in the fruit processing industry include drying by forced air, convection oven, microwaving, freeze-drying, fluidized-bed drying, osmotic dehydration, and vacuum drying [13, 26, 27].

Air- and oven-drying are the most commonly studied methods for drying apple tissues. However, the occurrence of shrinkage, non-enzymatic browning, and the loss of nutritional quality are recognized as major disadvantages associated with the use of these drying methods [26, 28, 29]. Air drying of apple tissues at 70°C and air velocity 1.5 m/s, resulted in breakage of the cell walls and formation of micro-cavities [29], which yields a lower quality end product. Oven drying of apple slices at 60°C resulted in poor quality in the final product because of uneven drying [30]. In oven drying, the product layer comes in direct contact with the hot surface of the dryer, which results an over-dried food product layer in contact. This may result in oxidation processes and loss of nutrients. Furthermore, high temperature application in air- and oven-drying has also been reported to result in loss of phenolic compounds [31]. The process of freeze-drying can help to retain the shape and nutrients in the final dried product [13, 26, 27]. However, freeze-dried apple slices resulted in the loss of crispiness due to sponginess of apple tissue resulting due to the formation of large cavities during freeze-drying [13, 29]. Microwave energy is another alternative method used to obtain greater quality dehydrated apple chips [32]. A method developed by Yücel *et al.* [33] applied high hydrostatic pressure (HHP) combined with conventional air drying at different pressure-time-temperature combinations (100–300 MPa for 5–45 min at 20 and 35°C) before drying. Significant increase of drying rate occurred when pressure of more than 100 MPa was applied as high pressure caused cell permeabilization. However, these alternative methods need to be explored for their impact on the phytochemicals in dried apple snacks.

The bioactive compounds (phenolic acids, anthocyanins, flavonols, and flavan-3-ols) present in apple are associated with the color, taste, and nutritional quality including their antioxidant activity [34, 35]. The impact of different drying methods on the phenolic compounds in apple tissue is compound dependent (Table 11.1). Phloridzin and quercitin-3-O-rhamnoside are well retained under the most commonly used drying process whereas the concentrations of catechin and epicatechin can get significantly reduced ( $P < 0.05$ ) in oven-dried apple slices. Compared to fresh apple slices, concentration of chlorogenic acid is also significantly reduced ( $P < 0.05$ ) in apple slices exposed to all of the drying processes. Air- and oven-drying of apple slices can cause significant loss of cyanidin-3-O-galactoside. However, the concentration of quercetin glycosides (with the exception of quercetin-3-O-rhamnoside) is well retained and shown to be significantly higher ( $P < 0.05$ ) in vacuum-dried apple slices as compared to fresh, oven-, and air-dried apple slices.

The varying effects of different drying methods on the individual phenolic compounds in dried apple slices can be due to their different thermo-stability properties and their susceptibility to the drying conditions. Phenolic compounds such as phloretin are found to be more stable under high temperature conditions (air- and oven-drying) than chlorogenic acid, catechin, epicatechin, and cyanidin-3-O-galactoside. Rupasinghe *et al.* [36] found that baked muffins (at 175°C for 20 min) containing apple peel powder resulted in a 784% increase in free phloretin levels due to the thermohydrolysis of glucosides of phloretin. The loss of phenolic compounds such as catechin and epicatechin during oven drying can be attributed to the application of high temperature which has shown to induce strong decomposition of these compounds [31]. In contrast to high temperature conditions, fresh samples prepared by freeze-drying have shown to minimize the loss of flavan-3-ols as compared to flavonols. Several studies have shown that freeze-drying process can significantly reduce the concentration of flavonoids including quercetin glycosides, whereas vacuum- and oven-dryings at low temperature (48 h at 40°C) have better potential for preserving flavonoids than freeze-drying [37–39]. Cannac *et al.* [37] reported a loss of about 39% of the total flavonols during

**Table 11.1** Concentration of phenolic compounds and vitamin C in fresh and dried apple slices (mg/100 g)

Phenolics and vitamin C	Apple flesh			Apple peel	
	Fresh	Vacuum-dried (30°C; 15 h)	Oven-dried (70°C; 8 h)	Air-dried (60°C; 0.8 m/s; 7 h)	Oven-dried (70°C; 8 h)
Catechin	0.30 ± 0.02 <sup>a</sup>	0.27 ± 0.02 <sup>ab</sup>	0.26 ± 0.01 <sup>b</sup>	0.29 ± 0.01 <sup>a</sup>	26.53 ± 2.27
Epicatechin	6.09 ± 6.09 <sup>a</sup>	4.71 ± 0.92 <sup>ab</sup>	3.11 ± 0.25 <sup>b</sup>	4.50 ± 1.84 <sup>ab</sup>	116.08 ± 0.74
Chlorogenic acid	191.86 ± 6.95 <sup>a</sup>	153.04 ± 3.71 <sup>b</sup>	138.84 ± 7.25 <sup>b</sup>	136.81 ± 29.31 <sup>b</sup>	51.21 ± 2.67
Cyanidin-3-O-galactoside	4.86 ± 0.79 <sup>a</sup>	3.86 ± 0.43 <sup>ab</sup>	2.97 ± 0.43 <sup>b</sup>	2.88 ± 1.18 <sup>b</sup>	49.45 ± 3.12
Phloridzin	46.88 ± 5.57 <sup>a</sup>	47.23 ± 4.94 <sup>a</sup>	35.44 ± 3.86 <sup>a</sup>	43.02 ± 13.44 <sup>a</sup>	11.52 ± 1.34
Phloretin	0.23 ± 0.00 <sup>b</sup>	0.24 ± 0.01 <sup>b</sup>	0.32 ± 0.01 <sup>a</sup>	0.32 ± 0.02 <sup>a</sup>	2.75 ± 0.23
Quercetin-3-O-rutinoside	1.37 ± 1.39 <sup>b</sup>	4.55 ± 2.28 <sup>a</sup>	1.71 ± 0.19 <sup>b</sup>	1.84 ± 0.51 <sup>b</sup>	13.11 ± 1.88
Quercitin-3-O-galactoside	10.88 ± 3.64 <sup>b</sup>	23.82 ± 6.23 <sup>a</sup>	10.49 ± 1.68 <sup>b</sup>	9.58 ± 2.95 <sup>b</sup>	249.00 ± 9.78
Quercitin-3-O-glucoside	5.56 ± 2.61 <sup>b</sup>	11.57 ± 3.28 <sup>a</sup>	5.93 ± 0.22 <sup>b</sup>	5.44 ± 1.40 <sup>b</sup>	25.21 ± 3.49
Quercitin-3-O-hamnoside	8.41 ± 2.21	11.66 ± 1.60	9.21 ± 0.45	8.25 ± 1.79	80.25 ± 0.89
Vitamin C	83.17 ± 9.43 <sup>a</sup>	65.87 ± 1.05 <sup>c</sup>	57.40 ± 4.15 <sup>c</sup>	77.39 ± 6.65 <sup>ab</sup>	nd

Source: Adapted with permission from Joshi *et al.* [10].

Data are expressed as mean ± SD ( $n = 3$ ) on a dried weight basis.

Means ± SD followed by the same letter, within each row (apple flesh), are not significantly different ( $P < 0.05$ ).  
nd, not determined.

pre-freezing process and a loss of 87% of flavonols throughout the entire freeze-drying process. The variation in phenolic compounds during freeze-drying can occur due to the interconversion of compounds by chemical or biochemical decomposition when submerging the samples in liquid nitrogen before freeze-drying [31]. van Sumere *et al.* [40] reported that phenolics can be lost during freeze-drying under high vacuum conditions as some low molecular weight compounds get volatilized and concentrated in the ice trap.

Similarly, drying processes impart significant effects on vitamin C concentration of apple slices (Table 11.1). The vitamin C concentration can be well retained in both air-dried and vacuum-dried apple slices as compared to oven drying. The loss of vitamin C during thermal processing has previously been reported by several other researchers [41, 42]. The oxidation of ascorbic acid under high temperature conditions and depletion of ascorbic acid due to its utilization for oxidative protection of polyphenols are main causes for vitamin C depletion [28, 43]. It has been reported that even drying in the absence of oxygen could not prevent the loss of vitamin C in potatoes [44].

### 11.3.2 Vacuum impregnation (VI)

Food fortification is a common practice used to further enhance the nutritional value of food products. For producing fortified, value-added fruit products, dipping fruits in fruit juices and sugar solutions containing minerals, vitamins, and other food ingredients is a commonly used processing method [7, 45]. To enhance the efficiency of these additional nutrient uptakes, VI processes can be used. It is a method which introduces controlled quantities of a solution to the porous structure of the fruit matrix [8, 46]. This method involves immersion of high porosity food samples in a solution containing desired solutes, under vacuum conditions [47, 48]. Incorporation of nutritional and functional food ingredients using VI has been found to be more effective in improving product quality than simple immersion treatments [49]. Thus, among numerous other methods, application of VI process can play a significant role in developing functional foods with desired food ingredients as minerals, vitamins, antioxidants, and antimicrobial agents, among others [9, 12, 49]. Incorporation of nutrients using VI process is achieved more quickly as compared to atmospheric impregnation. This technique was applied for incorporating probiotics into apple cylinders using vacuum pressure of 1.5 inch of mercury for a period of 10 minutes [44]. The same amount of calcium impregnated in apple tissues under atmospheric conditions after a period of 10 hours is obtained by 10 minutes exposure to VI [6]. Food products such as apples which have a higher porosity are more suitable for VI methods [47, 48], which allows impregnation with external solution and energy saving while processing. VI can also be studied to modify the compositional, thermal, and physicochemical properties of food products which, in turn, will increase the process efficiency in a manner beneficial for attaining desired product characteristics such as improved taste, texture, and shelf-life [8, 50]. In assessing the beneficial effects of VI, use of VI pre-treatment processes appears to be a good approach to develop value-added apple-based snack products.

## 11.4 Antioxidant capacity of dried apple snacks

Many *in vitro* methods have been developed to analyze antioxidant activity of food products. These methods each have different merits and limitations and to use any specific one as a

**Table 11.2** Total phenolic content and total antioxidant capacity in dried apple slices

Apple slices	Total phenolics ( $\mu\text{mol GAE}/100 \text{ g}$ )	FRAP ( $\text{mmol TE}/100 \text{ g}$ )	ORAC ( $\text{mmol TE}/100 \text{ g}$ )
Fresh	17.55 $\pm$ 1.13	0.99 $\pm$ 0.09	9.94 $\pm$ 0.37
Vacuum-dried ( $30^\circ\text{C}$ ; 15 h)	19.07 $\pm$ 0.33	1.00 $\pm$ 0.07	11.02 $\pm$ 0.72
Oven-dried ( $70^\circ\text{C}$ ; 8 h)	17.98 $\pm$ 1.22	1.00 $\pm$ 0.08	9.09 $\pm$ 1.64
Air-dried ( $60^\circ\text{C}$ ; 0.8 m/s; 7 h)	17.96 $\pm$ 4.98	0.92 $\pm$ 0.39	6.91 $\pm$ 3.08
Oven-dried apple peel ( $70^\circ\text{C}$ ; 8 h)	17.33 $\pm$ 0.09	20.27 $\pm$ 2.18	2.64 $\pm$ 0.43

Source: Adapted with permission from Joshi *et al.* [10].

Data are expressed as mean  $\pm$  SD ( $n = 3$ ) on a dried weight basis.

GAE, gallic acid equivalents; FRAP, ferric reducing antioxidant power; TE, trolox equivalents; ORAC, oxygen radical absorbance capacity.

measure of total antioxidant capacity is sometimes misleading. The mechanisms involved in these *in vitro* methods have been generally divided into two types: hydrogen atom transfer (HAT) and single electron transfer (SET) mechanisms. The Folin–Ciocalteu assay and the ferric reducing antioxidant power (FRAP) assay are *in vitro* systems which utilize a SET mechanism. The oxygen radical absorbance capacity (ORAC) assay is an example of an *in vitro* system involving a HAT mechanism.

Dehydration process of dried apple slices had promising effects on the total phenolic content (measured by using the Folin–Ciocalteu assay) and the total antioxidant capacity measured by using both FRAP and ORAC assays as they were well retained after dehydration (Table 11.2). Similar results have been reported where the drying of red grape pomace at  $60^\circ\text{C}$  for 9 hours showed no effect on its phenolic content and antioxidant capacity as compared to drying at  $100$  and  $140^\circ\text{C}$  for 5 and 4 hours, respectively [51]. Higher antioxidant activity in air-dried apple cubes of seven different cultivars ( $100^\circ\text{C}$  for 1 hour followed by  $85^\circ\text{C}$  at air velocity 1.75 m/s till final moisture content 7%) was observed by Sacchetti *et al.* [52]. The changes that phenolic compounds undergo during the drying process could increase the content of free phenolic compounds, which could, in turn, act as antioxidants or as new substrates for further oxidation [53, 54]. Thus, even after exposure to high temperature and atmospheric conditions during air- and oven-drying, the dried apple slices can show similar total phenolic content and total antioxidant capacity as compared to fresh apple slices.

Application of thermal treatments such as frying can significantly impact the bioactive compounds and the associated antioxidant capacity of the snacks (Table 11.3). Non-fried apple snacks showed approximately 20 times higher antioxidant capacity as compared to commercially fried potato snacks. The total phenolic content was found to be significantly lower ( $P < 0.05$ ) for fried potato snacks; however, no difference ( $P > 0.05$ ) in the total phenolic content was observed when non-fried apple snacks were compared with fried apple snacks.

A study was carried out to investigate the incorporation of different fruit juices into apple tissues before dehydration (Joshi and Rupasinghe, 2011; Unpublished data, Table 11.4). This resulted in further enhancement of antioxidant capacity and provided different colors to the apple snacks and different fruit juices showed varying abilities to be incorporated into the apple snacks. The FRAP values of dried apple snacks pre-treated with different juices varied considerably [6.3–14.0 mg trolox equivalents (TE)/g dried weight]. The overall trend for antioxidant capacity of the apple snack samples pre-treated with various solutions was

**Table 11.3** Total phenolic content and antioxidant capacity of snack products

Snack products	Total phenolics (µmol GAE/100 g)	FRAP (mmol TE/100 g)
Developed non-fried apple snacks	23.52 ± 0.97 <sup>a</sup>	2.05 ± 0.03 <sup>a</sup>
Commercial fried apple snacks	24.03 ± 1.7 <sup>a</sup>	1.60 ± 0.19 <sup>b</sup>
Commercial fried potato snacks	5.31 ± 0.59 <sup>b</sup>	0.11 ± 0.08 <sup>c</sup>

Source: Adapted with permission from Joshi *et al.* [11].

Data are expressed as mean ± SD ( $n = 3$ ) on a dried weight basis.

Means ± SD followed by the same letter, within each column, are not significantly different ( $P < 0.05$ ). GAE, gallic acid equivalents; FRAP, ferric reducing antioxidant power; TE, trolox equivalents.

as follows: cranberry juice > grape juice > carrot juice > apple juice > apple juice + calcium chloride > pineapple juice > maple syrup. This can be explained by the significant differences of antioxidant capacity of the juices, which were incorporated into the dried apple snacks. Therefore, the high antioxidant capacity of the juice can directly enhance the antioxidant potency of the apple snacks. Apple puree immersion in green tea extracts resulted in substantial levels of epigallocatechin (EGC), epigallocatechin gallate (EGCG), epicatechin gallate (ECG), and gallatecatechin gallate (GCG), as well as caffeine [55] in the products. The combination of osmotic pre-treatment mainly in sucrose solutions and microwave-vacuum dehydration of strawberries and apples preserved the cellular structure and vitamin C retention was around 60% with employing the microwave procedure [56].

**Table 11.4** ORAC and FRAP values of samples incorporated with different fruit juice

Juice	Treatment	ORAC (mmol TE/100 g)	FRAP (mmol TE/100 g)
Control	control	0.66 <sup>cde</sup>	4.60 <sup>1cd</sup>
Apple	dipping	0.62 <sup>cde</sup>	4.58 <sup>cd</sup>
Apple	vacuum	0.62 <sup>cde</sup>	5.62 <sup>bc</sup>
Apple + calcium chloride	dipping	0.56 <sup>de</sup>	5.00 <sup>cd</sup>
Apple + calcium chloride	vacuum	0.56 <sup>de</sup>	4.88 <sup>cd</sup>
Cranberry	dipping	1.22 <sup>a</sup>	6.21 <sup>ab</sup>
Cranberry	vacuum	0.97 <sup>abc</sup>	6.92 <sup>a</sup>
Carrot	dipping	1.12 <sup>ab</sup>	4.18 <sup>de</sup>
Carrot	vacuum	0.88 <sup>abcde</sup>	4.59 <sup>cd</sup>
Grape	dipping	0.92 <sup>abcde</sup>	4.72 <sup>cd</sup>
Grape	vacuum	0.89 <sup>abcde</sup>	5.05 <sup>cd</sup>
Pineapple	dipping	0.81 <sup>bcd</sup>	4.19 <sup>de</sup>
Pineapple	vacuum	0.93 <sup>abcd</sup>	4.02 <sup>de</sup>
Maple	dipping	0.53 <sup>e</sup>	3.44 <sup>ef</sup>
Maple	vacuum	0.71 <sup>cde</sup>	2.51 <sup>f</sup>

Source: Adapted from Joshi and Rupasinghe [2011, unpublished].

Data are expressed as mean ± SD ( $n = 3$ ) on a dried weight basis.

Means ± SD followed by the same letter, within each column, are not significantly different ( $P < 0.05$ ). ORAC, oxygen radical absorbance capacity; TE, trolox equivalents; FRAP, ferric reducing antioxidant power.

Hence, similar type of extracts can be used for preparing phytochemical enriched apple snacks using VI processes.

## 11.5 Compositional and nutritional characteristics of dried apple snacks

Apples are a good source of carbohydrates, ascorbic acid, phenolics, dietary fiber, minerals (such as P, K, and Ca), and vitamins (such as thiamin, niacin, and vitamin A) [57]. The phenolic compounds present in apples are of special interest as these act as a source of dietary antioxidants. The total antioxidant capacity of 100 g of whole apple is equivalent to the antioxidant capacity of 1500 mg of vitamin C [58]. The phenolic compounds, such as protocatechuic acid and chlorogenic acid have shown to alter the activity of enzymes involved in carcinogen activation, inhibit the formation of polycyclic aromatic hydrocarbon-DNA adducts in mouse epidermis, and decrease the level of lipid peroxidation in the epidermal microsomes [59]. Wu *et al.* [57] performed the chemical compositional studies on eight apple cultivars (Delicious, Golden Delicious, Ralls, Fuji, QinGuan, Jonagold, Granny Smith, and Orin); total phenolic content of these cultivars ranged from 26.21 to 88.27 mg/L, of which chlorogenic acid and epicatechin were the most predominant phenolics, followed by coumarin, phloridzin, catechin, and caffeic acid among all apple cultivars.

Application of VI process on apple slices resulted in uptake of calcium (780 mg/100 g) and vitamin E (168 mg/100 g) in the fruit matrix and thus, holds a great potential to prepare fortified apple-based snacks to meet the daily requirement of calcium and vitamin E in the consumer's diet. The calcium concentration in VI-treated apple slices as well as apple slices given anti-browning treatment was 0.78%. Increase in uptake of added calcium chloride by apple slices occurred during both of these pre-treatment processes (Table 11.5). Hence, this increase in calcium content in 100 g of apple snacks obtained from anti-browning and VI treatment was 780 mg of calcium which can help in providing 70% of the daily required calcium in the diet [daily reference intake (RDI): 1100 mg per day] [60]. The concentration of vitamin E in VI-treated apple snacks was 1.81 mg/g, thus 5 g of apple snacks would be sufficient to meet the daily requirements of vitamin E (10 mg per day) [60]. Increase in protein content in VI-treated apple slices was 65% when compared to that of the protein content of untreated apple slices which can be attributed to the addition of whey proteins.

VI process can be used as a successful tool for increasing the nutritional value of the food products [4, 5]. In a study by Xie and Zhao [7], fortification of 200 g of fresh-cut apples using VI methods increased calcium and zinc concentrations equivalent to 15–20 and 40% of RDI, respectively, as compared to fresh apple which provided about 0.84 and 2.30% of RDI of calcium and zinc, respectively. In another study, fortification of fresh-cut apples with vitamin E, calcium, and zinc using VI, resulted in an increased vitamin E (about 100-fold increase), calcium, and zinc contents (about 20-fold increase) as compared to the unfortified apples [12]. Hence, these fortified apple snacks can be introduced to the general public as a choice for delivering the required amount of dietary vitamins, minerals, and other nutritionally significant compounds.

Non-fried apple snacks showed comparable nutritional and compositional characteristics to commercially fried apple and potato snacks (Table 11.6). The amount of oil content was relatively higher in both commercial fried snack products and non-fried apple snacks. Generally, apple contains traces of lipids and for example "Empire" apples reported to have

**Table 11.5** Compositional and nutritional characteristics of different apple snacks

Proximate analysis	Unit	Pre-treatment before drying		
		Anti-browning treatment		VI treatment
		Untreated		
<b>Proximate composition</b>				
Dry matter	g/100 g	95.97	91.36	93.42
Crude protein	g/100 g	1.59	1.97	2.63
Crude fat	g/100 g	0.90	1.71	1.39
Ash	g/100 g	1.54	2.18	2.50
<b>Minerals</b>				
Calcium	mg/100 g	<50	780	780
Phosphorus	mg/100 g	70	50	70
Sodium	mg/100 g	50	50	50
Potassium	mg/100 g	680	480	620
Iron	mg/100 g	nd	0.71	1.15
Manganese	mg/100 g	0.26	0.26	0.26
Copper	mg/100 g	0.30	0.33	0.31
Zinc	mg/100 g	0.25	0.16	0.22

Source: Adapted with permission from Joshi *et al.* [10].Data are expressed as mean  $\pm$  SD ( $n = 3$ ) on a dried weight basis.

nd, not determined.

**Table 11.6** Compositional and nutritional characteristics of snack products

	Unit	Developed non-fried apple snacks	Commercial fried apple snacks	Commercial fried potato snacks
Water activity	$a_w$	0.24 <sup>a</sup>	0.26 <sup>a</sup>	0.19 <sup>b</sup>
<b>Proximate composition</b>				
Moisture	g/100 g	2.57 <sup>a</sup>	1.33 <sup>b</sup>	0.66 <sup>b</sup>
Protein	g/100 g	1.04 <sup>b</sup>	0.95 <sup>b</sup>	5.26 <sup>a</sup>
Oil	g/100 g	0.78 <sup>c</sup>	31.20 <sup>b</sup>	35.06 <sup>a</sup>
Ash	g/100 g	2.34 <sup>b</sup>	0.88 <sup>c</sup>	3.00 <sup>a</sup>
<b>Minerals</b>				
Calcium	mg/100 g	560 <sup>a</sup>	40 <sup>a</sup>	40 <sup>a</sup>
Phosphorus	mg/100 g	40 <sup>b</sup>	40 <sup>b</sup>	130 <sup>a</sup>
Sodium	mg/100 g	40 <sup>a</sup>	40 <sup>a</sup>	220 <sup>a</sup>
Potassium	mg/100 g	620 <sup>b</sup>	390 <sup>c</sup>	1190 <sup>a</sup>
Magnesium	mg/100 g	20 <sup>a</sup>	20 <sup>a</sup>	50 <sup>a</sup>
Iron	mg/100 g	1.65 <sup>b</sup>	2.12 <sup>b</sup>	23.33 <sup>a</sup>
Copper	mg/100 g	0.32 <sup>a</sup>	0.29 <sup>a</sup>	0.29 <sup>a</sup>
Manganese	mg/100 g	1.92 <sup>a</sup>	0.17 <sup>b</sup>	0.56 <sup>b</sup>
Zinc	mg/100 g	2.57 <sup>a</sup>	0.23 <sup>c</sup>	1.15 <sup>b</sup>

Source: Adapted with permission from Joshi *et al.* [11].Data are expressed as mean  $\pm$  SD ( $n = 3$ ) on a dried weight basis.Means  $\pm$  SD followed by the same letter, within each row, are not significantly different ( $P < 0.05$ ).

0.9% of lipid content [61]. Similarly, raw peeled potato naturally contains only trace of lipid [61]. Thus, the higher oil content in fried apple and potato snacks is the amount of oil gained during the frying process, as both apple and potato without any processing contain very low amount of oil. Differences in the compositional attributes as crude protein and ash contents can be attributed to the difference in the source and cultivar used for preparing fried and non-fried apple snacks.

## 11.6 Health benefits of fresh and dried apples

Though the reported literature on health benefits of dried apple products is scarce, scientific evidence for numerous health benefits of consumption of fresh apples is promising. The bioactive phytochemicals in apples contribute to high antioxidant capacity, antiproliferative activity, and cholesterol lowering effects, thereby promoting certain physiological functions in the human body associated with the reduced risk of cancer, heart diseases, asthma, and type-2 diabetes [62].

Apple phytochemicals have been shown to affect cholesterol biosynthesis, metabolism as well as the low-density lipoprotein (LDL) oxidation in different research model systems. A procyanidin-rich fraction isolated from apple polyphenols decreased the esterification of cholesterol and the secretion of apoB containing lipoprotein by human Caco-2/TC7 enteroctyes [63]. Freeze-dried apple peels and pulp fed to normal and atherogenic rats showed significant reduction in plasma total and LDL cholesterol [64]. Similar results were reported by Aprikian *et al.* [65] where male Wistar rats fed diets containing 0.3% cholesterol with lyophilized apples showed a reduction in cholesterol in triacylglycerol (TAG) rich lipoproteins, rise in high-density lipoprotein (HDL) fraction, and reduced malondialdehyde excretion in urine. The apparent absorption of dietary cholesterol was also markedly depressed.

Human studies involving apple and their consumption and dietary supplementation of their phytochemicals and health benefits are reported. For example, a 12-week ingestion of apple polyphenol containing capsules by healthy human subjects with moderate obesity significantly reduced the plasma total and LDL cholesterol [66]. Suppression of LDL oxidation *in vitro* was observed for apple extract where 16 mg/mL inhibited the oxidation by 81.9% [67]. Similarly, six commercial apple juices and extracts from “Red Delicious” apples inhibited LDL oxidation in an *in vitro* Cu<sup>2+</sup>-catalyzed human LDL oxidation system [68]. Interestingly, Seeram *et al.* [69] found that unblended apple juice consumption increased *ex vivo* Cu<sup>2+</sup>-mediated LDL oxidation lag time by 20% compared with the baseline.

## 11.7 Conclusions

The phytochemicals present in apples are associated with the color, taste, and nutritional quality including their antioxidant and biological activity. It is believed that growing interest in fruit-based healthy snack foods assures a promising future for the apple-based snack industry. Furthermore, convincing the consumer about the nature and healthiness of dried apple snacks is expected to influence the choice of selecting non-fried snacks over the current commercially available fried snacks. Food technology applications of modern drying processes alone or in combination with other techniques such as VI can increase the market potential of dried fruit products with promises of added health benefits.

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## **12 Phytochemicals and health benefits of dried apricots**

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### **12.1 Introduction**

Apricots (*Prunus armeniaca* L.) are classified under the *Prunus* species of the Rosaceae family. This type of fruit is produced by cultivation of wild apricot, called “Zerdali” [1] which has sweet and delicious taste and charming appearance with its yellow color and random reddish overlay.

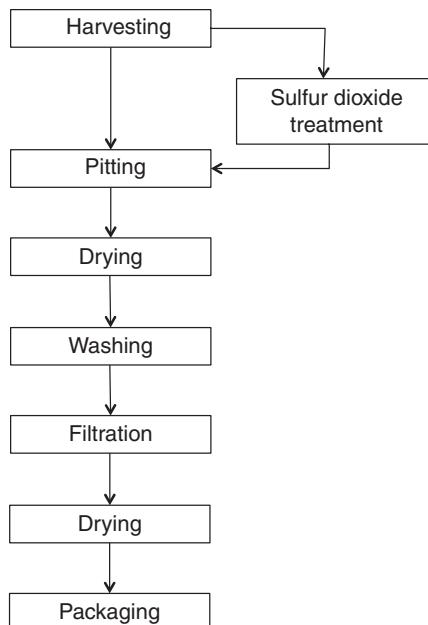
Apricots have been domesticated well over 5000 years ago in the area of Iran, Turkistan, Afghanistan, Middle Asia, and Western China [2]. Today, the greatest percentage of the world’s apricots is produced in the countries around Mediterranean Sea (such as Turkey, Spain, Italy, France, and Greece) [3]. Turkey is the leading apricot producer with 700,000 tonnes production in 2009, followed by Iran, Uzbekistan, Pakistan, Italy, China, and the United States [4].

Apricots have perishable nature and very short shelf-life, about 4–5 days under ambient conditions. Most of the apricots are either dried or consumed as fresh where they are grown [5]. Turkey, Iran, China, the United States, Australia, and South Africa are the major dried apricots producing countries. Turkey itself produces 80% of the dried apricots and exports 70% of the world’s dried apricots [2]. This chapter reports on the composition, nutritional value, phytochemicals, and health benefits of dried apricots. Chemical changes occurring during drying are also discussed along with the effect of sulfur dioxide treatment.

### **12.2 Production**

#### **12.2.1 Dehydration methods**

Drying is one of the oldest techniques used for food preservation [6, 7]. Drying lowers the water activity of foods and decreases the moisture content to a safe level. For storing and further processing, final moisture content of dried apricots must be less than 16–18% (by weight). It is also possible to produce 5% moisture content apricots with a second step drying [8].



**Figure 12.1** Flowchart of dried apricot production.

Sun drying is a widely used technique both in Turkey and elsewhere. Apricots, that are not suitable for fresh consumption or have high fiber content, are generally selected for drying. They are cut into half, pitted, and spread in depths on wooden trays. If sulfur dioxide-treated sun-dried apricots are produced, they can be treated with sulfur dioxide containing solutions or sulfur dioxide in gaseous form and then placed under sun. Unless they are sulfur dioxide-treated, they can directly be placed under sun [9]. Before marketing, they are being washed, filtered, dried, and packed. A flowchart for production of dried apricots is given in Figure 12.1. Drying time may vary between 2 and 8 days, depending upon the moisture content [10]. The dried apricots are stored at room temperature [9] and the yield from this process is approximately 5:1 [10].

After sun drying, it is possible to produce dried apricots having moisture content of less than 20% [10] with rich orange color, translucent appearance, and desirable gummy texture [11, 12]. Besides these advantages, dusts and insects may contaminate apricots when sun drying time is longer. Drying time required for apricots is around 3 to 4 weeks, depends on the thickness of the wet material layer, humidity, and temperature [13]. Longer drying time may cause significant economical loss. Therefore, an alternative technique instead of sun drying is required.

Solar drying is thought to be an alternative technique for apricot drying since it prevents microbial contamination, provides controllable drying parameters, and shortens the drying time. According to energy sources, solar dryers can be classified into three groups such as solar natural dryers (only use ambient energy sources), semi artificial natural dryers (have a fan driven by electrical motors to provide continuous air flow), and solar-assisted artificial dryers (use conventional energy source) [14].

## 12.3 Compositional and nutritional characteristics of dried apricots

Compositional and nutritional characteristics of fresh apricots and comparison with their dried counterparts are reported in the literature. However, dried apricots attracted much attention because of their mineral and vitamin contents in the last few years [15–17].

### 12.3.1 Proximate composition

Table 12.1 compares nutrient contents, including proximate composition, minerals, and vitamins of fresh and sulfur dioxide-treated dried apricots [18]. Moisture content of fresh apricots ranges from 75 to 95% [19]. Apricots can be dried until a desired moisture content, which is usually less than 20%, has been reached [1]. Moisture content of sulfur dioxide-treated dried apricots is around 7.5% in the data given by USDA [18]. Its carbohydrate

**Table 12.1** Nutrient composition of fresh and sulfur dioxide-treated dried apricots (values in per 100 grams edible portion in fresh weight basis)

	Unit	Fresh apricots	Dried apricots <sup>a</sup>
<b>Proximate composition</b>			
Water	g	86.35	7.50
Energy	kcal	48	320
Protein	g	1.40	4.90
Lipid	g	0.39	0.62
Ash	g	0.75	4.09
Carbohydrate	g	11.12	82.89
<b>Vitamins</b>			
Vitamin C	mg	10	9.5
Thiamin	mg	0.03	0.04
Riboflavin	mg	0.04	0.15
Niacin	mg	0.60	3.58
Pantothenic acid	mg	0.24	1.07
Pyridoxine	mg	0.05	0.52
Folate	μg	9.0	4.0
Vitamin A (RAE)	μg	96	633
<b>Minerals</b>			
Calcium	mg	13	61
Iron	mg	0.39	6.31
Magnesium	mg	10	63
Phosphorus	mg	23	157
Potassium	mg	259	1850
Sodium	mg	1.0	13
Zinc	mg	0.20	1.0
Copper	mg	0.08	0.58
Manganese	mg	0.08	0.37
Selenium	μg	0.1	nd

Source: Adapted from USDA [18].

RAE, retinol activity equivalents; nd, not detected.

<sup>a</sup>Sulfur dioxide-treated.

content is 82.89%, which is 7.5-fold more concentrated than that of fresh apricots. Sucrose is the major sugar in apricots. In fresh apricots, sucrose concentration ranges between 22.96 and 56.83 mg/100 g in dry weight basis [20]. Sorbitol, a sugar alcohol, is also present in apricots in significant amounts. Its concentration ranges between 2.47 and 26.80 mg/100 g (in dry weight basis) among different cultivars [20]. Protein content of sulfur dioxide-treated dried apricots is 4.90%, which is 3.5-fold more concentrated than that of fresh apricots.

### **12.3.2 Vitamins and minerals**

Apricots are an important source of vitamins such as thiamin, riboflavin, niacin, pantothenic acid, pyridoxine, folic acid, vitamin C, and vitamin A [21, 22]. Table 12.1 compares the contents of vitamins and minerals in fresh and sulfur dioxide-treated dried apricots [18]. On a dry weight basis, dried apricots contained lower amounts of vitamin C and folate than their fresh counterparts. Ascorbic acid (vitamin C) is indeed very sensitive to oxidation, hence, its loss may easily be accelerated depending on the oxidation potential of apricots and the drying temperature [22]. Other water-soluble vitamins do not change considerably by sulfur dioxide-treatment of apricots during drying. Sulfur dioxide-treated dried apricots are in fact a rich source of vitamin A and a 40 g portion of them provide 8% of reference dietary intake (RDI) of it [23]. For vitamin C, it also provides 4 and 5.04% of RDI for adult men and women, respectively [24].

Potassium is the most abundant mineral in dried apricots. Its content ranges between 1328 and 2087 mg/100 g on a dry weight basis [3] and this is followed by phosphorus, magnesium, and calcium (Table 12.1). According to the data established by the Food and Nutrition Center of the Institute of Medicine, 40 g edible portion of sulfur dioxide-treated dried apricot provides 15.6, 8.8, 8, and 2.4% of RDI of potassium, phosphorus, magnesium, and calcium, respectively, for adults [25]. Fresh and dried apricots are not good sources of selenium [20].

With regard to the amino acids content (Table 12.2), glutamic acid is the most predominant amino acid found in sulfur dioxide-treated dried apricots [18].

## **12.4 Phytochemicals in dried apricots**

Dried apricots are composed of certain phytochemicals mainly based on polyphenols and carotenoids. Major polyphenols and carotenoids found in dried apricots are shown in Figure 12.2.

### **12.4.1 Polyphenols**

Polyphenols are of much interest because of their high antioxidant capacity and effects in lowering the risk of chronic diseases [26]. In addition, they play a role as anti-carcinogenic, anti-microbial, anti-allergic, anti-mutagenic, and anti-inflammatory agents. Their effects on cardiovascular diseases (CVD) are also well known [27].

Flavonoids detected in fresh and sulfur dioxide-treated dried apricots are listed in Table 12.3 [28–30]. Radi *et al.* [31] identified major classes of phenolics in fresh apricot cultivars as procyanidins, anthocyanins, flavonols, and hydroxycinnamic acid derivatives. They reported chlorogenic acid, neochlorogenic acid, (+)-catechin, (-)-epicatechin, and rutin as principal phenolic compounds. Chlorogenic acid, which is a hydroxycinnamic acid

**Table 12.2** Amino acids in sulfur dioxide-treated dried apricots

Amino acids	Concentration (g/100 g)
Alanine	0.24
Arginine	0.19
Aspartic acid	1.12
Cystine	0.02
Glutamic acid	0.50
Glycine	0.15
Histidine <sup>a</sup>	0.08
Isoleucine <sup>a</sup>	0.15
Leucine <sup>a</sup>	0.29
Lysine <sup>a</sup>	0.34
Methionine <sup>a</sup>	0.02
Phenylalanine <sup>a</sup>	0.20
Proline	0.29
Serine	0.28
Threonine <sup>a</sup>	0.18
Tryptophan <sup>a</sup>	0.09
Tyrosine	0.11
Valine <sup>a</sup>	0.18

Source: Adapted from USDA [18].

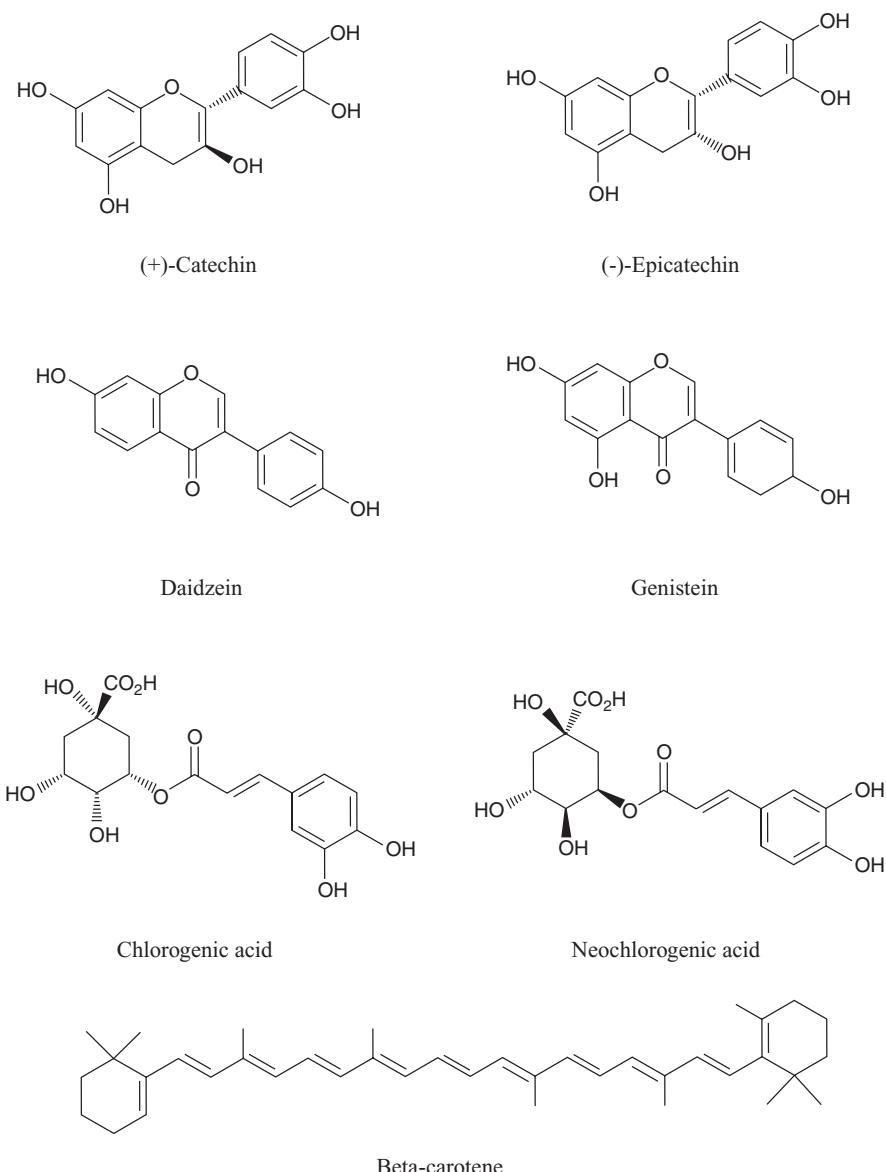
<sup>a</sup>Indispensable amino acids.

derivative, has been reported as the most dominant phenolic acid found in fresh apricots with 103–390 mg/g dry weight among nine cultivars [32]. Moreover, protocatechuic acid, and prunin along with procyanidins B2, B3, and C1 were characterized in fresh apricots [31]. (+)-Epicatechin, (-)-epicatechin, procyanidins B1, B2, and B4, some procyanidin trimers, quercetin 3-rutinoside, kaempferol 3-rhamnosyl-hexoside, quercetin 3-acetyl-hexoside, and cyanidin 3-rutinoside are the other phenolic compounds detected in fresh apricots by different researchers [20, 29, 32]. Sochor *et al.* [33] identified gallic acid, 4-aminobenzoic acid, chlorogenic acid, ferulic acid, caffeic acid, procatechin, salicylic acid, *p*-coumaric acid, quercetin, quercitrin, rutin, resveratrol, vanillin, epicatechin, and catechin in fresh apricots. Fernandez de Simon *et al.* [27] detected small amounts of coumarins such as aesculetin and scopoletin in fresh apricots and apricot juices.

Dried apricots contain daidzein, genistein, and biochanin A in very small amounts (Table 12.3). These are also known as phytoestrogens [34, 35]. Biochanin A is rarely found in most foods, less than 1 µg/100 g of fresh weight basis. The content of these phytoestrogens depends on a large number of genetic and environmental conditions such as variety, harvest, and processing [35].

### 12.4.2 Carotenoids

Carotenoids that have some protective effect against cancers and degenerative diseases are naturally occurring pigments in apricots [36]. They are classified into two major subgroups namely xanthophylls (with oxygen) and carotenes (without oxygen). As a source of provitamin A, 250 g of fresh apricots or 30 g of dried apricots provides 100% of RDI for adults [3].



**Figure 12.2** Chemical structures of some phytochemicals commonly found in dried apricots.

The most abundant carotenoid in apricots is  $\beta$ -carotene that is mainly responsible for the color of both fresh and dried apricots. Besides  $\beta$ -carotene, trace amounts of lutein, zeaxanthin,  $\beta$ -cryptoxanthin,  $\gamma$ -carotene, phytoene, phytofluene, and lycopene are found in fresh and dried apricots (Table 12.4) [36–38]. Several factors such as exposure time of apricots to sunlight, soil, season, region of cultivation, type of apricot, or stage of maturity affect the carotenoid levels [27]. In Turkish apricots, the total carotenoids range between 14.83 and 91.89 mg/100 g (dry weight basis). The percentage of  $\beta$ -carotene in total carotenoids varies

**Table 12.3** Flavonoids content of fresh and sulfur dioxide-treated dried apricots (values in mg per 100 grams edible portion)

Apricots	Flavonoids	Min-Max	Reference
<b>Fresh apricots</b>	<b>Flavan-3-ols</b>	(–)-Epicatechin (+)-Catechin	0.02–8.29 0.31–7.34 [28]
	<b>Flavonols</b>	Kaempferol	nd –1.32 [28]
		Quercetin	0.38–2.90 [28]
	<b>Proanthocyanidins</b>	Monomers	0.33–2.80 [29]
		Dimers	0.15–3.10 [29]
		Trimers	0.01–1.90 [29]
		4–6mers	4.90–4.90 [29]
		7–10mers	2.20–2.20 [29]
		Polymers	0.80–0.80 [29]
	<b>Isoflavones</b>	Daidzein	nd–0.01 [30]
		Genistein	nd–0.02 [30]
		Total isoflavones	nd–0.03 [30]
		Biochanin A	0.05 (mean) [30]

nd, not detected.

from 39 to 65% [20]. Kurz *et al.* [39] reported β-carotene (1.44–39.97 µg/g) as the dominant form of carotenoids in fresh apricots grown in Germany, followed by lutein (0.06–0.36 µg/g) and zeaxanthin (trace–0.46 µg/g).

Karabulut *et al.* [38] reported that apricots dried under hot air (80°C) contained 6.48 mg/100 g β-carotene, whereas sulfur dioxide-treated apricots dried under hot air (80°C) contained 7.17 mg/100 g β-carotene. In addition, sun dried and sulfur dioxide-treated sun-dried apricots had 3.38 and 3.87 mg/100 mg β-carotene, respectively. They reported that conditions of drying may affect the β-carotene content of dried apricots and sulfur dioxide treatment had no significant effect ( $P > 0.05$ ) on β-carotene content upon sun drying under the same conditions [38].

## 12.5 Antioxidant activity of dried apricots

Dried fruits represent a relatively concentrated form of fresh fruits. As a consequence of concentration, dried fruits have higher total energy, nutrient density, fiber content, and often greater antioxidant activity as compared to their fresh counterparts. Antioxidant activity is a result of the cumulative effect of losses and concentration of polyphenols during drying, and

**Table 12.4** Carotenoids found in fresh and dried apricots

Carotenoids	Reference
β-Carotene	[36–38]
β-Cryptoxanthin	[36, 37]
γ-Carotene	[36, 37]
Phytoene	[36, 37]
Phytofluene	[36, 37]
Lutein	[37]
Lycopene	[37]

**Table 12.5** ORAC values and total phenolic contents of fresh and partially dried apricots

Apricots	ORAC value (μmol TE/100 g)	Total phenolics (mg GAE/100 g)	Reference
<b>Fresh apricots</b>	1110	79	[40–42]
<b>Partially dried apricots (40% moisture)</b>	3234	248	[40]

ORAC, oxygen radical absorbance capacity; TE, trolox equivalents; GAE, gallic acid equivalents.

generation of certain Maillard reaction products. The antioxidant activity of some fruits and vegetables, including fresh and dried apricots, have been surveyed using the oxygen radical absorbance capacity (ORAC) assay, the ferric reducing antioxidant power (FRAP) assay, and the trolox equivalent antioxidant capacity (TEAC) assay [40–43]. The total antioxidant capacities of fresh and dried apricots are given in Table 12.5 [41–43]. However, lipophilic antioxidants account only for <3% of the total antioxidant activity [41–43].

Bennett *et al.* [44] found that total phenolic content of dried apricots was 19.1 μmol gallic acid equivalents (GAE)/g dried fruit and total antioxidant activity by FRAP assay was 39.6 μmol Fe<sup>2+</sup> reduced/g dried fruit. Among the dried ready-to-eat fruits, dried apricots were found to have less total phenolics and antioxidant activity than certain berries such as currants, prunes, and raisins [44]. Igual *et al.* [45] determined total phenolic content and 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activities of fresh and partially dried apricots. They found that total phenolic content of fresh and partially dried apricots was 16.6 and 64.73 mg GAE/100 g, respectively. Their corresponding DPPH scavenging activities were 2.4 and 3.8% for fresh and partially dried apricots [45].

The total antioxidant activities of different apricot forms are in the descending order of sulfur dioxide-treated sun dried > sun dried > fresh [46]. Sulphites, that are used to prevent flavor and color degradation in beverages and fruits, are reducing agents and weak antioxidants in foods. They react with molecular oxygen to form sulphates and also act as reducing agents that promote the formation of phenols from quinones, thereby preventing browning reactions [47].

## 12.6 Chemical changes during drying of apricots

Sun drying is the dominant mode of processing for the production of dried apricots, because it requires only free and renewable energy [9]. It is largely practiced in the provinces of Turkey where they are produced. There are also some other techniques such as cabinet/tunnel drying which use solar energy, hot air drying, and microwave drying that shorten drying time and have less effect on nutritional and functional composition of apricots [48].

There are certain chemical changes occurring in apricots during drying depending on the conditions (time, temperature, sulfur dioxide treatment, etc.). The major concern in the drying process of apricots is enzymatic browning catalyzed by polyphenol oxidase (PPO). Meanwhile, non-enzymatic browning such as sugar dehydration and Maillard reaction are also responsible for chemical changes in apricots during drying. The conditions of drying are favorable, especially for the Maillard reaction, a condensation reaction between carbonyls and amines leading to brown nitrogenous melanoidin polymers [49].

### 12.6.1 Enzymatic browning

PPO catalyzes the oxidation of phenolic compounds into quinones, which further form pigments in wounded tissues [50]. The action of PPO onto phenolic compound requires damage in the cells to let them come into contact [51]. In the presence of oxygen, two reactions begin to occur: the hydroxylation of monophenols (monophenolase activity) and the oxidation of *o*-diphenols to *o*-quinones (diphenolase activity) [52]. These reactions proceed by the polymerization of quinones leading to high molecular weight melanins with dark colors.

Phenolic compounds differ in their ability to act as substrate for PPO. Chlorogenic acid, which is the primary phenolic compound in apricots, is known as a suitable PPO substrate [50, 53]. Browning rate of apricots depends on several factors including concentration of PPO, type and concentration of phenolic compounds, presence and concentration of inhibitors (such as sulfur containing substances), oxygen, pH, and temperature [54]. During drying, PPO activity remains high for longer periods when temperature is around 55–60°C. On the other hand, exposure to 75–80°C in a shorter time inactivates the enzyme [39]. Queiroz *et al.* [50] expressed that optimum pH to PPO ranges from 5.0 to 7.5. Lowering the pH below 5.0 inhibits the enzyme. Several fruit's PPOs including almonds, apricots, peaches, and plums generally have maximal PPO activities at around pH 5.0 [55].

### 12.6.2 Non-enzymatic browning

Non-enzymatic browning in dried fruits is mainly associated with carbohydrate degradation reactions [56]. The Maillard reaction, which is mainly responsible for browning in foods containing reducing sugars and free amino groups, takes place during processing or storage of many foods [57]. It is controlled by different parameters such as pH, water activity, time, and temperature, as well as the concentration of reactants [49]. Hofmann [58] hypothesized that low molecular weight chromophores rather than high molecular weight melanoidins are mainly responsible for color formation in foods *via* the Maillard reaction. On the other hand, many researchers have related brown color with the formation of high molecular weight melanoidin polymers [59, 60].

5-Hydroxymethylfurfural (HMF) is a furane compound that forms as an intermediate in the Maillard reaction [61]. It is also formed from direct dehydration of hexose sugars under acidic conditions [62]. High temperature is known to accelerate the formation of HMF in sugar rich foods such as fruits and fruit-based products.

Sanz *et al.* [49] specified 2-furoylmethyl amino acids in dates, figs, apricots, and prunes. They observed 2-furoylmethyl-proline, 2-furoylmethyl- $\gamma$  aminobutyric acid, and furosine in all dried fruits analyzed. Furosine was the main compound found in figs and dried apricots. For dried apricots, the main compound was found to be 2-furoylmethyl- $\gamma$ -lysine (7.74 mg/100 g), followed by 2-furoylmethyl- $\gamma$ -proline (5.73 mg/100 g), and 2-furoylmethyl- $\gamma$ -aminobutyric acid (3.59 mg/100 g). No 2-furoylmethyl- $\gamma$ -alanine was detected in dried apricots [49].

## 12.7 Effects of sulfur treatment on phytochemical content of apricots

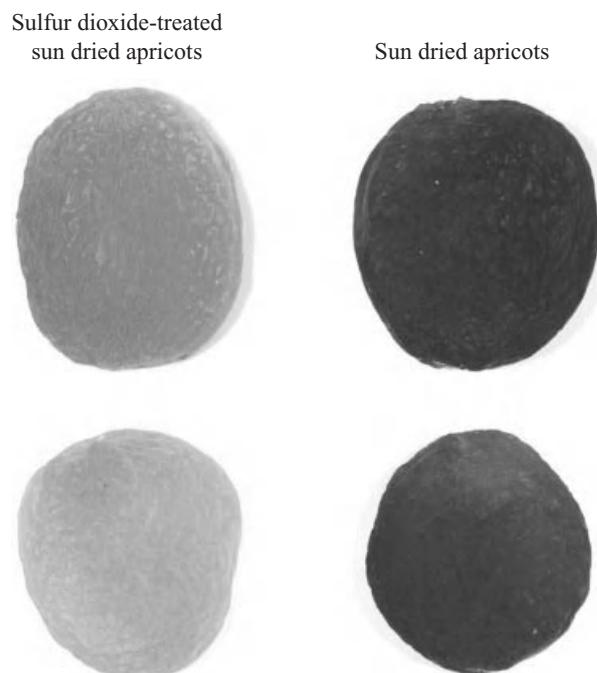
Sulfurization is a process that apricots are treated with sulfur dioxide gas or sulfur dioxide containing solutions. It is a pre-treatment that can be required to decrease the effect of

spoilage reactions, to facilitate the drying process, and to improve the quality [7, 8]. It also reduces fruit darkening rate by preventing enzymatic browning during drying. Sulfur dioxide also helps in stabilizing carotenes with its oxygen-scavenging action [5]. In practice, apricots are placed in fumigation rooms where sulfur is burnt to generate sulfur dioxide gas. They are exposed to sulfur dioxide for about 8–12 hours [50]. It is also possible to treat apricots with solutions of water-soluble sulphite salts such as potassium meta-bisulphite and sodium meta-bisulphite [8, 12].

Sulfur dioxide, sodium sulphite, sodium bisulphite, potassium bisulphite, sodium meta-bisulphite, and potassium meta-bisulphite have been recognized as “Generally Recognized as Safe” in foods and drugs [63]. There is an international maximum value, 2000 ppm, for residual sulfur dioxide in apricots. The residual sulfur is very important from a sensory point of view, because it affects both the color and the taste of dried apricots [8, 12].

Compounds that inhibit enzymatic browning are classified based on the inhibition mechanism as reducing agents, chelating agents, acidulants, enzyme inhibitors, enzyme treatments, and complexing agents [48]. Reducing agents prevent accumulation of *o*-quinones and the formation of melanins. They may also form colorless stable compounds. Sulphiting agents, especially sulfur dioxide, are able to inhibit PPO directly [55]. Therefore, sulfur dioxide-treated sun-dried apricots have golden yellow color, whereas sun-dried apricots have a brown color (Figure 12.3).

Sulfur dioxide-treated sun-dried apricots have some adverse effects on health such as asthma [64]. According to World Health Organization (WHO), the acceptable daily intake of sulfur dioxide in foodstuffs has been established as 0.7 mg/kg of body weight [48, 55]. Most consumers do not prefer sulfur-treated sun-dried apricots nowadays; sun-dried apricots that



**Figure 12.3** Typical images of sun-dried apricots with and without sulfur dioxide treatments. For color detail, see color plate section.

are produced without any treatments are most desirable. Consequently, sun-dried apricots have been produced as an alternative to sulfur dioxide-treated dried apricots in Turkey [38].

Sulfur dioxide treatment affects not only the color, but also phytochemicals, especially phenolic compounds. Even though sulfurization is known as an effective process in preventing the loss of natural color [10], it actually does not protect carotenoids. Dried apricots, sulfur dioxide treated or not, usually have similar contents of  $\beta$ -carotene [38]. However, phenolic profiles differ significantly in the two products. As shown in Figure 12.4, the most dominant phenolic compounds in sulfur dioxide-treated apricots are chlorogenic acid (167 mg/kg dry weight basis) and neochlorogenic acid (152 mg/kg dry weight basis). On the other hand, sun-dried apricots contain neither chlorogenic acid nor neochlorogenic acid [65].

The loss of phenolic compounds with sulfur dioxide treatment minimized the loss of total phenolics and total antioxidant capacity in sun-dried apricots. Thus, sulfur dioxide-treated dried apricots had a total phenolic content of 170.2 GAE/100 g compared to sun-dried apricots with 76.3 mg GAE/100 g dry weight. Dried apricots treated with sulfur dioxide have 2–6-fold more total antioxidant activity, and are measured by different assays [65].

Sulfur dioxide treatment has a significant impact on the pH of dried apricots. It was found that sulfur dioxide-treated dried apricots have an average pH of 4.20, whereas sun-dried apricots have 5.37. As a result of the dissolution of sulfur dioxide in apricot cells, pH of treated sun-dried apricots decreased by approximately one unit [65]. The pH of sun-dried apricots promotes the PPO activity, hence resulting in a complete loss of chlorogenic and neo-chlorogenic acids.

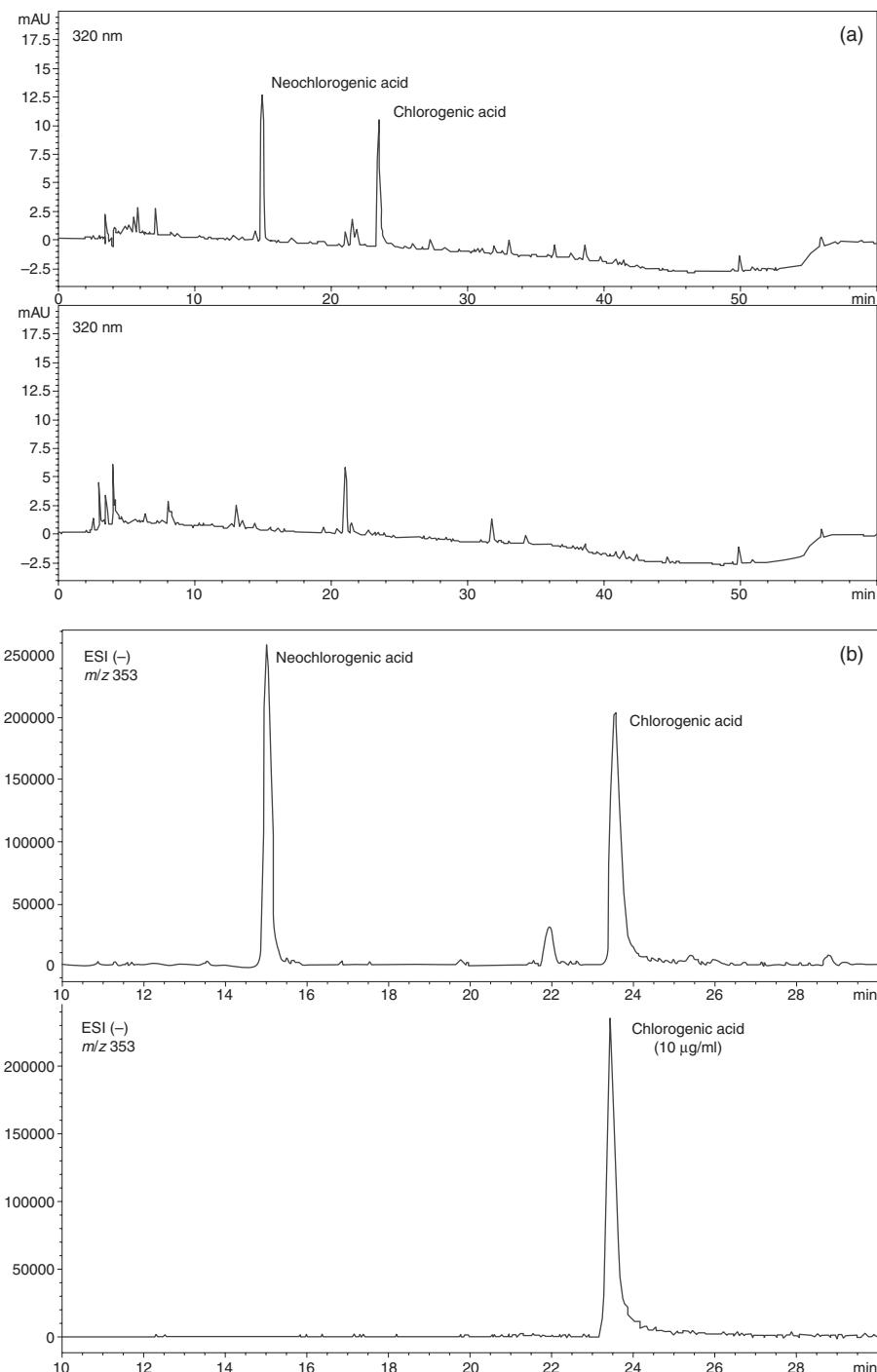
Low pH has an obvious effect on the HMF level of sulfur dioxide-treated sun-dried apricots as the formation of HMF proceeds better under acidic conditions. HMF contents of the sulfur-dioxide treated sun-dried apricots were significantly higher ( $P < 0.05$ ) than those of the sun-dried apricots. Figure 12.5 shows HMF levels of sulfur dioxide-treated sun-dried apricots and sun-dried apricots. The mean HMF levels were 21.48 and 1.19 mg/kg for sulfur dioxide-treated dried apricots and sun-dried apricots, respectively. Figure 12.6 illustrates the chromatograms of standard solution of HMF (1 mg/kg), a sulfur dioxide-treated sun-dried apricot and a sun-dried apricot [65].

The difference in the HMF contents can be considered as a result of high sugar dehydration under acidic conditions and proceeding of Maillard reaction on the route of Schiff base and consequently HMF formation. There is no need of high temperature for HMF formation under acidic conditions as drying temperatures of about 50–60°C is suitable for HMF formation.

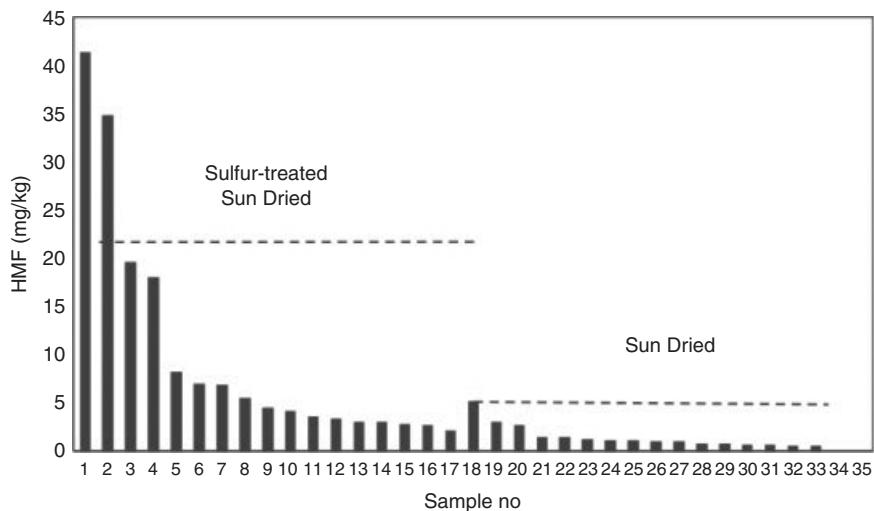
## 12.8 Health benefits of dried apricots

Foods, which are capable of providing additional physiological benefit, such as preventing or delaying the onset of chronic diseases, as well as meeting basic nutritional requirements, are described as functional foods [66]. Fruits and vegetables contain significant amounts of biologically active components and supply basic nutrition along with health benefits [67]. Dried apricots can be classified as functional foods with their concentrated nutritional content and phytochemicals. They are rich in phytochemicals, namely carotenoids and polyphenols. Consumption of plant foods rich in phenolic compounds counteracts the risk of CVD, cancer, and cataract as well as a number of other degenerative diseases [68].

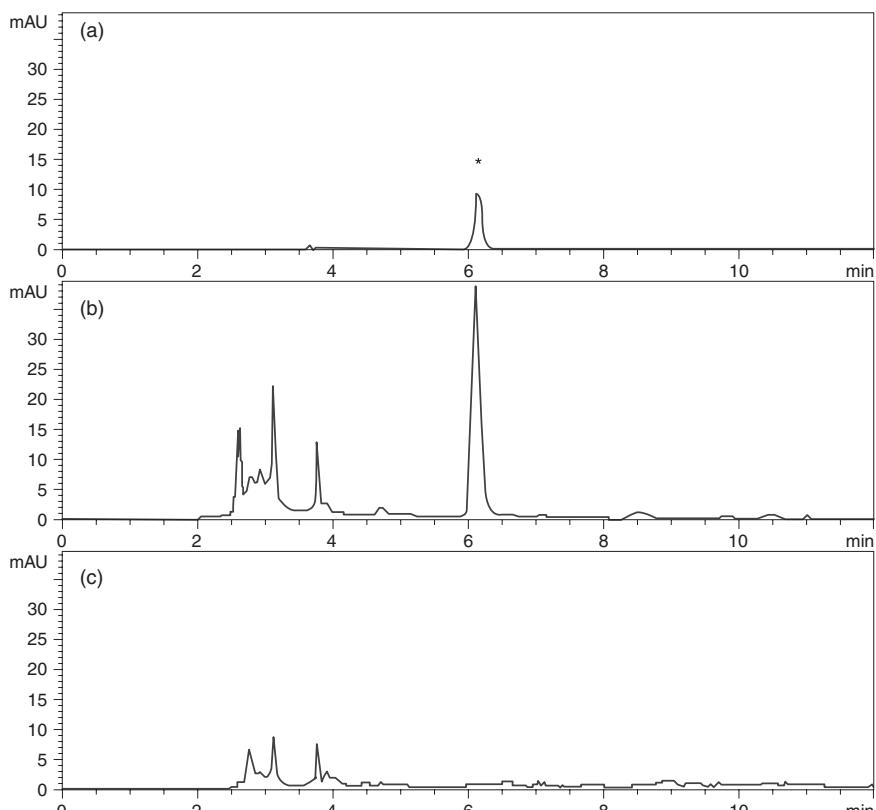
The effect of dried apricots in the prevention of CVD can be explained with different mechanisms. One of these mechanisms is the effect of antioxidants present. Carotenoids and



**Figure 12.4** (a) HPLC chromatograms (at 320 nm) of sulfur dioxide-treated sun-dried apricots (upper panel) and sun-dried apricots (lower panel) [65]. (b) LC-MS chromatograms (at  $m/z$  353) of sulfur dioxide-treated sun-dried apricots confirming the presence of chlorogenic and neochlorogenic acids as major phenolic compounds [65].



**Figure 12.5** Comparison of the occurrence of HMF in sulfur dioxide-treated sun-dried apricots and sun-dried apricots [65].



**Figure 12.6** Chromatograms illustrating in dried apricots: (a) standard solution of HMF at 1.0 mg/L; (b) sulfur dioxide-treated sun-dried apricot having 217.94 mg/kg of HMF; and (c) sun-dried apricot having 0.67 mg/kg of HMF [65].

flavonols found in dried apricots as phenolic compounds play a major role as antioxidants and take part in reducing the cholesterol oxidation in the arteries.  $\beta$ -carotene, the dominant carotenoid found in dried apricots, is the pioneer substance related to vitamin A. It is necessary for epithelial tissues covering our bodies and organs, eye-health, bone and teeth development, and working of endocrine glands [1]. Another mechanism is, with the help of soluble dietary fiber, the reduction of serum cholesterol level [67]. Dried apricots are a good source of dietary fiber and could play a role in the prevention of obesity [69]. In addition to weight control, dietary fiber consumption helps control serum cholesterol levels and blood sugar [70].

## 12.9 Conclusions

Dried apricots are appealing due to their health benefits, nutritional composition, and delightful taste. Their health benefits originate from their rich dietary fiber content, polyphenols (particularly chlorogenic and neochlorogenic acids), carotenoids (particularly  $\beta$ -carotene), and other minor components such as vitamins and minerals. Antioxidant activity of naturally occurring polyphenols and carotenoids particularly contributes to health benefits of dried apricots by taking role in the prevention of CVD. Sulfur dioxide-treatment of apricots has both beneficial and adverse effects in terms of food quality and safety. It protects phenolic compounds against oxidation and keeps the antioxidant activity high, but it also accelerates HMF formation due to higher acid conditions arising from the dissociation of sulfur dioxide.

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# 13 Dried cherries: phytochemicals and health perspectives

Letitia McCune

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## 13.1 Introduction

The United States Department of Agriculture (USDA) has recognized dried cherries as an expanding market for cherries produced in the United States [1]. Increased attention on cherries in general has been a result of cherries labeled as a “super food” and a “super fruit” following the recognition of an increased number of research articles focused on cherries’ high antioxidant levels and associated health benefits [2–4]. Considering that increasing consumption of fruits and vegetables is recognized as a method of improving overall health through nutrition, and that the dried fruit consumption in particular is an indicator of better nutrient intake and lower body weight measurements [5], dried cherries are a means of increasing health through consumption. This chapter presents some of the latest data on nutritive values and antioxidant phytochemicals as well as the potential health benefits of dried cherries in relation to cancer, cardiovascular disease (CVD), diabetes, and inflammation.

## 13.2 Production

Dried cherries are most often made from sour cherries (*Prunus cerasus* L.), for storage and supplementary sugar addition reasons, but they are also made from sweet cherries (*Prunus avium* L.). Both sweet and sour cherries are native to the European and Western Asia regions and currently are grown worldwide, especially in northern temperate regions. The Food and Agriculture Organization (FAO) 2008 data show Turkey as the leading producer of cherries at 338,361 metric tonnes (MT) followed by the United States at 225,073 MT. Under the category of sour cherries, Poland was the leading producer at 201,681 MT followed by Turkey at 185,435 MT with the United States at sixth with 97,250 MT [6]. In the United States, Michigan is the leading state in producing tart cherries while Washington is the leading state in producing sweet cherries.

Dried cherries are recognized as a form of processed cherries usually, but not always, produced from tart or sour cherries. There is limited data that separates out dried from

**Table 13.1** US cherry production and utilization amounts (2010 values)

	Tart cherry (in thousand MT)	Sweet cherry (in thousand MT)
Total produced	86.4	283.7
Fresh produced	0.4	225.3
Total processed	82.7	53.3
Frozen	56.2	—
Canned	16.0	2.8
Brined	—	30.9
Others	10.5 <sup>a</sup>	19.7 <sup>b</sup>

Source: Adapted from USDA [7].

<sup>a</sup>Includes juice, wine, brined, and dried.

<sup>b</sup>Includes California canned and all others processed (dried, frozen, and juice) from other states.

other forms of processed cherries. In 2010, the United States had bearing acreage of sweet cherries in the amount of 88,030 with a total production of 283.7 thousand MT and utilizing 225.3 thousand MT as fresh and 53.3 thousand MT as processed (Table 13.1). Of this, 19.7 thousand MT is for some forms of processed sweet cherries including dried. For tart cherries, the bearing acreage was 35,650 with a total production of 86.4 thousand MT with 0.4 thousand MT used as fresh and 82.7 thousand MT processed. Of those processed, 10.5 thousand MT fall under the category that includes dried cherries [7]. In 2004, 166 firms were recognized as processors of tart cherries in the United States. A survey sent to cherry processor firms in Michigan found that approximately 30% recognized that there had been an increase in dried cherries produced over the last 5 years, while approximately 70% of these firms recorded no change in dried fruit production (none were noted as recognizing a decrease) [8].

In general, the United States utilizes approximately 8% of all its non-citrus fruits, including cherries, in a dried form (2035.3 thousand MT in 2010) [7]. In 2005, the United States documented importing 188 MT of dried cherries. These numbers have gradually increased over the prior of 10 years with a spike in 2002 of 568 MT [9]. Customarily, it is the tart or the sour cherries that are dried considering the percentage of the sweet cherry harvest that is eaten fresh and the potential to add sugar to the dried tart cherry product to improve palatability. The Large Montmorency and Early Richmond are the typical US tart cherries that are dried while in the sweet cherry category it is often the Royal, Napoleon, Bing, and Lambert cultivars.

### 13.3 Methods of drying

Traditionally, cherries have been dried using open air drying in the sun or solar methods utilizing fans and greenhouses. Commercial drying techniques can also include chemical pretreatments to decrease loss of product and speed drying time. These methods often target the waxy cuticle of the fruit, creating small cracks to speed drying in addition to providing some antibacterial or antifungal properties. Fruit can be dipped in solutions of fatty acid esters (e.g., ethyl oleate), NaOH, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, or citric acid at different concentrations

and for different lengths of time. A study on sour cherries found that the best retention of color after drying was produced using a room temperature dipping solution of 2% ethyl oleate for 1 minute followed by drying at 45.2°C. [10]. Sulfur dioxide is sometimes added to prolong shelf life. Sweet cherries consumed fresh, on the other hand, can have post-harvest applications of oils and acids to delay ripening and deterioration before purchase [11]. With the increased demand for organic fruit products, many of these applications are being limited.

## 13.4 Nutritional characteristics

In contrast to fresh cherries, dried cherries can have the addition of oils, sugars, flavorings, or chocolate to the finished product. These additions can significantly change the nutritive values for dried cherries increasing caloric, fat, and carbohydrate levels as well as affecting glycemic index (GI). The contrast of these nutrient values between fresh and dried cherries can be seen in Table 13.2. Considering that 1 kg of dried cherries is produced from 6 to 8 kg of fresh cherries (cherry marketing board website facts), the amounts of calories and other components are increased in the same 100 g portion. However, a serving of dried fruit is usually considered less than half a cup (60 g) while a serving of fresh fruit is often 1 cup (140 g). Consuming dried cherries over fresh produce, therefore, not only has the potential to increase calories and sugars but also the amounts of protein, fiber, and vitamins.

### 13.4.1 Protein

The amount of protein in dried cherries is over three times that of fresh cherries. Dried cherries are, therefore, an efficient means to increase plant protein in the diet considering that the increased ratio of plant protein to animal protein in the diet is associated with increased health and decreased obesity [14]. This is also in agreement with the higher level of fruit and vegetable component of the healthy “Mediterranean diet” as compared to the unhealthy “Western diet” [15, 16]. In addition, the consumption of dried fruits has been linked to better quality dietary intakes and lower body weight [5]. Considering the many health benefits of increasing fruit and vegetable consumption, dried cherries is one method of incorporating fruit into the diet year round.

**Table 13.2** Some nutrition facts of dried and fresh cherries (tart and sweet) per 100 g

Nutrient	Unit	Dried cherries [12]	Tart cherries [13]	Sweet cherries [13]
Energy	kcal	340	50	63
Protein	g	3.29	1.0	1.06
Fat	g	0.1	0.3	0.2
Carbohydrate	g	82.2	12.2	16.0
Sugars	g	68.3	8.5	12.8
Fiber	g	2.57	1.6	2.1
Vitamin C	mg	<0.5	10	7
Vitamin A	IU	3701	1283	64
Potassium	mg	416	173	222

### 13.4.2 Fiber

Consuming dried cherries provides a higher amount of fiber in the diet than the same 100 g of fresh cherries (Table 13.2). At a rate of 2.57 g/100 g, this can contribute to the suggested consumption of 14 g/1000 kcal intake. Diets high in fiber have been linked to increased health and weight loss through decreases in cholesterol and blood glucose as well as through increased levels of satiety [17, 18]. While there has been some concern that higher levels of fruit fibers detrimentally affect the bioavailability of dietary antioxidants, it is likely the absorption of the antioxidants occurs in the colon rather than in the small intestine [19].

### 13.4.3 Vitamins

Vitamin C is decreased in the process of drying of cherries (Table 13.2). In studies of apple juice, it has been shown that UV radiation and higher temperatures lead to vitamin C degradation [20]. Such processing often results in the conversion of L-ascorbic acid (vitamin C) to dehydroascorbic acid and subsequent loss of biological activity.

Vitamin A, on the other hand, is present at a higher level in the dried product as compared to the fresh fruit. Dried cherries constitute a significant source of vitamin A; the amount in 100 g equaling 75% of the recommended daily intake (RDI) in a 2000-calorie diet. Vitamin A benefits many physiological functions including immunity, inflammation, vision, and reproduction. Deficiencies in vitamin A are particularly significant in malnourished populations contributing to infant mortality and blindness. Supplementation of wheat flour with vitamin A in relief projects has been recommended [21] as well as projects to recognize the importance of traditional sources of vitamin A in many Indigenous Peoples' food systems such as in Pohnpei, for the Karen People in Thailand, and the Awajun in Peru, etc. [22, 23].

Dried cherries also serve as a good source of potassium with amounts of 416 mg/100 g [12], almost twice that in fresh sweet cherries (222 mg/100 g) [13]. Higher consumption of potassium rich foods in conjunction with less sodium has been described in many studies as a means to lower high blood pressure and stroke risk [24, 25]. The Dietary Approaches to Stop Hypertension (DASH) intervention trial [26] consisted of a diet high in potassium rich foods including a high intake of fruits and vegetables and a reduced intake of saturated and total fat. High compliance with this diet as well as an increase in calcium and weight control has been shown to reduce hypertension [27]. Low potassium affects the hormones angiotensin II and aldosterone linked to sodium and potassium transport and cardiorenal damage as well as the adenosine triphosphate (ATP)-sensitive potassium channels responsible for maintaining glucose homeostasis [28, 29].

## 13.5 Antioxidant phytochemicals

Cherries are a good source of phenolic antioxidants with many different flavonoids including various anthocyanins [4]. Flavonols have been identified as the major class of polyphenols in tart cherries [30] with 7-dimethoxy-5,8,4'-trihydroxyflavone being the most active one in some antioxidant assays [31]. When tart cherries are converted to dried cherries, many derivatives of the anthocyanins and cyanidins appear [32]. Table 13.3 illustrates the amounts of many of these compounds in dried cherries from two tart cultivars, namely Balaton and Montmorency.

**Table 13.3** Antioxidant components of two cultivars of tart cherries

Antioxidant component	Montmorency (dried without sugar)	Montmorency (dried with sugar)	Balaton (dried without sugar)	Balaton (dried with sugar)
Total phenolics <sup>a</sup>	7813 ± 855	5103 ± 455	6343 ± 776	3522 ± 512
Total anthocyanins <sup>b</sup>	173 ± 31	62 ± 5.3	564 ± 65	273 ± 33
Cyanidin 3-sophoroside <sup>c</sup>	4.6 ± 0.8	1.9 ± 0.6	15.7 ± 4.3	13.9 ± 4.2
Cyanidin 3-glucosylrutinoside <sup>c</sup>	33.6 ± 6.4	11.1 ± 4.7	203.6 ± 44.2	64.8 ± 9.2
Cyanidin-3-glucoside <sup>c</sup>	0.7 ± 0.3	nd	7.6 ± 0.9	3.6 ± 0.7
Cyanidin-3-rutinoside <sup>c</sup>	19.5 ± 4.8	6.9 ± 0.9	24.9 ± 6.3	19.5 ± 4.8
Peonidin-3-glucoside <sup>c</sup>	4.5 ± 0.9	1.1 ± 0.6	16.2 ± 4.2	4.2 ± 0.9
Cyanidin <sup>c</sup>	0.3 ± 0.2	nd	1.6 ± 0.7	nd
Pelargonidin <sup>c</sup>	0.8 ± 0.3	0.3 ± 0.2	0.4 ± 0.2	nd
Isorhamnetin rutinoside <sup>c</sup>	383.1 ± 62.1	203 ± 52.1	35.8 ± 8.5	158.7 ± 44.5
Kaempferol <sup>c</sup>	16.9 ± 3.8	12.9 ± 4.1	42.9 ± 6.7	16.9 ± 4.4
Quercetin <sup>c</sup>	7.5 ± 0.9	8.8 ± 0.9	3.1 ± 0.8	1.9 ± 0.8

Source: Adapted with permission from Kirakosyan *et al.* [32].

Data are expressed as means ± standard deviation ( $n = 3$ ) on a dry weight basis.

nd, not detected.

<sup>a</sup>µg of gallic acid equivalents (GAE)/g.

<sup>b</sup>µg of cyanidin 3-glucoside equivalents (C3GE)/g.

<sup>c</sup>µg/g biomass.

Oxygen radical absorption capacity (ORAC) measurements, a standard antioxidant calculation based on µmoles of trolox equivalents (TE) per 100 g sample, indicate that dried cherries have an ORAC value of 6800 versus 2033 for frozen tart cherries and 1700 for canned tart cherries [2]. These high antioxidant values are likely due to the presence of antioxidants in the skins (Table 13.4). When scrutinizing the antioxidants present, one must consider the relative activity of each antioxidant. Kirakosyan *et al.* [32] suggests that cyanidin and its derivatives are the primary contributors to antioxidant activity in tart cherries. Processing of tart cherries into a dried form, however, has the potential of decreasing certain antioxidants when increased temperature is used in the process. Some anthocyanins may be unstable during processing (hence the derivatives of cyanidins seen in Table 13.3) and the

**Table 13.4** Montmorency tart cherry antioxidant measures

Portion	Anthocyanins (mg of C3GE/100 g)	Total phenolics (mg of GAE/g)	ORAC (µmoles of TE/g)
Edible portion	8.7 ± 0.8	4.07 ± 0.18	25.57 ± 3.99
Flesh	0.0 ± 0.09	3.01 ± 0.29	15.00 ± 1.00
Pits	0.8 ± 0.08	1.57 ± 0.02	9.78 ± 0.28
Skins	36.5 ± 1.6	5.58 ± 0.33	51.02 ± 1.97

Source: Adapted with permission from Chaovanalikit and Wrolstad [30].

Data are expressed as means ± standard deviation ( $n = 2$ ) on a fresh weight basis.

C3GE, cyanidin 3-glucoside equivalents; GAE, gallic acid equivalents; ORAC, oxygen radical absorbance capacity; TE, trolox equivalents.

antioxidant melatonin may also be affected [32]. To preserve melatonin, Kirakosyan *et al.* [32] indicated that individually quick freezing may provide the best method of processing tart cherries. Brining and canning of the fruit contributes to significant loss of antioxidants into the accompanying solution [30]. In contrast, dried cherries are more antioxidative than frozen, concentrated, or individually quick frozen products of the same cultivars [32]. Adding sugar to dried cherries appears to decrease the antioxidants available but still allows for antioxidant capacities to be substantial [32]. Synergistic actions of the antioxidant compounds in tart cherries contribute to its overall high antioxidant activity [33].

The choice of cultivar as well as elevation and harvesting time can have significant effects on the amount of antioxidants. Differences between the tart cherry cultivars Mortmorency and Balaton can be seen in Table 13.3. Balaton has higher levels of most of the anthocyanins while Mortmorency has higher total phenolics. Significant differences exist between early stage ripening and full ripened stages of harvest for dried sour cherries [34]. In addition, the growing location can affect antioxidant levels. Higher elevations were confirmed to increase phenolic and antioxidant content in four cultivars of sweet cherries in Greece [35]. This is in agreement with theories and studies on ecological conditions related to phytochemical production and antioxidant rates [36]. The stress conditions of the plant (including amounts of UV radiation, drought, and metals in the soil) can increase the antioxidant levels in the harvested plant part. In the conversion of grapes to wine the harvest year, with its associated differences in ecological stresses, can have an effect on phenolics and antioxidants. Further studies are needed in sour cherry cultivars.

Sour cherries have been ranked as one of the top 50 foods in terms of their antioxidant activity, according to the ferric acid in plasma assay (FRAP) analysis of 113 foods [37]. These rates were above that of such high antioxidant producers as grape juice, plums, and coffee. Sour cherries also ranked as 14th in their content of antioxidants present per serving; this is above the antioxidant content of red wine, cranberry juice, and oranges. It remains to be seen what ranking dried cherries would have considering the decrease in some antioxidant rates with processing (Table 13.3). Conversely, some of the antioxidants present in Table 13.3 have been shown to act synergistically, creating higher antioxidant activity in combination, particularly the pairing of cyanidin-3-rutinoside and isorhamnetin-3-rutinoside [33].

## 13.6 Health benefits

### 13.6.1 Inflammation

Cherries are a good source of antioxidants, many of which could influence the immune system. The immune system includes the production of pro-inflammatory cytokines such as interleukin (IL)-1, IL-6, and tumor necrosis factor (TNF) $\alpha$  that result in oxidative stress leading to tissue damage and pain. Antioxidants can influence the production of the cytokines, mediate the oxidative stress through the scavenging of free radicals and enhance endogenous antioxidant systems that help in tissue repair and recovery [38]. Natural antioxidants have been studied using the inhibition of the cyclooxygenase (COX-I and COX-II) enzymes that result in the production of prostaglandins leading to inflammation. The inhibition of these enzymes is the basis of the reduction of pain and inflammation by such products as ibuprofen.

In a cell system, studying these cyclooxygenase enzymes, Seeram *et al.* [39] found an inhibition of 25% in a COX-I assay and 38% in a COX-II assay using the anthocyanins

from tart cherries. These results were over 50% that of ibuprofen in the COX-I assay and comparable to the results for ibuprofen in the COX-II assay, thus indicating strong anti-inflammatory activity of isolated antioxidants from tart cherries (especially cyanidin). In some cases, the effect was stronger than that of aspirin in a human prostaglandin endoperoxide H synthase-1 (PGHS-1) isozyme assay [31].

In the Zucker obese rat model, Seymour *et al.* [40] found that rats fed a high fat diet in conjunction with whole tart cherry powder (1% weight/weight) for 90 days had a reduced amount of systemic and local inflammation as indicated by lowered levels of plasma and IL-6. Both this study and a previous one [41] on lean rats fed a low fat diet with cherry powder, found an affect on peroxisome proliferator-activated receptors (PPARs) often involved in inflammation.

A number of human trial studies, although of relatively small sample size, have followed these positive studies on anti-inflammatory activity of tart cherries in cellular systems and animal models. Recent studies have focused on exercise recovery using markers associated with inflammation and pain that represent a reduction of the damage caused by the inflammatory response after myofibril initial damage and the resulting oxidative stress. Three human studies have used a tart cherry juice blend with anthocyanin contents that can be extrapolated to dried cherry use. The drink was pasteurized and contained approximately 690 mg phenolics (gallic acid equivalents) and 46 mg anthocyanins (cyanidin-3-glucoside) consumed twice per day. For the same amount of phenolics, about three-fourth cup of unsweetened dried tart cherries (according to Table 13.3) would be required.

When long distance runners ( $n = 54$ ) ingested the cherry blended drink for 7 days before and during running, there was a significant reduction in the pain associated on the day of the race. Results were assessed using a visual analog scale of pain intensity [42]. Howatson *et al.* [43], using the same amount of juice blend product, found marathon runners ( $n = 20$ ) that consumed the cherry blend had significantly lower inflammation [IL-6, C-reactive protein (CRP), uric acid], increased total antioxidants, lower levels of oxidative stress [lipid peroxidation *via* thiobarbituric acid reactive substances (TBARS)] and quicker return of knee muscle strength as compared to the placebo. When healthy older individuals ( $n = 12$ ) consumed the cherry juice blend at a slightly lower dose over 14 days, decreased damage from forearm ischemia/reperfusion was noted as witnessed by the significant difference in integrated plasma F<sub>2</sub>- isoprostanate produced. The area-under-the-curve (AUC) pre-post as compared to the placebo was significantly lower as was the production of urinary oxidized nucleic acids [44]. Another study using a cherry concentrate (270 mg total anthocyanins twice per day for 10 days) with men ( $n = 10$ ) showed an effect on leg muscle exercise recovery after 7 days of consumption [45]. Force recovery was found to be faster, while the total and absolute increase in protein carbonyl activity (a measurement of oxidized proteins) was lower with cherry consumption.

Another potential use of the anti-inflammatory properties of the anthocyanins in tart cherries is for the alleviation of symptoms of inflammatory diseases such as arthritis and gout. He *et al.* [46] found in a rat model of human rheumatoid arthritis that a reduction of the amounts of prostaglandin E2 associated with inflammation following an injury was achieved with the administration of 40 mg/kg of anthocyanins from sour cherries for 28 days. Unfortunately, in humans (weighing 67.5 kg) the amount of anthocyanins would be 2720 mg/day which is close to 40 cups of dried cherries. In a preliminary study of healthy women ( $n = 10$ ), the levels of plasma urate were decreased with a single dose of 280 g of sweet cherries, more than the other fruits tested [47]. High level of urate is important in the

arthritic disease state of gout. A statistically insignificant trend was seen in the decrease of plasma levels of CRP and nitric oxide. In another human feeding study ( $n = 18$ ) using the same amount of sweet cherries for 28 days, there was a reduction of the two inflammatory markers, CRP in serum and nitric oxide in plasma [48]. However, further studies are needed in men (the primary contractors of gout). When these results are evaluated with the above research on inflammatory response and exercise, it appears that cherries have the ability to decrease inflammatory markers that could be significant in arthritis parameters. Larger, more targeted trials in diseased states are still needed.

### 13.6.2 Melatonin and sleep

Melatonin is a potent free radical scavenger and antioxidant produced in some plants as well as by the vertebrate pineal gland. It is most known for its potential use in improving sleep patterns, but other adjuvant uses have been analyzed [49]. Burkhardt *et al.* [50] has documented the amounts of melatonin in Montmorency and Balaton tart cherries to be in the order of 1350 and 200 ng/100 g of fresh cherry tissue, respectively. This was considered higher than sweet cherries (0–22.4 ng/100 g fresh weight [51]) and other fruits (13–29 ng/100 g for strawberries and pomegranates) as well as selected grains (87–187 ng/100 g) [52]. Although Kirakosyan *et al.* [32] described a loss of melatonin upon drying of tart cherries, they did not find this in freeze dried products. As the drying methods continue to improve with technology, the amount of melatonin in the final product should be monitored in order to maximize the presence of this compound.

Specific human trials of melatonin documentation upon cherry consumption are limited. Pigeon *et al.* [53] found in elderly insomniacs ( $n = 15$  in a cross-over design) that upon ingestion of a tart cherry juice blend for 2 weeks, there was a significant reduction of wakefulness after sleep onset as compared to the placebo. Garrido *et al.* [54] found in three age groups of healthy adults ( $n = 18$ , divided into 3) that consuming 27.85 g of a freeze dried sweet cherry product (equivalent to 142 g fresh) twice per day resulted in a significant increase in sleep time and a significant decrease in nocturnal activity across all three groups. The excretion of urinary 6-sulfatoxymelatonin also increased significantly in all groups. Further studies using cherries in human clinical trials are needed.

### 13.6.3 Cancer

Not only do cherries have a high level of antioxidants, but the antioxidants present include some that have been studied for their anti-cancer potential, including quercetin, anthocyanins, polyphenols, carotenoids, melatonin, and vitamin C. Oxidative stress is responsible for DNA damage leading to cancer initiation, while antioxidants have the potential to scavenge free radicals and support endogenous antioxidant systems to decrease the oxidative stress load.

Inclusion of cherry in the diet of mice induced with lipopolysaccharide (LPS) resulted in an apparent modulation of liver nuclear factor kappa B (NF- $\kappa$ B) production. NF- $\kappa$ B is important in the transcription of DNA [55]. In mice already with cancerous growths, Bobe *et al.* [56] found a decrease in intestinal tumorigenesis when anthocyanin rich extracts of tart cherry were fed to them. This study showed that when this extract was used in combination with an anti-inflammatory drug (sulindac), much lower doses of the drug could be used to reduce tumor amounts in the intestine. Kang *et al.* [57] in a study on mice and colorectal

cancer found those given a cherry diet, anthocyanins or cyanidin had fewer cecal tumors than those on sulindac or a control diet.

These animal model studies followed cancer cell line studies showing protective effects of cyanidin glucosides on improving apoptotic growth cycle arrest [58], protecting DNA cleavage, increasing levels of free radical scavenging, and inhibition of xanthine oxidase [59]. Cyanidin has been shown to increase cellular differentiation and decrease malignant transformation [60] as well as inhibit epidermal growth factor receptor [61]. Cherry anthocyanins caused cell cycle arrest and apoptosis in mutated cells [62, 63] and decreased growth in stomach and colon cancer cells [64]. Yoo *et al.* [65] found in Chinese hamster lung fibroblast cells that both cherry juice as well as individual phenolic cherry components reduced oxidative stress. In this study, cyanidin 3-glucoside was a stronger antioxidant than cyanidin 3-rutinoside.

Often antioxidants can work through synergistic mechanisms demonstrating the importance of the whole plant product rather than its individual chemical components. The antioxidant components in cherries, for example, have been shown to act synergistically [33]. The importance of whole foods is illustrated in the relation of diet and cancer [66] and the protection of DNA *via* the proportion of fruit and vegetables in the Mediterranean diet [67]. Anthocyanins have multifaceted pharmacological activities [68] just as quercetin has cancer pro-apoptotic effects [69], and dietary polyphenols have been reviewed for their anti-cancer properties *via* apoptosis [70]. Melatonin also has many mechanisms related to anti-tumor growth including immune, antioxidant, telomerase, and cell differentiation activity [71]. Given the above research in animal and cell models, human clinical trials with cherries, as with other high antioxidant foods and herbs, are now needed to directly link cherries with chemopreventive effects. In the interest of dried cherries, the aforementioned antioxidant components need to be documented in any product to extrapolate the research to the consumed product as well as the method of drying needs to ensure retention of the maximum amount of these antioxidant components.

### **13.6.4 Cardiovascular disease**

CVD by definition is a group of disorders associated with the heart and blood vessels with risk factors including obesity, high blood pressure, and high cholesterol. The risk of cardiovascular events (such as stroke or heart attack) is often related to the blockage of blood vessels with fatty deposits and associated with high levels of cholesterol and inflammatory markers [72]. As the Mediterranean diet's increase in fruits and vegetables is linked to lower levels of CVD [15], dried fruit consumption has also been linked to reduced rates of obesity [5]. Cherries are high in flavonoids which in general have been linked to lower rates of coronary heart disease (CHD) through the Zutphen Elderly Study [73]. Anthocyanins, one type of flavonoids in cherries, have been described as having cardiovascular effects through angiotensin-converting enzyme (ACE) and protein kinase B/endothelial nitric oxide synthase (Akt/eNOS) pathways (responsible for endothelial effects on blood vessel dilation) as well as vascular cell adhesion molecules [68]. Anthocyanins from some plant extracts have been shown to have vasoactive relaxation effects on excised porcine heart arteries [74].

Studies specific to cherry effects on CVD have focused on the effect of certain cherry anthocyanins on oxidative stress, arterial endothelial and foam cells, vascular inflammation, and ischemic injury to the heart. Bovine arterial endothelial cells exposed to cyanidin-3-glycoside increased nitric oxide production illustrating a potential ability to

decrease oxidant stress to the cardiac tissue [75]. In rat hearts with ischemic injury (and therefore irregular heartbeats), tart cherry seed extracts were found to decrease the incidence of irregular heartbeats and heart damage [76]. Cyanidin-3-O-glucoside was found to alter blood lipids in rats by modifying the level of vitamin E [77] and in mice cells to remove cholesterol from macrophage and foam cells [78]. In the Seymour *et al.* [40] study on fat Zucker rats, a tart cherry powder added to the diet resulted in lowered hyperlipidemia, decreased fat mass, lowered plasma expression of IL-6 and TNF $\alpha$ , and an increase in inflammation related peroxisome proliferation-activated receptor (PPAR) mRNA. Studies are now needed in human clinical trials to see if cherries have the same effect of lowering human lipid and inflammation parameters associated with CVD and risk. The use of dried cherries would depend on the level of associated anthocyanins proven in *in vitro* and animal models to have affected these parameters.

### 13.6.5 Diabetes

Metabolic syndrome is a group of risk factors that can lead to CVD and diabetes. Diagnosis focuses on central obesity and insulin resistance with three or more measurements of high fasting glucose, high blood pressure, large waist circumference, low low-density lipoprotein (LDL) cholesterol or high triacylglycerols (TAG). These health parameters encompass the health issues discussed above such that this section on diabetes also relies on the research on anthocyanins and cherries in the above sections on inflammation and CVD. In addition, recent research is linking many parameters of cancer and diabetes [79].

Oxidative stress is linked to many of the symptoms and complications of diabetes and as such the use of plant products high in antioxidants has the potential to ameliorate these symptoms [80, 81]. Jayaprakasam *et al.* [82] found in a cell culture study, as well as a mouse study [83], that anthocyanins and anthocyanidins from *Cornus* cherry fruit enhanced insulin production and improved glucose levels. The greater activity on insulin production was dependent on the number of hydroxyl groups on the B ring of the anthocyanins tested. In addition, Tsuda *et al.* [84] found that mice fed cyanidin 3-O- $\beta$ -D-glucoside rich color with their high fat diet for 12 weeks reduced their level of adipose accumulation and normalized hyperglycemic and hyperinsulinemia levels.

In specific animal models associated with diabetes, Seymour *et al.* [40] used the Zucker rat, an animal model of obesity often used in studies of type 2 diabetes, to show that dried tart cherry powder in their diet lowered fat mass, hyperlipidemia, and markers of inflammation. In reducing these parameters of metabolic syndrome, it was concluded that this could influence the onset of diabetes. In their studies in 2008, they used the lean Dahl salt-sensitive rat that has insulin resistance and hyperlipidemia. After similar feeding for 90 days, there was a decrease in fasting blood glucose and hyperinsulinemia, two factors important in diabetes.

Dried cherries often have added sugar which can be detrimental to diabetics. Cherries were initially documented as having a low GI of 22, but dried tart Montmorency cherries have recently been documented at a value of 58. More data are needed on the particular dried cherry product and the amount of sugar present. Jenkins *et al.* [85] found that low GI fruit consumption can reduce HbA1c levels (a measure of blood glucose representative of the past 8–12 weeks). In dried cranberry products, it was found that those with less sugar had significantly improved glycemic and plasma insulin response levels upon consumption [86]. In addition, as seen in Table 13.3, the phenolic and anthocyanin levels can be increased with less sugar in a dried cherry product.

## 13.7 Conclusions

Dried cherries have been found to be a good source of plant protein, fiber, vitamin A, and potassium, and the level of antioxidant phenolics and derivatives of anthocyanin and cyanidin rank it high in antioxidant foods. Lowered rates of local and systemic inflammation have been documented in cell and rat models, and in small studies on humans consuming tart cherry products. A couple of human pilot trials have also shown an effect of melatonin in tart cherries on sleep patterns. With regard to cancer, cell system studies have documented an improvement using cherry anthocyanins and cherry extracts added to the diet in animal models which were able to reduce the amount of anti-cancer drugs needed. The flavonoids and anthocyanins of cherries have been shown, in experimental systems, to lower the oxidative stress, blood lipids, and heart arrhythmias detrimental in cardiovascular and diabetes disease pathogenesis.

Most of the research presented here relates to dried cherries through the amounts of anthocyanins and use of tart cherry products (chiefly juice blends and dried powder). Improved methods of drying could cause some of the individual anthocyanin levels, as well as vitamin C and melatonin, to increase. Just as the method of drying could improve antioxidant levels (and thereby health parameters), a reduction in the sugar added to a dried cherry product may also improve antioxidant levels and health promotion. Further research is needed specifically using dried cherries over other forms of cherries as well as studies in human clinical trials over cell and animal systems. With designing human clinical trials, researchers must take into account the need for bioavailability measures to assess absorption, function, and synergistic action of antioxidant metabolites [87]. Extrapolation of the results presented here to dried cherries often relies on the amounts of phenolics and anthocyanins present in the product as well as in the blood stream and tissues of consumers.

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## **14 Dried citrus fruits: phytochemicals and health beneficial effects**

Tzou-Chi Huang and Chi-Tang Ho

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### **14.1 Introduction**

Citrus fruits make up the largest sector of the world's fruit production. Their worldwide production is over  $88 \times 10^6$  tonnes and one-third of the crop is processed. Oranges, lemons, grapefruits, and mandarins represent approximately 98% of the entire industrialized crop; among them oranges occupy approximately 82% of the total. In addition to fresh consumption, majority of citrus fruits are processed to obtain juice [1]. Part of the citrus wastes, including peels, seeds, and fruit pulp, remaining after juice extraction, are subjected to the extraction of flavonoids and essential oils [2]. Different from that of Western world, whole immature and mature citrus fruits and peels are dried, and widely used as remedies to stimulate the appetite, aid digestion, improve menopausal syndromes, alleviate cough, and improve inflammatory syndromes of the respiratory tract such as bronchitis and asthma in oriental countries [3].

According to the morphological system established by Tanaka [4], citrus genus is classified into two subgenera (*Archicitrus* and *Metacitrus*), 8 sections (*Papeda*, *Limonellus*, *Citrophorum*, *Cephacitrus*, *Aurantium*, *Osmocitrus*, *Acrmen*, and *Pseudo Fortunella*) and 16 subsections, involving 149 species. Citrus is a common term and genus of flowering plants in the family *Rutaceae*. Commercially important citrus fruits include oranges, grapefruits, lemons, some limes, and some tangerines. The name "orange" applies primarily to *Citrus sinensis*, which accounts for about 70% of world citrus production. Other citrus species known as oranges include:

- (1) *C. reticulata*, which itself has an enormous number of cultivars (most notably the satsuma (*C. unshiu*), tangerine (*C. tangerina*), and clementine (*C. clementina*)),
- (2) *C. bergamia* Risso, which is grown primarily in Italy and used primarily for the peel, and
- (3) *C. aurantium*, also known as Seville orange, sour orange, bitter orange, bigarade orange, and marmalade orange.

*C. limon* (L.) Burm.f. (Rutaceae) is an important fruit and medicinal plant. Lemon peel is utilized as a stomachic, carminative, diaphoretic, astringent, febrifuge, and diuretic agent in the traditional Indian medicine [5]. California and Arizona are the leading sources of lemons in the Western hemisphere. In recent years, grapefruit has received much attention because of its nutritional and antioxidant properties. It is cultivated principally to obtain the juice with high concentration of naringin. The beneficial effects of the grapefruit juice on human health, such as antioxidant, antiallergic, and anticarcinogenic benefits as well as protection against high blood pressure or cholesterol increase have been reported by Kawaii *et al.* [6]. Although grapefruit peels are the major sources of natural naringin, hesperidin, and other flavonoids, they are currently generally treated as waste by the juice producing industry [7]. This chapter outlines the phytochemicals and health beneficial effects of citrus fruits such as oranges, tangerines, grapefruits, lemons, and limes.

## **14.2 Compositional and nutritional characteristics of citrus**

### **14.2.1 Structure of citrus fruit**

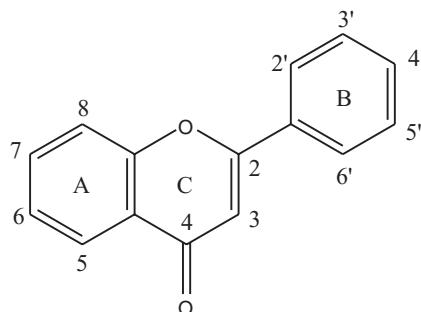
Citrus fruits consist of an epicuticular wax layer. Immediately under epidermis is located the flavedo characterized by a green, yellow, or orange color. Oil glands are interspersed around the flavedo layer and characterized by very thin and fragile walls. Beneath flavedo is the albedo that is composed of loosely packed, many branched, tube-like cells that form a continuous network with the greatest part of tissue volume. Albedo is the major source of citrus phytochemicals which impart a bitter taste to the juice and the health beneficial effects to human body. The edible part of the fruit with segments membrane containing juice sacs is the endocarp.

### **14.2.2 Nutritional characteristics of citrus fruits**

Citrus fruits are the principal source of various important nutrients. They contain vitamin C, folate, dietary fiber, and a number of physiologically functional components such as citric acid, minerals, and phytochemicals which are regarded as chemopreventive agents for various diseases [8]. Citrus soluble solids are on the average made up by a 70% of sugars, whilst pulp solids are made by a 40% of sugars, and by a 50% of polysaccharides. Citrus polysaccharides are mainly pectic acid (polygalacturonic acid). Commercial pectin is mostly derived from citrus peels including lime, grapefruit, and orange [9]. High dietary fiber powder preparations from citrus fruits contain pectin as their major constituent and are thus considered as having a better quality than other sources of dietary fiber due to the presence of associated bioactive compounds which may exert additional health promoting effects than the dietary fiber itself [10].

## **14.3 Phytochemicals in citrus**

At least five types of flavonoids (flavanones, flavones, polymethoxyflavones, flavonols, and anthocyanins) occur in citrus, and more than 60 individual flavonoids have been



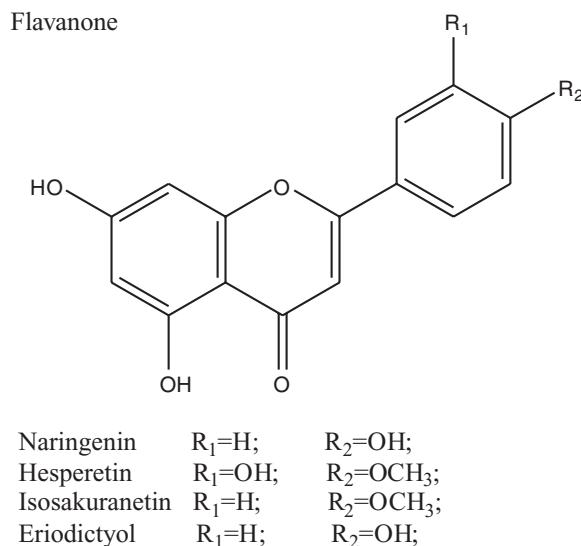
**Figure 14.1** The generic structure of flavonoids.

identified. The major flavonoids in orange peel are flavanone glycosides (narirutin 4'-*O*-glucoside, eriocitrin, narirutin, hesperidin, and isosakuranetin rutinoside) [11], flavone glycosides (diosmin, isorhoifolin, and rutin) [12], and C-glycosylated flavones (6,8-di-*C*-glucosylapigenin) [13]. Anthocyanins [cyanidin 3-glucoside and cyanidin 3-(6''-malonylglucoside)] occur only in blood oranges, whereas polymethoxyflavone (PMF) (sinensetin, hexa-*O*-methylquercetagettin, nobiletin, hexa-*O*-methylgossypetin, 3,5,6,7,8,3',4'-heptamethoxyflavone, tetra-*O*-methylscutellarein, tangeritin, and 5-hydroxy-3,7,8,3',4'-pentamethoxyflavone) distributed widely in citrus peels [14]. The highly methoxylated flavones exhibit higher biological activity even though they occur in relatively lower concentrations. Citrus flavonoids characterized with the various combinations of multiple hydroxy, methoxy, and *O*-glycoside group substituents on the basic benzo- $\gamma$ -pyrone (C6-C3-C6) as shown in Figure 14.1.

### 14.3.1 Flavanones

Flavanones are the most abundant flavonoids (e.g., 98% in grapefruits, 96% in limes, and 90% in lemons) in citrus [15]. The flavanones in citrus leaves, peels, and fruits are found mainly in glycosylated states. Flavanone glycosides including eriocitrin (eriodictyol 7-*O*-rutinoside), neoeriocitrin (eriodictyol 7-*O*-neohesperidoside), homoeriodictyol 7-*O*-rutinoside, hesperidin (hesperetin 7-*O*-rutinoside), neohesperidin (hesperetin 7-*O*-neohesperidoside), narirutin (naringenin 7-*O*-rutinoside), naringin (Naringenin 7-*O*-neohesperidoside), poncirin (Isosakuranetin 7-*O*-neohesperidoside), and neoponcirin (didymin, isosakuranetin 7-*O*-putinoside) have been identified in citrus fruits [16, 17]. The structures of major flavanone aglycones (naringenin, hesperetin, isosakuranetin, and eriodictyol) are shown in Figure 14.2.

The glycoside flavanone hesperidin is present predominately in the peels of orange (*Citrus sinensis*) and lemon (*Citrus limonium*) [18]. Hesperidin is the primary flavanone glycoside in Valencia, Navel, Temple, and Amber sweet oranges [19], whereas naringin is the dominant flavonoid in grapefruits (*Citrus paradisi*) [18]. Hesperidin accounts for more than 92% of the total flavanone glycosides in the peel extracts of lemon. In *C. reticulata* Blanco fruits, the highest flavanone glycoside contents were found in young fruits and hesperidin represented 49% of the dry weight (DW) of the fruit [20]. Wang *et al.* [21] characterized several rutinosides and neohesperosides of naringenin, eriodictyol, and hesperetin from a less commercialized *C.*



**Figure 14.2** Structures of citrus flavanone aglycone.

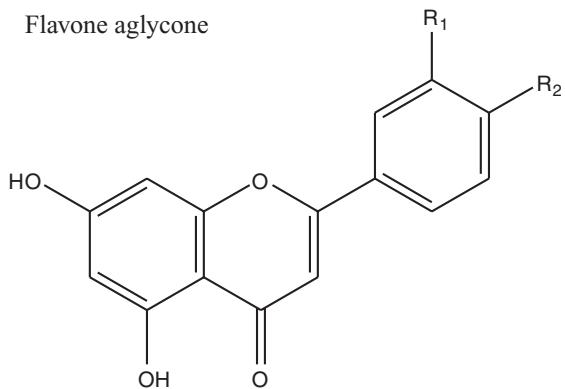
*bergamia* Risso. Among the neohesperidoside flavanones, including naringin, neohesperidin, and neoeriocitrin, are the most dominant flavonoid found in bergamot, grapefruit, and bitter orange juices, whereas rutinoside flavanones, such as hesperidin, narirutin, and didymin dominated in bergamot, orange, mandarin, and lemon juices [22].

On the other hand, naringin was the most abundant flavanone glycoside (92% of the total flavanone glycosides) in grapefruit peel and narirutin was the major flavanone glycoside in murcott [23]. Vanamala *et al.* [24] reported that naringin, narirutin, and poncirus were the major flavanone glycosides in grapefruits with concentrations of 30.4, 10.1, and 1.24 mg/100 mL of juice, respectively. Naringin was mainly found in lemon peel and seed as well as in mandarin seed, but not in the juices of these fruits [25].

Eriocitrin is particularly abundant in lemons and limes, while they are almost absent in other citrus fruits [26]. Lemon seeds contain large amounts of eriocitrin and hesperidin and a low level of naringin. On the contrary, the lemon peel is rich in neoeriocitrin, neohesperidin, and naringin and has a minor amount of narirutin [27].

### 14.3.2 Flavones

The flavones in citrus occur mainly in glycosylated states. Flavone glycosides including diosmin (diosmetin-7-*O*-rutinoside), neodiosmin (diosmetin-7-*O*-neohesperidoside), diosmetin 6,8-di-*C*-β-glucoside, diosmetin-6-*C*-β-glucoside, diosmetin-8-*C*-β-glucoside, vicenin-2 (apigenin 6,8-di-*C*-glucoside), apigenin-7-(malonylapiosyl)-glucoside, isorhoifolin (apigenin-7-*O*-rutinoside), rhoifolin (apigenin-7-*O*-neohesperidoside), lucenin-2 (luteolin 6,8-di-*C*-glucoside), luteolin 7-*O*-rutinoside, scoparin (chrysoeriol 8-*C*-glucoside), and stellarin-2 (chrysoeriol 6,8-di-*C*-glucoside), have been characterized [16, 28]. Figure 14.3 shows the structures of major flavones aglycones such as apigenin, luteolin, diosmetin, chrysoeriol, and chrysins.



Apigenin	$\text{R}_1=\text{H};$	$\text{R}_2=\text{OH};$
Luteolin	$\text{R}_1=\text{OH};$	$\text{R}_2=\text{OH};$
Diosmetin	$\text{R}_1=\text{H};$	$\text{R}_2=\text{OCH}_3;$
Chrysoeriol	$\text{R}_1=\text{OH};$	$\text{R}_2=\text{OCH}_3;$
Chrysin	$\text{R}_1=\text{H};$	$\text{R}_2=\text{H};$

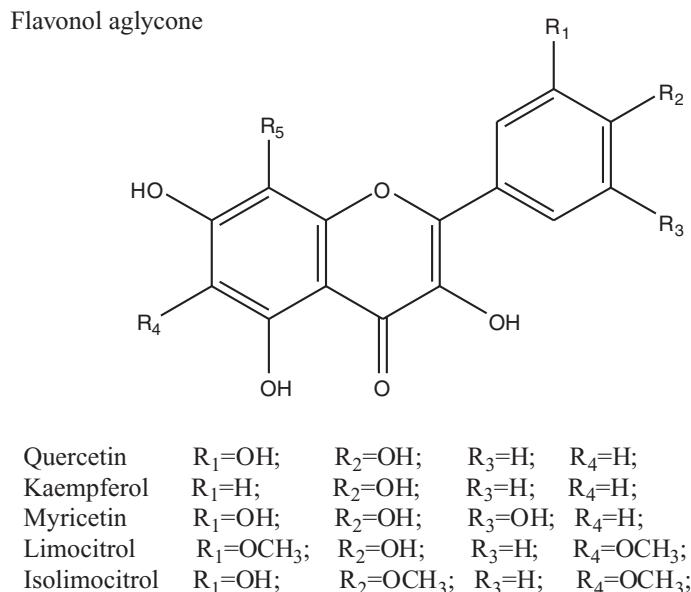
**Figure 14.3** Structures of citrus flavone aglycone.

Caristi *et al.* [29] reported that orange juice serves as a rich source of 6,8-di-*C*-glucopyranosylapigenin while lemon juice shows an abundance of 6,8-di-*C*-glucopyranosyldiosmetin. They found a 6,8-di-*C*-glucopyranosylapigenin content in the range of 70–76 mg/L in the commercially available Italian orange juices. Apigenin was identified in flower, leaf, and fruit (mesocarp and endocarp) extracts of *C. medica* cv Diamante, with values ranging from 941 mg/kg for flowers to 58 mg/kg for mature fruits endocarp in fresh weight (FW). Besides apigenin, quercetin (580.8 mg/kg) and diosmin (372.5 mg/kg) were also found in significant quantities in extracts of *C. medica* cv Diamante [30]. Recently, a new C-glycosyl flavonoid, lucenin-2, was identified in sour orange (*C. aurantium* L.) juice [28].

Diosmin is the major flavone in navel orange, bergamot, and lemon peels. Lemon peels contain three most abundant flavones: diosmetin 6,8-di-*C*-glucoside, vicienin-2, and diosmin [31]. Miyake *et al.* [32] isolated two C-glucosylflavones from the peel of lemon fruits: diosmetin 6,8-di-*C*-glucoside and diosmetin 6-*C*-d-glucoside. These flavones are also present in limes, but not in other citrus fruits. Recently, a new flavonoid possessing strong antioxidant activity [33] was characterized. The major isolated compound from *C. unshiu* peel was quercetagetin (3,5,6,7,3',4'-hexahydroxyflavone).

### 14.3.3 Flavonols

Flavonols, including rutin (quercetin 3-*O*-rutinoside), isolimocitrol 3- $\beta$ -D-glucoside, and limocitrin-3- $\beta$ -D-glucoside, have been identified [16] in citrus. Dugo *et al.* [34] reported that rutin and myrecetin were the most abundant flavonols identified in lemon juice, while quercetin and kaempferol were present in both peel and juice. Isolimocitrol 3- $\beta$ -D-glucoside,



**Figure 14.4** Structures of citrus flavonol aglycones.

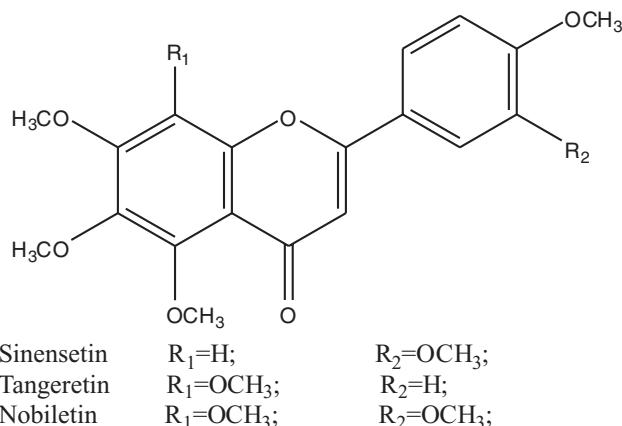
limocitrin 3- $\beta$ -D-glucoside, and limocitrol were identified as polymethoxylated flavonols, in citrus peels. Figure 14.4 shows the structures of major citrus flavonol aglycones such as quercetin, kaempferol, myricetin, limocitrol, and isolimocitrol.

#### 14.3.4 Polymethoxyflavones

Among the well-known citrus bioactive compounds, PMFs exist in citrus peel deserve special interest for their various biological activities [35]. These polymethoxylated flavones are scutellarein (5,6,7,4'-tetramethoxyflavone), sinensetin (5,6,7,3',4'-pentamethoxyflavone), tangeretin (5,6,7,8,4'-pentamethoxyflavone), quercetagetin (3,5,6,7,3',4'-hexamethoxyflavone), nobiletin (5,6,7,8,3',4'-hexamethoxyflavone), 3,5,6,7,8,3',4'-heptamethoxyflavone, 7-hydroxy-3,5,6,3',4'-pentamethoxyflavone, and 7-hydroxy-3,5,6,8,3',4'-hexamethoxyflavone [16, 36]. Nogata *et al.* [37] reported that nobiletin was the most abundant, while sinensetin was the least abundant of the PMFs. Figure 14.5 shows the structures of citrus PMFs (such as sinensetin, tangeretin, and nobiletin).

Recent studies attributed the beneficial function of chen-pi (dried orange peel) to the PMFs present in the orange peels [38]. Dancy tangerine (*C. tangerina*) and Ponkan, the two most widely used citrus species for the production of chen-pi in Chinese medicine, have the highest amounts of PMFs among citrus species. The typical quantities and distribution of PMFs in the extract of Ponkan peel were found to be in the range of between 6.41 and 12.8 mg/g solid extract. Nogata *et al* [39] analyzed the citrus PMFs in the dried edible parts of fruits. They found that the concentration of tangeretin (9.1 mg/100 g) in Ponkan was highest and that of nobiletin (12.8 mg/100 g) second highest among the 66 citrus species investigated. The level of sinensetin in the peel of Ponkan was determined as 6.6 mg/100 g.

## Polymethoxyflavones



**Figure 14.5** Structures of citrus polymethoxyflavones.

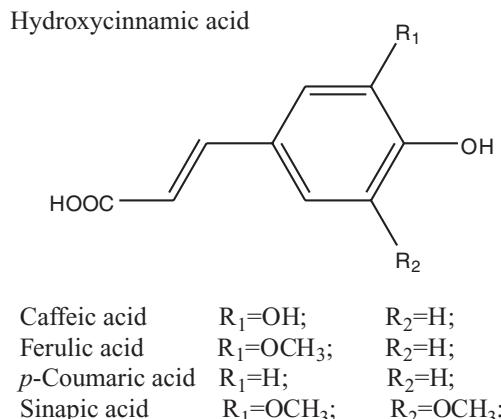
However, the relative non-polar PMFs may also appear in the juice products. The contents of hand-press Ponkan (*C. reticulata*) juice were estimated to be nobletin (3.56 mg/100 mL), tangeretin (4.10 mg/100 mL), and sinensetin (0.13 mg/100 mL), respectively [39]. Concentrations of PMFs (tangeretin, nobletin, and sinensetin) in hand-press Ponkan (*C. reticulata*) juice were found to be the highest among the three juices processed by in-line, chopper pulper, and hand-press extractions, respectively. Obviously, the destruction of peel structure leads to the accumulation of PMFs in juice although the level is relatively lower as compared with that in citrus peel.

### 14.3.5 Hydroxycinnamic acids

Although the main phenolic constituents of citrus peel are flavanone and flavone glycosides, some hydroxycinnamates at relatively low levels were also characterized. Most of the hydroxycinnamates in citrus occur as alkaline hydrolyzable esters [40]. The hydroxycinnamic acids identified were caffeic, ferulic, *p*-coumaric, and sinapinic acids as shown in Figure 14.6 [41]. Manthey and Grohmann [13] reported that the levels of lemon hydroxycinnamic acids were much higher in the peel than in the juice. Unlike other citrus varieties, the main hydroxycinnamic acid resulting after alkaline hydrolysis of lemon molasses was *p*-coumaric acid. In addition, some benzoic acids such as protocatechuic, *p*-hydroxybenzoic, and vanillic acids have also been identified in several citrus varieties cultivated in China [42]. Interestingly, two glycosides of phenolic acid, such as 1-feruloyl- $\beta$ -D-glucopyranoside and 1-sinapoyl- $\beta$ -D-glucopyranoside, were identified in lemon juice by Miyake *et al.* [43].

### 14.3.6 Limonoids

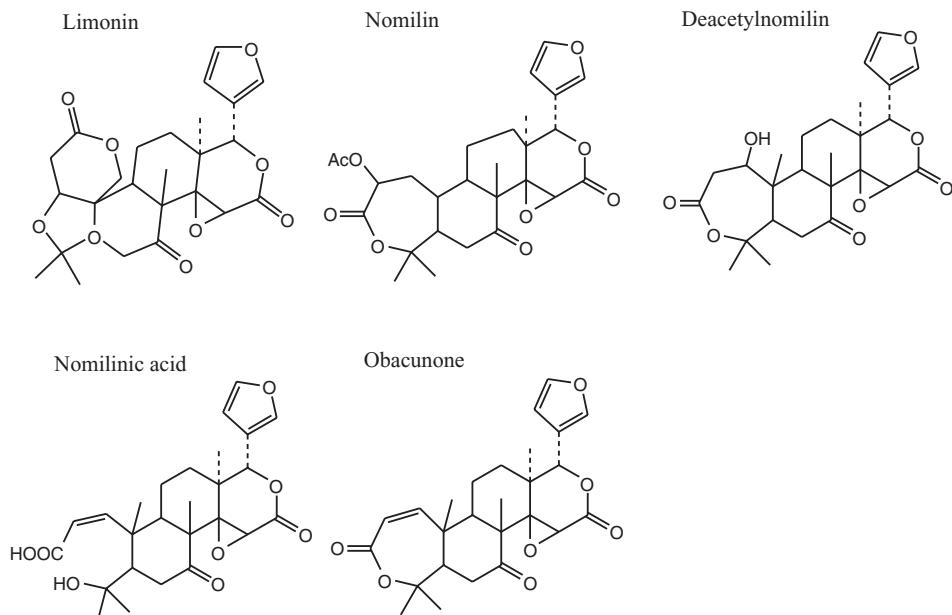
At least 39 limonoid aglycones and 21 glucosides have been isolated and characterized from citrus plants [44]. Five most found limonoid glucosides (limonin, nomilin, deacetylnomilin, nomilinic acid, and obacunone) (structures shown in Figure 14.7) have been identified from



**Figure 14.6** Structures of citrus hydroxycinnamic acids.

the tissues of members of the genus Citrus and related genera in the plant family Rutaceae [45]. Total limonoid glucosides can exceed 300 mg/kg in citrus fruit and exceed 500 mg/kg in citrus peel [46]. In citrus juices, limonin glucoside is present in about twice the amount of the other limonoid glucosides combined [47]. In citrus seeds, nomilin glucoside occurs in higher concentration than limonin glucoside [48].

Among the limonoid aglycones, limonin, and nomilin are most prevalent in citrus [49]. Sun *et al.* [50] investigated the limonin and nomilin contents in the tissues of flavedo, albedo,

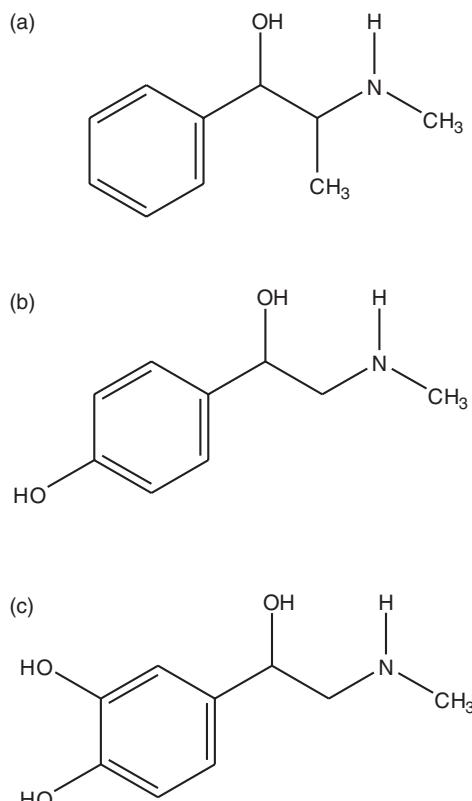


**Figure 14.7** Structures of citrus limonin, nomilin, deacetylnomilin, nomilinic acid, and obacunone.

segment membrane, and juice vesicles of four citrus cultivars, including *C. grandis*, *C. unshiu*, *C. reticulata*, and *C. changshanensis* cultivated in China. In albedo of *C. changshanensis*, they found limonin and nomilin contents of 0.578 and 0.635 mg/g DW and in segment membrane of *C. changshanensis* 3.52 and 2.94 mg/g DW, respectively.

### 14.3.7 Adrenergic amines

Adrenergic amines have been identified and quantified in citrus members of the Rutaceae family for weight management. At least, five adrenergic proto alkaloids including tyramine, *N*-methyltyramine, octopamine, hordenine, and synephrine in *C. aurantium* have been characterized [51]. Synephrine can potentially exist in three different structural or positional isomeric forms (para-*p*, meta-*m*, or ortho-*o*) [52]. Andrade *et al.* [53] reported that only *p*-synephrine can be found in *C. aurantium* fruits. Among the identified adrenergic proto alkaloids, *p*-synephrine has attracted much attention due to its lipolytic and thermogenic effects. Its chemical structure is similar to ephedrine in ephedra, aka, and ma-huang. Figure 14.8 shows the structures of adrenergic amines (ephedrine, *p*-synephrine, and epinephrine) in citrus.



**Figure 14.8** Structures of adrenergic amines (a: Ephedrine, b: *p*-synephrine, and c: Epinephrine).

The concentrations of *p*-synephrine in citrus were in the range of 0.001–0.3% in fruits from China [54], Japan [54], Italy [55], United States [56], and Brazil [57]. Mattoli *et al.* [56] analyzed the *p*-synephrine content of *C. aurantium* cultivated in Italy and reported that a high content of *p*-synephrine was found in tarocco orange freshly squeezed juice (26.65–33.22 µg/g) and in commercial red orange juices (29.9–32.07 µg/g). Recently, Arbo *et al.* [57] reported that the peel of *C. aurantium* contained a higher amount of *p*-synephrine than that in the pulp or albedo. The mean *p*-synephrine concentration in Seville orange juice samples was determined to be 56.9 µg/mL. They also compared the concentration of *p*-synephrine in unripe fruits and leaves from *C. aurantium* Lin, *C. sinensis* Osbeck, *C. deliciosa* Ten., *C. limon* Burm, and *C. limonia* Osbeck, collected in Southern Brazil. They found that both the *C. deliciosa* fruits and the leaves contained a higher concentration of *p*-synephrine than that in other citrus species.

## 14.4 Health effects of dried citrus peels

The health-related properties of phytochemicals in citrus are discussed in this section. The beneficial health effects of citrus flavonoids include antimicrobial, antiviral, antioxidant, anti-inflammatory, anti-allergic, hyperglycemic, antiproliferative, and cholesterol-lowering properties, and effects on capillary fragility and an ability to inhibit human platelet aggregation.

### 14.4.1 Antimicrobial activity

Natural phytochemical compounds, including phenolics and terpenoids, have been widely used as novel preservatives in the food industry. Apigenin has antibacterial activity over some Gram negative bacterial strains including *Enterobacter cloacae*, *Enterobacter aerogenes*, and *Pseudomonas aeruginosa* [58]. Quercetin also had antibacterial activity against *Bacillus cereus*, *Salmonella enteriditis*, *Listeria monocytogenes*, and *Pseudomonas putida* [59, 60]. Flavonoids, ponciretin, hesperetin, naringenin, and diosmetin extracted from citrus peels were active against *Helicobacter pylori* [63]. Rauha *et al.* [61] reported that naringenin exhibited strong activity against several bacteria including *Bacillus subtilis*, *Escherichia coli*, *Micrococcus luteus*, *Pseudomonas aeruginosa*, *Saccharomyces cerevisiae*, *Staphylococcus aureus*, and *Staphylococcus epidermidis*. Recently, the ethanolic fractions of Bergamot were tested against Gram-negative bacteria (*Escherichia coli*, *Pseudomonas putida*, and *Salmonella enterica*), Gram-positive bacteria (*Listeria innocua*, *Bacillus subtilis*, *Staphylococcus aureus*, and *Lactococcus lactis*) and the yeast *Saccharomyces cerevisiae*. Of the aglycones tested, eriodictyol was the most active and inhibited all the bacteria and the yeast *Saccharomyces cerevisiae* and the minimum inhibitory concentration (MIC) values were 200–800 µg/mL. Naringenin was the next most effective compound [62].

### 14.4.2 Antiviral activities

An important structure-activity relationship strongly influences the activity of a flavonoid against viruses. Kaul *et al.* [63] reported that quercetin and hesperetin inhibited the infectivity and/or replication of herpes simplex type, polio, parainfluenza type, and syncytial viruses. They postulated that the formation of quercetin-virus complexes may lead to the loss of the

ability to induce infection. Recent research demonstrates that nobiletin extracted from *C. unshiu* peel possesses anti-hepatitis C virus effect in MOLT-4 cells [64]. The anti-picornoviral activity of the PMF structure was dependent on the 3'-methoxy and the 4'-hydroxy function in the parent flavone structure.

#### 14.4.3 Antioxidant activity

The 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical-scavenging assay has been used to evaluate antioxidant activities of orange, pomelo, and lemon fruits. Ghasemi *et al.* [65] investigated the antioxidant activity of the extracts of 13 commercially available Citrus spp. peels and edible parts. By using DPPH method, they found the antioxidant activity with the half maximal inhibitory concentration ( $IC_{50}$ ) values ranged from 0.6 to 3.8 mg/mL. They attributed the DPPH radical-scavenging activities to the phenolics and flavonoids with contents varied from 66.5 to 396.8 mg gallic acid equivalents (GAE)/g of extract and from 0.3 to 31.1 mg quercetin equivalents (QE)/g of extract, respectively. Lee *et al.* [66] investigated relationship between the total polyphenol and flavonoid content and antioxidant activity of the seeds of *C. junos*. The hull and embryo of seeds were extracted with n-hexane and 70% ethanol. The DPPH radical-scavenging activity of hydroalcoholic extract was higher than that of n-hexane extract with  $IC_{50}$  values of 3.18–8.43 mg/mL. The scavenging effects of the *C. medica* cv Diamante extracts on DPPH were examined at different concentrations. The best DPPH free radical-scavenging activity was exerted by mesocarp of immature fruits ( $IC_{50}$  of 382 lg/mL), followed by flowers and leaves extracts with  $IC_{50}$  values of 425 and 502  $\mu$ g/mL, respectively [67].

#### 14.4.4 Hypoglycemic activity

The hypoglycemic potential of *C. medica* cv Diamante extracts was evaluated by the  $\alpha$ -amylase and  $\alpha$ -glucosidase inhibition assays [68]. It was found that the leaves extract inhibited  $\alpha$ -amylase activity with  $IC_{50}$  value of 438.5  $\mu$ g/mL. Interestingly, extract from endocarp of mature fruits inhibited the  $\alpha$ -amylase with  $IC_{50}$  value 2-fold higher than that of immature fruits. On the contrary, extract from the immature fruits showed a higher inhibition activity against the  $\alpha$ -glucosidase.

#### 14.4.5 Hypolipidemic activity

Accumulated studies indicate that certain citrus flavonoids may have a protective and therapeutic effect in coronary heart disease (CHD). Epidemiological studies show evidence that consumption of citrus fruits is associated with reduced risk of cardiovascular disease (CVD). This cardioprotective effect is thought to be due to the components of citrus phytochemicals. Several studies have shown that flavonoids, limonoids, and PMFs from citrus have cholesterol-lowering properties.

Accumulated clinical data indicate that consumption of citrus juice reduces the risk of CHD in human subjects. The hematological and serum chemical profiles on patients with CHD show significantly higher serum cholesterol. In a clinical experiment [69], sixteen healthy men and nine healthy women with elevated plasma total and low-density lipoprotein (LDL) cholesterol and normal plasma triacylglycerol (TAG) concentrations received

250 mL of orange juice sequentially in their diets over a period of 4 weeks. They reported that orange juice consumption significantly increased high-density lipoprotein (HDL) cholesterol by 21% and reduced the LDL/HDL cholesterol ratio by 16%. Kurowska *et al.* [69] conducted a similar experiment in which hyperlipidemic patients, aged 39–72 years, after coronary bypass surgery, were served with red grapefruit for 30 consecutive days. Diet supplemented with fresh red grapefruits was found to decrease serum lipid levels of total and LDL cholesterols, especially serum TAG. It was hypothesized that the hypocholesterolemic effects of citrus juices were due to the naringenin in grapefruit juice and hesperetin in orange juice.

Several animal model studies have revealed that citrus flavanone glycosides including hesperidin and naringin render cholesterol-lowering properties [70–73]. After 30 days of different feeding, Gorinstein *et al.* [74] found that diets supplemented with red grapefruit juice improved the plasma lipid levels in rats fed cholesterol and increased the plasma antioxidant activity. Recently, Miceli *et al.* [75] reported that chronic administration of *C. bergamia* (1 mL/rat/day) provoked a significant reduction in total and LDL cholesterols as well as TAG levels and an increase in HDL cholesterol level. Analysis showed that *C. bergamia* juice contained naringin (520 mg/kg), neoeriocitrin (370 mg/kg), and neohesperidin (310 mg/kg).

Systematic studies have been conducted to elucidate the mechanism of hypolipidemic activity of citrus flavanones. Borradaile *et al.* [76] examined the effects of citrus flavanones on the secretion of apolipoprotein B (apo B)-containing lipoproteins in the human hepatoma cell line HepG2. They reported that naringenin and hesperetin dose-dependently reduced the accumulation of apo B in the culture media (76–81% at 200 mM) over 24 hours. Reduced hepatic secretion of apo B-containing lipoproteins would be expected to contribute to a hypocholesterolemic effect of naringenin *in vivo*. Lee *et al.* [77] showed that naringenin lowered the plasma and hepatic cholesterol concentrations by suppressing HMG-CoA reductase (HMGR) and acyl CoA: cholesterol acyltransferase (ACAT) in male rats fed a high-cholesterol diet for 42 days. Borradaile *et al.* [78] indicated that naringenin reduced plasma lipids *in vivo* and inhibited apo B secretion, cholesterol esterification, and TAG transfer protein (MTP), a protein known to be essential for the assembly and hepatic secretion of apo B-containing lipoproteins activity in HepG2 human hepatoma cells. Jung *et al.* [79] attributed the plasma and hepatic cholesterol-lowering effect of hesperidin and naringin to the decreased hepatic 3-hydroxy-3-methylglutaryl-coenzyme (HMG-CoA) reductase and ACAT activities. Both enzymes are reported to regulate the extracellular and intracellular cholesterol metabolism [80].

On the other hand, citrus PMFs, especially tangeretin and nobletin displayed an even stronger potential lowering hepatic very low-density lipoprotein (VLDL), LDL, and total cholesterol than that observed for hesperidin and naringin. Borradaile *et al.* [76] reported that as compared with that of hesperetin, naringenin, and PMFs from tangerines presented a more pronounced reduction of medium apo B in a human liver HepG2 cell line. The IC<sub>50</sub> concentrations for hesperetin, naringenin, and PMFs were 43.0, 48.5, and 2.5 mg/mL, respectively. Kurowska and Manthey [81] found that diets containing 1% PMFs significantly reduced serum total and VLDL + LDL cholesterols by 19–27% and 32–40%, respectively, in hamsters with diet-induced hypercholesterolemia. Recent clinical trials demonstrated that citrus PMF extract (270 mg/d), in combination with palm tocotrienols (30 mg/d), reduced total cholesterol (20–30%), LDL cholesterol (19–27%), apo B (21%), and TAG (24–34%) [82].

### 14.4.6 Thermogenic and lipolytic activities

Traditionally, *C. aurantium* L. extracts were used in Chinese medicine to activate vital energy and circulation, eliminate phlegm, and disperse stagnation [3]. The immature dried fruit of *C. aurantium* has been used for the treatment of chest congestion and to stimulate gastrointestinal functions. The growing interest in sour orange products is due to the fact that they are rich in bioactive synephrine alkaloids [83]. Synephrine is a sympathomimetic amine with structural similarities to ephedra. Commercial synephrine (*C. aurantium* extract) is obtained by extraction from immature fruits of *C. aurantium* L. Recently, products containing sour orange extracts have been exploited for the production of ephedrine-free dietary supplements for weight loss and appetite control.

The biological benefits of *p*-synephrine include thermogenic and lipolytic activities [84], weight management [85], and athletic performance [86] as well as the controversial effects on blood pressure and heart rate have been discussed. Several human clinical studies have indicated that *p*-synephrine exhibits remarkable thermogenic and lipolytic activities [87–89].

### 14.4.7 Antiproliferative activity

#### 14.4.7.1 Antiproliferative effects of citrus flavonones

The antiproliferative activity of fresh fruit juices containing flavanone glycosides was evaluated. All tested citrus juices exhibited evident antiproliferative activities toward the human chronic myelogenous leukemia K562, human leukemia HL-60, and human breast adenocarcinoma MCF-7. By using high performance liquid chromatography (HPLC), the contents of flavanone glycosides of the tested citrus juices was 7.90–53.57 mg/100 mL for fruits including *C. sinensis*, *C. deliciosa* cv. Avana, *C. clementina* cv. Nules, and *C. aurantium* subsp. *Myrtifolia*. They attributed the antiproliferative activity to the presence of citrus flavanones [90].

Hesperidin is the most abundant flavanone glycoside in citrus fruits such as lemons and oranges [91]. Hesperidin has a dose-dependent cytotoxic effect on human colon cancer cells, accompanied by DNA fragmentation and caspase-3 activation [92]. Hesperidin has been reported to inhibit cell cycle progression in human pancreatic cells [93]. It has been shown that hesperidin possesses cancer chemopreventive effect on the 1,2-dimethylhydrazine induced colon carcinogenesis in male Wistar rats [94]. On the other hand, naringenin found in grapefruit was associated with cancer prevention [95].

Menon *et al.* [96] found that naringenin possessed an excellent antitumor potential and antioxidant effect. The decreased levels of the superoxide and hydroxyl radicals in cells were attributed to the free radical scavenging effects of naringenin. Kooststra *et al.* [97] also showed the protective effect of naringenin against UV-induced DNA damage. Due to its antioxidant properties and the ability to absorb UV light, naringenin was expected to act in all stages of the carcinogenic process: damage to the DNA (or initiation step), tumor growth (or promotion step), and invasion (or proliferative step).

In addition to the direct radical scavenging activity, the aglycone of hesperidin was reported to be a promoter of cellular antioxidant defense-related enzyme activities as well [98]. Choi [99] reported that the reduced catalase and total superoxide dismutase (SOD) activity by 7,12-dimethylbenz(a)anthracene (DMBA) were restored with the pretreatment of hesperitin a mice model. Recently, Ekambaram *et al.* [100] indicated that administration of naringenin

to gastric carcinoma-induced rats could have up-regulated the redox status *via* increasing the expression of SOD, catalase (CAT), and glutathione peroxidase (GPx) to decrease the risk of cancer by antioxidant potential.

Glutathione (GSH), a major nonenzymatic antioxidant in conjugation with GPx and glutathione S-transferase (GST), protects cells against cytotoxic and carcinogenic chemicals [101]. Evidence showed that naringenin enhanced glutathione level and GST expression in rats [102]. Hesperetin treatment significantly increased the GSH/oxidized glutathione (GSSG) ratio in the DMBA-treated group in a dose-dependent manner. Gao *et al.* [103] provided another anti-cancer pathway for citrus flavonoids. They reported that an increased dietary intake of naringenin induced DNA repair enzyme expression in a hormone-responsive human prostate cancer cell line (LNCaP).

#### **14.4.7.2 Antiproliferative effects of citrus flavones and flavonols**

Many studies have revealed that apigenin exhibited cytotoxicity *in vitro* to human cell lines, including those of colon cancer [104], hepatoma [105], prostate carcinoma [106], and human cervical carcinoma [107]. Other reports indicated that luteolin exhibited cytotoxicity to colon cancer [108] and human cervical carcinoma cells [109]. For flavonol, quercetin was found to show apoptotic effect on both hepatoma [110] and prostate carcinoma cells [111]. A number of reports in different cell lines, animal models and human epidemiological trials have pointed out an association between intake of citrus flavones and flavonols and reduced risk of cancer [112, 113].

Zhang *et al.* [114] studied the molecular mechanisms responsible for the cytotoxic effects of citrus flavones and flavonols and showed that both were able to induce cytotoxicity in KYSE-510 cells in a dose- and time-dependent manner. Their cytotoxic potency was in the order of: luteolin > quercetin > chrysanthemum > kaempferol > apigenin > myricetin. They indicated that all the tested citrus flavonoids caused G2/M arrest through up-regulation of p21waf1 and down-regulation of cyclin B1 at the mRNA and protein levels.

#### **14.4.7.3 Antiproliferative effects of citrus polymethoxylated flavones**

Manthey and Guthrie [115] have shown that PMFs exhibited a higher antiproliferative activity than other citrus flavonoids. Lipophilic citrus nobiletin and tangeretin inhibited the cell growth of squamous cell carcinoma in a dose-dependent manner [116]. Abe [117] found that a standardized preparation of orange peel extract with 30% PMFs decreased development of an atypical hyperplastic lesion and increased apoptosis in ductal epithelial cells of C57Bl/6 mice. The orange peel extract containing tangeretin (19.0%), heptamethoxyflavone (15.24%), tetramethoxyflavone (13.6%), nobiletin (12.49%), hexamethoxyflavone (11.06%), and sinensitin (9.16%) was used in the experiment. Fan *et al.* [118] reported that after feeding 0.5% orange peel extract in new Western-style diet, the development of tumors markedly decreased, with multiplicity decreasing 49% in the small intestine and 38% in the colon.

The antiproliferative effects of individual citrus PMFs, especially tangeretin and nobiletin have been investigated. Hirano *et al.* [119] showed that tangeretin induced apoptosis in human promyelocytic leukaemia HL-60 cells. Lust *et al.* [120] explored the mechanism of cell death of tangeretin in K562 breakpoint cluster region-abelson murine leukemia (Bcr-Abl+) cells. Zheng *et al.* [121] reported that nobiletin had apoptosis-inducing effects in a concentration- and time-dependent manner in human colon cancer cells. Yoshimizu *et al.*

[122] confirmed the antitumour effects of nobiletin extracted from *C. depressa* Hayata on several human gastric cancer cell lines. Suzuki *et al.* [123] found that nobiletin feeding on 5-week-old male F344 rats reduced the cell-proliferation activity and increased the apoptotic index in colonic adenocarcinoma and/or colonic mucosa. Tang *et al.* [124] investigated the influence of nobiletin on prostate carcinogenesis using transgenic rats developing adenocarcinoma of the prostate (TRAP) and human prostate cancer cells. Nobiletin (powder diet containing 500 mg/kg nobiletin) caused significant reduction in the ventral, lateral, and dorsal prostate lobes.

#### 14.4.7.4 Antiproliferative effects of *citrus limonoids*

Experimental evidence has revealed that citrus limonoids are biologically active, displaying antibacterial, antifungal, antiviral, antimalarial, anticancer, and other pharmacological activities on humans [125]. Citrus limonoids, especially obacunone, limonin, and nomilin were able to inhibit chemically induced carcinogenesis and were effective in a series of human cancer cell lines, with remarkable cytotoxicity against lung, colon, oral, and skin cancer in animal models and human breast cancer cells [126].

*In vitro* limonin, nomilin, and limonoid glucosides proved to have a significant ability to inhibit proliferation of human breast cancer. Among the tested limonoids, nomilin was the most effective followed by limonin and limonoid glucosides; these compounds showed an IC<sub>50</sub> of 0.4, 12.5, and 75 µg/mL, respectively [127]. Limonin 17-β-D-glucopyranoside was responsible for the decreased colon tumour-genesis associated with feeding orange juice [128]. Pure limonin glucoside and limonin were also found to possess significant anti-tumor properties in animal models and with human cells [129]. Obacunone and its glucoside inhibit the proliferation of estrogen positive and negative human breast cancer cells [130] as well as colon adenocarcinoma cells [131]. Results from *in vivo* studies suggested that obacunone could inhibit carcinogen-induced colon cancer by blocking the development of a precursor lesion, aberrant crypt foci, and induction of apoptosis [132].

### 14.4.8 Anti-inflammatory activity

Chronic inflammation is induced by microbial and viral infections; exposure to allergens, radiation, and toxic chemicals; tobacco use and obesity. Accumulated epidemiological and experimental data indicate a close link between inflammation and cancer. The prolonged inflammatory/oxidative environment results in the damage of healthy neighboring cells and leads to carcinogenesis [133]. Overexpression of cyclooxygenase-2 (COX-2) and inducible nitric oxide synthase (iNOS) leads to the accumulation of prostaglandin E2 (PGE2) and nitric oxide (NO), respectively, and plays a major role in oxidative stress-induced inflammation [134]. Inhibitions of COX-2 and iNOS expression are the major targets of anti-inflammatory phytochemicals.

#### 14.4.8.1 Anti-inflammatory of *citrus flavonols*

Rutin has been shown to have significant anti-inflammatory properties in an adjuvant arthritis rat model [135]. Several *in vitro* studies have shown that quercetin, the aglycone moiety of rutin, is capable of inhibiting lipopolysaccharide (LPS)-induced cytokine production. Boots

*et al.* [136] found that quercetin inhibits the gene expression of TNF $\alpha$  via modulation of NF-kappaB in human peripheral blood mononuclear cells.

#### 14.4.8.2 Anti-inflammatory of citrus flavones

Apigenin blocks the development of mouse skin tumours and the proliferation of human breast-cancer cells. It is a potent antioxidant, PGE2 and NO production inhibitor, cell cycle inhibitor, protein kinase C inhibitor, and apoptosis inducer. Apigenin is also found to inhibit the adhesion of monocytes to human umbilical vein endothelial cells and the expression of cellular adhesion molecules [137].

#### 14.4.8.3 Anti-inflammatory of citrus flavanones

Da Silva *et al.* [138] tested the functionality of citrus flavonoids in rats and mice models and found that hesperidin may have potential therapeutic use as mild anti-inflammatory agents. Benavente-Garcia *et al.* [10] reported that several citrus flavanones exhibited potent inhibitory activity on the catalytic function of lipoxygenase and cyclooxygenase. Sakata *et al.* [139] indicated that hesperidin inactivated the LPS-induced overexpression of cyclooxygenase-2 and iNOS in a mouse macrophage cell model. Kim *et al.* [140] showed that hesperetin suppressed NF-kappaB activation and related gene expressions in kidneys of 6- and 24-monthold rats. They postulated that hesperetin suppresses NF-kappaB activity through four signal transduction pathways, NIK/IKK, ERK, p38, and JNK.

#### 14.4.8.4 Anti-inflammatory of citrus polymethoxyflavones

Murakami *et al.* [141] studied the antiinflammatory activities of 31 citrus fruits. The suppressive activity of peel and juice extracts toward NO generation in murine macrophage RAW264.7 cells stimulated with LPS. They found that the inhibitory activities of peel parts containing nobiletin as the major PMFs were largely higher than those of the corresponding juice sac parts. The effects of citrus phytochemicals on a variety of inflammatory processes have been extensively studied and it has been demonstrated to inhibit several enzymes that are activated in certain inflammatory conditions [142]. The content of nobiletin in the peel extracts of 20 citrus fruits has been shown to correlate well with their inhibitory activities on NO production in the LPS-activated RAW264.7 cells [143]. Ho and Lin [144] showed that PMFs but not flavanone glycosides, were the major contributors to the NO-suppressing activity of heat-treated chen-pi. The content of PMFs (nobiletin and tangeretin) was found to be highly correlated with anti-inflammatory activity.

Wu *et al.* [145] reported that nobiletin could alleviate the airway inflammation of asthmatic rats. Nobiletin significantly reduced ovalbumin (OVA)-induced increases in eosinophils, remarkably lowered the level of eotaxin in blood and broncho-alveolar lavage fluid (BALF) of asthmatic rats. Lin *et al.* [146] indicated that nobiletin downregulated the interleukin (IL)-1-induced gene expression and production of proMMP-1/procollagenase-1 as well as proMMP-3/prostromelysin-1 in human synovial fibroblasts. They claimed that nobiletin has anti-inflammatory actions similar to those of dexamethasone.

On the other hand, tangeretin suppresses IL-1- $\beta$ -induced COX-2 expression [147]. The effects of tangeretin on the expression of COX-2 in human lung epithelial carcinoma cells, A549, and human non-small cell lung carcinoma cells, H1299 were examined. Tangeretin

was found to exert a much better inhibitory activity than nobiletin against IL-1- $\beta$ -induced production of COX-2 in A549 cells. Li *et al.* [148] interpreted that the hydrophobic nature of the PMFs enables them to cross the intestinal membrane easily leading to the remarkable anti-inflammatory activities. They regarded citrus PMFs as promising therapeutic phytochemicals.

## 14.5 Food application of citrus and their by-products

At least one third of citrus fruits are used for juice production. During juice processing, peels are the major by product. It is well established that phytochemicals beneficial to human health are more abundant in citrus peels rather than the juice. As manufacturing processes can modify the level of the biologically active phytochemicals present in processed products, various processing methods to increase the biological activities of citrus were developed basically by trial and error in ancient China. Table 14.1 lists citrus varieties, especially those dried to produce value-added products.

### 14.5.1 Dried citrus peels

Chen-pi (dried citrus peels) has long been used as a remedy to help digestion and to treat inflammatory syndromes including bronchitis and asthma in China, Japan, Korea, and Taiwan. Varieties of *C. unshiu* Markovich, *C. reticulate* Blanco, and *C. tachibana* Makino Tanaka, are most frequently used. Some other citrus immature peels, such as *C. reticulata* Blanco (“Qing-Pi”), *C. aurantium* L., and *C. wilsonii* Tanaka (“Zhi-Ke”), are used in Chinese folk medicine preparation as well [149].

A modified intermittent drying process was developed by ancient Chinese to produce Chen-pi. Modified intermittent drying techniques for Chen-pi manufacturing are characterized with several tempering periods which allow moisture diffusion from the interior to the external surface to achieve a concentrating effect. The interaction between enzyme and substrate leads to the brown or dark brown appearance of the finished dried products.

Although sun drying is a common dehydration process used in the traditional Chinese medicine industry, high temperature treatment is found to enhance the antioxidative and antiinflamatory activity [146]. Heat treatment of citrus peels was found to enhance the antioxidant activity, perhaps due to the release of phenolic compounds from an unextractable form covalently bound to insoluble polymers to an extractable free form [150]. Interestingly, heat treatment at 100°C for 2 h also significantly increased the anti-inflammatory activity of

**Table 14.1** Commercial dried citrus fruits

Common name	Scientific name	Part used	Products
Ponkan	<i>Citrus reticulata</i>	Peel	Folk medicine
Dancy tangerine	<i>Citrus tangerina</i>	Peel	Folk medicine
Satsuma	<i>Citrus unshiu</i>	Peel	Weight loss formula
Kumquat	<i>Fortunella margarita</i> S.	Whole	Preserved fruit
Sour orange	<i>Citrus aurantium</i>	Whole	Weight loss formula
Lemon	<i>Citrus lemon</i> L.	Whole	Dried slice, whole
	<i>Citrus aurantifolia</i>		

citrus peels as evaluated by their ability to inhibit NO production in LPS-activated RAW264.7 macrophages. Jung *et al.* [151] proposed that PMFs were released by heat treatment and act as the key determinants of the anti-inflammatory activity of Chen-pi.

### **14.5.2 Dried sour orange**

Sour orange (*C. aurantium*) is dried in Taiwan to make suan-gang tea. The entire production process of suan-gang tea is quite complicated and time-consuming. Similar to that of Chen-Pi, a modified intermittent drying process is applied to process dried sour orange. The aged suan-gang tea is charcoal black in color and has a pleasant fragrance when brewed. Before brewing, it is required to chop the product into smaller pieces. Some of the tea shops would provide the aforementioned service. A steaming hot cup of suan-gang tea tastes amazingly soothing and refreshing.

### **14.5.3 Preserved kumquat**

Kumquats (*Fortunella margarita* S.) have a sweet outer coat and a tart, juicy center, and they can be dried and processed into preserves. Dried whole kumquats are often used as folk medicine to cure inflammatory syndromes of the respiratory tract, such as coughing, hoarseness, and sore throats [152]. Preserved kumquat is processed following several steps of material selection, washing, puncturing, color protection, blanching, vacuum sugar-dipping, draining, and drying in Taiwan.

### **14.5.4 Dried lemon**

#### **14.5.4.1 Dried lemon slices**

Dried lemon slices are now commercially available in Taiwan. Traditionally, lemon slices are dried by conventional hot air drier. Recently, a closed-type dryer associated with a photovoltaic system (PV) was developed by Chen *et al.* [153]. Dried lemon slices using a closed-type dryer have better quality in terms of their sensory parameters. There are significant color differences resulting from the browning reaction experienced under the two drying methods. The constant (at 60°C) drying using hot air drier resulted in a deeper brown color than did the closed-type dryer.

#### **14.5.4.2 Dried black lemon**

For decades, people in Eastern Guatemala dried native lemon (*C. aurantifolia* L.) and this practice dates back to the ancient Mayan civilization. *C. aurantifolia* originated in Asia but has adapted well to Guatemala and can be cultivated in warm temperate climates. The lemons are small and round measuring from 30 to 50 mm in diameter.

The lemon dehydration process developed in Guatemala involves the complete drying of lemons in direct sunlight [154]. Ripe fruit is picked, spread uniformly on raised earth beds (1.5 m wide) covered with black plastic held in place by stones or other heavy objects at the sides. Lemons are sun-dried on the black plastic for 3–4 months until 80–90% water is removed. Lemons are constantly turned and moved around to ensure homogenous drying. They are daily covered with the black plastic in the late evening and are uncovered to expose

them to direct sunlight in the morning. Optimal conditions are reached when the lemons turn brown or black and have a slightly burnt look. Products include whole sun-dried lemons, available in different sizes (Jumbo 40 mm, 30–40 mm, 20–30 mm, and Baby) and ground lemon. Most of the dried lemon is exported to the Middle Eastern countries.

## 14.6 Conclusions

Among world fruit production, citrus is undoubtedly the largest one. Different from that of Western world in which citrus fruits are processed for juice production, in Oriental countries the whole immature and mature citrus fruits and peels are dried, and widely used as remedies for health promotion. Citrus phytochemicals, particularly flavonoids have wide ranges of health beneficial properties such as antioxidant, hypoglycaemic, hypolipidemic, and anticancer activities, among others.

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# **15 Functional characteristics of dried figs**

Cesarettin Alasalvar

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## **15.1 Introduction**

Figs (*Ficus carica* L.) are native to southwest Asia and the eastern Mediterranean region, belonging to the Moraceae family [1, 2]. Figs are a widespread species commonly grown, especially in warm and dry climates and an important crop worldwide for fresh and dried consumption. The world production of figs was around 1,024,138 metric tonnes (MT) in 2008 [3], 70% of which was grown in the countries of the Mediterranean coast. Egypt is the world's largest fig producer, followed by Turkey, Algeria, and Morocco. The majority of fig production is for dry consumption. Since figs are highly perishable fruits, they have to be preserved in the dried form [4]. World dried fig production was approximately 105,453 MT in 2011 [5].

Fresh fig colors vary from dark purple to green. They can be eaten whole and raw, but are often peeled; the flesh is eaten and the skin often discarded [6]. Whereas, dried figs are available in many forms: whole for the consumers and, in industrial products, as paste, concentrate, nuggets, powder, and diced forms [7]. Potassium sorbate is added to dried figs to inhibit yeast fermentation and mould growth. Dried figs are processed to bring their moisture content up to 14–20% to as high as 30% [7]. Compared to other dried fruits such as apricots and apples, color in certain varieties may be stabilized by the addition of low levels of sulfur dioxide.

Some important aspects such as compositional/nutritional characteristics, phytochemicals, and health benefits of dried figs are considered in this chapter. Where available, comparison is made with fresh figs.

## **15.2 Compositional and nutritional characteristics of fresh and dried figs**

Table 15.1 lists the compositional and nutritional characteristics of fresh and dried figs [8]. Figs are low in fat (0.30 g/100 g for fresh and 0.93 g/100 g for dried) and high in fiber (2.9 g/100 g for fresh and 9.8 g/100 g for dried). Dried figs are excellent sources of sugar

**Table 15.1** Compositional and nutritional characteristics of fresh and dried figs (values in per 100 g edible portion)

Nutrient	Units	Fresh figs	Dried figs
<b>Proximate composition</b>			
Water	g	79.11	30.05
Energy	kcal	74	249
Protein	g	0.75	3.30
Lipid	g	0.30	0.93
Ash	g	0.66	1.86
Carbohydrate	g	19.18	63.87
Dietary fiber	g	2.9	9.8
Sugars	g	16.26	47.92
<b>Minerals</b>			
Calcium	mg	35	162
Copper	mg	0.07	0.29
Iron	mg	0.37	2.03
Magnesium	mg	17	68
Manganese	mg	0.13	0.51
Phosphorus	mg	14	67
Potassium	mg	232	680
Selenium	µg	0.2	0.6
Sodium	mg	1.0	10
Zinc	mg	0.15	0.55
<b>Vitamins</b>			
Betaine	mg	nd	0.7
Choline	mg	4.7	15.8
Folate	µg	6.0	9.0
Niacin	mg	0.4	0.62
Pantothenic acid	mg	0.3	0.43
Pyridoxine	mg	0.11	0.11
Riboflavin	mg	0.05	0.08
Thiamin	mg	0.06	0.09
Vitamin A (RAE)	µg	7.0	tr
Vitamin C	mg	2.0	1.2
Vitamin E (ATE)	mg	0.11	0.35
Vitamin K	µg	4.7	15.6
<b>Amino acids</b>			
Alanine	g	0.045	0.134
Arginine	g	0.017	0.077
Aspartic acid	g	0.176	0.645
Cystine	g	0.012	0.036
Glutamic acid	g	0.072	0.295
Glycine	g	0.025	0.108
Histidine <sup>a</sup>	g	0.011	0.037
Isoleucine <sup>a</sup>	g	0.023	0.089
Leucine <sup>a</sup>	g	0.033	0.128
Lysine <sup>a</sup>	g	0.030	0.088
Methionine <sup>a</sup>	g	0.006	0.034
Phenylalanine <sup>a</sup>	g	0.018	0.076
Proline	g	0.049	0.610
Serine	g	0.037	0.128
Threonine <sup>a</sup>	g	0.024	0.085
Tryptophan <sup>a</sup>	g	0.006	0.020
Tyrosine	g	0.032	0.041
Valine <sup>a</sup>	g	0.028	0.122

Source: Adapted from USDA [8].

Note: Some numbers are rounded to the second digit after decimal point.

RAE, retinol activity equivalents; ATE, alpha-tocopherol equivalents; nd, not detected; tr, trace.

<sup>a</sup>Indispensable amino acids.

(47.92 g/100 g); fructose and glucose are the main sugars. Trace amounts of sucrose and galactose are also available [8]. Levels may differ according to drying method, regional, and varietal factors.

Based on USDA National Nutrient Database [8], dried figs provide more fiber (9.8 g/100 g) than other dried fruits (Chapter 1, Table 1.2). The recommended dietary fiber intake is 14 g/1000 calories of food consumed each day. This means 25–38 g of fiber per day depending on age and gender [9]. On a per serving basis (40 g dried figs or one-fourth cup and 150 g fresh figs or 1 cup or 3 medium size figs), dried figs deliver between 11.2 and 15.7% of the recommended daily intake of fiber as compared to their corresponding fresh fig counterparts (between 12.5 and 17.4%).

With respect to nutritional aspects, percentage of recommended dietary allowances (RDA) or adequate intake (AI) for minerals for adult males and females (aged 15–50 years) are also given in Table 15.2. Dried figs compare favorably in their daily mineral requirement values to fresh figs. Dried figs, in general, serve as a good source of calcium, copper, iron, magnesium, manganese, phosphorus, and potassium. Consuming 40 g (on a per serving basis) of dried figs (Table 15.2) supplies 6.5% of calcium, 12.9% of copper, 4.5–10.2% of iron, 6.6–8.6% of magnesium, 8.9–11.3% of manganese, 3.8% of phosphorus, and 5.8% of potassium for RDA or AI for adults [8, 10–12]. These values are comparable with their corresponding fresh

**Table 15.2** Percentage of RDA values for adults (aged 19–50) in fresh and dried figs

Mineral	RDA or AI*	Unit	Fresh figs (150 g serving basis) <sup>a</sup>	Dried figs (40 g serving basis) <sup>b</sup>	Reference
<b>Males</b>					
Calcium	1000 mg/day*	mg	5.3	6.5	[8, 10]
Copper	0.9 mg/day	mg	11.7	12.9	[8, 11]
Iron	8 mg/day	mg	6.9	10.2	[8, 11]
Magnesium	400–420 mg/day	mg	6.2	6.6	[8, 10]
Manganese	2.3 mg/day*	mg	8.5	8.9	[8, 11]
Phosphorus	700 mg/day	mg	3.0	3.8	[8, 10]
Potassium	4700 mg/day	mg	7.4	5.8	[8, 12]
Selenium	55 µg/day	µg	0.5	0.4	[8, 13]
Sodium	1500 mg/day	mg	0.1	0.3	[8, 12]
Zinc	11 mg/day	mg	2.0	2.0	[8, 11]
<b>Females</b>					
Calcium	1000 mg/day*	mg	5.3	6.5	[8, 10]
Copper	0.9 mg/day	mg	11.7	12.9	[8, 11]
Iron	18 mg/day	mg	3.1	4.5	[8, 11]
Magnesium	310–320 mg/day	mg	8.1	8.6	[8, 10]
Manganese	1.8 mg/day*	mg	10.8	11.3	[8, 11]
Phosphorus	700 mg/day	mg	3.0	3.8	[8, 10]
Potassium	4700 mg/day	mg	7.4	5.8	[8, 12]
Selenium	55 µg/day	µg	0.5	0.4	[8, 13]
Sodium	1500 mg/day	mg	0.1	0.3	[8, 12]
Zinc	8 mg/day	mg	2.8	2.8	[8, 11]

RDA, recommended dietary allowances; AI\*, adequate intake.

<sup>a</sup>150 g serving basis (1 cup): Around 3 medium size figs.

<sup>b</sup>40 g serving basis (one-fourth cup): Around 4–5 medium size figs.

fig counterparts (on a 150 g serving or one-fourth cup or 3 medium size figs) and dependent upon variety. Based on RDA and AI values, dried figs contain more calcium, magnesium, and manganese than any other dried fruits (Chapter 1, Table 1.3). O'Brien *et al.* [14] found that fruit-eating animals regularly prefer to eat figs even when other food is abundant. They proposed that high calcium levels contribute to the desirability of figs as food for many forest animals. In addition, unlike most fruits figs are considered a “keystone” plant resource for fruit-eating birds and mammals throughout the tropics [15].

Dried figs contain both water-soluble (choline, folate, niacin, pantothenic acid, pyridoxine, riboflavin, thiamine, and vitamin C) and fat-soluble vitamins (A, E, and K) (Tables 15.1 and 15.3). With regard to RDA of vitamins, 40 g dried figs provide up to 3.4% of pantothenic acid and pyridoxine, 2.5–2.9% of riboflavin, 3.0–3.3% of thiamine, and 5.2–6.9% of vitamin K for RDA or AI for adults [8, 11, 13, 16]. These values are lower than that of their corresponding fresh figs (on a 150 g serving or one-fourth cup or 3 medium size figs). Among eight dried fruits, prunes, apricot, and peaches contain higher amounts of vitamins than other dried fruits including figs (Chapter 1, Tables 1.2 and 1.4).

**Table 15.3** Percentage of RDA values for adults (aged 19–50 years) in fresh and dried figs

Vitamin	RDA or AI*	Unit	Fresh figs (150 g serving basis) <sup>a</sup>	Dried figs (40 g serving basis) <sup>b</sup>	Reference
<b>Males</b>					
Choline	550 mg/day*	mg	1.3	1.1	[8, 16]
Folate	400 µg/day	µg	2.3	0.9	[8, 16]
Niacin	16 mg/day	mg	3.8	1.6	[8, 16]
Pantothenic acid	5 mg/day*	mg	9.0	3.4	[8, 16]
Pyridoxine	1.3 mg/day	mg	12.7	3.4	[8, 16]
Riboflavin	1.3 mg/day	mg	5.8	2.5	[8, 16]
Thiamin	1.2 mg/day	mg	7.5	3.0	[8, 16]
Vitamin A (RAE)	900 µg/day	µg	1.2	tr	[8, 11]
Vitamin C	90 mg/day	mg	3.3	0.5	[8, 13]
Vitamin E (ATE)	15 mg/day	mg	1.1	0.9	[8, 13]
Vitamin K	120 µg/day*	µg	5.9	5.2	[8, 11]
<b>Females</b>					
Choline	425 mg/day*	mg	1.7	1.5	[8, 16]
Folate	400 µg/day	µg	2.3	0.9	[8, 16]
Niacin	14 mg/day	mg	4.3	1.8	[8, 16]
Pantothenic acid	5 mg/day*	mg	9.0	3.4	[8, 16]
Pyridoxine	1.3 mg/day	mg	12.7	3.4	[8, 16]
Riboflavin	1.1 mg/day	mg	6.8	2.9	[8, 16]
Thiamin	1.1 mg/day	mg	8.2	3.3	[8, 16]
Vitamin A (RAE)	700 µg/day	µg	1.5	tr	[8, 11]
Vitamin C	75 mg/day	mg	4.0	0.6	[8, 13]
Vitamin E (ATE)	15 mg/day	mg	1.1	0.9	[8, 13]
Vitamin K	90 µg/day*	µg	7.8	6.9	[8, 11]

RDA, recommended dietary allowances; AI\*, adequate intake; RAE, retinol activity equivalents; ATE, alpha-tocopherol equivalents; tr, trace.

<sup>a</sup>150 g serving basis (1 cup): Around 3 medium size figs.

<sup>b</sup>40 g serving basis (one-fourth cup): Around 4–5 medium size figs.

Vinson *et al.* [17] compared six fresh fruits (apricots, cranberries, dates, figs, grapes, and plums) with their corresponding dried versions with respect to nutrients for a serving size of the fruit. Dried figs were ranked number 2 in two nutrients, dietary fiber and calcium, and had the best nutrient score among the dried fruits (tied with dried apricots). The nutrient score was significantly ( $P < 0.01$ ) better for dried fruits compared to their fresh counterparts. The best nutrient score of the fresh fruits belonged to dates, which in fact had the best nutrient score of all the fruits.

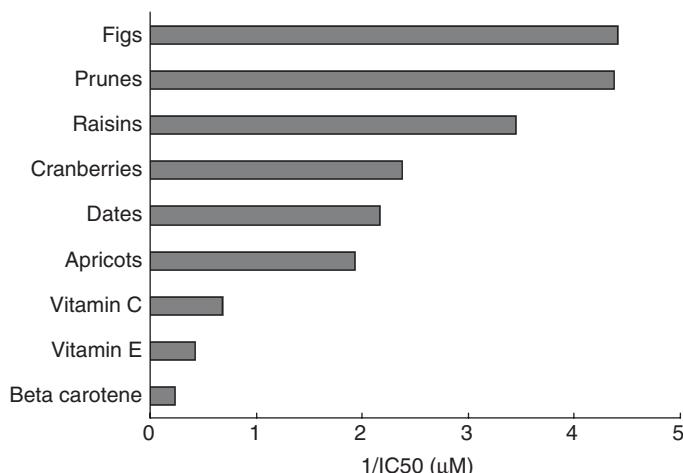
Despite the fact that fresh and dried fruits contain all indispensable amino acids, in general, they are not good sources of amino acids due to their low content of protein (Table 15.1). Aspartic acid, proline, and glutamic acids are the major amino acids in fresh and dried figs.

## 15.3 Phytochemicals in dried figs

### 15.3.1 Antioxidant activity and quality of antioxidants

The oxygen radical absorbance capacity (ORAC) of a selection of dried fruits is shown in Chapter 1, Table 1.5. Raisins (golden seedless) have the highest ORAC value (10,450  $\mu\text{mol}$  trolox equivalents [TE]/100 g), whereas dates (Deglet noor) have the lowest ORAC value (2387  $\mu\text{mol}$  of TE/100 g). Dried figs contain 3383  $\mu\text{mol}$  of TE/100 g [18, 19]. Values are much higher for dried figs than their corresponding ORAC values for fresh, since antioxidants are concentrated during the drying process.

A comparison of antioxidant quality of vitamins and dried fruits is shown in Figure 15.1 [17]. The higher the value of  $1/\text{IC}_{50}$ , the better the quality. Among dried fruits, figs have the highest value and approximately 10-fold higher than vitamin C, vitamin E, and  $\beta$ -carotene. Therefore, polyphenols from dried fruits, including figs, can serve as potent antioxidants at physiological concentrations [17].



**Figure 15.1** Comparison of quality of antioxidants of vitamins and dried fruits. (Adapted with permission from Vinson *et al.* [17]).

In a human study, plasma antioxidant capacity is measured by trolox equivalent antioxidant capacity (TEAC). The plasma TEAC value has been reported to be 9% after eating dried figs (40 g serving) [17]. This value after drinking one serving of green tea by normal subjects compared to baseline is 4% [20]. This shows that dried figs produce a much greater increase in plasma TEAC than green tea. Besides figs, the only other dried fruit to demonstrate human *in vivo* antioxidant activity is raisins from white grapes. In this study, subjects consumed 3 g/kg (about 5 serving) of raisins for a week and the fasting TEAC increased 8% [21].

Slatnar *et al.* [22] measured antioxidant activity of fresh and dried figs and found that antioxidant activity measured by 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging activity was significantly 2-fold higher in dried figs than fresh ones.

### 15.3.2 Phenolics

Flavonoids are another group of phenolic compounds that can be classified into flavanones, flavones, isoflavones, anthocyanidins, flavonols, and flavanols or flavan-3-ols [23]. Literature on flavonoid profiles, particularly anthocyanins, in dried figs are scarce. Solomon *et al.* [6] analyzed total phenolics, total flavonoids, total anthocyanins, and antioxidant capacity of six commercial varieties of figs, differing in color (black, red, yellow, and green) (Table 15.4). The dark-purple mission variety contained the highest levels of phenolics, flavonoids, and anthocyanins and exhibited the highest antioxidant capacity among the tested varieties. The order of total phenolics, flavonoids, anthocyanins, and antioxidant capacity of figs were in the order of skin > fruit > pulp. Recently, Çalışkan *et al.* [24] analyzed phytochemical and antioxidant properties of 76 fig cultivars (green, yellow, purple, black, and brown) from the eastern Mediterranean region of Turkey. Black fig cultivars had the highest total antioxidant capacity (range of 7.9–16.1, mean 1.2 Fe<sup>2+</sup> mmol/kg fresh weight), total anthocyanins (range of 32.3–356, mean 128.4 µg cyanidin-3-rutinoside/g fresh weight), and total phenols (range of 69.1–220, mean 118.9 mg gallic acid equivalents [GAE]/100 g fresh weight). These black-fruited cultivars had 2-fold greater total antioxidant capacity, 15-fold greater total anthocyanin, and 2.5-fold greater total phenolics than green and yellow fig cultivars. Similar results were obtained by Del Caro and Piga [25] who found that black figs were significantly richer in polyphenols (phenolic acids, flavonols, and anthocyanins) than the green ones. They also found that polyphenols were mainly concentrated in the peel rather than pulp of fresh figs. Slatnar *et al.* [22] reported that total phenolics were in the range from 7.49 mg GAE/100 g in fresh figs to 53.02 mg GAE/100 g in dried figs.

Solomon *et al.* [6] measured the total anthocyanins of various colored fresh fig fruits, skins, and pulps (Table 15.4). In all figs tested, anthocyanins concentrated in the fruit skin and constituted the main coloring compounds. Vallejo *et al.* [26] studied phenolic compounds of fresh figs and found that high concentrations of phenolic compounds are present either in the skin (mainly anthocyanins) and pulp (mainly proanthocyanidins). The average daily intake of anthocyanins per person has been estimated to reach 200 mg [27]. Fig skins are major sources of anthocyanins and polyphenols; therefore consumption of whole ripe fruit is recommended [6].

Table 15.5 lists the anthocyanins found in different colored fresh figs, skins, and pulps [6, 25, 26, 28–32]. In total, 19 different anthocyanins have been reported in different varieties and colored figs, three of which are major pigments found in figs and their skin (cyanidin

**Table 15.4** Total phenolics, flavonoids, anthocyanins, and TEAC values of 100 g of fresh figs, skins, and pulps

Fig type & color	Total phenolics (mg of GAE/100 g)		Total flavonoids [mg of (+)-catechin/100 g]		Total anthocyanins (mg of cyn-3-glu/100 g)		(μmol of TE/100 g)
	Total phenolics (mg of GAE/100 g)	Total flavonoids [mg of (+)-catechin/100 g]	Total anthocyanins (mg of cyn-3-glu/100 g)	Total anthocyanins (mg of cyn-3-glu/100 g)			
<b>Fig fruits</b>							
Mission (dark purple)	281.1 ± 3.0 <sup>a</sup>	21.5 ± 2.7 <sup>a</sup>	10.9 ± 1.3 <sup>a</sup>	10.9 ± 1.3 <sup>a</sup>	716.3 ± 52.6 <sup>a</sup>	716.3 ± 52.6 <sup>a</sup>	
Chechick (dark purple)	80.6 ± 7.2 <sup>b</sup>	15.9 ± 1.7 <sup>b</sup>	1.8 ± 0.2 <sup>b</sup>	1.8 ± 0.2 <sup>b</sup>	192.1 ± 16.1 <sup>b</sup>	192.1 ± 16.1 <sup>b</sup>	
Brown Turkey (purple-red)	58.1 ± 6.3 <sup>bc</sup>	3.6 ± 0.4 <sup>c</sup>	1.3 ± 0.1 <sup>b</sup>	1.3 ± 0.1 <sup>b</sup>	120.7 ± 11.3 <sup>c</sup>	120.7 ± 11.3 <sup>c</sup>	
Bursa (purple-red)	56.0 ± 6.2 <sup>c</sup>	2.7 ± 0.3 <sup>c</sup>	0.3 ± 0.1 <sup>c</sup>	0.3 ± 0.1 <sup>c</sup>	100.3 ± 8.6 <sup>c</sup>	100.3 ± 8.6 <sup>c</sup>	
Brunswick (yellow-green)	50.0 ± 4.6 <sup>c</sup>	2.3 ± 0.3 <sup>c</sup>	nd	nd	69.5 ± 7.8 <sup>cd</sup>	69.5 ± 7.8 <sup>cd</sup>	
Kodara (yellow)	48.6 ± 3.8 <sup>c</sup>	2.1 ± 0.2 <sup>c</sup>	nd	nd	25.0 ± 3.1 <sup>d</sup>	25.0 ± 3.1 <sup>d</sup>	
<b>Fig skins</b>							
Mission (dark purple)	463.0 ± 44.3 <sup>a</sup>	45.6 ± 3.7 <sup>a</sup>	27.3 ± 2.3 <sup>a</sup>	27.3 ± 2.3 <sup>a</sup>	1987.0 ± 175.4 <sup>a</sup>	1987.0 ± 175.4 <sup>a</sup>	
Chechick (dark purple)	164.2 ± 10.5 <sup>b</sup>	42.9 ± 4.1 <sup>a</sup>	7.7 ± 0.5 <sup>b</sup>	7.7 ± 0.5 <sup>b</sup>	602.5 ± 58.1 <sup>b</sup>	602.5 ± 58.1 <sup>b</sup>	
Brown Turkey (purple-red)	141.1 ± 12.4 <sup>bc</sup>	13.4 ± 1.4 <sup>b</sup>	6.5 ± 0.7 <sup>b</sup>	6.5 ± 0.7 <sup>b</sup>	302.2 ± 20.3 <sup>c</sup>	302.2 ± 20.3 <sup>c</sup>	
Bursa (purple-red)	123.0 ± 13.4 <sup>c</sup>	10.1 ± 1.3 <sup>b</sup>	4.1 ± 0.3 <sup>c</sup>	4.1 ± 0.3 <sup>c</sup>	292.5 ± 24.6 <sup>c</sup>	292.5 ± 24.6 <sup>c</sup>	
Brunswick (yellow-green)	65.5 ± 5.6 <sup>d</sup>	3.8 ± 0.5 <sup>c</sup>	0.7 ± 0.1 <sup>d</sup>	0.7 ± 0.1 <sup>d</sup>	101.2 ± 7.8 <sup>d</sup>	101.2 ± 7.8 <sup>d</sup>	
Kodara (yellow)	41.7 ± 3.8 <sup>d</sup>	2.2 ± 0.3 <sup>c</sup>	nd	nd	82.0 ± 5.1 <sup>d</sup>	82.0 ± 5.1 <sup>d</sup>	
<b>Fig pulps</b>							
Mission (dark purple)	100.6 ± 8.6 <sup>a</sup>	5.7 ± 0.5 <sup>a</sup>	0.3 ± 1.3 <sup>a</sup>	0.3 ± 1.3 <sup>a</sup>	357.5 ± 30.6 <sup>a</sup>	357.5 ± 30.6 <sup>a</sup>	
Chechick (dark purple)	36.5 ± 4.2 <sup>d</sup>	4.5 ± 0.4 <sup>b</sup>	0.1 ± 0.2 <sup>b</sup>	0.1 ± 0.2 <sup>b</sup>	88.4 ± 7.1 <sup>b</sup>	88.4 ± 7.1 <sup>b</sup>	
Brown Turkey (purple-red)	42.9 ± 4.7 <sup>d</sup>	1.6 ± 0.2 <sup>d</sup>	0.1 ± 0.1 <sup>b</sup>	0.1 ± 0.1 <sup>b</sup>	79.3 ± 6.3 <sup>b</sup>	79.3 ± 6.3 <sup>b</sup>	
Bursa (purple-red)	73.7 ± 6.2 <sup>b</sup>	3.2 ± 0.3 <sup>c</sup>	0.1 ± 0.1 <sup>c</sup>	0.1 ± 0.1 <sup>c</sup>	107.8 ± 9.6 <sup>b</sup>	107.8 ± 9.6 <sup>b</sup>	
Brunswick (yellow-green)	37.0 ± 4.6 <sup>d</sup>	1.6 ± 0.3 <sup>d</sup>	nd	nd	36.5 ± 2.8 <sup>c</sup>	36.5 ± 2.8 <sup>c</sup>	
Kodara (yellow)	59.1 ± 6.8 <sup>c</sup>	2.1 ± 0.2 <sup>c</sup>	nd	nd	20.8 ± 3.1 <sup>c</sup>	20.8 ± 3.1 <sup>c</sup>	

Source: Adapted with permission from Solomon *et al.* [6].TEAC, trolox equivalent antioxidant capacity; GAE, gallic acid equivalents; cyn-3-glu, cyanidin-3-glucoside; TE, trolox equivalents; nd, not detected. Different letters in the same column indicate significant differences ( $P < 0.05$ ).Data expressed as means ± standard deviation ( $n = 3$ ) on a fresh weight basis.

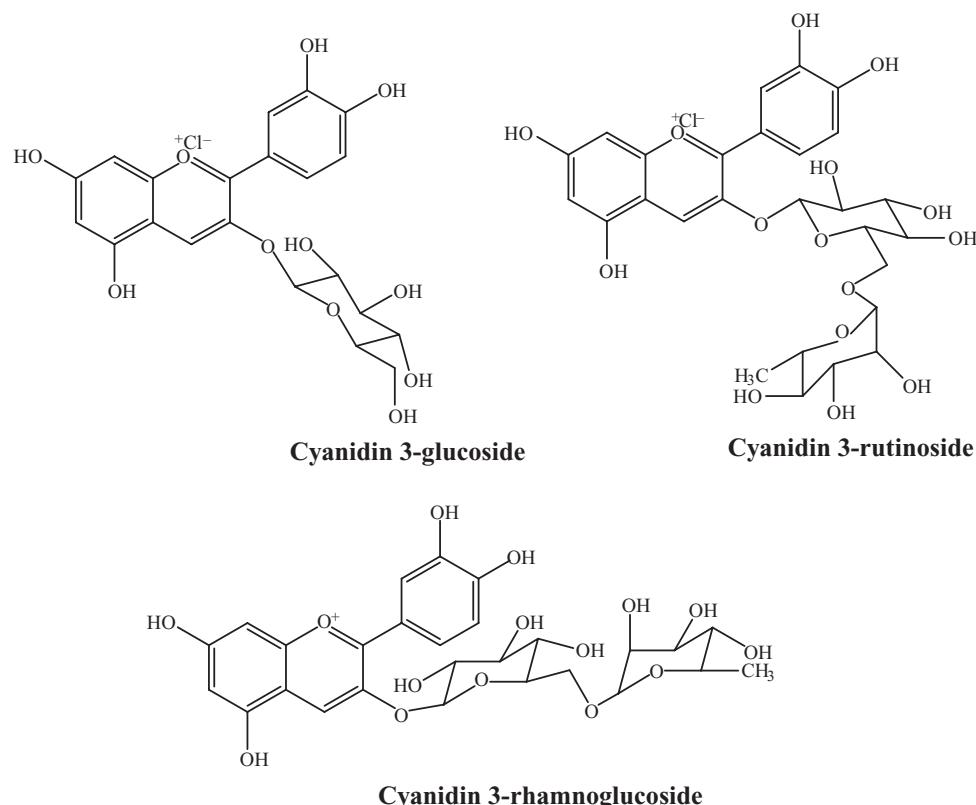
**Table 15.5** Anthocyanins found in different colored fresh figs, skins, and pulps

Anthocyanin	Reference
Cyanidin 3-glucoside	[28]
Cyanidin 3-rhamnoglucoside	[29]
Cyanidin 3,5-diglucoside	
Pelargonidin 3-rhamnoglucoside	
Cyanidin 3-glucoside	[6, 30]
Cyanidin 3-rhamnoglucoside	
Cyanidin 3-rutinoside dimer	[31]
(Epi)catechin-(4–8)-cyanidin 3-glucoside	
(Epi)catechin-(4–8)-cyanidin 3-rutinoside	
Cyanidin 3,5-diglucoside	
(Epi)catechin-(4–8)-cyanidin 3-rutinoside	
(Epi)catechin-(4–8)-pelargonidin 3-rutinoside	
(Epi)catechin-(4–8)-pelargonidin 3-rutinoside	
5-Carboxypyranocyanidin-3-rutinoside	
Cyanidin 3-malonylglicosyl-5-glucoside	
Cyanidin 3-glucoside	
Cyanidin 3-rutinoside	
Pelargonidin 3-glucoside	
Pelargonidin 3-rutinoside	
Peonidin 3-rutinoside	
Cyanidin 3-malonylglicoside	
Quercetin-3-rutinoside	[25]
Cyanidin 3-glucoside	
Cyanidin 3-rutinoside	
Quercetin-3-rutinoside	[32]
Cyanidin 3-glucoside	[26]
Cyanidin 3-rutinoside	

3-glucoside, cyanidin 3-rutinoside, and cyanidin 3-rhamnoglucoside) (Figure 15.2). Dark-purple and purple colored fig varieties contain much higher anthocyanins than their yellow- and red-fruited varieties [6, 32].

Phytoestrogens comprise three major classes: isoflavones, lignans, and coumestans [33]. The content of daidzein and genistein, which are classes of isoflavones, in some dried fruits (such as apricots, currants, dates, figs, prunes, and raisins) has been reported [33, 34]. Raisins are the richest source of daidzein and genistein (183.64 µg/100 g), primarily genistein, among six dried fruits (Table 15.6). Dried figs contain relatively low amount of isoflavones (5.97 µg/100 g) as compared to other dried fruits, except dried apricots (4.27 µg/100 g). More detailed information about phytoestrogen content of some dried fruits (apricots, currants, dates, prunes, and raisins) is given in Chapter 1, Table 1.7.

Vallejo *et al.* [26] reported that dried figs contained higher amounts of phenolics than the pulp of fresh figs, due to the contribution of dry skin. Four flavonols (such as kaempferol-rutinoside, quercetin-acetylglucoside, quercetin-rutinoside, and quercetin-glucoside) have been reported in three dried fig cultivars [26] and are given in Figure 15.3. Among them, quercetin-rutinoside is the major one (Table 15.7). All dried fig cultivars showed similar amounts of flavonols to fresh ones. Same authors have also reported that no anthocyanins and proanthocyanidins were found in green colors of dried fig cultivars.



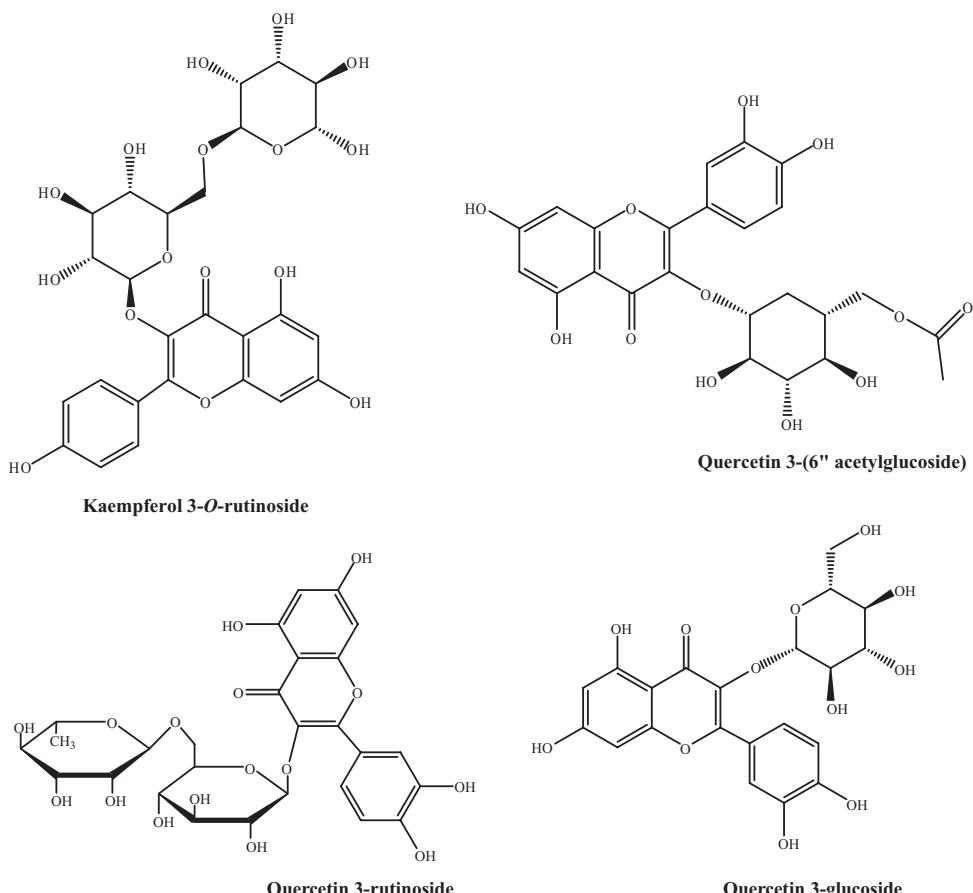
**Figure 15.2** Chemical structures of major anthocyanins found in figs.

Recently, Slatnar *et al.* [22] measured the effect of different drying on fig phenolics (Table 15.8). Eight phenolics in fresh and dried figs, belonging to four groups of hydroxycinnamic acids, flavan-3-ols, flavonols, and anthocyanins were identified. The predominant phenolic compound was epicatechin; in very small amounts of luteolin-8-C-glucoside. Analysis of individual phenolic compounds revealed a higher content of all phenolic groups determined after the oven-drying process, with the exception of cyanidin-3-O-rutinoside.

**Table 15.6** Daidzein and genistein content of some dried fruits ( $\mu\text{g}/100 \text{ g}$  edible portion)

Dried fruits	Daidzein	Genistein	Total	Reference
Apricots	4.27	nd	4.27	[34]
Currants	2.20	10.00	12.20	[33]
Dates	1.72	5.16	6.88	[34]
Figs	1.77	4.2	5.97	[34]
Prunes	4.26	8.53	12.79	[34]
Raisins	58.99	124.65	183.64	[34]

nd, not detected.



**Figure 15.3** Chemical structures of flavonols found in dried figs.

Similarly, higher total phenolic content and antioxidant activity were determined after the drying process [22].

Finally, two flavones (luteolin 6C-hexose-8C-pentose and apigenin-rutinoside) have been reported in fresh fig skins [26]. These compounds were not detected in fig pulps and dried figs.

**Table 15.7** Flavonol content of three dried figs (mg/100 g edible portion)

Dried fig variety (green color)	Kaempferol- rutinoside	Quercetin- acetylglucoside	Quercetin- rutinoside	Quercetin- glucoside
Unknown Turkey	2.0 <sup>a</sup>	2.6 <sup>a</sup>	10.2 <sup>a</sup>	2.5 <sup>a</sup>
Cuello Dama	1.0 <sup>b</sup>	2.1 <sup>b</sup>	13.0 <sup>b</sup>	1.0 <sup>b</sup>
Unknown Spain	2.0 <sup>a</sup>	2.8 <sup>a</sup>	10.9 <sup>c</sup>	0.7 <sup>c</sup>

Source: Adapted from Vallejo *et al.* [26].

Different letters in the same column indicate significant differences ( $P < 0.05$ ).

**Table 15.8** Content of phenolic compounds (mg/100 g) in fresh and dried figs of two drying methods at different sampling dates

Drying methods	Sampling date		
	July 9	July 15	September 11
<b>Chlorogenic acid</b>			
Fresh	1.33 ± 0.15 <sup>a</sup>	2.78 ± 0.46 <sup>a</sup>	4.91 ± 1.00 <sup>a</sup>
Sun drying	9.84 ± 1.41 <sup>b</sup>	15.88 ± 1.07 <sup>b</sup>	3.42 ± 0.54 <sup>a</sup>
Oven drying	13.96 ± 1.48 <sup>c</sup>	32.42 ± 0.89 <sup>c</sup>	19.92 ± 2.56 <sup>b</sup>
<b>Catechin</b>			
Fresh	1.36 ± 0.24 <sup>a</sup>	2.67 ± 0.17 <sup>a</sup>	2.88 ± 0.18 <sup>a</sup>
Sun drying	11.46 ± 2.45 <sup>b</sup>	5.88 ± 0.60 <sup>b</sup>	6.60 ± 1.18 <sup>b</sup>
Oven drying	16.16 ± 1.32 <sup>b</sup>	15.57 ± 2.04 <sup>c</sup>	19.75 ± 0.68 <sup>c</sup>
<b>Epicatechin</b>			
Fresh	7.58 ± 1.64 <sup>a</sup>	8.67 ± 1.12 <sup>a</sup>	7.11 ± 0.54 <sup>a</sup>
Sun drying	23.30 ± 3.12 <sup>b</sup>	20.37 ± 0.70 <sup>b</sup>	10.44 ± 0.86 <sup>b</sup>
Oven drying	34.65 ± 2.63 <sup>c</sup>	36.65 ± 2.46 <sup>c</sup>	26.66 ± 1.85 <sup>c</sup>
<b>Kaempferol-3-O-glucoside</b>			
Fresh	0.04 ± 0.00 <sup>a</sup>	0.10 ± 0.00 <sup>a</sup>	0.13 ± 0.01 <sup>a</sup>
Sun drying	0.46 ± 0.04 <sup>b</sup>	0.31 ± 0.04 <sup>b</sup>	0.59 ± 0.06 <sup>b</sup>
Oven drying	0.99 ± 0.09 <sup>c</sup>	0.56 ± 0.05 <sup>c</sup>	1.43 ± 0.07 <sup>c</sup>
<b>Luteolin-8-C-glucoside</b>			
Fresh	nd	nd	nd
Sun drying	0.15 ± 0.02	0.13 ± 0.01	0.16 ± 0.02
Oven drying	0.39 ± 0.03	0.21 ± 0.02	0.45 ± 0.04
<b>Rutin</b>			
Fresh	0.61 ± 0.14 <sup>a</sup>	1.86 ± 0.63 <sup>a</sup>	0.89 ± 0.20 <sup>a</sup>
Sun drying	6.66 ± 1.39 <sup>b</sup>	12.06 ± 1.00 <sup>b</sup>	1.38 ± 0.37 <sup>a</sup>
Oven drying	7.03 ± 1.03 <sup>b</sup>	14.62 ± 1.81 <sup>b</sup>	3.75 ± 0.29 <sup>b</sup>
<b>Quercetin-3-O-glucoside</b>			
Fresh	0.18 ± 0.04 <sup>a</sup>	0.60 ± 0.17 <sup>a</sup>	0.41 ± 0.09 <sup>a</sup>
Sun drying	2.40 ± 0.46 <sup>b</sup>	3.35 ± 0.19 <sup>b</sup>	0.56 ± 0.12 <sup>a</sup>
Oven drying	2.23 ± 0.24 <sup>b</sup>	2.98 ± 0.27 <sup>b</sup>	1.10 ± 0.06 <sup>b</sup>
<b>Cyanidin-3-O-rutinoside</b>			
Fresh	0.21 ± 0.05 <sup>a</sup>	0.31 ± 0.05 <sup>b</sup>	0.62 ± 0.04 <sup>c</sup>
Sun drying	0.26 ± 0.06 <sup>a</sup>	0.12 ± 0.01 <sup>a</sup>	0.13 ± 0.05 <sup>a</sup>
Oven drying	0.16 ± 0.02 <sup>a</sup>	0.12 ± 0.01 <sup>a</sup>	0.31 ± 0.05 <sup>b</sup>

Source: Adapted with permission from Slatnar *et al.* [22].

Data are expressed as mean ± standard deviation ( $n = 5$ ) on a fresh weight basis.

Different letters in columns indicate significant differences ( $P < 0.05$ ) in the contents of individual compounds between the treatments for each set of sampling dates.

nd, not detected.

**Table 15.9** Contents of free and bound phenolic acids in dried figs (mg/100 g)

Phenolic acid	Free phenolic acids	Bound phenolic acids	Total
Chlorogenic	0.40 ± 0.06 <sup>a</sup>	2.60 ± 1.01 <sup>b</sup>	3.00
Ferulic	0.31 ± 0.01 <sup>a</sup>	6.88 ± 0.01 <sup>b</sup>	7.19
Gallic	tr	tr	tr
p-Coumaric	0.25 ± 0.01 <sup>a</sup>	9.64 ± 0.01 <sup>b</sup>	9.89
Protocatechuic	0.43 ± 0.35 <sup>a</sup>	1.53 ± 2.16 <sup>b</sup>	1.96
Syringic	0.51 ± 0.60 <sup>a</sup>	0.93 ± 0.94 <sup>b</sup>	1.44
Vanillic	3.47 ± 0.05 <sup>a</sup>	29.88 ± 2.61 <sup>b</sup>	33.35

Source: Adapted from Aegean Exporter's Associations [35].

Data are expressed as mean ± standard deviation ( $n = 3$ ) on a fresh weight basis.

Different letters in the same row indicate significant differences ( $P < 0.05$ ).

tr, trace.

### 15.3.3 Phenolic acids

Phenolic acids in foods occur in the free and bound forms. Free forms are known to contribute to the taste of foods. The bound forms contribute to the antioxidant activity. Seven phenolic acids (free and bound), four of which are hydroxylated derivatives of benzoic acid (gallic, protocatechuic, syringic, and vanillic acids) and three are cinnamic acid derivatives (chlorogenic, ferulic, and *p*-coumaric acids), have been reported and tentatively identified in dried figs [35]. Bound phenolics were most abundant in dried figs and are significantly higher ( $P < 0.01$ ) than free phenolics (Table 15.9). Among the identified phenolic acids, vanillic acid was most abundant in dried figs, followed by *p*-coumaric acid, and ferulic acid. Recently, Vallejo *et al.* [26] have found only one phenolic acid (chlorogenic acid) in dried fig cultivars, ranging from 1.4 to 2.0 mg/100 g edible portion. Veberic *et al.* [32] have identified three phenolic acids in fresh fig cultivars, chlorogenic acid (1.71 mg/100 g fresh weight) being the most abundant, followed by gallic acid (0.38 mg/100 g fresh weight), and trace amounts of syringic acid (0.10 mg/100 g fresh weight). Dark cultivars exhibited a higher level of phenolic acids in comparison to the white fruit cultivar. Ferulic and *p*-coumaric acids have been reported as being more antioxidative than syringic, vanillic, and protocatechuic acids [36].

### 15.3.4 Carotenoids

Five carotenoids in an unknown variety of fresh figs ( $\alpha$ -carotene,  $\beta$ -carotene,  $\beta$ -cryptoxanthin, lutein, and lycopene) have been reported, with lycopene being the most abundant one, followed by lutein and  $\beta$ -carotene [37]. Based on USDA [8] data,  $\beta$ -carotene and lutein + zeaxanthin are present in dried figs. Both fresh and dried figs contain most carotenoids appearing in plasma, albeit at relatively low concentrations (470 µg/100 g in fresh figs and 38 µg/100 g in dried figs). The low level of carotenoids in dried figs may be due to the drying process since carotenoids are heat sensitive. As compared to other dried fruits, dried apricots contain the highest carotenoids (2163 µg/100 g), followed by dried peaches (2080 µg/100 g), and prunes (692 µg/100 g) [8].

## 15.4 Health benefits of dried figs

Dried figs are an excellent source of nutrients such as minerals (calcium), fiber (soluble), and sugars (fructose and glucose) and thus a good choice for snacking. Besides nutrients, they contain an array of health promoting bioactive compounds [2].

It has been estimated that up to 70% of incidences of cancer are related to diet. Previously, it was thought that the antioxidant vitamins, such as vitamins C, and E, and  $\beta$ -carotene, were responsible for the beneficial effects of fruits and vegetables as shown by epidemiological studies across many cultures. However, recent supplement studies have not supported this hypothesis. More than 200 epidemiological studies now support the fact that phytochemicals in the fruits and vegetables (including dried fruits) are responsible for the reduced cancer-risk benefits offered by fruits and vegetables [7]. Major antioxidant activity of fruits including dried fruits is due to the presence of flavonoids and phenolic acids. The antioxidant activity of several flavonoids, measured as scavenging of peroxyl radicals, were found to be higher than that of vitamins E and C, and glutathione [38].

The Mediterranean diet has been reported to promote health and quality of life, specifically by preventing pathophysiological conditions related to coronary heart disease (CHD) and cancer. The high consumption of natural antioxidants and health promoting phytochemicals, achieved by consuming salads, vegetables, fruits, and their derived products, is generally considered to be a major beneficial contributor to the Mediterranean diet. Among them, olives and figs are characteristic and abundant fruits in this diet [6, 7, 17].

Dried fig antioxidants can enrich lipoproteins in plasma and protect them from subsequent oxidation. In addition, they produce a significant increase in plasma antioxidant capacity for 4 hours after consumption, and overcome the oxidative stress of consuming high fructose corn syrup in a carbonated soft drink [17].

Besides their ubiquitous polyphenols, figs have other compounds with anticancer activity, specifically benzaldehyde and coumarins [7]. Benzaldehyde has been used successfully to treat terminal human carcinomas [39]. Coumarins are the major compounds isolated from volatile extracts of figs [40]. The furanocoumarins identified in figs include angelicin, marmesin, psoralen, umbelliferone, and bergapten [41]. Coumarins have also been used for the treatment of prostate cancer [42, 43]. Psoralens, such as in the fig compound angelicin, are currently being investigated for the treatment of skin cancers and have been recommended for clinical trials because they have low skin phototoxicity [44]. These compounds produce free radicals and photoadducts of DNA that inhibit proliferation of the cancer cells [45]. Moreover, potent *in vitro* suppressors of cancer cell proliferation have been found in a fraction isolated from figs [46].

Dietary phytoestrogens present in dried figs have attracted much interest in recent years because of their potential protective effects against many diseases and conditions including cancer, cardiovascular disease (CVD), osteoporosis, and menopausal symptoms [47–53].

## 15.5 Conclusions

Dried figs are an excellent source of fiber, minerals, and certain phytochemicals and possess strong antioxidant activities. They are low in fat and sodium. Dried figs retain most of the nutritional benefits and health protective bioactive compounds of fresh figs. When fresh figs

are not available, properly dried figs could thus be used as a valuable substitute in diets that aim to prevent certain diseases.

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# **16 Drying nectarines: functional compounds and antioxidant potential**

Daniel Valero, Huertas María Díaz-Mula,  
and María Serrano

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## **16.1 Introduction**

Nectarines are delicious summertime fruits, mainly consumed fresh. Genetically, nectarine fruits are related to peaches since they belong to the same species, *Prunus persica*, and nectarines being *P. persica* var. nectarines. Peaches and nectarines can be differentiated by skin texture; nectarines have smooth skin, while peaches have fuzzy or velvety skin. Both fruits are available in clingstone and freestone types. Nectarines, as other stone fruits, are characterized by highly lignified endocarp (pit or stone), fleshy mesocarp (pulp), and thin epicarp (skin). Production of peaches and nectarines worldwide was about 20,000 million tonnes in 2009, these fruits having the highest production among stone fruits. The main producer is China, with more than 10,000 million tonnes, followed by Italy, the United States, and Spain [1].

In general, nectarine cultivars are grouped into two types: soft flesh and tough flesh. The latter has a longer shelf life and is most preferred by consumers. Also, the flesh of nectarines can be white or yellow, depending on the variety, while all of them have smooth and red skin. Nectarines are not only sweet and tasty, but they are loaded with innumerable health benefits [2–4].

From the point of view of nectarine fruit quality and consumer acceptance, several authors have found a linear relationship between total soluble solids (TSS) and consumer acceptance, showing that TSS below 11 to 12% is considered as being unacceptable, although for low-acid cultivars the acceptance by consumers depends more on the TSS/total acidity (TA) ratio than TSS alone [5, 6]. In addition, consumer acceptability is also dependent on fruit firmness, since too soft or too firm flesh impacts negatively on quality attributes [7]. Color changes that are associated with ripening strongly influence both visual and eating quality of nectarines. In this sense, genotype differences markedly affect color intensity, the main pigments responsible for color (both skin and flesh) being carotenoids [8].

Fruits are an important part of our daily diet and their increased intake has been associated with reduced incidence of human diseases due to their antioxidant potential attributed to several compounds which vary widely in chemical structure and function in plant tissues and are grouped into vitamins (C and E), carotenoids, phenolics, and thiol compounds [9–11].

Nectarines are mainly consumed fresh worldwide. However, as in other climacteric fruits the ripening process evolves quickly after harvesting, leading to quality losses and reducing the fruit shelf life. Therefore, canning and freezing have traditionally been used in the fruit processing industry to extend their shelf life. The drying process is another mode of fruit preservation consisting of the removal of water vapors from the system after they have separated from the fruit tissues. This process tends to extend the storage life by months or even years. In spite of this, there are some chemical and physical changes that occur during and/or after processing, which leads to a gradual loss of quality, such as discoloration and off-flavor development [12]. This chapter reports the available information about the nutritive properties of dried nectarines, with special emphasis on their antioxidant properties due to the content of bioactive compounds such as carotenoids and phenolics, as compared with those present in fresh nectarines.

## 16.2 How to dry nectarines

The earliest recorded mention of dried fruits can be found in Mesopotamian tablets dating back to about 1700 bc, which contain what are probably the oldest known written recipes. Traditional dried fruits were either sun-dried or dehydrated in wind tunnels and they have a long history of food safety. The high drying and processing temperatures, the intrinsic low pH of the fruit, the low water activity, and the presence of natural antimicrobial compounds in dried fruits make them a remarkable stable food. There is no known incident of a food-borne illness related to dried fruits. Dried nectarines are not a common food as other fruits such as prunes or raisins, although in the recent years some dried nectarine types can be found in the market.

Traditionally, nectarines were sun-dried, although this process was dependent on weather conditions of each year and had risks due to attack by insects and fungi that produce phytotoxins. Therefore, various methods of drying chambers or tunnels under controlled conditions have been developed in recent years for this purpose, which show some interesting advantages against the traditional sun-drying. Principally, the drying time is shortened and different combinations of air velocity, temperature, and time can be used, leading to lower changes in color, taste, and nutritional values than those occurring when high drying temperatures and times are used [13]. In addition, the drying process is under better sanitary conditions, because of a reduction in contamination by dust and other forcing matter and dehydration is not conditioned by rain or weather changes. Thus, dried nectarines are prepared from sound, mature fresh nectarines which have been washed, peeled, pitted, cut into slices, sulfured for color retention, and dried to remove the greater portion of moisture. Nectarine slices should be dried to a moisture content of 18 to 20%, until their water activity falls below 0.6, which is the industry standard for storage of dried fruits. After the drying process, nectarines have a pronounced sweet flavor, chewy texture, and a deep red-orange blush.

## 16.3 Compositional and nutritional characteristics of dried nectarines

Compositional and nutritional characteristics of dried nectarines as compared to that of fresh ones are shown in Table 16.1 [14–16]. Moisture content of fresh and dried nectarines is

**Table 16.1** Compositional and nutritional characteristics of fresh and dried nectarines (values in per 100 g edible portion)

Nutrient	Units	Fresh nectarines [14]	Dried nectarines [15, 16]
<b>Proximate composition</b>			
Water	g	87.6	20
Energy	kcal	44	220–280
Protein	g	1.08	4–6
Lipid	g	0.32	0.6
Ash	g	0.48	
Carbohydrate	g	10.55	46–66
Dietary fiber	g	1.7	5–7
Sugars	g	7.89	
<b>Minerals</b>			
Calcium	mg	6	26
Copper	mg	0.09	–
Iron	mg	0.28	3
Magnesium	mg	9	–
Manganese	mg	0.05	–
Phosphorus	mg	26	–
Potassium	mg	201	960
Selenium	μg	nd	–
Sodium	mg	nd	5
Zinc	mg	0.17	–
<b>Vitamins</b>			
Betaine	mg	0.2	–
Choline	mg	6.2	–
Folate	μg	5	–
Niacin	mg	1.13	–
Pantothenic acid	mg	0.19	–
Pyridoxine	mg	0.03	–
Riboflavin	mg	0.03	–
Thiamin	mg	0.03	–
Vitamin A (RAE)	μg	17	21
Vitamin C	mg	5.4	10
Vitamin E (ATE)	mg	0.77	–
Vitamin K	μg	2.2	–

RAE, retinol activity equivalents; ATE,  $\alpha$ -tocopherol equivalents; nd, not detected.

Some numbers are rounded to the second digit after decimal point.

around 88 and 20%, respectively. Dried nectarines tend to be higher in calories than fresh nectarines, as the reduction in water condenses the fruit. Thus, dried nectarines are relatively calorie-dense, since 100 g provides 220 to 280 kcal, which is 12% of the suggested daily intake of 2000 calories, while fresh nectarines would contain just 44 kcal. Dried nectarines, similar to other fruits, are a rich source of carbohydrates, with concentration of 46 to 66 g/100 g, while fresh nectarines contain 10.55 g/100 g. Dried nectarines provide more than threefold higher dietary fiber than fresh ones. Both fresh and dried nectarines are poor sources of lipid and protein. Information about vitamin content of dried nectarines is scarce, and only vitamins A and C have been found in dried nectarines. Finally, dried nectarines

are a good source of mineral, especially potassium, with concentration of approximately 1 g/100 g (Table 16.1).

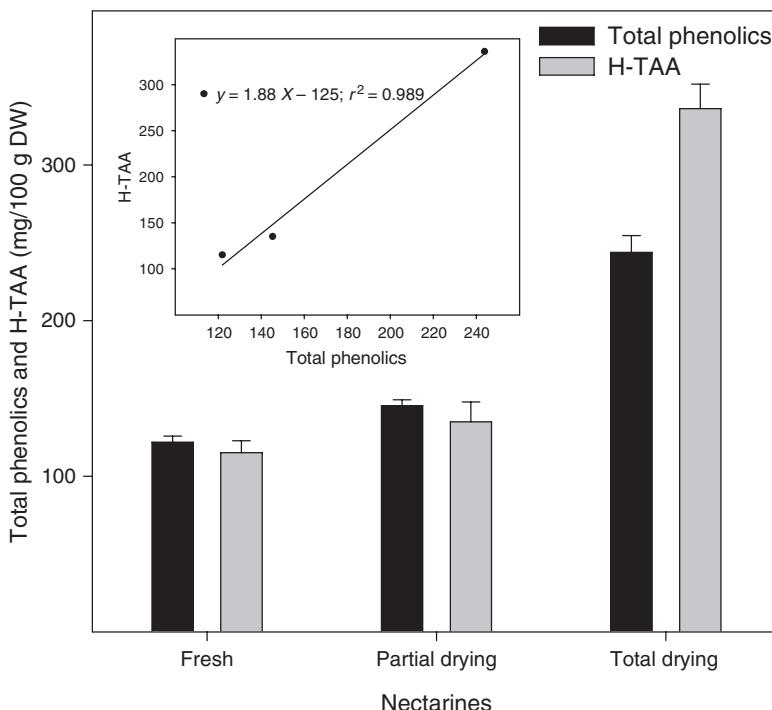
## 16.4 Phytochemicals in dried nectarines

The health benefits associated with fresh fruit consumption are broadly known and linked with convincing evidence for lowered risk of cardiovascular disease (CVD) [17], cancer [18], and antioxidant activity [19].

It has been reported that nectarines contain different bioactive compounds with antioxidant activity such as polyphenols and carotenoids with large variation among round and flat nectarine cultivars [2–4, 20, 21]. In particular, polyphenols and their associated antioxidant properties are increasingly linked with health and lowering of the risk of chronic diseases. Phenolic compounds are not uniformly distributed within the tissue of fruits, and more of them are concentrated in the epidermal and subepidermal tissues of the fruit as has been reported for peaches, nectarines, and plums [2, 4, 22]. However, the effects of drying practices on polyphenols and antioxidant activities have not been systematically studied in fruits in general and no evidences exist in the literature about this issue in dried nectarines.

We have analyzed the effect of drying process on total phenolics, total carotenoids, and total antioxidant activity in both hydrophilic and lipophilic extracts (H-TAA and L-TAA, respectively) from nectarines. Nectarines were first dried till they had 50% of water content (partial drying) and then totally dried in an oven at 60°C for 24 and 72 hours, respectively. Total phenolic content in fresh nectarines was 121.9 mg gallic acid equivalents (GAE)/100 g dry weight basis (DW), which is within the range of nectarines in the literature (10 to 80 mg GAE/100 g of fresh weight depending on cultivars) [2, 3, 20]. Results showed an increase in total phenolic content and H-TAA upon drying of nectarines (Figure 16.1). It has recently been reported that total phenolic content increases during the drying process of two grape cultivars due to increases in phenolic acids, flavans, flavonols, and anthocyanins [23]. Rababah *et al.* [24] reported that the levels of total phenolics were higher in dried apples, strawberries, and peaches than in fresh fruits. Slatnar *et al.* [25] have recently shown that individual phenolic compounds and total phenolics were at higher concentration in dried figs than their fresh counterparts. In addition, total phenolic concentration in apricots increased after hot drying treatments, combined or without microwave energy, although some individual phenolic acids, such as caffeic and gallic acids, decreased [26]. Phenolic acids such as chlorogenic and neochlorogenic acids have been reported to be the dominant phenolic compounds in nectarines [20].

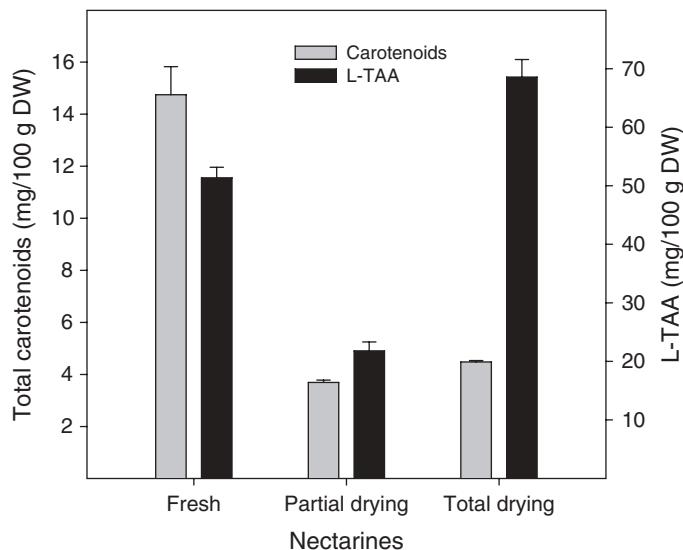
The increment on phenolic concentration upon drying process could be due to greater ease in the extraction of these compounds as a result of cell structure alteration and breakage of the skin during the drying process. Thus, dried fruits represent a shelf-stable and rich source of dietary polyphenols, compared with polyphenolic-rich fresh fruits. Moreover, phenolic content and antioxidant activity in dried fruits remained unchanged after long-term storage [27]. Dried nectarines could fulfill consumer's wishes for a diet with health benefits [28]. However, the drying process can also lead to loss in total phenolic compounds or changes in the ratio of free to total polyphenols [29]. Hot drying of raspberries at 77°C for 4.5 hours significantly reduced the total phenolic content and antioxidant activity, mainly due to the degradation of anthocyanins, which are less stable to temperature treatments than



**Figure 16.1** Total phenolic concentration (milligrams of gallic acid equivalents per 100 g of dry weight, DW) and hydrophilic total antioxidant activity (H-TAA, milligrams of trolox equivalents per 100 g of DW) in fresh nectarines and after partial and total drying (unpublished data).

polyphenols [30]. Thus, high-temperature treatments of drying fruits could lead to loss of bioactive compounds, especially in those fruits with a high anthocyanin concentration.

H-TAA also increased in both partially and totally dried nectarines with respect to fresh ones (Figure 16.1). It has been reported that the antioxidant activity was significantly increased in dried apricots and raisins with respect to their fresh counterparts [26, 31]. Moreover, the antioxidant activity was higher in dried strawberries, apples, and peaches than those of fresh fruits. This increase was higher if ascorbic acid was added before drying [24]. H-TAA was highly correlated with total phenolic concentration in other dried fruits [23, 24, 27] as well as in a wide range of fresh nectarine cultivars [2–4], showing that, as for fresh fruits, the antioxidant activity in the hydrophilic fraction of dried fruit extracts is mainly due to phenolic compounds [22, 32, 33]. Thus, total phenolics could be considered the main bioactive compounds contributing to H-TAA, since it has been reported that vitamin C (another hydrophilic antioxidant compound) makes a low contribution to H-TAA. This compound was found at low concentrations in peach and nectarine cultivars [21, 34]. Nevertheless, loss of vitamin C as a consequence of thermal processing has been reported in fruits, probably due to its utilization for protection against the oxidation of polyphenols in fruit tissues [35]. The elevated antioxidant activity in dried nectarine could also be due to the generation of Maillard reaction products (MRPs) during the drying process, which can enhance antioxidant potential in dried fruits [36]. The contribution of the MRPs to the antioxidant capacity of dried fruits is supported by the findings of Madrau *et al.* [37], who reported



**Figure 16.2** Total carotenoid concentration (milligrams of  $\beta$ -carotene per 100 g of dry weight, DW) and lipophilic total antioxidant activity (L-TAA, milligrams of trolox equivalents per 100 g of DW) in fresh nectarines and after partial and total drying (unpublished data).

an increase in antioxidant activity after the drying process of apricots in spite of a decrease in phenolics present. Moreover, the contemporary decrease in polyphenols and increase in antioxidant activity could also be due to an increased antioxidant power of polyphenols in an intermediate state of oxidation.

Total carotenoid content decreased with drying, from 14.74 mg/100 g (DW) in fresh nectarines to 4.48 mg/100 g (DW) in dried nectarines (Figure 16.2). These carotenoid contents are within the range of reported values for other round white-fleshed peaches and nectarines in which the major carotenoid is  $\beta$ -carotene followed by  $\beta$ -cryptoxanthin and lutein + zeaxanthin [2, 4, 14, 21, 34, 38]. Lavelli *et al.* [39] reported a decrease in the content of  $\beta$ -carotene after thermal processing of nectarine purées at 100°C for 5 minutes. However, García-Parra *et al.* [40] have recently shown that less intense stabilization treatment, as 80°C for 5 minutes, does not affect the total carotenoid content or the individual carotenoid compounds. Very few reports have examined the antioxidant activity in the hydrophilic and lipophilic fractions separately, although evidences exist for some fresh peaches, nectarines, and plums, in which correlations exist between carotenoids concentration and L-TAA [4, 22, 38, 39, 41]. In other stone fruits (such as sweet cherries, apricots, peaches, and plums), L-TAA as well as the content of tocopherols ( $\alpha$ ,  $\beta$  +  $\gamma$ , and  $\delta$ ) in the skin was determined, although no correlations were established [42]. Thus, tocopherols as other lipophilic substances might contribute to the L-TAA.

## 16.5 Health benefits of dried nectarines

The growing demand for healthy and nutritive foods in the world today has made nutrient analyses a major area in quality control studies. The antioxidant capacity of fruits varies

in relation to antioxidant compounds present in different species, although variations can occur among cultivars within a single species [2, 3, 22, 32, 34]. Dietary phenolic intakes, in particular, are known to reduce coronary heart diseases (CHD) and cancer, as well as to act as antimicrobial, antiallergic, antimutagenic, and anti-inflammatory agents due to their antioxidant properties [43]. The antioxidant activity of phenolic compounds is based on their ability to scavenge free radicals, chelate pro-oxidant metal ions, and inhibit some oxidant enzymes. In addition, polyphenols of fruits have an inhibitory effect in fat cell development and intracellular fat deposition, that is, they have antiadipogenic activity leading to reduction of the risk for the development of obesity [30]. Thus, since dried nectarines have even greater content of phenolic compounds and higher antioxidant potential than fresh ones, the consumption of this commodity could be a good alternative to the intake of health beneficial compounds when fresh nectarines are not available in the market.

## 16.6 Commercial products and industrial applications of dried nectarines

The commercialization of dried nectarines around the world is not as high as that of other dried fruits such as plums or raisins, and only a few companies make dried nectarines, especially in the United States (such as Sunsweet Nutrition, Sid Wainer & Son, Barry Farm Foods, California Gourmet Company, Bella Viva Orchards, and Steward and Jasper Orchards, among others). However, this is an interesting product, with possibilities of reaching new markets, due to their high-quality attributes, with special emphasis on high phenolic content and antioxidant activity upon drying process, leading to health beneficial effects when consumed.

## 16.7 Conclusions

Nowadays, there is an increasing demand for dried fruits in several parts of the world, such as the United States, the United Kingdom, Germany, and Australia, partly due to the presence of bioactive compounds with beneficial health effects. The production of nectarines as dried fruits is scarce around the world, although it is an interesting fruit to be used for drying process, leading to new market opportunities to solve the problem of their harvest in a very short season. In addition, the content of bioactive compounds, such as polyphenols, and the antioxidant activity increase upon drying process and then the consumption of dried nectarines could have even more health beneficial effect for consumers than those of fresh nectarines.

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## 17 Phytochemical composition and health aspects of peach products

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### 17.1 Introduction

Peaches (*Prunus persica*) are juicy, sweet drupe fruits belonging to the Rosaceae family, which are categorized as “stone fruits” because their seeds are enclosed in a hard, stone-like endocarp. They originated in China and were introduced to Persia and then to Europe by the Romans, and later on to the rest of the world by the Spaniards. Commercially, they can be classified as clingstone and freestone, depending on whether the flesh sticks to the stone or not. They can also be classified as white or yellow, according to their flesh color. Clingstone are especially used in the processing industry, while freestone are used mainly as fresh fruits [1].

World production of peaches has shown a 52% increase since 1999, with a total production of more than 20 million tonnes in 2009. In a recent study, Konopacka *et al.* [2] reported that among 4271 European consumers, 39% consumed three to five peaches per week, and 23.8% more than five fruits per week. China is the main producer with a 50% share of the total production in 2009, followed by Italy, United States, Spain, Greece, and Turkey, with an overall share of 26.5% of the world production [3]. In 2008, 48% of the total production of peaches in the United States was consumed fresh. Canned (37.6%) and frozen (9.8%) are the main processed peach products consumed in the United States. Dried peaches represent approximately 1% of the total production, while other products such as juices, jams, and jellies represent around 3%. Due to the increase in scientific information on the health benefits of consumption of fresh fruits, there has been a decrease (~10%) in the consumption of canned peaches, due to an increase of fresh (~2%), frozen (~7%), and juice (~2%) use compared to the 1980. In the same period of time, the consumption of dried peaches has shown only a slight decrease (0.27%) [4].

Dried peaches are defined by the US standard as “the halved and pitted fruit of the peach tree (*Prunus persica*) from which the greater portion of moisture has been removed. Before packing, the dried fruit is processed to cleanse the fruit and may be treated with sulfur dioxide in order to retain its characteristic color.” Federal inspection certificates indicate the moisture content of the finished product not more than 25% by weight [5]. Production of dried peaches

involves washing, peeling, cutting, blanching with hot water, and/or ascorbic acid, or other antioxidants to minimize discoloration, and finally sun or oven drying. It is generally known that during processing, there is a decrease in the phytochemical content of dried products. This chapter summarizes the effect of drying on the phytochemical content and antioxidant capacity of fresh and dried peaches, where available the possible health benefits of dried peaches and other minor products are discussed.

## 17.2 Compositional and nutritional changes of peaches during dehydration

Among the most complete compositional database of peaches, the USDA [6] proposes the nutrient database information for the edible portion of raw peaches. Table 17.1 summarizes the compositional and nutritional characteristics of raw, dried, and dehydrated peaches [6]. Water represents 88.87% of peaches, hence an energy value of 39 kcal/100 g of edible portion. However, after drying the water content is 31.8 and 7.5% for dried (uncooked, sulfur dioxide-treated dried) peaches and dehydrated peaches, respectively, affecting the contents of all nutritional components [6]. Energy value increases to 239 and 325 kcal/100 g for dried and dehydrated peaches, respectively (Table 17.1).

Protein content of fresh peaches is approximately of 0.91 g/100 g, aspartic acid being the most abundant amino acid. After drying or dehydration, the protein content increases to 3.61 and 4.89 g/100 g, respectively. However, if the analysis is done on a dry weight basis, it is possible to observe a reduction in the protein content from 8.18 g/100 g for fresh peaches to 5.29 g/100 g for dried peaches. This reduction could be due to deteriorative reactions or to lixiviation during the drying process. In all cases, aspartic and glutamic acids remain the major amino acids present. Lipid content in fresh peaches is 0.25 g/100 g, of which 7.6% are saturated fatty acids (SFA), 26.8% monounsaturated fatty acids (MUFA), and 34.4% polyunsaturated fatty acids (PUFA). This composition remains practically unchanged during the drying process. These values suggest that peaches are a good source of PUFA. As in the case of protein, lipid content increases to 0.76 and 1.03 g/100 g for dried and dehydrated peaches, respectively. The total carbohydrate and dietary fiber of raw peaches are 9.54 and 1.5 g/100 g, respectively. Sucrose is the most abundant sugar, followed by glucose and fructose. These three sugars also remain the most abundant in dried peaches (Table 17.1).

The main minerals found in peaches are K, P, Mg, Ca, Fe, Zn, Cu, and Mn. Concentration of all of these minerals increases in dried and dehydrated peaches. The edible portion of raw peaches possesses a variety of fat- and water-soluble vitamins. Most of these compounds can be classified as labile structures, sensitive to light and high temperature, among other factors, that can be involved in the dehydration procedure. Even when no drying conditions are reported in the USDA database, it is evident that drying drastically reduces vitamin E content (Table 17.1). Thiamine, folic acid, and ascorbic acid (vitamin C) are also reduced in dried peaches, but show a recovery in the dehydrated form, probably due to water loss. Reduction in thiamine is associated with the use of sulfur dioxide, which is known to destroy this vitamin [7].

Considering that the drying process can have very drastic effects on the content of natural bioactive compounds of raw peaches, several mechanisms can be contemplated to prevent this loss [8]. For many years, sulfur dioxide has been used as antioxidant in the drying process of peaches, in order to prevent the loss of carotenoids and ascorbic acid. Packaging material and

**Table 17.1** Compositional and nutritional characteristics of fresh, dried, and dehydrated peaches (values in per 100 g edible portion)

Nutrient	Units	Fresh	Dried	Dehydrated
<b>Proximate composition</b>				
Water	g	88.87	31.8	7.5
Energy	kcal	39	239	325
Protein	g	0.91	3.61	4.89
Lipid	g	0.25	0.76	1.03
SFA	g	0.02	0.08	0.11
MFA	g	0.07	0.28	0.38
PUFA	g	0.09	0.37	0.50
Ash	g	0.43	2.50	3.39
Carbohydrate	g	9.54	61.33	83.18
Dietary fiber	g	1.5	8.2	nr
Sugars	g	8.39	41.74	nr
Fructose	g	1.53	13.49	nr
Glucose	g	1.95	12.83	nr
Sucrose	g	4.76	15.42	nr
<b>Minerals</b>				
Calcium	mg	6	28	38
Copper	mg	0.07	0.36	0.493
Fluoride	µg	4.0	nr	nr
Iron	mg	0.25	4.06	5.51
Magnesium	mg	9	42	57
Manganese	mg	0.06	0.30	0.41
Phosphorus	mg	20	119	162
Potassium	mg	190	996	1351
Selenium	µg	0.1	0.5	nr
Sodium	mg	nd	7	10
Zinc	mg	0.17	0.57	0.78
<b>Vitamins</b>				
Betaine	mg	0.3	nr	nr
Choline	mg	6.1	12.7	nr
Folate	µg	4	nd	7
Niacin	mg	0.81	4.38	4.82
Pantothenic acid	mg	0.15	0.56	0.52
Pyridoxine	mg	0.03	0.07	0.16
Riboflavin	mg	0.03	0.21	0.07
Thiamin	mg	0.02	tr	0.04
Vitamin A (RAE)	µg	16	108	71
Vitamin C	mg	6.6	4.8	10.6
Vitamin E (ATE)	mg	0.73	0.19	nr
Vitamin K	µg	2.6	15.7	nr
<b>Amino acids</b>				
Alanine	g	0.028	0.215	0.292
Arginine	g	0.018	0.092	0.124
Aspartic acid	g	0.418	0.602	0.817
Cystine	g	0.012	0.029	0.040
Glutamic acid	g	0.056	0.548	0.743
Glycine	g	0.021	0.126	0.171
Histidine <sup>a</sup>	g	0.013	0.067	0.091

(continued)

**Table 17.1** (Continued)

Nutrient	Units	Fresh	Dried	Dehydrated
Isoleucine <sup>a</sup>	g	0.017	0.104	0.141
Leucine <sup>a</sup>	g	0.027	0.204	0.277
Lysine <sup>a</sup>	g	0.030	0.116	0.157
Methionine <sup>a</sup>	g	0.010	0.087	0.118
Phenylalanine <sup>a</sup>	g	0.019	0.114	0.154
Proline	g	0.018	0.152	0.206
Serine	g	0.038	0.167	0.226
Threonine <sup>a</sup>	g	0.016	0.141	0.192
Tryptophan <sup>a</sup>	g	0.010	0.010	0.014
Tyrosine	g	0.014	0.094	0.128
Valine <sup>a</sup>	g	0.022	0.197	0.267

Source: Adapted from USDA [6].

Some numbers are rounded to the second digit after decimal point.

SFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids; RAE, retinol activity equivalents; ATE,  $\alpha$ -tocopherol equivalents; nr, not reported; nd, not detected; tr, trace.

<sup>a</sup>Indispensable amino acids.

packaging atmosphere can be used to control sulfur dioxide loss from dried peaches during extended storage; nitrogen packaging also reduces the loss of sulfur dioxide from dried peaches and helps to maintain higher levels of antioxidant compounds. This information reveals that due to their composition, dry peaches represent a healthy consumption option, rich in fiber and bioactive compounds, being also an interesting option for the agribusiness to develop functional foods.

## 17.3 Phytochemicals in fresh and processed peaches

Phytochemicals are defined as bioactive nonnutritive plant compounds found in fruits, vegetables, grains, and other plant-derived foods that have been linked to reducing the risk of major chronic diseases [9]. The major phytochemicals found in peaches are polyphenolic compounds, carotenoids, and nondigestible carbohydrates such as pectin and dietary fiber.

### 17.3.1 Polyphenolic compounds and antioxidant capacity

Polyphenolic compounds are secondary metabolites of plants with an aromatic ring bearing one or more hydroxyl groups in their structure. They are usually classified into two main groups of flavonoids and non-flavonoids, and each group can be further classified according to the number of carbon atoms, phenol rings, and structural elements that bind these rings [10]. The main classes of flavonoids are flavones, flavonols, flavanones, flavan-3-ols, anthocyanidins (anthocyanins when glycosylated), and isoflavones, among others. Meanwhile, the main classes of non-flavonoids are hydroxybenzoic acid and hydroxycinnamic acid derivatives. Polyphenolic compounds are recognized for their high antioxidant capacity; the antioxidant activity of individual phenolics depends on several structural features, including position and number of hydroxyl groups [11]. The total antioxidant capacity of fruits is

usually highly correlated with concentrations of total or individual polyphenols, indicating that these compounds are the main contributors to the antioxidant capacity of fruits [9].

Concentrations of total phenolics, total antioxidant capacity, major flavonoids, and carotenoids reported in fresh (raw) and processed peaches are shown in Table 17.2 [12]. Total phenolic compounds in fresh peaches range from 38 [13] to over 300 mg gallic acid equivalents (GAE)/100 g [14] of fresh fruit, with an average concentration of 133 mg GAE/100 g [15]. These wide variations may be due to natural causes such as differences among cultivars, geographical area, maturity stage, agronomic, and postharvest practices; but they are also caused by differences in the analytical methods, especially in the extraction procedures and solvents. The major classes of phenolic compounds found in peaches are flavan-3-ols (catechin, procyanidin B1, and epicatechin) followed by hydroxycinnamic acid derivatives (such as chlorogenic and neochlorogenic acids). Structures of some phytochemicals found in peaches are given in Figure 17.1. The peels of some red-colored peach cultivars are also rich in anthocyanins [16]. Peaches contain relatively low concentrations of flavonols (quercetin glucosides). Total antioxidant capacity of raw peaches is 1922  $\mu\text{mol}$  of trolox equivalents (TE)/100 g of fresh sample [15].

Processing of peaches may cause some alterations in the contents of phenolic compounds and antioxidant activity in peach products, depending on the type and intensity of the process. Canning is the most common form of peach processing; however, few studies exist on the effect of canning on the content of phenolic compounds in peaches. Thermal processing during canning induces the loss of total phenolic compounds and procyanidins (polymeric flavan-3-ols) in peaches [17, 18]. However, these losses are dependent on the processing temperature. Processing at 90°C for 40 minutes did not result in any significant loss in total polyphenolic compounds [17]. For procyanidins, these losses were also dependent on the degree of polymerization of the compound. Thus, octamers were completely lost in the process while monomers to heptamers were reduced by 6–30% and could be detected in the syrup in quantities that accounted for the loss in the peach tissue [18]. Cold storage at 4°C for 14 days or freezing and storing at –12°C for 3 months produced no loss in total polyphenolic compounds in peaches [17].

Peach juices are common peach products; fresh peach juices contain between 68.8 and 75.4 mg GAE/100 g total phenolic compounds, the main compounds quantified are catechin (2.0–3.4 mg/100 g juice) and chlorogenic acid (1.2–1.9 mg/100 g juice), followed by iso-quercetin (quercetin-3-glucoside, 0.52–0.71 mg/100 g juice) [19]. Purees and concentrates are intermediate products in the elaboration of commercial fruit juices. The contents and types of phenolic compounds in these products have been determined by several authors. Bengoechea *et al.* [20] found that chlorogenic acid and catechin were the major polyphenolic compounds in peach purees, while chlorogenic and neochlorogenic acids were major phenolics in peach concentrates. No flavonols were found in these products. The authors concluded that phenolic compounds can be helpful in the characterization of fruit purees and concentrates as well as in the detection of adulteration in the manufacturing of commercial fruit juices. Talcott *et al.* [21] demonstrated that the production of peach purees without periderm removal increased the processing yield and levels of polyphenolic compounds and antioxidant capacity, without significantly impacting product quality attributes. The major polyphenolic compounds found were chlorogenic and neochlorogenic acids, followed by catechin. They also found that blanching time impacted the antioxidant capacity and contents of phenolic compounds in purees. However, the losses during processing (steam-blanching, blending, and pasteurization) or storage were low, in fact a long blanching time (20 minutes) enhanced

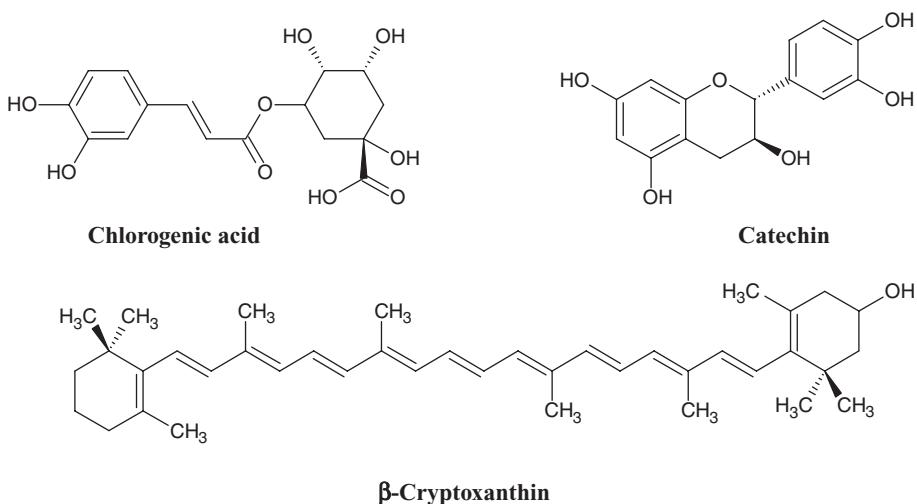
**Table 17.2** Phenolic compounds, antioxidant capacity, and carotenoids of raw and processed peaches (values in per 100 g edible portion)

	<b>Fresh peaches (white flesh)</b>	<b>Canned peaches</b>	<b>Dry peaches (40% moisture)</b>	<b>Reference</b>
Total phenolics (mg of GAE)	133 ( <i>n</i> = 15)	nr	73 ( <i>n</i> = 2)	[15]
Total antioxidant capacity (μmol of TE)	1922 ( <i>n</i> = 15)	nr	436 ( <i>n</i> = 2)	[15]
<b>Individual flavonoids (mg)</b>				
Catechin	4.92 ( <i>n</i> = 49)	12.25 ( <i>n</i> = 30)	1.87 ( <i>n</i> = 1)	[12]
Epicatechin	2.34 ( <i>n</i> = 49)	4.09 ( <i>n</i> = 30)	nd	[12]
Epigallocatechin	1.04 ( <i>n</i> = 14)	nr	nr	[12]
Cyanidin	1.61 ( <i>n</i> = 45)	0.97 ( <i>n</i> = 30)	nd	[12]
Quercetin	0.66 ( <i>n</i> = 40)	0.45 ( <i>n</i> = 30)	nd	[12]
Kaempferol	0.22 ( <i>n</i> = 3)	nr	nd	[12]
<b>Carotenoids (μg)</b>				
α-Carotene	nd	nd	3 ( <i>n</i> = 0)	
β-Carotene	162 ( <i>n</i> = 32)	nr	1074 ( <i>n</i> = 0)	[6]
β-Cryptoxanthin	67 ( <i>n</i> = 32)	nr	444 ( <i>n</i> = 0)	[6]
Lutein + zeaxanthin	91 ( <i>n</i> = 8)	nr	559 ( <i>n</i> = 0)	[6]

Some numbers are rounded to the second digit after decimal point.

Data in parentheses show the number of data points.

GAE, gallic acid equivalents; TE, trolox equivalents; nr, not reported; nd, not detected.



**Figure 17.1** Structures of some phytochemicals found in peaches.

the yield of some phenolic compounds in the purees. Antioxidant capacity of peach purees was highly correlated with the concentration of chlorogenic acid [21]. Production of peach purees at room temperature, followed by heat treatment, reduced the contents of polyphenolic compounds in the purees in comparison with a traditional process of hot pulping/finishing, probably due to a lower extraction yield [22]. Loss of individual polyphenols calculated with respect to the amounts present in fresh fruits varied from 5 to 82% depending on the individual compound, peach variety, and type of process. Loss of cyanidin-3-glucoside was considered favorable, since the presence of this anthocyanin in purees was correlated with an undesirable color [22].

Very few studies have analyzed the contents of phenolic phytochemicals and antioxidant capacity of dried peaches or the effect of dehydration on them (Table 17.2). Rababah *et al.* [23] studied the effect of ascorbic acid addition on the concentrations of total phenolics, antioxidant capacity, and anthocyanins of fresh and dried peaches. They found that addition of ascorbic acid had a minor impact while dehydration significantly increased the levels of total phenolics, antioxidant capacity, and anthocyanins (Table 17.3). This is expected, since water elimination from the fresh fruits concentrated all the compounds in the peach tissues.

**Table 17.3** Effect of drying on phenolic compounds and antioxidant capacity of peaches

	Fresh peaches	Dry peaches
Total phenolics (mg of GAE/100 g)	197.3	759.0
Total antioxidant capacity ( $\mu$ mol of TE/100 g)	1140	6760
Total anthocyanins (mg of cyn-3-glu/100 g)	1.9	5.1

Source: Adapted with permission from Rababah [23].

Data expressed as means ( $n = 3$ ) on a fresh weight basis.

GAE, gallic acid equivalents; TE, trolox equivalents; cyn-3-glu, cyanidin-3-glucoside.

Threlfall *et al.* [24] also found that polyphenolic compounds, antioxidant capacity, and anthocyanins were higher in dry peaches than those of their fresh counterparts. More studies on the effect of drying on peach polyphenolic compounds and antioxidant activity are needed. Nevertheless, it can be said that drying is a convenient method of peach processing, which effectively concentrates phenolic compounds and therefore increases antioxidant capacity in the dried products.

### 17.3.2 Carotenoids

There are over 600 known carotenoids that are synthesized by fruits and vegetables [25]. Carotenoids along with anthocyanins are the major pigments in peaches. As in the case of other phytochemicals such as polyphenols, carotenoid contents in peaches vary greatly among cultivars due to genotype, stage of maturity, climatic conditions, and postharvest practices, among others. Maturity is one of the main factors that control the amount of carotenoids in peaches, since during ripening there is an increase of carotenogenesis [26]. It has been reported that carotenoid content in yellow-flesh peaches (0.1–2.8 mg  $\beta$ -carotene equivalents/100 g) is higher than in white-fleshed cultivars (0.025–0.08 mg  $\beta$ -carotene equivalents/100 g) [27, 28].  $\beta$ -Carotene (0.004–0.31 mg/100 g) and  $\beta$ -cryptoxanthin (0.04–0.34 mg/100 g) [22, 29–32] are the main provitamin A carotenoids identified in peaches. Other carotenoids include  $\alpha$ -carotene (0.0082 mg/100 g), lutein (0.075 mg/100 g), and zeaxanthin (0.025 mg/100 g) [29]. Khachik *et al.* [33] reported a large difference between fresh and dried peaches (0.122 versus 4.47 mg/100 g). According to the USDA nutrient database [6], the main carotenoids in fresh and dried peaches are  $\beta$ -carotene,  $\beta$ -cryptoxanthin, and lutein + zeaxanthin. Their contents are 162, 67, and 91  $\mu$ g/100 g for fresh (raw) peaches and 1074, 444, and 559  $\mu$ g/100 g for dried peaches, respectively (Table 17.2). These results suggest that drying increases carotenoids concentration because of removal of water that concentrates the phytochemicals.

Gil *et al.* [30] reported that carotenoids were concentrated mainly in the peel, and  $\beta$ -carotene in the peel was two to six times higher than that in the flesh. Caprioli *et al.* [34] found that concentration of total carotenoids in peaches was higher than the sum of individual carotenoids determined by high-performance liquid chromatography (HPLC) and suggested that this may be due to different maximum absorption wavelength for each individual carotenoid, which is not taken into account with the spectroscopic method. Tavarini *et al.* [27] found no correlation between peach carotenoids and antioxidant capacity measured by the ferric-reducing antioxidant power (FRAP) assay.

Peach processing has been associated with a decrease in carotenoid content, which has also been correlated with a decrease in the chroma values of the processed peach products [32]. McHugh and Huxsoll [35] reported that color changes in extruded peaches were attributed to carotenoid degradation and nonenzymatic browning. This behavior has also been observed in fresh-cut peaches treated with a precutting heating at 50°C for 10 minutes [36], decreasing both the chroma value and the  $\beta$ -carotene content.

Canned peaches are by far the most commonly consumed form of processed peaches in the United States. There are few studies that report the effect of canning on the content of carotenoids in peaches. Khachik *et al.* [33] reported an increase in the concentration of total carotenoids in canned peaches (as per 100 g edible portion); however, they argued that these results may not reflect the expected carotenoid losses during processing since no information about the moisture content of fruits or initial carotenoid concentration of peaches

before processing was available. When the variations in carotenoid content of fresh and canned peaches were analyzed, a 50% reduction in both  $\beta$ -carotene and  $\beta$ -cryptoxanthin was observed [37, 38]. In a later study, a 10% increase in the content of *cis*-isomers was observed during processing, due to light, heat, and acid conditions [25]. It has been reported that this isomerization process changes the bioavailability and biological activity of carotenoids, because *cis*-isomers are less absorbed [25]. Other factors such as canning material and storage can also change the carotenoid content. Kaushal *et al.* [39] observed less carotenoid concentration in jars compared to cans under the same processing conditions. This reduction in the content of carotenoids during processing can be due to their decomposition which depends on several factors such as carotenoid structure, nature of the system, available oxygen, exposure to light, water content, temperature, atmosphere, and presence of antioxidants, prooxidants, and free radicals [26].

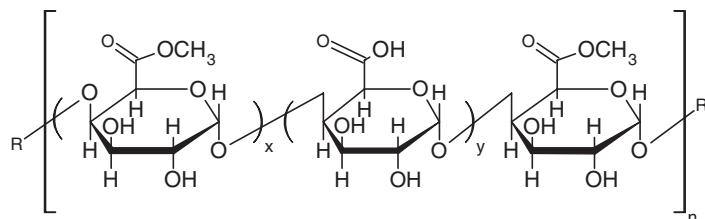
Other commonly consumed peach products are purees and nectars. Purees are intermediate moisture products that are used in the formulation of nectars. Lavelli *et al.* [22] reported a 48–65% reduction in carotenoid concentration, during puree processing, depending on peach variety and processing procedures. They observed a larger reduction in carotenoid concentration in Elegant Lady variety, which is more susceptible to enzymatic browning, than in Redhaven, which is a variety normally used for puree and nectar production. No further decrease in carotenoid content with respect to purees was observed during nectar production and storage for as long as 3 months. However, carotenoid concentration in lye-peeled nectars was lower than the whole peach nectars [22, 31]. These results are in agreement with the higher carotenoid concentration in peel than in flesh observed by Gil *et al.* [30].

It is well known that air-dried products undergo a significant reduction in carotenoids concentration. Higher carotenoid concentrations are reported in cabinet-dried vegetables than their solar-dried counterparts [25]. However, there is little information on carotenoid content in dried peaches. Two early studies suggested that peaches retained only 42% of their carotenoid content during dehydration [37, 40]. Mackinney *et al.* [40] observed that sulfur dioxide treatment reduced carotenoid losses during drying.

The main concern when analyzing carotenoids in dried fruits is to prevent their loss; however, in the several last years there has been an increased interest in analyzing the effect of processing on the bioavailability of carotenoids which suggest that their bioavailability is higher compared to the unprocessed samples [26].

### **17.3.3 Pectin and other nondigestible carbohydrates**

Pectin or pectic substances refer to a group of heteropolysaccharides that consist predominantly of partially methylated galacturonic acid residues [41]. Together with cellulose and hemicelluloses, they are the main components of the vegetable cell walls, and their molecular configuration is determinant of the textural properties of fresh and processed peaches [42]. Pectins are not digested and absorbed in the human small intestine; therefore they are part of the dietary fiber fraction of peaches and other fruits. Total dietary fiber constitutes 1.5 g/100 g of the edible portion of fresh peaches (Table 17.1), while in dried peaches it represents 8.2 g/100 g [6]. Total dietary fiber components are usually classified as insoluble (cellulose, hemicellulose, and the non-polysaccharide lignin) and soluble (pectins,  $\beta$ -glucans, and arabinoxylans) dietary fibers. Soluble dietary fiber content is high in fruits, vegetables, and legumes and is associated with colonic degradation and high fermentability, prebiotic properties, slow glucose absorption, lower serum cholesterol levels, and enhanced immune function



**Figure 17.2** Structure of pectin backbone found in peaches. Solubility and functional properties of pectins depend on the chain length ( $n$ ) and relation between methylated ( $x$ ) and free ( $y$ ) galacturonic acid residues.

[43]. Fresh and processed peaches are good sources of soluble dietary fiber (mainly pectins). Fresh and canned peaches contain 0.60 and 0.49 g of soluble fiber/100 g of edible portion, respectively [44]. Peach concentrate is rich in total dietary fiber (33.2 g/100 g), consisting of 11.3 g/100 g soluble and 21.9 g/100 g insoluble fibers [45].

Pectin is the most studied component of peach dietary fiber (Figure 17.2), mainly because of its profound effects on the textural properties of food products. The changes in the physicochemical characteristics of pectins during peach dehydration, and their relationship to changes in the texture of the dried products, have been studied [46]. It was found that fresh peaches (Carson variety) contain 2.63% pectin (on a dry weight basis) and that osmotic drying increased total and oxalate-soluble pectins (extracted in 0.005 M sodium oxalate solution, pH 5.6) while decreasing the content of water-soluble pectin and protopectin. However, the decrease in protopectin was minimal, and therefore the firmness and organoleptic properties of the dried peaches were not affected. Forni *et al.* [46] found that peaches behaved better than apricots when processed by osmotic dehydration. Later on, Levi *et al.* [42] studied the effect of blanching and thermal (oven) drying on the pectic constituents of peaches and found that adequate blanching stabilized pectins of the dehydrated peaches, so the higher the rehydration capacity, the lower the rehydration losses after 5 minutes of blanching. Total pectin in fresh peaches was 509 mg/100 g, of which 60% was soluble pectin, 25% protopectin, and 15% calcium pectate. After dehydration, total and soluble pectins were reduced, but protopectin was more stable. The stability of protopectin was also important for the rehydration properties of the peaches [42].

The health effects of pectin are receiving increased attention. Evidence exists that pectin can lower cholesterol and serum glucose levels and may also have anticancer activities [47]. However, to the best of our knowledge, no studies exist on the health benefits or biological activity of peach pectins.

## 17.4 Health effects of peaches

Fresh and processed peaches are good sources of nutrients such as carbohydrates, proteins, amino acids, vitamins, and minerals as well as health-promoting bioactive compounds such as phytochemicals and soluble dietary fiber. Therefore, peach products contribute to the intake of several types of phytochemicals having a positive influence on human health. Peaches may represent a significant contribution to the daily uptake of carotenoids and polyphenolic

compounds. They are highly consumed [2] and their serving size is often larger than that for other fruits [48].

It is well known that high intakes of carotenoids and polyphenolic compounds are associated with the prevention or reduction of the risk of some diseases, such as cardiovascular disease (CVD) [49] and certain types of cancer [50]. Therefore, peach consumption may aid in the prevention of such disorders. However, studies dealing with the healthful properties of fresh and processed peaches are very scarce.

Phenolic compounds extracted from peel and flesh of fresh peaches inhibited the copper-catalyzed human low-density lipoprotein (LDL) oxidation *in vitro* [51] and the proliferation of HepG2 human liver cancer cells [52]. Polyphenol-rich extracts of yellow-fleshed peaches also inhibit the proliferation of an estrogen-independent breast cancer cell line (MDA-MB-435) with a 50% inhibitory concentration ( $IC_{50}$ ), three-fold lower than for the inhibition of a noncancerous breast cell line (MCF-10A) [53].

One *in vivo* study was carried out in rats fed on a diet with or without 1% cholesterol and 10% whole dry peaches, apples, or pears. Peach supplementation did not affect serum or liver lipid levels in rats fed a cholesterol-free diet. Addition of cholesterol to the diet significantly increased total cholesterol, LDL-cholesterol, and triacylglycerols (TAG) in the serum and total cholesterol in the liver. Peach supplementation to the cholesterol-containing diet significantly hindered the rise in plasma and liver lipids, although the values were still higher than those of rats fed cholesterol-free diets [54]. Oxidation levels of serum lipids were evaluated by means of the thiobarbituric acid reactive substances (TBARS) assay and plasma antioxidant capacity was also measured as an indicator of *in vivo* oxidative status. Peach supplementation had no effect on either of these two variables independent of the presence or absence of cholesterol in the diet, suggesting that peaches have no effect in regulating oxidative status *in vivo* [54]. Apples were found to be more effective than peaches and pears in regulating lipid levels and markers of oxidative status [54]. The authors argue that this may be due to the higher concentrations of phenolic compounds found in apples and explain that the effects on lipid levels may also be dependent on the fiber content, which was high in all fruits tested [54]. As mentioned earlier, peaches are good sources of soluble dietary fiber [45], and it is known that dietary fiber intake provides many health benefits including reduction in the risk of developing coronary heart disease (CHD), stroke, and gastrointestinal disorders, among others [55]. In a different *in vivo* study, peach juice consumption in humans had a short-term effect on the antioxidant status of human plasma, evaluated using dichlorofluorescein. Consumption of 120 mL of peach juice (and other fruit juices) induced an increment in the plasma antioxidant status within 30 minutes after juice consumption; but the effect was lost after 2 hours [56].

A specific health benefit of peach consumption was found by an epidemiological cross-sectional cohort study [57]. The association between glaucoma and the consumption of specific fruits and vegetables was studied in a cohort of women aged 65 and older, participating in the study of osteoporotic fractures. The odds of glaucoma risk were found to decrease by 47% in women who consumed at least one serving per week of canned or dried peaches compared to those who consumed less than one serving per month. Consumption of one, two, or more servings of fresh peaches per week did not have any effect compared to less than one serving per week [57]. The protective effect of canned/dried peaches may be due to their content of vitamin A or provitamin A carotenoids, especially cryptoxanthin, which may become more bioavailable due to processing [25, 57].

Peach consumption may also have some potentially negative health effects. Fresh peaches may cause food allergies, due to the presence of the lipid transfer protein (Pru p3), which is the major allergen of peach in some populations [58]. Production of dried peaches is usually achieved by thermal drying procedures such as sun drying [59] or oven drying [60], and sulfites (sulfur dioxide or potassium meta-bisulfite) are used as preservatives and antioxidants [59, 60]. However, ingested sulfites may cause several mild to severe, and even fatal, adverse effects to the asthmatic population, including broncho-constriction, urticaria, and anaphylaxis, among others [61]. Therefore, consumption of dried peaches (and other dried fruits) containing high levels of sulfites may pose a threat to sensitive individuals, and use of alternative treatments to help preserve the quality of fruits throughout dehydration and storage is advisable [62, 63].

## 17.5 Dry peaches and their by-products

Drying is one of the less used processing options for peaches. This fruit is principally canned, and a small proportion is frozen, dried, or used to prepare other products such as jams, preserves, or beverages. The steps involved in common pre-drying of peaches are selection and sorting for size, maturity, and firmness; washing; peeling by hand, lie solution, or abrasion; cutting into halves, slices, cubes, or segments; and sulfating [8]. The quality of dehydrated peaches depends on many factors, such as raw material, drying temperature, process time, moisture content, and sulfur dioxide concentration. Dried peaches are utilized as pie, tart, and turnover filling, while their powder provides excellent purees, spreads, or glazes, after proper dehydration and preparation [8].

The processing of peaches results in the generation of waste in the form of peel, seeds, and trimmings. In the past, this costly problem has been mitigated to some extent by processing the by-products further to yield a product that presents less of disposal problem or that has some marginal economic value [64]. The processing of dried peaches could be improved by developing higher value use for the by-products. For instance, several patents have been published relating the use of peaches as a source of nutraceutical and cosmetic compounds [65, 66]. It has been found that fruit by-products contain high levels of various health-enhancing substances that can be extracted from the by-products to provide nutraceuticals [54, 67, 68].

Peach seeds are considered low-value agro-industrial residue. To achieve the most economical and efficient utilization of these seeds, more information on their varieties, properties, and composition is required [69]. Cyanoglycoside in peach kernel, also called amygdaline, can represent about 71–72 mg/100 g of HCN [70]. In Chinese medicine, peach kernel is one of the nine plant ingredients used in a cocktail for CVD [71]. Peach kernel contains 63.8% oleic acid, 15.4% linoleic acid, 20.7% SFA, and 27.5% protein [72]. Essential amino acids make up 32–34 g/100 g of total amino acids found in apricot kernels [69]. Protein values, which range from 17.11 to 21.33 g/100 g, are comparable with those of black beans, soy beans, and peanuts [73]. Peach seed is an agro-industrial residue that corresponds to approximately 10% of the fruit weight. Peach kernel flour was produced by drying at 45, 55, and 65°C, with or without maltodextrin.

Several potential uses can be considered for dry peach by-products, one of the most interesting options can be as food additives (antioxidants, antimicrobials, colorants, flavorings, and thickeners). It can be considered that the high content of bioactive compounds present

in peach by-products can be used as natural food additives. If this approach is realized, it would be feasible to fulfill the requirements of consumers for natural and preserved healthy food. In addition, the full utilization of peach fruits could lead the industry to a lower waste agribusiness and increasing industrial profitability.

## 17.6 Conclusions

Peaches are good sources of phytochemicals, mainly polyphenolic compounds and carotenoids. They can be consumed as both fresh and processed products. Among the existing processing options, drying or dehydration is not a very common form of peach preservation. However, this process has the advantage of concentrating the phytochemicals in the final product. Generally speaking, processing induces degradation of phytochemicals, depending on the fruit variety, processing technique, and type of phytochemicals present. However, very few studies have analyzed the effect of drying on the degradation of phenolic compounds and carotenoids in peaches. There are also few studies on the health effects of peach products. One of the most relevant studies showed that consumption of dried or canned peaches, but not fresh peaches, may protect individuals from glaucoma. This may bring about interest for studying, not only the concentration, but also the bioavailability of phytochemicals in dried peaches and their effect on different human and animal models. Finally, production of dry peaches generates large amounts of by-products (mainly kernels) that can be used as sources of economically important natural products.

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# **18 Dried pears: phytochemicals and potential health effects**

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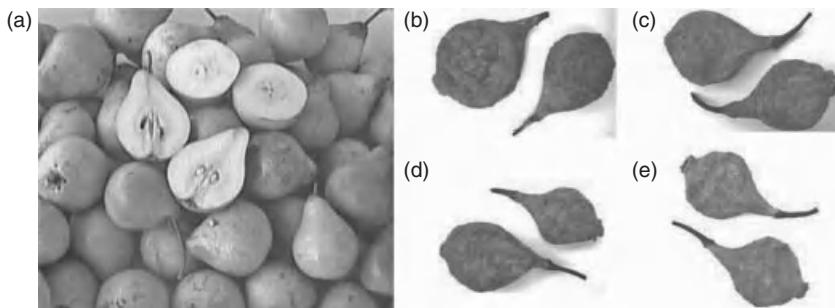
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## **18.1 Introduction**

The pears (*Pyrus communis* L.) are the pomaceous fruits of the trees within the same genus, *Pyrus*. They grow in temperate zones of Western Europe, among other regions. There are over 2000 varieties of pears, but only a few of them are commercialized [1]. They are produced from the flowers of their trees that often grow in cooler climates. They range in color from red, green, yellow, and white, and in shape, from oblate to globule to the most recognizable cultivar shape: pyriform, with an elongated portion ending in a bulbous bottom [2]. On the average, pears contain carbohydrates (11%), which include reducing sugars and dietary fiber (cellulose, hemicellulose, and pectins), proteins (1.5%), and lipids (0.1–0.5%), making them an important part of the human diet [1, 3–5]. The health benefits of dietary fibers are well known, as recently reviewed by Anderson *et al.* [6]. In addition, pears contain vitamins, minerals, organic acids, and phenolic compounds that contribute to the human health promotion. Pears are widely consumed in the fresh form. However, they can also be consumed, among others, in yogurt, juice, frozen, and dried forms, in order to provide a more stable and good quality dehydrated fruit.

The fruits of *Opuntia matudae*, a cactus variety, is also named “pear,” specifically, “prickly pear” and have been shown many human health benefits. Its origin, physical aspect, and composition have no resemblance to *P. communis* L. pear fruit. This plant grows in desert climates and its fruits can be consumed in fresh form, as well as mashed into dips and salsas for certain sour species [7]. They are a good source of fiber and minerals, such as iron, zinc, calcium, potassium, and magnesium [8, 9]. The peel or skin of *O. matudae* fruit is rich in phenolic compounds, namely gallic acid, vanillic acid, 4-hydroxybenzoic acid, vanillin, and catechin. Also, the indole-derived pigments betacyanins and betaxanthins are present in these fruits. In this way, these fruits, derived from *Opuntia* genus, should not be confused with those from *Pyrus* genus, the subject of the present chapter.

One of the traditional and well-appreciated Portuguese food products is a sun-dried small pear (S. Bartolomeu) of reddish brown color which has unique elastic properties [4, 5]. In Portugal, the tradition of drying the S. Bartolomeu pear by direct sun exposure is still used,



**Figure 18.1** The S. Bartolomeu pears: (a) fresh pears and pears dried by different technologies, (b) traditional, (c) large glass greenhouse with air convection (GH1), (d) small greenhouse with natural convection (GH2), and (e) hot air tunnel in the absence of light (HAT). (Adapted with permission from Coimbra *et al.* [14]). For color detail, see color plate section.

although the development of new drying methods, such as greenhouses with or without air convection and a hot air tunnel have recently been tested [10] (Figure 18.1). Pears are rich in phenolic compounds, which are the main phytochemicals present in this fruit, in both the fresh and dried forms [11]. The presence of these compounds has been associated with the high antioxidant activity of pears [12]. However, the content of total phytochemicals present in this fruit may vary, depending on a number of factors, such as cultivar type, environmental growth conditions, harvest, ripening, drying, and storage conditions [1, 11, 13]. Furthermore, during the drying process, both enzymatic and nonenzymatic reactions between reducing carbohydrates and proteins/amines promote the formation of volatile flavor components and brown compounds that change the color, flavor, and texture of the dried product [14]. Phenolic compounds, namely caffeoylquinic acid, (+)-catechin, (-)-epicatechin, and proanthocyanidins, are also responsible for the changes in organoleptic properties (color and specific flavors) during the drying process of pears [4, 11, 15]. The texture of dried pears is also altered due to the modifications in the chemistry of cell wall polysaccharides [1, 4, 15].

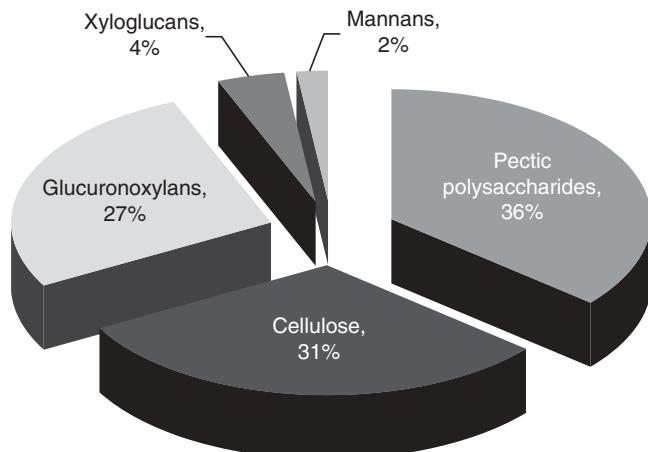
Chemical and sensory transformations that occur during the drying process influence the quality of the end-product, having a decisive relevance toward its attractiveness to the consumer, in both physical and nutritional aspects. Thus, this chapter seeks to clarify the role of the main phytochemicals present in dried pears and to understand their relevance as potential benefits to human health.

## 18.2 Phytochemicals in pears

Much attention has recently been paid to phytochemicals of pears due to their positive association with human health [16]. In the following sections, the amount and structure of carbohydrates, proteins, and phenolic compounds present in pears are described.

### 18.2.1 Carbohydrates

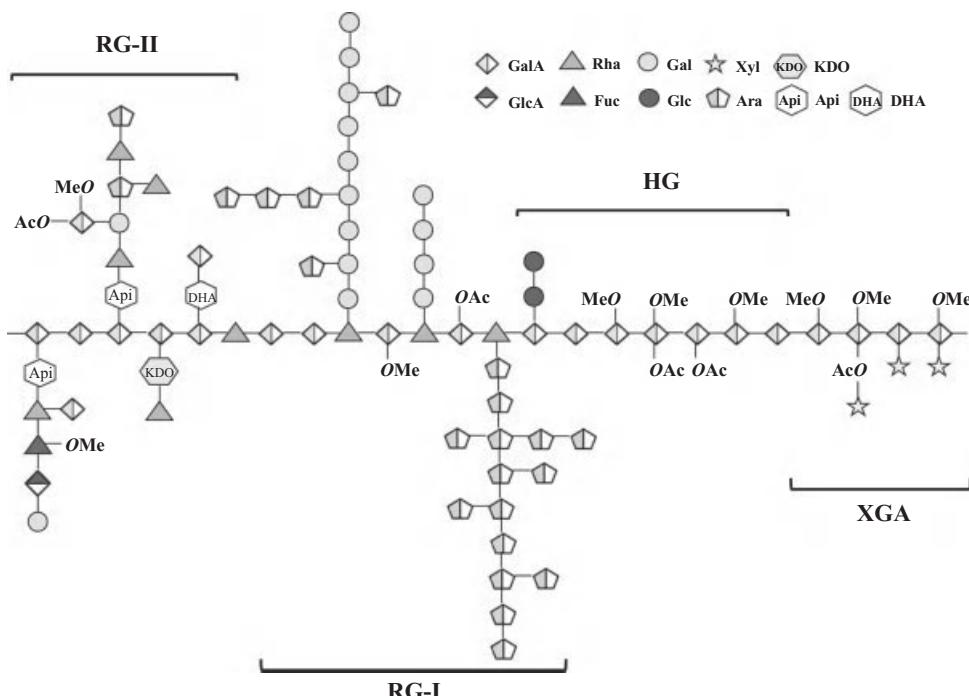
Pear fruit is composed of pectic polysaccharides (36%), cellulose (31%), and hemicellulose, which includes glucuronoxylans (27%), xyloglucans (4%), and mannans (2%) (Figure 18.2)



**Figure 18.2** Relative amount of cell wall polysaccharides of S. Bartolomeu fresh pulp pears. (Adapted from Ferreira [17]).

[17]. Pectic polysaccharides are a complex class of polysaccharides rich in galacturonic acid (GalA). Rhamnose (Rha), arabinose (Ara), and galactose (Gal) residues are also present. The occurrence of glucose (Glc) residues glycosidically linked to GalA backbone has been found in pectic polysaccharides of different fruits, including pear. Thus, this structural feature could also be common to other pectic polysaccharides.

The composition of pectic polysaccharides includes different associated polysaccharides, such as homogalacturonans (HG), xylogalacturonans (XGA), type I rhamnogalacturonans (RG-I), type II rhamnogalacturonans (RG-II), arabinans, and arabinogalactans [18, 19] and all these types of structures can be found in pear fruit [4, 20]. The most abundant pectic polysaccharides in pears are HG. They are linear homopolymers of  $\alpha$ -1,4-linked galacturonic acid in the pyranose form (GalpA), comprising about 60–70% of total amount of pectic polysaccharides. HG could partially be methylesterified at C-6 carboxyl group and/or O-acetylated at O-2 and/or O-3 (Figure 18.3), according to the source [21–23]. Pectic polysaccharides are also composed of xylose ( $\beta$ -D-Xylp) residues substituted at C-3 of GalpA backbone, forming XGA (Figure 18.3). Although xylose is mainly present as single residues, it can occur, occasionally, as an additional  $\beta$ -2-linked or  $\beta$ -4-linked Xylp, to form a disaccharide [21–24]. Moreover, the GalpA residues comprising the XGA backbone can be partially methylesterified and the methyl esters seem to be equally distributed among the substituted and unsubstituted GalpA residues [25]. RG-I like polysaccharide has a backbone composed of repeating units of  $\alpha$ -2-linked Rhap and  $\alpha$ -4-linked GalpA,  $[\rightarrow 2)\text{-}\alpha\text{-L-Rhap-(1}\rightarrow 4)\text{-}\alpha\text{-D-GalpA-(1}\rightarrow]$ . The residues of Rha can be substituted (20–80%) at O-4 with Gal and/or Ara residues. In these side chains, single residues of  $\beta$ -D-Galp as well as linear or branched polymers of arabinogalactans and/or arabinans have been identified [4, 20]. Furthermore, the GalpA residues in the RG-I backbone may be highly acetylated in O-2 and/or O-3 positions (Figure 18.3) [26]. RG-II are the most complex pectic polysaccharides, with an HG backbone constituted of, at least, 8 1 $\rightarrow$ 4-linked  $\alpha$ -D-GalpA residues with branching chains consisting of 12 different types of sugars in over 20 different linkages. Four different side chains have been described in the RG-II structure, with peculiar sugar residues, namely apiose (Api), aceric

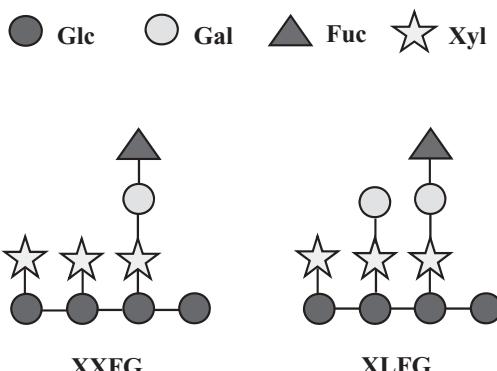


**Figure 18.3** Schematic structure of pectic polysaccharides. HG, homogalacturonan; XGA, xylogalacturonan; RG-I, type I rhamnogalacturonan; RG-II, type II rhamnogalacturonan; GalA, galacturonic acid; GlcA, glucuronic acid; Rha, rhamnose; Xyl, xylose; Ara, arabinose; Fuc, fucose; Gal, galactose; KDO, 3-deoxy-D-manno-octulosonic acid; DHA, 3-deoxy-lyxo-2-heptulosaric acid; Api, apiose. (Adapted from Ferreira [17]).

acid (AceA), 3-deoxy-*lyxo*-2-heptulosaric acid (DHA), and 3-deoxy-*manno*-2-octulosonic acid (KDO) (Figure 18.3) [18, 19, 26].

Cellulose is the second major carbohydrate found in pears. This polysaccharide is constituted by  $\beta$ -4-linked Glc residues,  $[\rightarrow 4]\text{-}\beta\text{-D-Glc}p\text{-(}\rightarrow 1]$ , that associate with other cellulose chains by hydrogen bonding and van der Waals forces, yielding microfibrils [19].

Glucuronoxylans, xyloglucans, and mannans are regarded as hemicellulosic compounds and are present in pear fruit, although in lesser amount than pectic polysaccharides and cellulose. Glucuronoxylans are about 27% of polysaccharides of fresh S. Bartolomeu pulp cell wall. They are composed of  $\beta$ -(1 $\rightarrow$ 4)-D-Xylp backbone with  $\alpha$ -D-GalpA residues in O-2 position of the backbone and/or their derivative 4-O-methylated. The high content of these compounds is also observed in Brancilla pear, and probably they are derived from secondary cell wall of sclereids [27]. Xyloglucans have been found comprising a core backbone structure composed of 4-linked  $\beta$ -D-GlcP residues, with regular branches at O-6 of  $\alpha$ -D-Xylp residues. In S. Bartolomeu pears, decoration with Gal and fucose (Fuc) also occurs, yielding XXFG- and XLFG-type blocks, in which G = Glcp; X = Xyl-(1 $\rightarrow$ 6)-GlcP-; L = Galp-(1 $\rightarrow$ 2)-Xylp-(1 $\rightarrow$ 6)-GlcP-; and F = Fucp-(1 $\rightarrow$ 2)-Galp-(1 $\rightarrow$ 2)-Xylp-(1 $\rightarrow$ 6)-GlcP- (Figure 18.4) [17]. The occurrence of mannans (1 $\rightarrow$ 4-linked  $\alpha$ -D-Manp residues) in pears is probably related to the presence of glucomannans, which are present in the secondary cell wall of sclerotic cells, although in small amounts [17].



**Figure 18.4** Schematic structures of xyloglucans found in *S. Bartolomeu* pears. XXFG, G = Glc; X = Xyl-(1→6)-Glc-; L = Gal-(1→2)-Xyl-(1→6)-Glc-; F = Fuc-(1→2)-Gal-(1→2)-Xyl-(1→6)-Glc-. Glc, glucose; Gal, galactose; Fuc, fucose; Xyl, xylose. (Adapted from Ferreira [17]).

### 18.2.2 Proteins

The protein content of pears may range from 1.5 to 2.6% of dry mass, according to their variety [5]. Pears are composed mainly of glutamic acid (Glu)/glutamine (Gln), determined as Glx, and leucine (Leu), accounting for 20–19 mol.%, each, followed by aspartic acid (Asp)/asparagine (Asn), determined as Asx, contributing 17–13 mol.% for *S. Bartolomeu* pear variety [14]. The designations Asx and Glx derive from the fact that the methodology did not allow the distinction between the amide and carboxylic acid functions for Asn and Asp, as well as for Gln and Glu. In addition, isoleucine (Ile), alanine (Ala), and valine (Val) are present, accounting for 10–7, 8–7, and 7 mol.%, respectively [14, 28]. Despite these protein amino acids, 4-hydroxyproline (Hyp) was found in Beurré variety, but not in *S. Bartolomeu* variety [14]. Hyp occurs in extensins (hydroxyproline-rich proteins) and arabinogalactan-rich glycoproteins of *P. communis* L. [10]. Finally, serine (Ser) is found in some Chinese pear varieties [29].

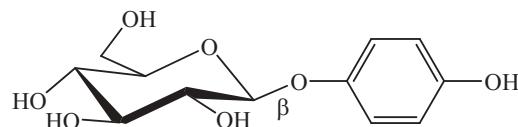
Amino acids can also occur in the free form. The most abundant free amino acids in pears are Asx and Glx, accounting for 45–20 and 38–29 mol.%, respectively. Ala and Val are also found, although, in smaller quantities (17–9 and 9–7 mol.%, respectively), as well as proline (Pro) and glycine (Gly) [14, 28].

### 18.2.3 Phenolic compounds

Phenolic compounds are widely distributed in pear fruit [11]. The pulp of fresh pears contains 3.7 g/kg phenolics, mainly composed of procyanidins (96%), with a mean degree of polymerization (mDP) of about 13–14. (–)-Epicatechin (99%) is the most abundant monomer in the procyanidin structure with only 1% (+)-catechin. Hydroxycinnamic acids, arbutin, and monomeric catechins are also present, accounting for 2.0, 0.8, and 0.7%, respectively [11].

#### 18.2.3.1 Arbutin

The simple phenolic arbutin, 4-hydroxyphenyl- $\beta$ -D-glucopyranoside (Figure 18.5), is a hydroquinone glucoside characteristic of *P. communis* L. pear, including the varieties of



**Figure 18.5** Structure of arbutin.

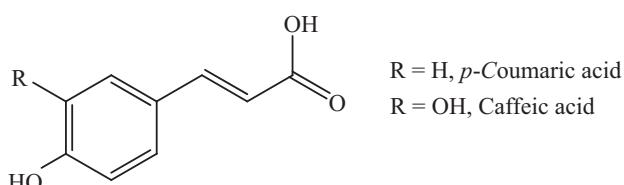
S. Bartolomeu [11], d'Anjou, Red Williams, Alexander Lucas [30], and Decana [31]. This phytochemical can occur in the leaves of *P. communis* L. [32], as well as in pear juice [33]. It is diagnostic of the occurrence of pear pulp in fruit purees (30 mg/kg of fresh pulp), allowing their distinction from other pome fruits, such as apples [34, 35]. There was little change in arbutin content between fresh and dried pears [14].

#### 18.2.3.2 Phenolic acids

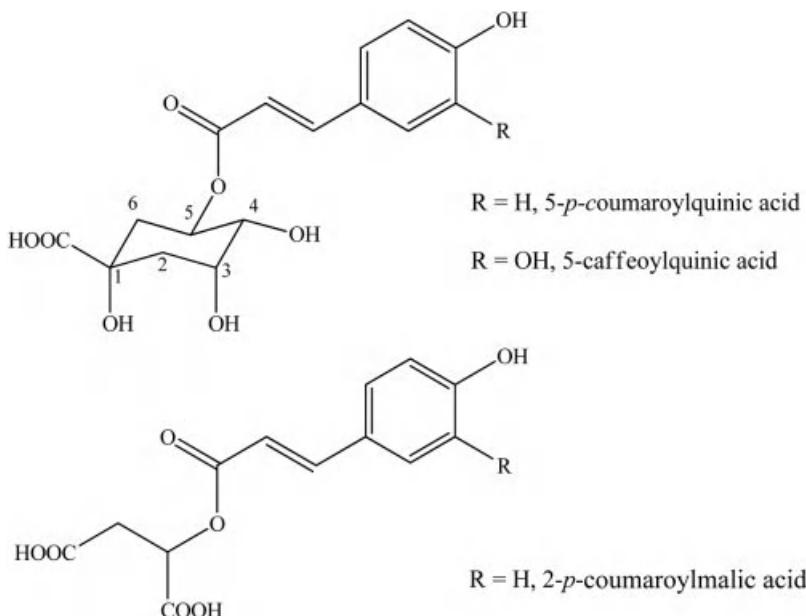
Phenolic acids comprise the broadly distributed hydroxybenzoic and hydroxycinnamic acids. In pears, hydroxycinnamic acids are the most abundant, accounting for about 85 mg/kg of fresh pulp [11]. These phytochemicals have a C6–C3 structure, with *p*-coumaric or caffeic acids (Figure 18.6) being most abundant. Caffeic acid has been found in the pulp of some pear varieties [12, 31, 36], as well as in pear juice, together with *p*-coumaric acid [33]. Hydroxycinnamic acids are present mainly as derivatives, as esters of caffeic and coumaric acids linked to the hydroxyl groups of quinic or malic acids forming coumaroylquinic, caffeoylquinic, and coumaroylmalic acids. 5-Caffeoylquinic acid (40–141 mg/kg of fresh pulp), a chlorogenic acid (Figure 18.7), is the most abundant hydroxycinnamic acid in pears, as reported for varieties such as S. Bartolomeu [11], d'Anjou, Bosc [37], Williams, Guyot, and Conference [38], Comice and Abbe Fetel [39], Decana, Prassagrana [31], Alexander Lucas [30], as well as in some Chinese pear varieties [12]. In addition, chlorogenic acid occurs in pears juice [40]. 5-*p*-Coumaroylquinic acid (Figure 18.7) has been found in S. Bartolomeu variety [11] and, together with 2-*p*-coumaroylmalic acid (Figure 18.7), is present in Guyot pear variety [41]. 2-*p*-Coumaroylmalic acid (Figure 18.7) (about 15 g/kg of fresh pulp) occurs in S. Bartolomeu [11] and Conference pear varieties [38], as well as in Comice and d'Anjou pear juice [33]. All of these hydroxycinnamic acid esters also occur in other varieties of pear [41].

#### 18.2.3.3 Flavonoids and procyanidins

Flavan-3-ols, which are included in the flavonoid family, can be present as monomeric (named catechins), oligomeric, and polymeric forms. Monomeric catechins, namely (+)-catechin and (-)-epicatechin (Figure 18.8), have been reported in several varieties of pear,



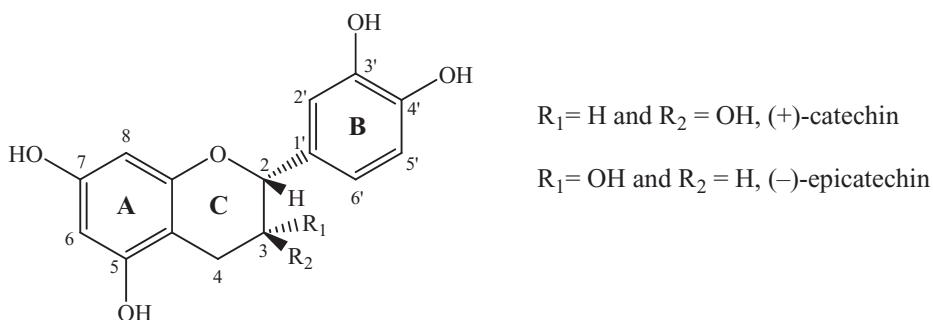
**Figure 18.6** Structure of hydroxycinnamic acids.



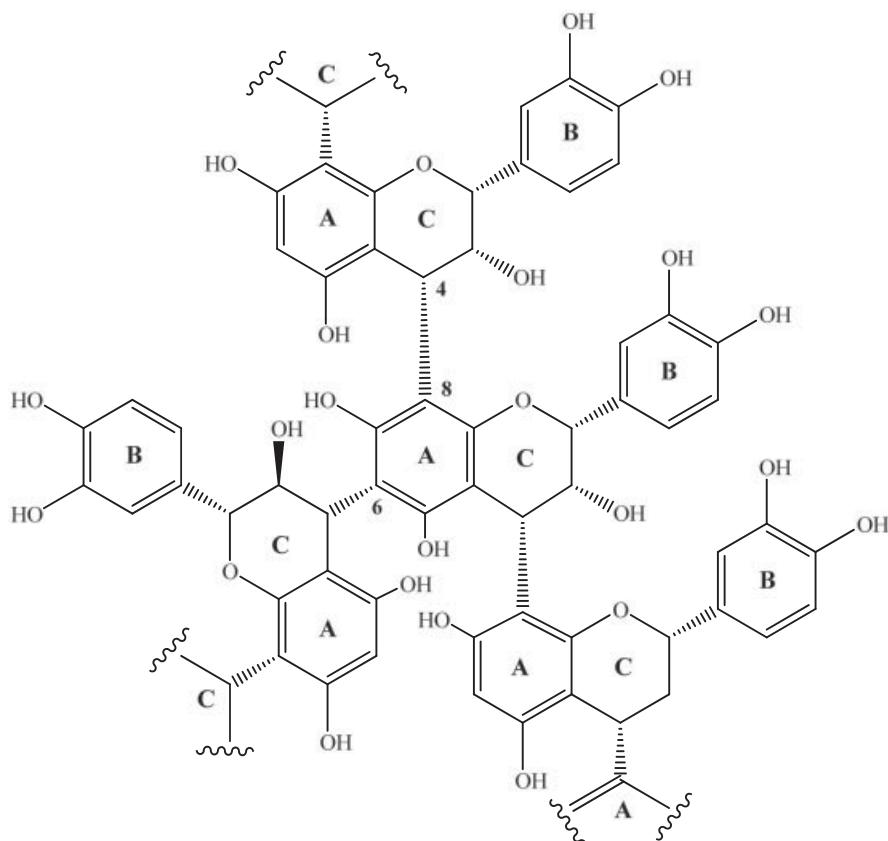
**Figure 18.7** Structure of hydroxycinnamic esters.

such as S. Bartolomeu [11], Guyot, Comice, Conference, and Williams (13–26 mg/kg of fresh pulp) [39], among others [30, 42], in which (−)-epicatechin is the main monomer (about 88%). On another study, Schieber *et al.* [30] reported the highest epicatechin content in Red Williams cultivar.

Oligomeric as well as polymeric forms of flavan-3-ols are known as proanthocyanidins (condensed tannins). Proanthocyanidins are colorless precursors of anthocyanidins, the aglycone form of anthocyanins (pigments with red, blue, or purple color), formed upon the rupture of C–C bond, which is cleaved after being heated in acidic solutions. In this way, the terminal flavan unit is released from the oligomers as carbocations that are then oxidized to colored anthocyanidins by atmospheric oxygen [3]. Proanthocyanidins, which are composed

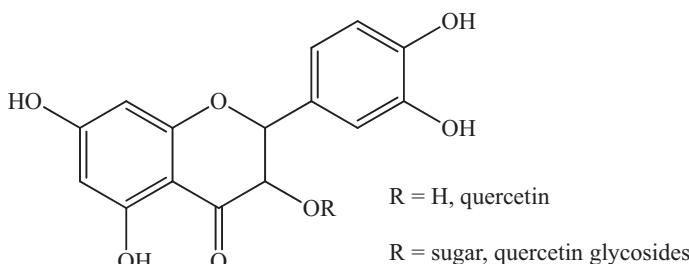


**Figure 18.8** Structure of monomeric catechins.



**Figure 18.9** Partial structure of procyanidins group B.

by (+)-catechin and/or (-)-epicatechin units, are known as procyanidins due to the release of cyanidin units after being heated in acidic solutions. In the procyanidin structures, both C–C and C–O bonds are possible to occur (procyanidins of group A), but usually a C–C bond from the C-4 of one unit to the C-6 or C-8 of the other (procyanidins of group B) is found in pears (Figure 18.9). Procyanidin dimers of group B with C<sub>4</sub>–C<sub>8</sub> bond, such as B1 [43], B2 [33, 43], and B4 [33] have been reported in different pear varieties, as well as polymeric procyanidins [11]. For example in fresh pears, procyanidins B2 account for about 3.6 g/kg of the fresh pulp, where (-)-epicatechin (99%) is in higher amount, rather than (+)-catechin, which account only for 1% of the total procyanidin monomers [11]. The high degree of polymerization of procyanidins seems to affect the sensory properties such as the enhancement of astringency [44, 45], as is observed for fresh S. Bartolomeu pear [11]. The sensation of astringency occurs due to the specific interaction between phenolic compounds and proteins [46], leading to the precipitation of salivary proteins [47]. Furthermore, oligomeric forms seem to be related to the bitterness of pears [44]. Flavonols and their glycosidic forms are also identified in pears. Quercetin, in both aglycone and glycoside forms (Figure 18.10), is the main flavonol found in pears, as well as isorhamnetin glycosides [41, 48]. Quercetin 3-O-glycosides, identified as rutinoside, glucoside, and malonyl glucoside, and the isorhamnetin



**Figure 18.10** Structure of quercetin and its O-3-derivatives.

3-O-glycosides determined as rutinoside, galactorhamnoside, glucoside, malonyl galactoside, and malonyl glucoside have been reported in Bartlett and Bon Chretien pears, as well as in Packington variety [41, 48]. In addition, isorhamnetin-3-rhamnogalactoside and a derivative of isorhamnetin-3-glucoside as well as isoquercitrin (quercetin-3-glucoside) are present [48, 49]. Kaempferol, another flavonol, has been found in pears, although in small quantities [12, 48].

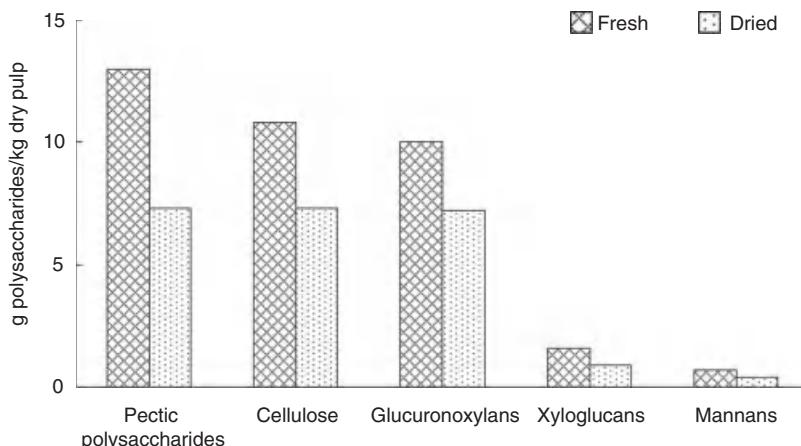
### 18.3 Changes in phytochemical compounds during drying of pears

Drying of fruits is probably the oldest practice for food preservation. In Portugal, the tradition of drying of S. Bartolomeu pear by direct sun exposure is still in use. After harvesting, the fruits are peeled and dried in sunlight and in open air for about 5 days. Then, the pears are laid in baskets and covered with a cloth for 2 days, in order to obtain pears with the needed elasticity to flatten, without breakage. After this, the fruits are submitted to a second sun-drying process [4]. The final product is a much appreciated sun-dried small pear with singular organoleptic characteristics, such as reddish brown color (Figure 18.1) and unique elastic properties [4, 5]. During the drying process, the astringency is lost and the fruit acquires a typical sweet flavor and chewy texture [5].

This section reviews the changes occurring in cell wall polysaccharides and in protein and free amino acid profiles, as well as the changes associated with the nonenzymatic browning reactions (Maillard reaction). The changes of phenolic compounds during the drying process of pears are also presented.

#### 18.3.1 Carbohydrates

After drying, pears have a moisture content of about 20%, representing a 75% decrease of moisture content compared to the fresh pear [17, 50]. Dried pear is mainly composed of cellulose (33%), pectic polysaccharides (32%), and glucuronoxylans (30%), followed by xyloglucans (3%) and mannans (1%) [17]. Compared with fresh pears, a slight decrease in relative amounts of pectic polysaccharides, xyloglucans, and mannans may be observed. Contrarily, the relative amount of cellulose and glucuronoxylans increased slightly with the sun-drying process. The increase in the relative amount of glucuronoxylans can be explained



**Figure 18.11** Composition of cell wall polysaccharides (g/kg of dry pulp) of *S. Bartolomeu* fresh and dried pears. (Adapted from Ferreira [17]).

with the rise of polymerization degree in these structures, possibly due to the continuing development of sclereid cells during the drying in the sun, as was observed during Blanquila pear ripeness [27]. In terms of dry weight of pulp, sun-drying of pears accounts for a 36% decrease in total cell wall polysaccharides, in which xyloglucans are most affected (49%; Figure 18.11) [17]. This fact is probably related to the depolymerization of backbone and/or loss of residues from xyloglucan side chains, affecting the solubility of these compounds. Furthermore, cellulose content decreased 32% in dry weight of pulp, compared to the fresh form, suggesting the degradation of cellulose microfibrils and solubilization of glucans. The amount of glucuronoxylans and mannans decreased by 28 and 43%, respectively. Pectic polysaccharides in dried pears showed a decrease of 43%, which can be explained by the degradation of the galacturonan backbone, mainly of arabinan and/or galactan and/or arabinogalactan side chains, which in turn were also reduced (52%). The changes in the composition of sugars of these polysaccharides may contribute to the changes in their solubility in the cell walls of dried pears [17]. The same results were found for sun-dried Bartlett pears [1], where a positive correlation with the decrease of RG-I–arabinan side chains and the solubility of pectic polysaccharides was observed.

### 18.3.2 Proteins

The drying of pears with different methods, such as Portuguese traditional sun-drying method, in a large glass greenhouse with air convection (GH1), in a small greenhouse with natural convection (GH2), or using a hot air tunnel in the absence of light (HAT), did not seem to significantly affect the proteic amino acid profile of the fruit, when compared to its fresh counterpart [14]. For all dried pears protein, Glx (26–22%), Leu (19–17%), and Asx (14–13%) were the predominant amino acids, contrasting with the high content Asx (35%) and low Glx (8%) and Leu (5%), found in the literature for fresh pear (*P. communis* L.) [28]. The occurrence of high amount of Glx in dried *S. Bartolomeu* pear seems to be related to the presence of arabinogalactan-rich glycoproteins in the fruit [10]. In addition, other amino

acid proteins, namely Ile, Ala, and Val, were present in higher abundance in dried pears, accounting for 11–8, 9–5, and 8–7%, respectively. The higher differences observed between fresh and traditional dried pears are the decrease of the content of Pro and the increase of the content in Glx. Also, a loss in relative content of phenylalanine (Phe), lysine (Lys), and threonine (Thr) also occurred [14]. The decrease of Pro and Lys contents also occurs in the other drying methods, although to different extent, depending on the type of processing. The highest loss of Lys was observed in GH1 and traditional processed pears, followed by GH2 and no loss of Lys was noted in HAT processed fruits. Also, the relative content of Glx increased in all processed S. Bartolomeu pears [14].

Similar to that observed for S. Bartolomeu fresh pear, dried pears processed according to different methodologies also contain Ala, Gly, Val, Pro, Asx, and Glx, as free amino acids, in quantifiable amounts. Thr, Leu, Ile, Phe, and Lys also occur, but in lesser amounts. In dried pears, Pro is the most abundant free amino acid, except for the pears obtained with GH1 drying process, where Glx was most abundant [14]. For all dried fruits, Pro accounted for 48–21% of the free amino acids and Glx contributed 24–12%. Ala also accounted for 17–8%. Val, Asx, and Gly were present in all dried pears, accounting for 15–9, 15–8, and 12–3%, respectively. In general, all other free amino acids decreased upon all drying processes. The decrease in the total free amino acid content was related to the low water activity of fruits, promoting the Maillard reaction at room temperature. Compared with free amino acid profile from fresh S. Bartolomeu pears, all drying processes increased the content of Pro. In fact, the increase in the synthesis of Pro has been reported as a response of fruits to stress conditions [51–53], namely due to the modulation of the expression of proline-rich glycoproteins (extensins) [14]. Also, the high increase of Pro is in accordance with the higher decrease in Pro as integrated protein, as well as the lower amounts in Glx found as free amino acid, in agreement with its high content in the protein.

### 18.3.3 Phenolic compounds

Similar to that observed for polysaccharides and proteins, sun-drying of pears leads to a slight modification in the profile of their phenolic compounds [11]. Dried S. Bartolomeu pear seems to have a loss of about 64% (in dry weight pulp) of the total amount of phenolic compounds, compared with the fresh form. With the exception of arbutin, all other phenolics appear to be affected by the drying process [11]. Procyanidins were the most abundant phenolic compounds in dried pears, although a decrease of 68% occurred. However, its degree of polymerization was not affected. As observed for fresh pears, (–)-epicatechin was the most abundant flavan-3-ol monomer, accounting for 77%. In sun-dried pear, B2 dimer of procyanidin was not present. The hydroxycinnamic acids, namely chlorogenic acid, as well as monomeric catechins seem to be most affected (decreased 96 and 91%, on a dry weight basis, respectively) [11].

Arbutin was not affected by the sun-drying process [11]. A similar result was observed in pear juice [33]. In fact, it has been postulated that polyphenoloxidase (PPO) might have less influence on the concentration of arbutin than on chlorogenic acid and catechins, as was observed in d'Anjou and Bosc pears [37].

The decrease of polymeric procyanidins and the absence of procyanidin B2 in sun-dried pear, as well as their high insolubility [11], are probably due to the involvement of these compounds in coupled oxidation reactions, as also observed in apple juice [54]. For example,

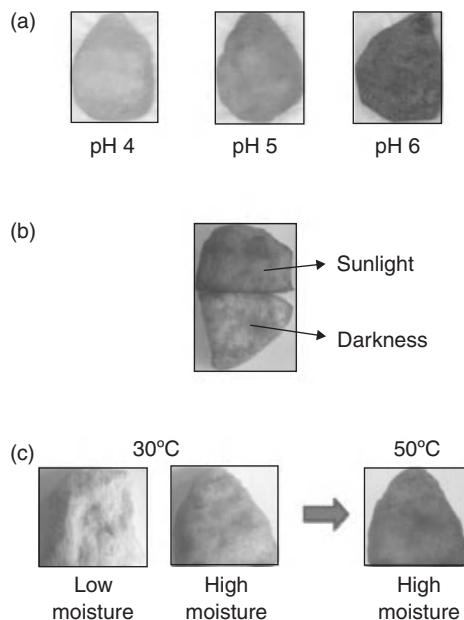
in apple juice, procyanidins are oxidized and highly reactive oxidized intermediates react irreversibly with each other and with proteins to form insoluble complexes [54]. Polymeric procyanidins have been shown to affect sensory properties, such as astringency [44]. The sensation of astringency provided by some fresh pears, such as S. Bartolomeu pear, seems to be lost during the drying process, probably due the decrease of polymeric procyanidins and their insolubility [11]. Furthermore, the reaction of these compounds with other components present in cell wall, such as polysaccharides, could explain the physical characteristics of sun-dried pears, since phenolic compounds form an additional, less hydrophilic, network in these fruits [11].

During processing of fruits, changes in color also occur. Chlorogenic acid and catechins (*o*-diphenols) are involved in enzymatic browning of pears [38, 55]. In this way, the browning of pears, observed during sun-drying process seems to be related with the oxidation of these compounds catalyzed by cathecolase of pear PPO. Consequently, the oxidation of these *o*-diphenols leads to the formation of *o*-quinones, which are rapidly polymerized, yielding brown pigments [34, 56]. The oxidation of these phenolic compounds by PPO could be the cause of their decrease in the pulp-dried pear. Moreover, since the PPO was shown to have higher affinity for chlorogenic acid than for catechins this may explain the higher reduction in caffeoylquinic acid in dried S. Bartolomeu pear [57, 58].

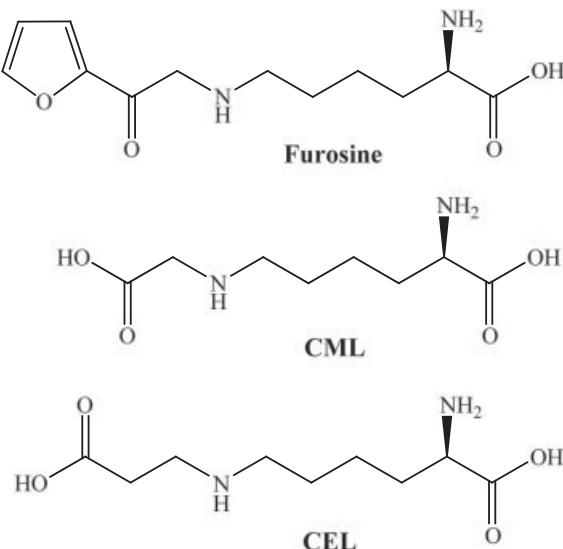
### 18.3.4 Maillard reactions

Apart from enzymatic reactions involving phenolic compounds and PPOs, the browning of sun-dried pears was recently associated with the presence of Maillard reaction products (MRPs) [14]. Maillard reaction, also called nonenzymatic browning or glycation, comprises a reaction between reducing sugars and the free amino groups of amino acids, peptides, or proteins [59] and has been shown to play an important role in the browning and loss of nutritional value of proteins (e.g., loss of available Lys) during food drying [14, 60]. In addition, MRPs account for both desirable [61, 62] and unpleasant [56, 63, 64] flavors and aroma of processed or stored food. It is known that browning reactions are favored during the dehydration process [65], under conditions of pH 5–7, with intermediate moisture content and temperatures over 50°C, using long processing times [66]. After the immersion of pieces of freeze-dried pulp of S. Bartolomeu fresh pear in buffer solutions with a large range of pH, a fast darkening of the tissues immersed in the solutions with higher pH than the other ones [14] was observed. Major color variations were observed in the pH interval of 4–6, whereas at pH 5.0 the color of the tissue approached the reddish brown color characteristic of the traditional product (Figure 18.12a). In addition, the intensity of color in the pear tissues exposed to sunlight was higher when compared with the same samples placed in the dark (Figure 18.12b). In addition, high temperature under high moisture conditions also promoted the formation of the reddish brown color of the pear tissues (Figure 18.12c) [14].

Maillard reaction comprises three stages: the early, the advanced, and the final Maillard reaction steps, which can occur simultaneously [67]. Amadori compounds, formed during the early stage of Maillard reactions [68, 69], have been detected in dried pears as furosine, 2-furoylmethyllysine (Figure 18.13) [14], a good indicator of the first step of these reactions in dairy products [70, 71]. Taking into account the different drying methodologies of pears (see Section 18.2.2), the content of furosine was higher for S. Bartolomeu pears dried by the traditional sun-drying process (247 mg/100 g protein) and lower for pears dried in a



**Figure 18.12** Effect of (a) pH variation, (b) sunlight exposure, and (c) moisture and temperature on the development of color of pear tissues. (Adapted from Coimbra *et al.* [14]). For color detail, see color plate section.



**Figure 18.13** Maillard reaction products identified in dried pears. CML, carboxymethyllysine; CEL, carboxyethyllysine.

HAT (80 mg/100 g protein). Pears dried in a GH1 and GH2 showed intermediate levels of furosine (182 and 136 mg/100 g protein, respectively). These amounts of furosine are similar to those observed for products to which moderate heat treatment is applied, such as ultra-high-temperature (UHT) milk products [72, 73], jams, and fruit-based infant foods [71] and cooked salmon [74]. During intense heating or prolonged storage of foods, Amadori compounds may undergo several rearrangements and degradation reactions, yielding the so-called advanced glycation end-products, AGEs (advanced stage) [67].

Carboxymethyllysine (CML) and carboxyethyllysine (CEL) have been shown to be useful markers in this step of browning reactions (Figure 18.13) [75–77]. Both of these AGEs (CML and CEL) were found in dried pears, accounting for 96 mg/g protein for traditional sun-drying method and 37 mg/g protein for HAT. Dried pears in GH1 and GH2 (94 and 71 mg/g protein, respectively) showed intermediate amounts of CML and CEL, which suggests that the sun-drying process of pears is a more severe treatment than HAT. The content of MRPs present in dried pears seem to influence their color, since the reddish brown color observed in traditional dried fruits (Figure 18.1b) is in accordance with the high content of these compounds. On the other hand, HAT-dried pears showed a less intense color (yellow-orange color, Figure 18.1e), which is probably related to their low content of MRPs [14]. Taking into account the decrease in the amount of each amino acid after drying pears with different methodologies and the content of MRPs formed, a positive correlation between the amount of these compounds and a decrease in the relative amount of Lys can be observed.

The loss of Lys can be used as a marker of Maillard reactions [78], since it is the most reactive residue undergoing chemical changes under these conditions [68]. Contrarily, the nutritional value of S. Bartolomeu pear was not affected when pears were dried in HAT process, since the loss of Lys does not occur [14]. The final stage of Maillard reactions is marked by the presence of melanoidins [68]. These compounds, resulting from numerous rearrangements and polymerization reactions of Amadori compounds, as well as AGEs, are commonly described as brown-colored high-molecular-weight peptide-bound MRPs, since the information of their exact chemical structure is still scarce [68]. Melanoidins have been found in several heat-processed dairy foods such as coffee, bread [79, 80], meat [81], and tomato sauce [82]. However, as far as we know, these compounds have not been reported in dried pears.

## 18.4 Bioavailability and potential health effects

Epidemiological and clinical investigations strongly suggest that the consumption of fruits, including pears, is associated with a decrease of developing chronic diseases, such as cardiovascular diseases (CVD), cancer, and other pathologies [83–86]. The lower incidence of human pathologies has been mainly ascribed to phenolic compounds present in fruits, due to their high antioxidant activity [16, 87]. Furthermore, positive effects in the intake of dietary fiber, widely distributed in pears, are also known [88, 89]. The potential health effects of phytochemicals depend on their bioavailability, which includes absorption in human gastrointestinal tract, metabolism, and excretion [87].

Pear fruit is consumed globally, in both the fresh and dried forms. Few studies have been performed in order to understand the influence of the sun-drying process in the chemical and sensory properties of pears [11, 14]. However, as far as we know, no data are available from *in vitro* and/or *in vivo* experiments with phytochemicals of dried pears in order to evaluate their

impact on human health. As the compounds present in pears also occur in other matrices, and some of them have also been isolated and used for the evaluation of bioavailability and potential health effects, the information available in the literature concerning the potential health benefits of these compounds are discussed and related to dried pears with respect to phenolic compounds (Table 18.1) and dietary fiber (Table 18.2).

### 18.4.1 Phenolic compounds

#### 18.4.1.1 Bioavailability

Phenolic compounds, as the major antioxidants present in pears, cannot exert any biological effects unless they are absorbed, metabolized, and distributed in the body [90]. However, little information exists about the bioavailability of these phytochemicals from whole foods, including pears. Thus, as far as we know, information concerning the bioavailability of arbutin, the phytochemical characteristic of pears, is not known.

It is estimated that the total intake of phenolic compounds from fruits and beverages (fruit juice, wine, tea, coffee, chocolate, and beer) is about 1 g/day [91]. Among flavonoids (total 650 mg/day), flavonols account for about 23 mg/day in human dietary, in which about 70% (16 mg/day) is attributed to quercetin and 17% (4 mg/day) to kaempferol [90]. The procyanidin content in food may vary according to the source. Apple fruit is one major source of procyanidins, accounting for 12.3–252.4 mg/serving, depending on its variety. On average, procyanidins from apple are about 147.1 mg/day [92]. The daily intake of flavan-3-ol (catechin and epicatechin) may range between 100 and 500 mg/day, depending on the fruits and beverages ingested [43, 91]. Despite the amount of intake, only about 5–10% of the total phenolic compounds are absorbed in the small intestine [91, 93]. Unabsorbed phenolic compounds reach the large intestine, where they become fermentable substrates for bacteria. Those that are not fermented remain in the colonic microflora, where they may contribute to a healthy antioxidant environment by scavenging free radicals and counteracting the effects of dietary pro-oxidants [94]. Several studies have reported the absorption of these phytochemicals in the small intestines in humans and animals. One *in vitro* study performed in an isolate rat intestine model showed the absorption of chlorogenic and caffeic acids [95]. In another study, injected chlorogenic and caffeic acids showed 33 and 95%, respectively, of absorption in the small intestines of ileostomized humans [96]. Traces of chlorogenic acids and 11% of caffeic acid were recovered in the urine after 24 hours, suggesting that part of the chlorogenic acids from foods will enter the bloodstream, but most will reach the large intestine and may be metabolized by the gut microflora [96]. Furthermore, rats fed with chlorogenic acids excreted very low amount of chlorogenic acids in their urine, but instead they excreted mainly microbially produced metabolites of chlorogenic acids such as hippuric acid and m-coumaric acid [97]. Several studies have demonstrated the absorption of flavonols in humans [98, 99], but in which form they are absorbed, for example, as an aglycone, glycoside, or both, remains to be answered. A study reported that quercetin-3-rutinoside (rutin) is hydrolyzed in the gastrointestinal tract to quercetin aglycone by glycosidases released from gut microflora [100]. Others have suggested that quercetin glucoside is better hydrolyzed to quercetin in small intestines by glucosidases and is then absorbed [101]. A previous study on ileostomized patients on different forms of quercetin reported the absorption as 52% for glucosides, its major dietary form, 24% for aglycone, and 17% for quercetin-3-rutinoside [98]. In addition, another study involving humans suggested the quercetin bioavailability from apples (rich in

**Table 18.1** Summary table of some potential health effects of phenolic compounds present in dried pears

Biological activity	Phytochemicals	Biological assays	Findings	Reference
Antioxidant activity	Phenolic acids and flavonoids	<i>In vitro</i>	Phenolic extracts of pears have antioxidant activity	[12]
Anti-inflammatory activity	Quercetin	<i>In vivo</i> <i>In vitro</i>	Positive influence on plasma lipid levels and on plasma antioxidant capacity of rats Inhibition at 20 $\mu\text{M}$ for LPS-induced NO and 50 $\mu\text{M}$ for TNF- $\alpha$ production in RAW cells	[112] [124]
Prevention of CVD	Phenolic acids and flavonoids	<i>In vivo</i> <i>In vitro</i>	Inhibition of collagen-induced platelet aggregation at a concentration that can be achieved by the diet No correlation between the high content of phytochemicals and anti-inflammatory activity.	[126]
Cancer effect	Hydroxycinnamates Procyandins Caffeic acid	<i>In vitro</i> <i>In vitro and/or in vivo</i> <i>In vivo</i>	Inhibition of LDL oxidation (quercetin was the most effective inhibitor) Inhibition of platelet aggregation ( $\text{IC}_{50}$ 556 $\mu\text{M}$ ; human plasma $\approx$ 3 $\mu\text{M}$ ) No direct effect on blood vessel function Carcinogenic at 2% Tumor promoter at 0.5–1.0% Anticarcinogenic at 0.05–0.5% Chemopreventive potential against colon carcinogenesis in rats	[119] [126]
	Chlorogenic acid	<i>In vivo</i>	No significant anticarcinogenic effects At 50 $\mu\text{M}$ showed inhibitory effect; reduction of melanin per cell (39%); and reduction of tyrosinase activity.	[145]
	Arbutin	<i>In vivo</i>	Reduction on TCCSUP human bladder carcinoma cell proliferation concentrations of <500 $\mu\text{g}/\text{ml}$ . High protection of gastric lesions (antiluler effect).	[146] [86]
	Procyandins	<i>In vivo</i>		

CVD, cardiovascular disease; LPS, lipopolysaccharide; NO, nitric oxide; TNF- $\alpha$ , tumor necrosis factor- $\alpha$ ; LDL, low-density lipoprotein.

**Table 18.2** Summary table of some potential health effects of dietary fiber present in dried pears

Biological activity	Phytochemicals	Biological assays	Findings	Reference
Prevention of CVD	Soluble fiber	<i>In vivo</i>	Reduction of total plasma and LDL-cholesterol levels with daily intake of 2–10 g; no changes in HDL-cholesterol or TAG in blood	[162]
Pectins (HMP and LMP) and cellulose			Intake ≈ 6 g/day reduced on serum LDL-cholesterol levels of ≈ 5.4% and risk of CHD of ≈ 9% [6]	
Soluble fiber of fruits			Improve blood glucose control in type 1 diabetes 10 and 15% of HMP decreased the body weight; probably HMP is associated with high viscosity	[169]
Soluble and insoluble fibers		Prospective study <i>In vivo</i>	No correlation with reduction risk of type 2 diabetes 26 g/day of dietary fiber (≈ 6 sun-dried pears) leads to a 22% lower risk of developing diabetes	[163]
		<i>In vivo</i>	Enhanced weight loss (1.22 kg) compared with fibers from oat cookies (0.88 kg)	[173]
			Reduction of blood pressure	[172]
			Reduction of CRP levels with ≈ 30 g/day fiber intake	[175]
			Reduction in blood cholesterol level through inhibition cholesterol synthesis	[177]
Propionate (SCFA)		Meta-analysis Randomized trial <i>In vivo</i>	Anti-inflammatory effect by influencing NF-κB activation in a human colonic epithelial cell line	[179]
Butyrate (SCFA)		<i>In vitro</i>	Reduction of tumor growth and cancerous cell migration in rats fed modified citrus pectin	[186]
Cancer effect	Pectin	<i>In vivo</i>	Improve the stool weight, thereby promoting normal laxation	[192]
	Soluble and insoluble fibers	<i>In vivo</i>	Positive correlation with lower pancreatic and breast cancer risk	[196]
		Case-control studies	No correlation with lower breast and colorectal cancer risks	[193, 194]
		Cohort studies		[191, 195]

CVD, cardiovascular disease; HMP, high-methoxy pectins; LMP, low-methoxy pectins; SCFA, short-chain fatty acids; LDL, low-density lipoprotein; HDL, high-density lipoprotein; TAG, triacylglycerol; CRP, C-reactive protein; NF-κB, nuclear factor-κappaB.

both quercetin glucosides and aglycone) and pure rutin to be only 30% of that of quercetin from onions (rich in quercetin glucosides) [99]. Thus, it may be inferred that humans absorb quercetin and that its absorption may be enhanced in the form of quercetin glucosides.

Procyanidins, the major phenolic compounds present in pears, as well as flavan-3-ol monomers (catechin and epicatechin), were absorbed by the small intestinal epithelial cells, although in limited concentrations [102, 103]. It has been suggested that the major bioactive forms of flavan-3-ol monomers and procyanidins *in vivo* are probably in the form of their metabolites and/or conjugates of epicatechin [104]. In fact, (–)-epicatechin monomers were strongly metabolized to O-methylated forms and/or conjugated to glucuronides and sulfates during absorption into the circulation, which were detected in the plasma, liver, kidneys, and urine of grape seed extract-fed rats [103]. The amounts of (+)-catechin and (–)-epicatechin metabolites excreted in urine relative to the quantity of the monomers ingested were 27 and 36%, respectively, after 24 hours. Low amounts of procyanidins were also detected in the urine of rats, providing evidence that depolymerization to monomers does not occur in the gastrointestinal tract and these have high stability in the stomach [105]. These results are in accordance with the study conducted by Donovan *et al.* [106], which detected 37% urinary excretion after feeding rats with (–)-epicatechin, supporting the hypothesis that procyanidins are not depolymerized after ingestion. The same findings were also reported in both *in vitro* and *in vivo* models [107].

There are evidences indicating that dietary fiber [107–109], as well as proteins [110, 111], interact with food antioxidants, influencing their absorption and consequently their bioavailability in human bloodstream.

#### 18.4.1.2 Antioxidant activity

The antioxidant capacity of phenolic compounds of fruits has been extensively studied over the years and their potential effects in lowering human pathologies have been suggested [16, 87, 112–114]. In addition, compared to vitamins C and E, phenolic compounds are more effective as antioxidants *in vitro*, suggesting their potential protective effects *in vivo* [115, 116]. The mechanism of antioxidant action of these phytochemicals is based on their radical-scavenging activity, donation of hydrogen atoms/electrons, or metal-chelating capacity, which in turn is related to their chemical structure [87]. Recently, the antioxidant capacity of five commercial Chinese pear cultivars was evaluated and showed that the extracts obtained from different pear cultivars exhibited varying degrees of antioxidant activity [12]. This antioxidant activity was highly correlated with the contents of phenolic acids and flavonoids. The antioxidant activity of fruit phenolics appears to be higher than common synthetic antioxidants. A study involving Mediterranean fruits, including four varieties of pears, and tropical fruits was performed in order to assess their antioxidant activity compared with that of common food additives [such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and propyl gallate, (PG)] [117]. The results showed very good scavenging activity against hydroxyl radicals ( $\text{HO}^{\bullet}$ ) for all Mediterranean and tropical fruits, protecting deoxyribose better than BHA and BHT. However, hypochlorous acid ( $\text{HOCl}$ )-scavenging activity of all pear varieties was weak compared to other fruits. The inhibition of oxidation and prevention of DNA damage are crucial in lowering human diseases risk, such as CVD (e.g., atherosclerosis) [118–120] and certain types of cancer [84]. A positive influence on plasma lipid levels and on plasma antioxidant capacity of rats by phenolic acids and flavonoids from pears and apples (peel and pulp) was observed [112].

#### 18.4.1.3 Anti-inflammatory activity

Numerous studies have suggested a positive correlation between the radical-scavenging activity of phenolic compounds from fruits and their anti-inflammatory activities [121, 122]. However, the opposite has been reported by Li *et al.* [12] who found no correlation between the total phenolic content (mainly phenolic acids and flavonoids) of five pear cultivars and their anti-inflammatory capacity in *in vivo* models. The authors suggested that the observed anti-inflammatory effect in those extracts may be due to the presence of other phytochemicals such as sterols and triterpenes (phytosterols) [123]. Quercetin has been shown to possess anti-inflammatory activities by inhibiting, *in vitro*, lipopolysaccharide (LPS)-induced nitric oxide (NO) and tumor necrosis factor- $\alpha$  (TNF- $\alpha$ ) production in a dose-dependent manner [124].

Quercetin accounted for more than 75 and 80% of inhibition at a concentration of 20  $\mu\text{M}$  for LPS-induced NO and 50  $\mu\text{M}$  for TNF- $\alpha$  production, respectively, in RAW cells. TNF- $\alpha$ , an antitumor cytokine, and NO (cytokine mediator), has been shown to play an important role in the pathogenesis of diseases during acute inflammation [124]. However, their overproduction by activated macrophages may lead to several pathophysiological conditions during acute and chronic inflammation [124].

#### 18.4.1.4 Prevention of cardiovascular diseases

CVD are the main cause of death and disability in the world [125]. Both *in vitro* [126–128] and *in vivo* [129–131] studies have demonstrated that some phenolic compounds (e.g., procyanidins, flavan-3-ol, and quercetin) are able to inhibit platelet aggregation, suggesting a reduction in thrombosis risk. The effects of hydroxycinnamates and quercetin on platelet activation and cell signaling *in vitro* were evaluated [126].

Hydroxycinnamates inhibited platelet function with collagen as agonist, although not at levels that can be achieved in human plasma by diet ( $\text{IC}_{50}$  556  $\mu\text{M}$ ; human plasma:  $\approx 3 \mu\text{M}$  [132]). Therefore, these compounds seem to be inefficient as inhibitors of platelet aggregation *in vivo*. On the contrary, quercetin inhibited collagen-induced platelet aggregation *in vitro* at a concentration that can be achieved by diet. This shows that quercetin may have potential effect as inhibitor of platelet aggregation *in vivo* [126]. As procyanidins do not break down in the gastrointestinal tract into their flavanol monomers [107, 133], dietary procyanidins do not make any marked contribution to the systemic pool of flavanols in humans, since they are not absorbed and consequently, their direct effect on blood vessel function is limited [133]. Many studies have shown the capability of flavonoids in inhibiting low-density lipoprotein (LDL) oxidation, which is associated with cell aging and chronic diseases, such as atherosclerosis [134].

#### 18.4.1.5 Cancer effects

Most investigations, both *in vitro* and *in vivo*, have suggested the anticancer action of some phenolic compounds present in fruits. However, there are other studies that show no effect or even cancer-inducing effect of these phytochemicals [135]. For example, caffeic acid has been demonstrated to have both carcinogenic and anticarcinogenic effects in *in vivo* studies [135]. It can be carcinogenic at 2% [136], tumor promoter at 0.5–1% [137, 138], and anticarcinogenic at 0.05–0.5% [135, 139]. The lower quantities found in dried pears may infer that these compounds should have a protective effect.

Chlorogenic acid has been shown to have chemopreventive potential against colon carcinogenesis in rats [140]. However, no significant anticarcinogenic effects were observed in other studies [86, 141]. The effect of procyanidins and chlorogenic acid, extracted from Winter Nelis pear fruit, was investigated in ethanol-induced gastric ulcer in rats [86]. After oral administration of 20 mg/rat before 60% ethanol treatment, procyanidins showed a high level of antiulcer capacity, probably due to their strong antioxidant activity. Interestingly, chlorogenic acid, which acts as an antioxidant, had no protective effect on ulcers induced by ethanol [86]. In addition, chlorogenic acid is thought to inhibit human immunodeficiency virus (HIV) activity [142].

Numerous studies have demonstrated that arbutin inhibits tyrosinase, a key enzyme to melanin biosynthesis in melanocytes [143–145]. Melanin is the major pigment responsible for skin color. In this way, arbutin has been used as a whitening agent in cosmetics. Arbutin can also be a potential drug in the treatment of melanin-associated hyperpigmentation disorders. A recent study reported the inhibitory effects of arbutin on melanin production in B16 cells of brownish guinea pig and human skin tissues induced with alpha-melanocyte stimulating hormone ( $\alpha$ -MSH) through the reduction of tyrosinase activity in a cell-free system [143]. The maximum arbutin concentration without inhibitory effect on B16 melanoma cell growth was 50  $\mu$ M [145]. At this concentration, a significant decrease (about 39%) on melanin content per cell was observed, accompanied by a reduction of tyrosinase activity [145]. Arbutin showed significant reduction in TCCSUP human bladder carcinoma cell proliferation in dose-response and time-response at concentrations of <500  $\mu$ g/mL [146]. Based on the content of arbutin in dried pears and on the serving dose, it is not probable that arbutin could have any anticancer effect by ingestion but its topical use may be beneficial. In addition, arbutin has diuretic and urinary anti-infective properties [147].

## 18.4.2 Dietary fiber

### 18.4.2.1 Bioavailability

Epidemiologic studies have estimated that the recommended acceptance intake of dietary fiber for adults is 25 g/day for women and 38 g/day for men to ensure optimum CVD protection [148]. Dietary fiber of pears (1 pear = 4 g of total dietary fiber) includes pectic polysaccharides (pectins) as soluble fiber and cellulose, glucuronoxylans, and xyloglucans as insoluble fiber [4, 148, 149]. Their bioavailability defines the utilization and potential biological effect of dietary carbohydrates [150]. Due to the nature of their glycosidic linkages, these compounds cannot be hydrolyzed by the endogenous enzymes of the small intestine, flowing directly into the large intestine. In the colon, the soluble dietary fiber is a potential substrate for the fermentation of the gut microflora, yielding short-chain fatty acids (SCFA), as by-products, that can be absorbed and utilized by the host as an energy source [150]. In a recent study, human subjects with short bowel syndrome were fed with a custom pectin-based supplement (4 g) to evaluate their small intestinal absorption capacity. Evidences showed that 80% of pectin was fermented by the gut microflora, associated with the increase of SCFA detected in the feces, suggesting that soluble fiber intake enhances colonic SCFA production [151]. SCFA have been shown to be involved in numerous physiological processes promoting health [152] and some of them are described below. Insoluble fibers, which are more difficult to ferment, have a bulking action by absorbing water as it moves through the digestive system leading to an easier defecation.

#### 18.4.2.2 Prevention of cardiovascular diseases

Hypertension, hypercholesterolemia, obesity [153], and diabetes [153, 154] are the major risk factors associated with CVD. Higher intake of dietary fiber, particularly soluble fiber, reduced the risk of CVD and coronary heart disease (CHD) [155]. Also, an inverse relation between the intake of dietary fiber from fruits and risk of CHD has been reported [156]. Several mechanisms have been postulated to elucidate protective effects of dietary fiber intake against CVD. Viscous fibers, particularly the soluble ones (e.g., pectins), seem to improve blood lipid profiles [157–160], thus avoiding other inflammation pathologies such as atherosclerosis [160]. Dietary fiber intake has been associated with their ability in lowering serum LDL-cholesterol levels, which is the major risk factor for CVD [161]. Brown *et al.* [162] evaluated the cholesterol-lowering effects of various soluble fibers, including pectin and oat bran, and their influence on blood lipid changes in adults subjects. The authors showed a good correlation between the daily intake of 2–10 g different soluble fibers and significant decrease of serum total cholesterol and LDL-cholesterol concentrations by similar amounts. Furthermore, they also observed no changes in high-density lipoprotein (HDL)-cholesterol or triacylglycerol (TAG) concentrations in blood with soluble fiber. Some random studies estimated that the consumption of 12–24 g pectin/day (about three pears) in divided amounts was associated with 13% reduction in LDL-cholesterol values [6, 162]. Soluble fiber intake of about 6 g/day is accompanied by reductions in serum LDL-cholesterol levels of around 5.4% and estimated risk of CHD of about 9% [6]. Viscosity is thought to be an essential feature in the lowering of cholesterol, although solubility and molecular weight of dietary fibers also determine the cholesterol-lowering ability. Fietz *et al.* [163] evaluated the effects of high- and low-methoxy pectins (HMP and LMP, respectively) and cellulose on serum cholesterol levels, as well as TAG in hyperlipidemic rats over 30 days. HMP-fed rats (10 and 15%) significantly decreased the body weight with increased dietary fiber concentrations, suggesting that higher molecular weight fibers are associated with increased viscosity. Soluble and viscous fibers tend to bind to bile acids in the small intestine, making them less likely to enter the body [6]. *In vivo* experiments showed in response to this fact that LDL-cholesterol is removed from blood and converted into bile acids/salts by the liver to replace the bile acids lost in the feces (35–65%) [164, 165]. Therefore, total plasma and LDL-cholesterol concentrations are reduced, but no changes in HDL-cholesterol were observed [166, 167]. The same viscosity seems to improve blood glucose control in type 1 diabetes [168, 169], either by delaying [170] or reducing [171] glucose intestinal absorption, thus lowering postprandial glucose and attenuating insulin responses. The consumption, on an average of 26 g/day, of dietary fiber (equivalent to six sun-dried pears) leads to a 22% lower risk of developing diabetes [172]. On the contrary, except for fiber from cereals, some recent studies have reported no correlation between the consumption of soluble fiber from fruits and vegetables and a reduced risk of type 2 (non-insulin-dependent) diabetes [173, 174]. Dietary fiber has also been shown to regulate energy intake [171], thereby enhancing loss of weight [175] or preserving a healthier body weight. In one study, women (30–50 years of age) were randomized to receive one of three dietary supplements: apples, pears, or oat cookies, three times a day in a total of six meals a day, in order to evaluate the effect of fruit intake on body weight change [175]. After 12 weeks of follow-up, the fruit group lost 1.22 kg, whereas the oat group had an insignificant weight loss of 0.88 kg. Furthermore, a significantly greater decrease of blood glucose was observed among those who had eaten fruits compared with those who had eaten oat cookies, but the glucose to insulin ratio was not statistically different

from baseline to follow-up. The mechanisms of how dietary fiber enhances the weight loss are still unclear. Nevertheless, it has been suggested that glucagon-like peptide, a hormone produced as a result of soluble fiber fermentation in the large intestine, may be responsible for the satiety, which refers to the state in which further eating is inhibited and occurs as a consequence of having eaten [148].

Fermented dietary fiber leads to an increase in SCFAs such as acetate, propionate, and butyrate as products by gut microflora. These SCFAs, particularly propionate, have been shown to contribute to a decrease in blood cholesterol level through inhibition of cholesterol synthesis [176, 177]. In addition, butyrate has been associated with anti-inflammatory effects [178]. Dietary fibers also affect blood pressure, as well as C-reactive protein (CRP). Many studies have demonstrated that the prevention of hypertension could be achieved with the consumption of dietary fiber [179–181]. Moreover, it has been observed that the decrease in blood pressure is higher in older humans and in hypertensive populations [179]. CRP is a sensitive marker of inflammation, and thus, CRP has been shown to be a strong predictor of CVD [182, 183]. It is produced by the liver and is present in low amounts ( $\leq 1$  mg/L) in the blood of healthy subjects. Investigations have shown an inverse association between the intake of dietary fiber and CRP [184, 185]. Moreover, it has also been suggested that the levels of CRP can be reduced with 30 g/day fiber intake from a diet naturally rich in fiber or from a fiber supplement [186].

#### 18.4.2.3 Cancer effects

The relationship between dietary fiber intake from fruits and risk in developing cancer is still inconclusive. Although some epidemiological studies have suggested an inverse association between the consumption of dietary fiber from fruits and cancer risk [187–189], others have not found this correlation [190, 191]. For example, Terry *et al.* [188] concluded that individuals who consumed less than 1.5 servings of fruits and vegetables per day had a higher risk for developing colorectal cancer than individuals who consumed more than 2.5 servings. Pectins, the main soluble fiber occurring in dried pears, may play a role in cancer prevention. Meanwhile, Nangia-Makker *et al.* [192] demonstrated the ability of pectin in binding to galectin-3, thus decreasing tumor growth and cancerous cell migration in rats fed modified citrus pectin, suggesting the importance of dietary fibers as cancer-preventive and/or -therapeutic agents. The reduced risk of breast cancer associated with high consumption of dietary fiber has also been shown [193]. The same findings were reported for pancreatic cancer, in which fiber intake from fruits led to a low risk in developing the pathology [194].

However, several studies disagree with these promising results. A pooled analysis of cohort studies of breast cancer found no association between the intake of fruits and vegetables during adulthood and lower breast cancer risk [191]. Similarly, a recent investigation involving 58,279 men found no relationship between dietary fiber and colorectal cancer [195]. Despite these controversial results concerning the potential effects of dietary fibers on cancer, these phytochemicals have been demonstrated to offer potential benefits, such as improving the stool weight, thereby promoting normal laxation [196].

## 18.5 Conclusions

Pears (*P. communis* L.) are an excellent source of nutrients and phytochemicals for maintaining good health and defending against a large number of diseases. Due to their high

fiber content they help against constipation and lower cholesterol. The presence of phenolics also helps ameliorating cardiovascular and neurodegenerative diseases and certain types of cancer.

The traditional sun-drying of *S. Bartolomeu* pear is still practiced to obtain well-appreciated small sun-dried edible products with reddish brown color and unique elastic properties. The several chemical and sensory changes, responsible for interesting features of dried pear, have been poorly explored. In general, a decrease in the amount of all phytochemicals is observed when the fruit is dried. No reports are available for *in vitro* and/or *in vivo* studies concerning phytochemicals of dried pears. However, we did provide an analogical approach of bioavailability and potential health benefits of dried pears phytochemicals based on the information available in the literature, concerning the observed human health effects of these compounds found in other matrices. Thus, it is possible to infer that some phenolic compounds, as well as dietary fibers that are described to exist in dried pear, should be able to exert human health benefits. In order to support the real implications of dried pear components as health protectors, an extensive investigation in this area is crucial.

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# **19 Prunes: are they functional foods?**

Alessandra Del Caro and Antonio Piga

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## **19.1 Introduction**

It is widely recognized that regular consumption of different foods, particularly fruit and vegetables, may help to promote an optimal health and lower or reduce the risk of different chronic diseases. The above-cited effects are associated to naturally present or process-induced biologically active compounds. Foods with these characteristics are often classified as functional foods. Prunes have long been recognized as having beneficial effects on human health, thus they can surely be included in the functional foods [1]. Prunes are obtained from drying fresh plum fruits (*Prunus domestica* L.) that are thought to originate in the Caucasus Mountains. The actual polyploidy species are the results from two wild plums, the diploid *Prunus cerasifera* Ehrh (cherry plum) and the tetraploid *Prunus spinosa* L. (blackthorn) [2]. The cross-breeding generated an appreciated fruit species that was propagated worldwide during the centuries. Prunes are industrially obtained by tunnel air drying up to 20–24% in moisture at temperatures ranging from 60 to 85°C [3]. They can also be rehydrated up to 35% in moisture. Prune juice may be obtained by boiling prunes in water up to 18.5% solid content. Other products can be obtained from prunes, such as purees and powders. Most prunes are obtained from cv. D'Agen plums and until 2000 California was the dominant world prunes supplier with a market share of over 70%. Nowadays, other countries in the world are emerging and can become rivals with regard to prune production [3]. One of these countries is Chile, which ranks second in prune production, with an estimated 55,000 metric tonnes (MT) produced in 2009, compared to US production of 139,000 MT. Argentina is third in the world prune production with a 25% increase in production to an expected 50,000 MT over the next 5 years.

A certain number of articles have been published on biological effect of prunes on human health. The main compounds claimed to have beneficial effects are mainly phytochemicals. This chapter outlines the present state of knowledge about composition, nutritional characteristics, phytochemicals, health effects, and food applications of prunes and their by-products.

## 19.2 Compositional and nutritional characteristics of prunes

### 19.2.1 Proximate composition

There is extensive literature that summarizes the current knowledge of the proximate composition of prunes [1], but most of the scientific papers show mainly data related to fresh plum cultivars [4–13]; some refer to prune juice [14–16] and others to dried prunes [17–19].

Table 19.1 reports the nutrient composition of prunes. Their content vary considerably, even in the same cultivar, surely due to the growing conditions, geographic area, and degree of ripeness. Prunes contain a considerable amount of carbohydrates compared to the fresh fruit due the dehydration process, so they can be considered a good source of energy.

### 19.2.2 Dietary fiber

Dietary fiber has been reported to have some biological activities, such as lowering of serum cholesterol and postprandial glycemia [20, 21] and reductions in chronic disease, such as coronary heart disease (CHD), diabetes mellitus, cancer [22–25], and irritable bowel syndrome [26, 27].

Prunes have been reported to contain from 6.0 to 16.1 g/100 g of dietary fiber (Table 19.1). This wide range could be due to the different analytical methods employed and variety. USDA Food Composition Tables [28] report 7.0 g/100 g of dietary fiber in prunes. Tinker *et al.* [29] reported 6.0 g/100 g of dietary fiber in prunes, while Labavitch *et al.* [30] found 6.2 g/100 g of dietary fiber. Recently, Cheryl *et al.* [31] analyzed the dietary fiber content of prune and prune preparations and expressed the content as percent of dry weight. After converting the values from percentage dry weight to fresh weight, the following amounts were obtained: 10.8, 8.4, 8.0, and 5.3 g/100 g in prune powders, prunes, pitted prunes, and prune puree, respectively. These values are lower than those reported by the European Food Composition Tables [32], which give a value of 16.1 g/100 g. The French Prune Association [33] reports similar values of 13–16 g/100 g. These data show that prunes, along with dried figs, are probably the fruits with the highest dietary fiber content.

Data on the composition of the dietary fiber show different values for soluble and insoluble fibers. An ethanol extract of prune has been reported to have 49% of soluble and 51% of insoluble dietary fiber [34], while a methanol extract afforded 42% of insoluble and 58% of soluble dietary fiber [35].

With respect to prune juice which is lower in fiber, values ranging from 0.01 to 1.1 g/100 g have been reported [31, 36]. Some prune by-products such as waste cake and prune pits contain 6.0 and 70.4 g/100 g of dietary fiber, respectively [31].

### 19.2.3 Sugars

Individual sugar contents (Table 19.1) reported in several studies [11, 37–39] show wide ranges, probably due to the variations in drying conditions employed. The sugar content is different for each species, for example, apricots contain more sucrose and much less sorbitol than prunes [39]. These individual sugars are also present in the fresh fruit but their percentages change upon drying [17]. During processing, sucrose is hydrolyzed to fructose

**Table 19.1** Nutrient composition of prunes (values per 100 g edible portion)

Nutrient	Unit	Prunes	References
<b>Proximate composition</b>			
Water	g	30.9–32.4 <sup>a</sup>	[37, 47]
Energy	kcal	240	[47]
Protein	g	2.2–2.6	[37, 47]
Lipid	g	0.4–0.5	[37, 47]
Carbohydrate	g	62.7–63.9	[37, 47]
Dietary fiber	g	6.0–16.1	[32, 47, 48]
<b>Sugars</b>			
Fructose	g	13.1	[11, 38, 39]
Glucose	g	23.1	[11, 38, 39]
Sucrose	g	0.6	[11, 38, 39]
Sorbitol	g	14.7	[11, 38, 39]
<b>Minerals</b>			
Boron	mg	2.2	[48]
Calcium	mg	43–78	[42, 43, 47, 48]
Copper	mg	0.3–0.4	[47, 48]
Fluoride	µg	4.0	[47]
Iron	mg	0.9–3.9	[42, 47, 48]
Magnesium	mg	41–45	[47, 48]
Manganese	mg	0.2–0.3	[47, 48]
Phosphorus	mg	69–85	[42, 47, 48]
Potassium	mg	732–990	[42, 43, 47, 48]
Selenium	µg	0.3	[47]
Sodium	mg	2–8	[42, 47, 48]
Zinc	mg	0.4–0.5	[42, 47, 48]
<b>Vitamins</b>			
Betaine	mg	0.4	[47]
Choline	mg	10.1	[47]
Folate	µg	3.7–4.0	[47, 50]
Niacin	mg	2.0	[50]
Pantothenic acid	mg	0.46	[50]
Pyridoxine	mg	0.21–0.28	[47, 50]
Riboflavin	mg	0.16–0.19	[47, 50]
Thiamin	mg	0.05–0.08	[47, 50]
Vitamin A (RAE)	µg	39	[47]
Vitamin C	mg	0.6–4.0	[47, 48, 50]
Vitamin E (ATE)	mg	0.43	[47]
Vitamin K	µg	5.5–59.5	[47, 50]

RAE, retinol activity equivalents; ATE,  $\alpha$ -tocopherol equivalents.

<sup>a</sup>Range (minimum–maximum).

and glucose, which can undergo Maillard reaction as a result of drying up to their total loss. Sorbitol is extremely important since it represents one of the criteria used to select the plum cultivar for drying [40]. In fact, this sugar is responsible for the laxative effect of dried prunes at low doses (70 g/day) and prevents excessive browning in prunes due to its resistance to caramelization and to the fact that it is not a reactant molecule in the Maillard reaction [41].

### 19.2.4 Minerals

Table 19.1 shows the content of minerals present in prunes. Prune-making plums, once subjected to the dehydration process, maintain the same mineral content as the fresh fruit [1, 42]. A study on California prunes with 19% of moisture showed an iron content of 3.2 mg/100 g of dry weight, while potassium was 990 mg/100 g and calcium 78 mg/100 g [43]. Rehydration does not cause any significant loss of minerals. For this reason, a 100 g serving of prunes can supply 20% of the daily reference value (DRV) for potassium, 20% of the reference daily intake (RDI) for copper, 14% of RDI for iron, about 10% of the RDI for zinc and magnesium, and 10% of intake of manganese. Moreover, prunes contain significant amounts of boron [44]. A 100 g serving of prunes is equal to an average daily intake for adult males of about 2.2 mg of boron [45], where the dietary requirement could be 1 mg/day.

### 19.2.5 Vitamins

The content of vitamins in prunes is reported in Table 19.1. Some vitamins are perhaps lost during the dehydration process, due to the high temperature used, especially ascorbic acid, as reported in the literature [19, 46]. There is a wide difference in the content of vitamin C reported in the United States (0.6 mg/100 g) [47] with respect to Europe (4.0 mg/100 g) [48]. A large serving of dried prunes could provide 6–10% of the RDI of vitamin C, whereas 9% of RDI for vitamin E. Other tocopherols are present, but only in trace amounts as  $\beta$ -tocopherol and  $\gamma$ -tocopherol. Dried plum also contains a high amount of vitamin K (up to 59.5 mg phylloquinone/100 g) among commonly consumed foods [49].

## 19.3 Phytochemicals in prunes and their by-products

Phytochemicals are generally referred to as nonnutritive plant compounds, which may affect health through protective or disease-preventive properties. More than several thousand phytochemicals have so far been reported. Some of the well-known phytochemicals belong to the classes of phenolics, carotenoids, organosulfur compounds, nitrogen-containing compounds, and alkaloids. Prunes and their by-products are rich in phytochemicals, mainly polyphenols, but minor amounts of carotenoids and other compounds are also present.

### 19.3.1 Polyphenols

This class of compounds is well represented in fresh-prune-making plums and, in spite of the known heat damage caused by the drying process, they are still present in prunes. Dried prunes have a high content of polyphenols. The main compounds are hydroxycinnamic acids, namely 3-*O*-caffeoylequinic acid (neochlorogenic acid) and 5-*O*-caffeoylequinic acid (chlorogenic acid). Table 19.2 reports the range of polyphenols found in prunes and prune juices.

Hydroxycinnamates found in prunes have been reported by different authors [15, 19, 50–53]. All of these authors found a higher amount of neochlorogenic acid than chlorogenic acid in the products. Both acids account for 95–98%, but their content declined to 75% when another isomer, 4-*O*-caffeoylequinic acid (cryptochlorogenic acid), was present [51]. Higher amount of neochlorogenic and chlorogenic acid was found by Piga *et al.* [19] in

**Table 19.2** Content (mg/kg dry weight basis) of phenolic compounds in prunes and prune juices

<b>Phenolics</b>	<b>Prunes</b>	<b>Prune juices</b>	<b>References</b>
Neochlorogenic acid	928–3045 <sup>a</sup>	225	[15, 19, 51, 53]
Chlorogenic acid	67–562	193–335	[14, 15, 19, 51, 53]
Caffeic acid	1–35	3–45	[14, 15, 19, 51–53]
p-Coumaric acid	2–43	4	[15, 19, 51–53]
Protocatechuic acid	0.5–2	–	[52]
Cyanidin 3-rutinoside	15	–	[19, 53]
Rutin	3–89	4	[15, 19, 51–53]
(–)-Epicatechin	7.2	–	[52]
Catechin	–	126–169	[14]

<sup>a</sup>Range (minimum–maximum).

President prunes obtained by high-temperature drying. According to the literature, prunes are the richest fruits in neochlorogenic acid. It is important to highlight that the use of drying temperatures higher than 75°C reduces considerably the depletion of these two phenolic acids, due to the fact that the degradation process is mediated by polyphenoloxidase [19, 50]. Kayano *et al.* [54] reported different caffeoylquinic acid isomers in prunes for the first time. Caffeic and coumaric acids, which are absent in fresh fruits, appear in prunes [15, 19, 51–53], probably due to the hydrolysis of cinnamic acid during drying.

Other compounds found in prunes are rutin, (–)-epicatechin, protocatechuic acid, coniferin, vanillic acid, scopoletin, magnolioside, anthocyanidins, and proanthocyanidins [15, 19, 51–55]. Catechin has been found in dried fruits by Raynal *et al.* [50], but they provided separate data for pulp and exocarp, thus it is not simple to report the exact amount of phenolic content in whole dried fruits. Rutin accounted for about 2–4% of the total polyphenol content. Anthocyanins have been found in prunes at very low concentrations due to their rapid degradation during the first phase of drying [55]. Literature reports the presence of peonidin 3-rutinoside, peonidin 3-glucoside, cyanidin 3-rutinoside, and cyanidin 3-glucoside [19, 55], but data are available only for cyanidin 3-rutinoside [19, 53], for the reason given earlier as noted by Raynal *et al.* [50]. Coniferin, vanillic acid, scopoletin, and magnolioside have been reported for the first time by Kayano *et al.* [56]. Recently, Kimura *et al.* [57] found an oligomeric proanthocyanidin in a prune extract. The oligomer is composed mainly of epicatechin units with catechin as a terminal unit. Other important components found in prunes include two lignans [58].

Prune juices are the main product derived from prunes. They are obtained using different processing technologies, with respect to the other fruit juices. In fact, there is no pressing and refining operation, but only water extraction by boiling dried prunes until 18.5% sugar content is achieved. This process surely results in further depletion of polyphenols. Donovan *et al.* [15] found significantly lower content of polyphenols in prune juices than in prunes. They also noticed a decreased ratio of neochlorogenic acid to chlorogenic acid. Apart from these two compounds, they detected low amounts of caffeic and coumaric acids as well as rutin. It is important to note that the boiling treatment increases the concentration of hydroxymethylfurfural, an intermediate compound in the Maillard reaction. Catechin is also reported in prune juices [14]. To best of our knowledge, data on other prune derivatives or by-products have not been published.

**Table 19.3** Carotenoid composition of prunes (values per 100 g edible portion)

Nutrient	Unit	Prunes	References
α-Carotene	μg	31–57	[47, 59]
β-Carotene	μg	140–394	[47, 59]
β-Cryptoxanthin	μg	93	[47]
Lutein + zeaxanthin	μg	148	[47]

### 19.3.2 Carotenoids

Carotenoids are yellow to red fat-soluble pigments that may be converted to vitamin A in the body, provided they have a β-ionone ring. Table 19.3 shows carotenoid and xanthophyll profiles (α-carotene, β-carotene, β-cryptoxanthin, and lutein + zeaxanthin) of prunes. Among these, β-carotene acts as provitamin A. Finnish researchers found very low amounts of α-carotene, β-carotene, and lutein, in particular, with respect to the content of the fresh plums [59]. One hundred grams of prunes may provide only 5% of RDI. This low RDI contrasts with the European Tables and US claim of 22 and 25% RDI, respectively [1, 32]. Scientific literature also includes a study by Bolin [43] who reported that steam-rehydrated Californian prunes contained 0.56 mg β-carotene/100 g of fresh weight, which is less than half of the provitamin A activity reported by the USDA Food Composition Tables [28]. Similar results have also been obtained by Korobkina [60] with four cultivars of Uzbek prunes.

When looking for changes in carotenoid content after drying of fresh plums, a detailed study was carried out by Moutounet [61]. In particular, the author demonstrated that drying results in a 45–75% loss of total carotenoids, β-carotene being less susceptible. It is interesting to note that the paper reports that prunes dehydrated in two harvesting seasons had very different carotenoid contents.

Prune juice contains only traces of vitamin A activity [47], probably due to the hot water extraction used to obtain the prune juice.

### 19.4 Natural antioxidant in prunes

A large group of phytochemicals, which have protective effects against cell oxidation, have been discovered. These naturally occurring compounds act as antioxidants in the body by scavenging harmful free radicals, which are implicated in most degenerative diseases. Thus, they may well be defined as the substances that are capable of quenching or stabilizing free radicals. Epidemiological studies have established a positive correlation between the intake of fruits and vegetables and prevention of diseases such as atherosclerosis, cancer, diabetes, arthritis, and ageing. Vitamins (A, C, and E) present in dried prunes are all considered as natural antioxidants. The other natural antioxidants in prunes can be phenolic compounds, such as flavonoids and phenolic acids, among others. The antioxidant properties of phenolics are mainly due to their redox properties, which allow them to act as reducing agents, hydrogen donators, and singlet oxygen quenchers. Prunes and prune juices are an excellent source of dietary antioxidants [15]; in fact they are characterized by high concentrations of hydroxycinnamic acids, especially neochlorogenic and chlorogenic acids that are predominant. The prune extracts, as well as neochlorogenic and chlorogenic acids, exhibit antioxidant activity

by inhibiting low-density lipoprotein (LDL) oxidation *in vitro*. Other phenolic compounds present in prunes, such as rutin and caffeic acid, have been reported in the literature as active inhibitors of human LDL oxidation [62].

## 19.5 Health effects of prunes

It is well known that certain foods help to keep us healthy and prevent chronic disease [63]. Above all, consumption of fruits and vegetables has shown to reduce the risk of cancer, heart disease, and stroke [64]. These foods are often classified as functional foods, and dried prunes fall into this category. The literature reports many biological effects of prunes, whereas the most known is the laxative effect.

Prunes alleviate constipation with an effect on the bowel actually, which is not well understood. It is reasonable to ascribe this action to the prune fiber content. Probably, the combination of soluble and insoluble fibers acts in a gentle way in the lower intestine, softening the stool, increasing its bulk, and promoting in this way the intestinal mobility. In addition, prunes contain sorbitol that is known to cause a laxative action in animals and humans [65]. Phenolic compounds can also contribute to the laxative effect.

Prunes have the ability to lower the glycemic index (GI) in humans [66, 67]. They provide reasonable amount of energy (239 kcal/100 g), due to their high sugar content, but do not increase the blood level of sugar and their GI is in the moderate range (54 against 100 for the GI of glucose) [67]. Besides, prunes reduce the plasma insulin concentration and C-peptide, a product of insulin breakdown. This action reduces the level of insulin secretion in humans who consume dried prunes. This behavior is linked to the sugar and fiber content of prunes; in fact, the combination of glucose, fructose, and sorbitol with significant amounts of dietary fiber has a beneficial influence on glucose metabolism and diabetes management [66].

Phenolic compounds appear to have some effect on glucose absorption and metabolism, as reported by Welsch *et al.* [68], where the responsible compound is chlorogenic acid, and can decrease 80% of glucose active transport capacity. Phenolic compounds also have the ability to inhibit the formation of endogenous glucose in the liver, where chlorogenic acid is responsible for inhibition of glucose-6-phosphate translocase in the enzyme system of microsomes in rat liver [69].

Prunes have a very important role in bone metabolism. Several studies are reported in the literature that evidence the important role of prune consumption in both preventing and reversing bone loss in male and female animal models of osteoporosis [70]. In addition to the animal studies, the results of a short-term clinical trial indicated that the consumption of prunes (100 g/day) by postmenopausal women significantly increased markers of bone formation such as serum total alkaline phosphatase (ALP) activity, bone-specific ALP activity, and insulin-like growth factor-I (IGF-I) that is reported to correlate with bone formation and bone mass in women [71]. Prunes contain about 50 mg of calcium, the same quantity of magnesium, and 80 mg of phosphorus per 100 g of fruit. Even if these minerals are not high in concentration, compared with the RDI for these nutrients, the absorption of bone-building minerals can be improved due to the high organic acid content of prunes. Besides, they contain boron and vitamin K [49], which are responsible for influencing bone-building process. Boron has the ability to increase plasma steroid hormone concentrations and reduce the urinary excretion of calcium in both humans and laboratory animals [72, 73]. Therefore, boron can be considered as an important nutritional factor in the prevention of

the incidence of osteoporosis. Regarding vitamin K, studies in the literature report that it influences bone health by improving calcium balance. It is also considered as a cofactor needed for  $\gamma$ -carboxylation of osteocalcin.  $\gamma$ -Carboxylated osteocalcin promotes normal bone mineralization by regulating the growth of hydroxyapatite crystals [74].

Many studies in the literature have reported the role of bioactive phenolic compounds (isoflavones and lignans) on bone health [75, 76]. Prunes are an important source of phenolic compounds, such as neochlorogenic acid and chlorogenic acid, which act as antioxidants and inhibit bone resorption and stimulate bone formation [77]. Therefore, the beneficial effects of dried prunes on bone may be mediated, in part, through their antioxidant properties. Dried prunes polyphenols seem to be able to suppress osteoclast differentiation and activity under normal, oxidative stress, and inflammatory conditions *in vitro* [78]. Another study on ovariectomized rats evidenced the role of prunes in bone metabolism [79] as linked to the high content of phenolic compounds. However, some researchers suggest the presence of boron as an agent which prevents bone loss [1].

Prunes are also responsible for beneficial influences on cardiovascular health. They have a role on three major risk factors involved in the cardiovascular diseases (CVD) such as hypertension, dyslipidemia, and oxidative stress [1]. With regard to hypertension, prunes with their high potassium and low sodium content can protect against hypertension, especially by preventing the adverse effects of high sodium diets [80].

Prunes are able to control dyslipidemia due to the significant quantities of soluble fiber in the form of pectin responsible for decreasing the plasma cholesterol [29]. Studies on ovariectomized female rats fed with dried powdered prunes [81] indicated that their cholesterol-lowering effect was probably due to both their high fiber content and some estrogen-like actions [82]. Prunes also have the capacity of binding bile acids. Binding of bile acids and increasing their fecal excretion has been hypothesized as a possible mechanism by which dietary fibers lower cholesterol [83].

Prunes are responsible for inhibiting human LDL oxidation *in vitro* [84, 85]. In particular, the antioxidant activity of prunes is very high in comparison to the antioxidant activities of other fruits and vegetables on the basis of the oxygen radical absorbance capacity (ORAC) [86]. It is well known that neochlorogenic, chlorogenic, and cryptochlorogenic acids exhibit antioxidant activity against human LDL oxidation [62], scavenge reactive oxygen and nitrogen species [51], and inhibit the formation of conjugated dienes from linoleic acid oxidation. It is reported that the antioxidant activity of prunes is highly dependent on caffeoylquinic acid isomers [1, 87]. However, the contribution of caffeoylquinic acid isomers to the antioxidant activity of prunes has not yet been proven, as reported by Kayano *et al.* [54]. Another recent study [57] shows proanthocyanidin oligomers as contributing to the antioxidative activity of prunes. The results of this study suggest that the high antioxidative activity of prunes depends on the effects of both proanthocyanidin oligomers and caffeoylquinic acids. Prunes also contain small amounts of flavonoids, especially quercetin, which influences the enzyme system involved in immune response and generation of inflammatory process by decreasing the synthesis of prostaglandins, inhibiting histamine release, and reducing cell aggregation or adhesion in various types of cells. In addition, flavonoids can exert an antithrombotic effect, causing a decrease in the incidence of heart attack and stroke [88]. The presence of copper in prunes can be considered as beneficial for cardiovascular health, since copper is needed for the integrity of blood vessels and hemoglobin formation. Many oxidative and antioxidative enzymes are copper dependent, so it can be useful for maintaining the oxidant/antioxidant balance.

Prunes also have a role against cancer. It is known that phenolic compounds are responsible for the inhibitory effect on the carcinogenic action of many chemical carcinogens. In particular, caffeic and chlorogenic acids are able to suppress the mutagenic activity of *N*-methyl-*N'*-nitro-nitrosoguanidine (MNNG) in *Salmonella typhimurium* test [89]. Chlorogenic acid is responsible for the reduction of tumors such as adenocarcinomas, hemangiomas, and liver cell adenomas in methylazoxymethanol-injected hamsters [90]. Consumption of foods rich in fiber diminishes the risk of colon and rectal cancer [91]. Prune extracts have been evaluated *in vitro* for their antiviral, antibacterial, and antifungal activities, but they showed a very low level of activity, as compared to other fruits [92–95].

## 19.6 Food application of prunes and their by-products

Food applications of prunes include the use of prune itself as well as its derived products.

### 19.6.1 Whole prunes

Whole prunes may be sold intact or be processed as juice or juice concentrate. Prune juice is obtained from extraction in boiling water, pressing or centrifugation, clarification, concentration up to a minimum of 18.5% soluble solids, pasteurization, and bottling. This juice after depectinization may be vacuum evaporated at low temperature up to 60°Brix (48°C), then packed in cans, and frozen [96]. A more concentrated juice, up to 72°Brix, may be produced for industrial markets. Concentrated juice is used to make prune juice after reconstitution. Apart from its direct use, prune juice has been reported for a number of applications, as listed below:

- (a) in bread preparation [97];
- (b) for preparing sauces [98];
- (c) for extending the shelf life in baked goods [99] due to the mold control exerted by malic acid and the humectant function of sorbitol, fibers, and monosaccharides that result in maintaining a soft and moist texture;
- (d) as antioxidant in precooked roast beef [100];
- (e) as natural preservative in whole grain bread [101]; and
- (f) for controlling pathogen growth [102].

### 19.6.2 Pitted prunes

Pitted prunes may be sold as whole, canned, chopped, and diced and used to make pastes and purees, granules and powder (low moisture content), fiber, fillings, and toppings.

Significant amounts of prune products are bought by institutional users. Derived products may have different food applications. Pitted canned prunes are produced in three types: (a) regular, packed in sugar syrup; (b) nectarized, water-packed; and (c) moist pack, regular pitted prunes with higher moisture content. Their uses are for direct consumption. The main food applications come from puree, fiber, fillings, and toppings. Prune puree, obtained from whole prunes by extrusion, is in the form of homogenous paste and has a number of applications, such as fat replacer for reducing fat content in a series of goods. The main segments of the food industry in which prune puree has been experimented are bakery, confectionery,

and meat. In fact, the unique multifunctional “fruit system” of prunes confers prunes the particular fat-sparing capacity. This characteristic is due to the presence of

- (a) pectins, with the properties of creating a stable film during mixing and of flavor entrapping and gradual releasing during mastication;
- (b) very high content of sorbitol and reducing sugars, providing humectancy; and
- (c) malic acid, which acts as flavor enhancer.

All of these characteristics match the need to lower the fat content of food while imparting delicious flavor. Thus, fruit purees have been proposed as moisture enhancer in precooked beef, pork, lamb, turkey, and chicken products to retain moisture particularly after freezing, reheating, and holding [103] as well as on hot dogs [104], as a fat replacer and moisture enhancer in ground beef for school lunch hamburgers [105], for replacing shortening and thus reducing trans fat in baked goods [106], for salt reduction in bakery and meat production [107], and for adding protein value in underutilized meats [108], as well as for all the features cited for juice. Moreover, dried prune powder has been demonstrated to reduce lipid oxidation in meat [109]. All of these literature reports confirm the important technological functionality of prune derivatives.

## 19.7 Conclusions

Prunes have attracted the attention of consumers mainly for their bowel function, but nowadays there is increasing scientific evidence for their nutritional and technological functionality. Prunes' high amounts of dietary fiber, sorbitol, boron, potassium, and phenolics may be beneficial in regulating digestion and sugar metabolism, in lowering plasma cholesterol concentration and reducing the risk of bowel cancer, in maintaining cardiovascular health, and in improving bone metabolism. Phenolic compounds, on the other hand, due to their antioxidant properties, may have a role in preventing or decreasing the risk of various diseases.

The particular composition of prunes confers them technological functionality, such as fat replacer in meat and bakery products, antioxidant effect in roast beef, and preservative in bread, or for inhibiting pathogen growth. Despite the above-cited functions, more research is needed on the composition, in particular on the amounts of carotenoids, vitamin E, and other vitamins and on the relationship between prune consumption and disease risks. Thus, only a multidisciplinary research program could reveal the exact potential related to the functionality of prunes.

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## **20 Raisins: processing, phytochemicals, and health benefits**

Fereidoon Shahidi and Zhuliang Tan

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### **20.1 Introduction**

Raisins are defined as grapes that have been dried and have a sweet taste and a wrinkly texture. The word raisin comes from the French “*raisin sec*,” which literally means “dried grapes.” The French word itself comes from the Latin term *racemes*, meaning “a bunch of grapes” [1]. Raisins have been consumed as food since 1490 BC due to their high nutritional value and the presence of high levels of micronutrients [2]. They are known as nature’s candy and counted among the most nutritious dried fruits globally. Popularity of raisins as healthy food for millennia is due to their nutritional value and the enjoyable taste. They may be eaten as such or included in breakfast cereals, dairy, and bakery as well as confectionery products and nutrition bars [3].

Raisins are of major commercial interest as they are the most important horticultural products. They are the second most important product of grapevine after wine [1]. The world production of raisins from 2005 to 2010 by different countries is given in Table 20.1 [4]. The United States is the largest raisin producer in the world, followed by Turkey. Both countries typically account for more than 95% of production among the major northern hemisphere producing countries and, generally, about 80% of global production. The other major raisin producers include Iran, China, Chile, South Africa, and Afghanistan, among others.

Studies on raisins have shown that they are rich sources of natural bioactive compounds [5, 6]. In this chapter, the processing of raisins will be presented and the characteristic phytochemicals are summarized. The bioactivities and health benefits of raisin consumption are also discussed.

### **20.2 Types of raisins**

Four main grape varieties used for raisin production are Thompson seedless, Muscat, Sultana, and black Corinth. Thompson seedless is the most common variety that constitutes 90% of the total raisin supply in the United States [7]. Dark raisins, golden raisins, Sultanas, Zante

**Table 20.1** World raisin production by countries (metric tonnes, dry weight basis)

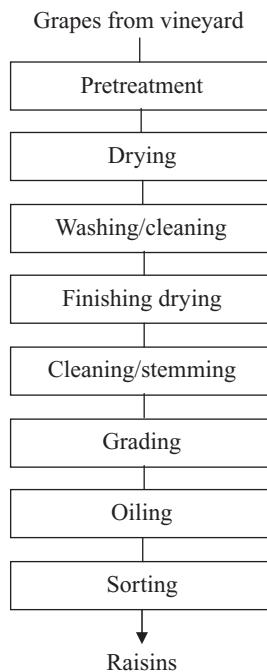
<b>Production</b>	<b>2005/2006</b>	<b>2006/2007</b>	<b>2007/2008</b>	<b>2008/2009</b>	<b>2009/2010</b>
United States	316,245	274,877	321,143	347,452	294,835
Turkey	250,000	280,000	250,000	310,000	260,000
Iran	155,000	130,000	150,000	60,000	100,000
China	105,000	125,000	150,000	135,000	150,000
Chile	65,500	61,500	67,350	80,000	67,000
South Africa	36,000	41,800	40,200	28,000	43,000
Afghanistan	31,000	20,000	25,000	25,300	29,000
Australia	30,400	15,000	12,000	16,000	14,000
EU-27	30,000	20,000	10,000	10,000	12,000
Uzbekistan	26,000	30,000	37,000	25,700	26,000
Argentina	25,000	36,000	33,000	30,000	36,000
Mexico	8,200	8,500	8,500	8,500	8,300
Total	1,078,345	1,042,677	1,104,193	1,075,952	1,040,135

Source: Adapted from USDA [4].

currants, and Monukka raisins are among the most popular types of raisins [7]. Dark raisins are most commonly found in the marketplace, usually made from Thompson seedless grapes. Although they start as green grapes, the fruit naturally darkens as it dries. Golden raisins, also known as Muscats, are generally made of white Muscat grapes. They are oven-dried rather than being dried by sun and are treated with sulfur dioxide in order to retain their light color. Some of the golden raisins may also be made from Thompson seedless. Sultanas are more popular in Europe and originate from seedless yellow grapes; they are usually softer and sweeter than other varieties. The American variety of Sultana grape is the Thompson seedless. Zante currants are made from black Corinth grape. Tiny dried currants are very sweet and aromatic [7]. Other criteria can also be used to classify raisin products or distinguish them from one another; these include the method of drying (natural, golden-bleached, sulfur-bleached, and lexia), the place of origin (Vostizza, Patras, Pyrgos, Smyrne, Malaga, and Valencia), the conditions under which the product is offered for sale (layers, loose, and seeded), the size grades (4 crown, 3 crown, and 2 crown), the US maturity grades (B or better, C, and substandard), and the quality grades (extra standard, standard, substandard, extra fancy, choice, etc.) [1].

### 20.3 Processing of raisins

Drying is the process of removing moisture through simultaneous heat and mass transfer and is a classical method of food preservation that provides longer shelf life and reduces weight and volume [8]. It is probably the oldest and one of the most cost-effective methods for preserving fruits, including grapes. The preservation of grapes by drying is a major industry in many parts of the world where grapes are grown. The technique for drying of grapes into raisins has been in use since ancient times. Raisins were produced in Persia and Egypt as early as 2000 BC with one of their first mention being in the Old Testament [9]. A typical block flow diagram for modern raisin production is given in Figure 20.1.



**Figure 20.1** Raisin production by drying.

The grape with an outer layer waxy cuticle and a pulpy material inside is a complex product for dehydration as the outer layer cuticle controls the moisture diffusion rates during drying [1]. The low diffusivity implies that there is a formidable barrier that gives consistency to the skin of grape, which may lead to a time-consuming drying process [10]. Thus, a chemical or physical pretreatment is generally applied to decrease skin resistance and, hence, improving moisture diffusion through the waxy cuticle [11]. The commonly used chemical pretreatment in grape drying includes dipping the grapes in hot water and using chemicals such as sulfur dioxide, caustic, and ethyl oleate or methyl oleate emulsions [1]. Different physical treatments have also been reported; for example, superficial abrasion [12], microwave heating [13], and ohmic heating have been used [14].

Drying of grapes is largely traditional and varies in different parts of the world, depending on the cultivation conditions. There are three main methods that are widely used in raisin production, namely, sun drying, solar drying, and mechanical drying [15]. Comparison of the different drying techniques is given in Table 20.2. Historically, the production of raisin from grapes by open sun drying can be traced back to 1490 BC in Greece since it is a simple and cost-effective method [16]. Some of the traditional sun drying methods include open sun drying without cover, open sun drying with cover, and natural rack dryer [11]. Traditionally, the natural sun drying of grapes is carried out in trays. More recently, a new natural sun drying method named within-row-alternate-bearing drying-on-vine (WRAB DOV) has been developed. Compared with the traditional method of hand-harvest, the dried-on-vine raisins are machine harvested, thus reducing human contact and production costs. This novel method also eliminates the need for intensive cultivation to prepare terraces down

**Table 20.2** Comparison of different drying techniques employed in raisin production

Drying method	Advantages	Disadvantages
Sun drying	Simple Cost effective Most efficient use of solar energy	Long drying time (8–10 d) Possibility of contamination Uncontrolled drying conditions
Solar drying	Renewable energy source Controllable process Short drying time (within 4 d)	Specially designed dehydrator Moderate equipment investments Small drying capacity
Mechanical drying	Rapid drying rate (within hours) Controllable processing Minimizing the composition, texture, and color changes Slightly higher air-stream grade	High initial investment Significantly higher operational cost High energy cost Only cost effective for specialty, high-valued products such as sulfured raisins or reconditioned rain-damaged fruit

More than any other factor, raisin quality is directly influenced by fruit maturity which is determined by the soluble solid content of the grapes.

row middles [17]. Although sun drying is a popular and inexpensive method, a considerable risk of deterioration of quality due to dust, insect infection, undesirable changes in color, and the presence of foreign matters exists. The other main disadvantage of sun drying is the uncontrollable drying conditions such as weather, intensity of radiation, and ventilation, among others. The basic principle of a solar dryer is that air is heated by the sun in a collector and then passed over the grapes, which are to be dried. It has been established that solar drying is the most technically and economically viable option for most developing countries, especially for those countries within the belt of good solar radiation [18]. Solar dryers for raisin production can be broadly classified into three types, namely, direct type, indirect type, and mixed type. Grapes are exposed directly to solar radiation in the direct type of solar dryer. However, in the indirect type of solar dryer, air heated by solar radiation is made to flow through grapes. Depending on the air circulation, the indirect type solar dryers can be further classified into natural circulated or forced circulated solar dryers. The mixed type of solar dryer combines the advantages of the above two types of solar dryers, in which grapes are exposed directly to solar radiation and hot air is also allowed to flow through them [19]. Advantages and disadvantages of various solar dryer systems that have been developed, fabricated, and tested for effective grape drying are discussed by Pangavhanne and Sawhney [15] and Jairaj *et al.* [19]. Mechanical drying, which is safe, rapid, and controllable, is attractive to raisin production, when high throughput is needed. Freeze and microwave vacuum dehydration have also been employed to minimize the compositional changes in grapes during the drying process [20–22]. The industrial application of microwave heating for the preparation of dried grapes has been reported in the literature [23]. The main disadvantages of mechanical drying are the high initial investment and additional operation and running energy cost.

The dried grapes, by either sun drying or other drying techniques, are then delivered to an appropriate unit for further processing. Water is first used to wash and eliminate foreign materials such as dust and soil. Cleaning involves individualizing the dried grapes, removal of stems and foreign materials, and removal of off-grade raisins. During the above two

processing steps, rehydration, leakage of some of the dissolved sugars of the dried grapes into the washing water, and extension of micro-cracks and skin wounds are the main changes that may affect dried raisins [11]. To control the amount of moisture in the final products, one more step, finishing drying, is needed, especially for rehydrated dried raisins during the washing or the grapes that have been partially dried or washing off the grapes before packaging. The efficiency and quality of the finishing drying operations are significantly influenced by biomechanical and physical properties of the dried grapes [24].

The criteria for quality determination of raisins have been summarized by Winkler *et al.* [25] based on color, appearance, texture, free flow (having nonsticky surface), flavor, and nutritional value of raisins, which are the main attributes for quality evaluation of raisins and their consumer acceptance. As detailed in the US Standards for Grades of Processed Raisins [26], which became effective December 1, 1978, several factors may affect the grading and quality of raisins. These include maturity and size of grapes, hue, uniformity, and brilliance of the color, condition of the grape surfaces, texture of the skin and pulp, moisture content, chemical composition, presence of decay or rot, mould, yeast, and foreign matters, insect infection, and pretreatment methods as well as drying and storage conditions [1, 11].

## 20.4 Composition of raisins

Raisins, similar to other dried fruits, have an appealing, sweet taste, and high nutritional value. They provide essential nutrients, dietary fiber, and other bioactive compounds. The nutrient composition, including proximate composition, minerals, and vitamins, of grapes and raisins is given in Table 20.3 [27]. Grapes and raisins are essentially the same, as raisins are dehydrated grapes. The fresh grapes normally contain 80% water. However, the moisture content in raisins is decreased to 15% after the drying process. Consequently, macronutrients such as total protein, carbohydrates, sugars, and fiber become concentrated in raisins compared with fresh grapes. The high sugar and low moisture content of raisins makes them naturally resistant to spoilage during storage. It is important to note that the high content of dietary fiber (3.7–4.0 g/100 g raisins) in raisins helps meet dietary fiber recommendations (14 g of fiber for every 1000 calories of food) [28]. Higher fiber content of 5.05–5.37 g/100 g raisins has also been reported [29]. High-fiber diets help reduce the risk of developing various conditions, including constipation, heart disease, diabetes, colon cancer, and obesity [30]. As indicated in Table 20.3, the content of minerals in raisins is generally 3–7 times higher than those in fresh grapes. Raisins are rich in potassium, phosphorus, magnesium, and calcium, but very low in sodium. It is known that the drying process induces compositional changes in the type of sugar, enzymes, and certain pigments. Grapes contain pentose and furanose, as compared to hexose in raisins as a main sugar group. The polyphenol oxidase, which is present in grapes, does not occur in raisins. Chlorophyll *a*, chlorophyll *b*, xanthophylls, and carotenes are the main pigments identified in grapes, but these are not present in raisins [31]. The content of vitamins C, E, and K is deceased in raisins, while that of other vitamins, namely, thiamine, riboflavin, niacin, vitamin B<sub>6</sub>, folate, and choline, remains at the same level or is increased compared with fresh grapes. The decrease in vitamins may be caused by the drying process or the chemical pretreatment [32]. Raisins, like other fruits, contain very low levels of fat and are devoid of cholesterol. Raisins are also an important source of dietary boron, which is not listed in Table 20.3. According to a study by Rainey *et al.* [33],

**Table 20.3** Nutrient composition of grapes and raisins (values per 100 g grapes or raisins)

Nutrient	Units	Grapes (American type)	Grapes (European type)	Raisins (golden seedless)	Raisins (seedless)
<b>Proximate composition</b>					
Water	g	81.30	80.54	14.97	15.43
Protein	g	0.63	0.72	3.39	3.07
Total lipid	g	0.35	0.16	0.46	0.46
Ash	g	0.57	0.48	1.66	1.85
Carbohydrate	g	17.15	18.10	79.52	79.18
Fiber	g	0.90	0.90	4.00	3.70
Sugars	g	16.25	15.48	59.19	59.19
<b>Minerals</b>					
Calcium	mg	14.00	10.00	53.00	50.00
Iron	mg	0.29	0.36	1.79	1.88
Magnesium	mg	5.00	7.00	35.00	32.00
Phosphorus	mg	10.00	20.00	115.00	101.00
Potassium	mg	191.00	191.00	746.00	749.00
Sodium	mg	2.00	2.00	12.00	11.00
Zinc	mg	0.04	0.07	0.32	0.22
Copper	mg	0.04	0.13	0.36	0.32
Manganese	mg	0.72	0.07	0.31	0.30
Selenium	μg	0.10	0.10	0.70	0.60
<b>Vitamins</b>					
Vitamin C	mg	4.00	10.80	3.20	2.30
Thiamin	mg	0.09	0.07	0.01	0.11
Riboflavin	mg	0.06	0.07	0.19	0.13
Niacin	mg	0.30	0.19	1.14	0.77
Vitamin B6	mg	0.11	0.09	0.32	0.17
Folate	μg	4.00	2.00	3.00	5.00
Choline	mg	5.60	5.60	11.10	11.10
Vitamin E	mg	0.19	0.19	0.12	0.12
Vitamin K	μg	14.60	14.60	3.50	3.50

Source: Adapted from USDA [27].

The numbers are rounded to the second digit after decimal point.

raisins have the highest concentration of boron at 2.2 mg/100 g among the 50 major food contributors of boron in the American diet.

## 20.5 Phytochemicals in raisins

Phytochemicals or plant chemicals are known to possess certain biological and physiological activities. These include antioxidant activity, inhibiting cholesterol absorption, blocking the activity of bacteria or viral toxins, decreasing platelet aggregation, or destroying the harmful gastrointestinal bacteria [34]. In recent years, phytochemicals originating from fruits, vegetables, tree nuts, cereals, and other plant food products have attracted much attention by the functional food and nutraceutical market due to their potential health benefits and therapeutic value [35]. In addition to providing essential nutrients, raisins are also a rich source of phytochemicals. The known phytochemicals in raisins include

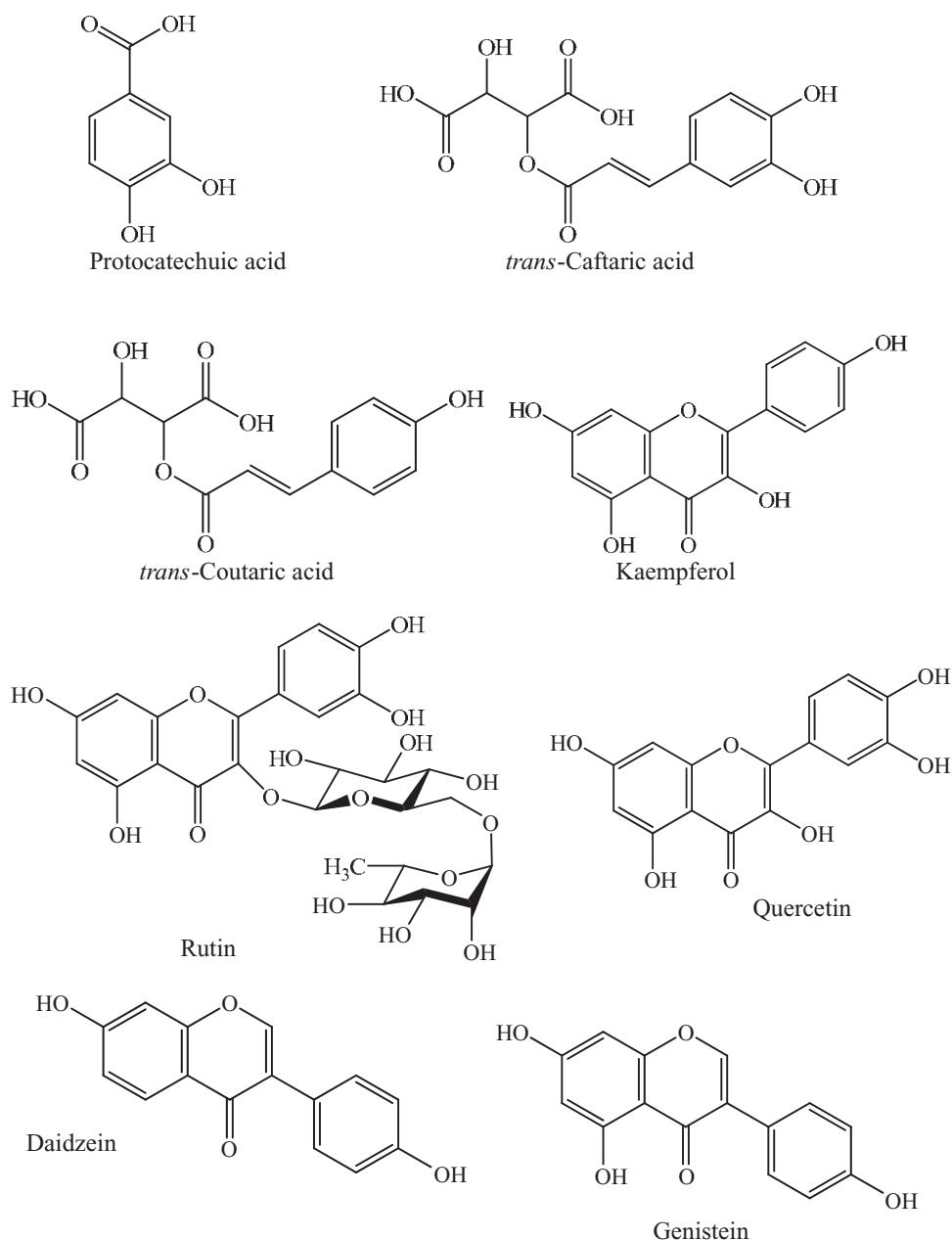
phenolics, prebiotics, tartaric acid, and other minor phytochemicals which may positively affect human health.

### 20.5.1 Phenolics

Phenolic compounds are ubiquitous and widely distributed secondary metabolites in the plant kingdom. They contain at least one aromatic ring with one or more hydroxyl groups attached to it and play a very important role in plants and plant-derived foods [36]. A wide range of beneficial physiological properties, such as anti-allergic, anti-atherogenic, anti-inflammatory, antimicrobial, anti-thrombotic, cardioprotective, and vasodilatory effects, have been attributed to phenolics [37]. Phenolic compounds may serve as a major determinant of antioxidant potential of foods because of their ability to donate a hydrogen atom or an electron in order to form stable radical intermediates. Different mechanisms may be used to explain their antioxidant activity including scavenging of free radicals, quenching of reactive oxygen species, inhibition of oxidative enzymes, chelating of transition metals, or interaction with biomembranes [38]. The major phenolics found in raisins are phenolic acids, flavonols, isoflavones, and their derivatives. The chemical structures of representative phenolics found in raisins are given in Figure 20.2.

While the phenolics composition of grapes, grape juices, and wines has been extensively investigated, few studies have explored the phenolics composition of raisins. The total phenolics content (TPC) and antioxidant capacity of selected dried fruits and grapes are presented in Table 20.4. The TPC of raisins is higher than fresh grapes since the phenolics become concentrated and possibly be partially modified during the dehydration process [39].

The phenolic profiles of raisin as reported by Karadeniz *et al.* [40] and Parker *et al.* [41] are summarized in Table 20.5. The difference in phenolics content between raisins and fresh grapes is striking, partially due to the enzymatic oxidation and nonenzymatic browning reactions happening during the drying process. Similar trends have been reported in both studies; for example, raisins possess higher levels of phenolics than grapes in most cases. Phenolic acids and flavonols are the two major types of phenolics in both raisins and grapes. Phenolic acids, namely, caftaric and coutaric, exist mainly as *trans* isomers. Due to sulfur dioxide pretreatment, higher levels of *trans*-caftaric and *trans*-coutaric acids are present in golden raisins. Protocatechuic acid was detected only in sun-dried raisins and dipped raisins. Among the flavonols, quercetin glycosides have the highest concentration, followed by kaempferol glycosides and rutin. Except the similar trends mentioned above, there are also certain inconsistencies between these two reports. The content of some phenolics given in the two reports varied considerably. The difference was up to 12 times as indicated by the content of *trans*-caftaric acid in fresh grapes. Ninety percent of caftaric and coutaric acids were lost when fresh grapes were processed into sun-dried, dipped, and golden raisins as reported by Karadeniz *et al.* [40]. However, in the report by Parker *et al.* [41], the content of these two phenolic acids in raisins was higher than that in their corresponding fresh grapes. According to the study of Karadeniz *et al.* [40], procyanidins and flavanols were completely degraded during raisin formation. This is also inconsistent with the USDA database [42], which reported that raisins contain catechin (0.42 mg/100 g), epicatechins (0.10 mg/100 g), and cyanidin (0.03 mg/100 g). The inconsistency may be explained by the use of different samples of grapes/raisins, highly complex structures produced during the drying process, difficulty in working with the raisins matrix as well as interference with non-phenolic



**Figure 20.2** Structures of representative phenolics found in raisins.

**Table 20.4** Total phenolics and antioxidant capacity of dried fruits and grapes

Food	TPC (mg of GAE/g)	TAC (μmol of TE/g)	L-ORAC <sub>FL</sub> (μmol of TE/g)	H-ORAC <sub>FL</sub> (μmol of TE/g)
Medjool dates	5.72	23.87	0.27	23.60
Figs	9.60	33.83	1.83	32.00
Prunes	11.95	85.78	1.79	83.99
Raisins	10.65	30.37	0.35	30.02
Green grapes	1.45	11.18	na	nc
Red grapes	1.75	12.60	na	nc

Source: Adapted from Wu *et al.* [39].

TPC, total phenolics content; TAC, total antioxidant capacity; L-ORAC<sub>FL</sub>, lipophilic-oxygen radical absorbance capacity; H-ORAC<sub>FL</sub>, hydrophilic-oxygen radical absorbance capacity; GAE, gallic acid equivalents; TE, trolox equivalents; na, not available; nc, not calculated.

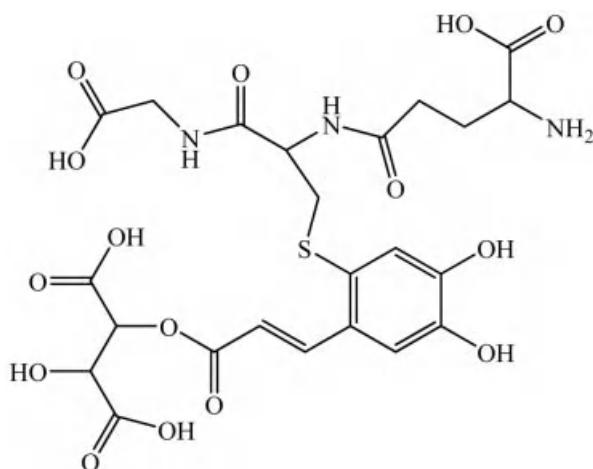
compounds [43]. The discrepancy may also be explained by the different extraction conditions employed. Zhao and Hall [44] studied the optimization of solvent extraction of raisins phenolics. Their results indicated that the extraction method, such as the types of solvent, pH, temperature, and other factors, plays a major role in the yield of phenolics and hence the apparent composition of products. In their study, except the phenolics mentioned above, they also reported the presence of gallic acid, ferulic acid, chlorogenic acid, and (+)-catechin in raisin extracts. However, Ong and Nagel [45] reported that chlorogenic acids are absent in grapes, and phenolic acids were present mainly as tartaric and not quinic acid esters in grapes. Thus, the presence and source of chlorogenic acid in raisins may still remain unclear and more research is needed to shed light on the composition of phenolics in raisins.

Other minor phenolics reported in raisins include isoflavones, 2-S-glutathionylcaftaric acid, and other oxidized cinnamics. Isoflavones such as daidzein and genistein are thought to protect against chronic diseases that are common in the Western countries, such as cancer,

**Table 20.5** Phenolics composition in raisins and fresh grapes (mg/kg of sample)

Food	Reference	CAA		COA		2-S-GCA	PA	RU	QG		KG	
		trans	cis	trans	cis				A	B	A	B
Sun-dried raisins	[40]	39.6	nd	6.7	nd	nd	6.8	5.2	7.3	34.7	11.2	23.7
	[41]	41.4	nr	nd	nr	nd	4.4	8.3	15.6	6.5	7.0	9.3
Golden raisins	[40]	84.3	nd	27.3	nd	nd	nd	3.5	41.5	37.1	6.5	7.6
	[41]	130.4	nr	31.4	nr	nd	nd	14.4	65.7	43.4	9.8	14.3
Dipped raisins	[40]	45.2	nd	7.7	nd	8.1	2.8	6.5	20.6	39.0	16.7	29.5
Fresh grapes	[40]	100.7	2.7	31.8	8.0	nd	nd	0.9	21.9	3.9	nd	19.4
	[41]	7.9	nr	14.8	nr	8.8	nd	tr	15.2	25.6	tr	tr
Frozen grapes	[40]	18.2	nd	1.2	nd	nd	nd	0.9	21.9	3.9	nd	19.4
	[41]	7.9	nr	nd	nr	12.1	nd	tr	21.5	27.7	tr	tr

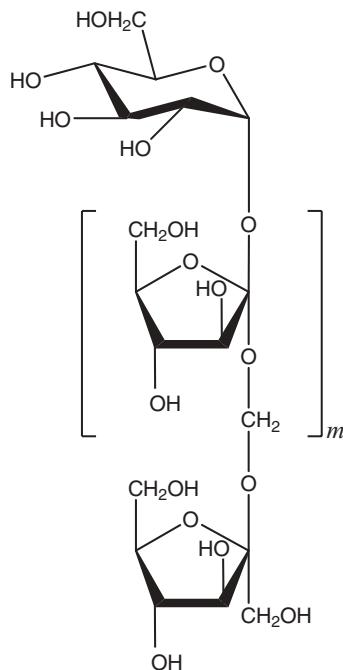
CAA, caftaric acid; COA, coutaric acid; 2-S-GCA, 2-S-glutathionylcaftaric acid; PA, protocatechuic acid; RU, rutin; QG, quercetin glycoside; KG, kaempferol glycoside; nd, not detected; nr, not reported; tr, trace.



**Figure 20.3** Chemical structure of 2-S-glutathionylcaftaric acid as oxidation product of glutathione and caftaric acid.

osteoporosis, and coronary heart diseases (CHD) [46]. California raisins are the richest sources of daidzein and genistein among 36 samples of fruits and nuts that contain daidzein or genistein, being 2.25 and 1.84 mg/kg, respectively [47]. 2-S-Glutathionylcaftaric acid (also known as grape reaction product, its structure is shown in Figure 20.3) is formed when glutathione and caftaric acids are decompartmentalized upon processing [48]. The amount of 2-S-glutathionylcaftaric acid present in a wine provides information on the oxidation history of the wine over its elaboration and aging [49]. The content of 2-S-glutathionylcaftaric acid in different raisin and grape samples from two sources is shown in Table 20.5. Karadeniz *et al.* [40] reported that 2-S-glutathionylcaftaric acid exists only in dipped raisins. This may indicate that enzymatic oxidation reactions probably occur during the drying process as the polyphenol oxidase is only partially inactivated in the dipped raisins during production. In contrast, in sun-dried raisins, 2-S-glutathionylcaftaric acid does not normally form due to the compartmentalization of glutathione and caftaric acid, and in golden raisins, pretreatment with sulfur dioxide inhibits phenolic oxidation. However, different results about the content of 2-S-glutathionylcaftaric acid have been reported by Parker *et al.* [41]. A similar level of 2-S-glutathionylcaftaric acid is present in grapes, with a higher level in frozen grapes than in fresh ones. The different sample preparation methods may contribute to such difference as explained by the authors [41].

High level of resveratrol has been reported in both grapes and wine [50–52]; however, no resveratrol has been reported in raisins by Karadeniz *et al.* [40] and Parker *et al.* [41]. This may be partially explained by the fact that grapes used for raisin production are normally fully ripened and grapes are known to lose their capacity to produce resveratrol during ripening even in the face of fungal infection [53, 54] and have a reduction in their content of resveratrol. However, resveratrol (40–1088 µg/g) in raisin extracts was reported by Zhao and Hall [44] who were using different extraction solvents and various concentrations and combination.

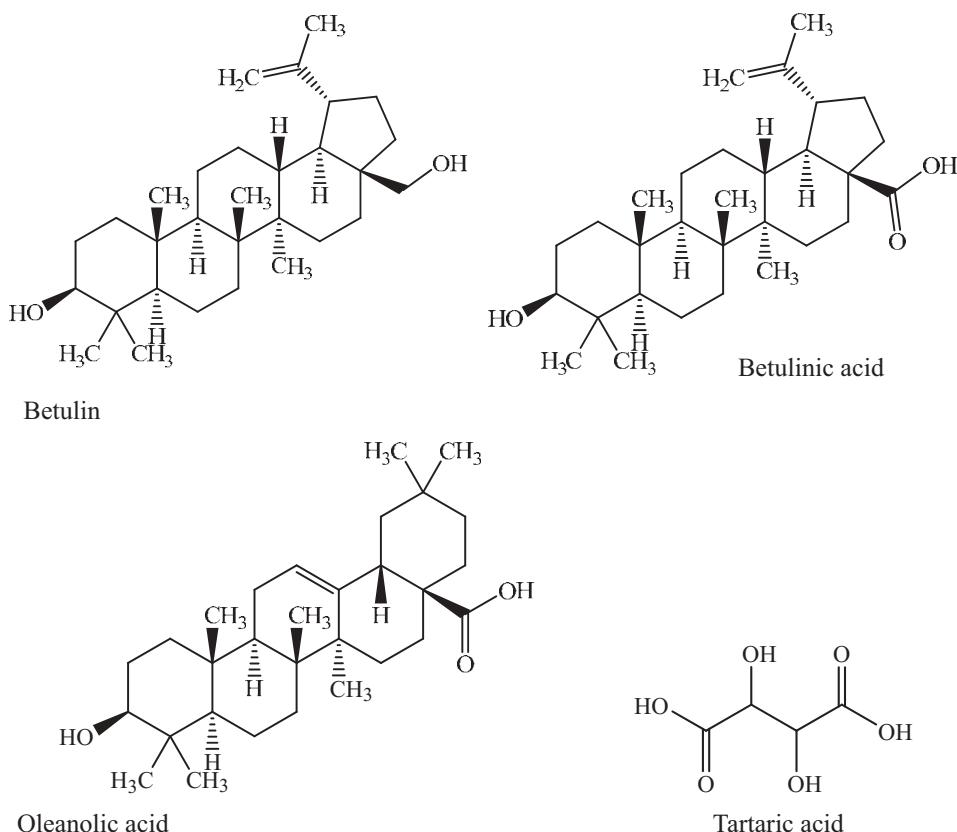


**Figure 20.4** Structure of fructan.

### 20.5.2 Prebiotics

A prebiotics is defined as a nonviable food component that confers a health benefit on the host associated with modulation of the microbiota [55]. Inulin, fructooligosaccharides (FOS), galactooligosaccharides (GOS), soya oligosaccharides, xylooligosaccharides, pyrodextrins, isomalto-oligosaccharides, and lactulose are the commonly used prebiotics. The majority of studies have, so far, focused on inulin, FOS, and GOS [56, 57]. Inulin and FOS are two subgroups of fructans, also known as polyfructoses (Figure 20.4), and differ in their molecular size. The larger sized polyfructoses (more than 10 fructose units,  $m > 10$ ) are known as inulin while the smaller ones (chain length of 3–10 fructose units,  $m = 3–10$ ) are known as FOS [58]. Fructans can reach the large intestine practically intact and are then fermented by bacteria that can cleave the  $\beta(2-1)$ -glycosidic bonds between fructosyl units and act as prebiotic compounds by selectively stimulating the growth of beneficial intestinal microflora, namely, *Bifidobacteria* and *Lactobacilli*. Clinical studies have shown that fructans increase the number of these health-promoting bacteria in the colon mucosa when taken in the diet [59]. Prebiotics, such as fructans, not only help keep microbial balance in the intestinal track, but also offer cardiovascular benefits through a triacylglycerol (TAG)- and cholesterol-lowering effect. They may also increase the absorption of calcium and magnesium and so enhance bone mineralization during growth and prevent osteoporosis [60].

While fresh grapes have no detectable fructans, the dehydration process converts grape sugars into fructans. Thus raisins, unlike fresh grapes, are a rich source of prebiotics in the diet. Sun-dried raisins contain 5.7 g fructans per 100 g of fruit [29], which is the highest among all commonly consumed fruits [61]. Carugh [62] reported that the inulin content



**Figure 20.5** Structures of some minor phytochemicals in raisins (betulin, betulinic acid, oleanolic acid, and tartaric acid).

in raisins ranged between 0.7 and 1.2% and FOS between 0.78 and 0.96%, thus having the highest content of prebiotics in commonly consumed fruits. The type of dehydration, storage, and grape variety also influenced the content of fructans in raisins.

### 20.5.3 Other minor phytochemicals

Triterpenoids are terpenoid derivatives with 30 carbon atoms. The structures of betulin, betulinic acid, and oleanolic acid belonging to this group are given in Figure 20.5. This group of compounds exhibits a wide range of bioactivities including antiretroviral, antimarial, anti-inflammatory, and anticancer properties. The main plant source for triterpenoids includes birch bark, rosemary leaves, apple peel, and mistletoe shoots [63–65]. Triterpenoids, namely oleanolic acid, oleanolic aldehyde, betulin, and betulinic acid, have been isolated and identified in raisins. However, there is no quantitative report of their presence in raisins [66, 67].

Tartaric acid (Figure 20.5) is a diprotic organic acid and occurs naturally in many plants, especially grapes, raisins, bananas, and tamarinds, and is used as both a flavorant and an antioxidant in the food industry. Tartaric acid is of interest in studies of fiber and health as

it is known to affect colon function. Tartaric acid and fiber in raisins work synergistically to maintain a healthy digestive system [68]. The content of tartaric acid in grapes and raisins is 0.6–0.9 and 2.0–3.5 g/100 g, respectively [69].

The high content of phytosterols (200 mg/kg of fresh weight), with dominance of  $\beta$ -sitosterol, has been reported in grapes [70]. However, there is no report on the composition of phytosterols in raisins, a subject that deserves more attention.

## 20.6 Bioactivities and health benefits of raisins

### 20.6.1 Antioxidant activity of raisins

Phenolic compounds are believed to account for a major portion of the antioxidant capacity in many plants [71]. Antioxidant activity of raisins has been studied by several groups of researchers as it is the most notable bioactivity of phenolics in raisin. Antioxidant activity assays such as oxygen radical absorbance capacity (ORAC), total radical-trapping antioxidant parameter (TRAP), trolox equivalent antioxidant capacity (TEAC), ferric-reducing antioxidant power (FRAP), and cellular antioxidant activity (CAA) have been employed to evaluate the antioxidant potential of raisins [39, 41, 72–74]. Comparison of the antioxidant activity of two types of raisins and Thomson seedless grapes is shown in Table 20.6. As shown, raisins generally possess a higher antioxidant activity than fresh grapes because of the removal of water and concentration of antioxidants during the drying process. Parker *et al.* [41] indicated that the ORAC value of golden raisins was much higher than that of the sun-dried raisins, possibly because the pretreatment with sulfur dioxide in the production of golden raisins may inactivate polyphenol oxidase and minimize nonenzymatic browning. Thus, more phenolics are retained during the drying process. The lipophilic and hydrophilic antioxidants are shown in Table 20.4 for dried fruits such as dates, prunes, and raisins. For all those dried fruits, the hydrophilic antioxidants contributed more than 94% to the total antioxidant activity [39]. The antioxidant activity measured by FRAP, TRAP, and TEAC is reported by Pellegrini *et al.* [73]. In their study, raisins showed a moderate antioxidant activity in all three assays employed among several dried fruits examined, including prune, apricot, chestnut, and fig.

Antioxidants can inhibit copper-induced oxidation of human low-density lipoprotein (LDL) and very low density lipoprotein (VLDL) particles as estimated using the thiobarbituric acid reactive substances (TBARS) [75]. The quality of antioxidants in raisin extracts has

**Table 20.6** Antioxidant activity of raisins and grapes using different methods

Food	ORAC ( $\mu\text{mol of TE/g}$ )		FRAP (mmol antioxidant content/100 g) [72]
	[39]	[41]	
Sun-dried raisins	na	37.4	0.78
Golden raisins	30.37	104.5	na
Thompson seedless grapes	11.80	10.8	0.13

ORAC, oxygen radical absorbance capacity; FRAP, ferric-reducing antioxidant power; TE, trolox equivalents; na, not available.

also been reported as IC<sub>50</sub> (the concentration to inhibit *in vitro* oxidation of LDL particles by 50%) using this method. Values of 1/IC<sub>50</sub> (reciprocal of the amount needed to inhibit oxidation by 50%) for fresh cranberries, green grapes, and plums are 1.16, 1.32, and 1.42 [76], respectively, compared to values for dried cranberries, raisins, and dried plums of 2.38, 3.45, and 4.38, respectively [77]. This is in agreement with the conclusions reached by Wu *et al.* [39] that antioxidant activity improved during the drying process.

It is reported that consumption of phenolic-rich foods can increase serum antioxidant capacity in humans [78]. Study of serum antioxidant capacity after consumption of raisins/grapes was carried out by Parker *et al.* [41]. Long-term consumption of raisins/grapes (4 weeks) increased serum antioxidant capacity by the second and third week of sample consumption. However, values fell again in the fourth week. They speculated that there may be a physiological plateau approximately 2 or 3 weeks after consistent consumption; Cao *et al.* [79] reported similar results. However, serum ORAC values after 1 and 2 h of raisins/grapes consumption weekly during each of 4-week consumption indicated increased oxidation. The authors speculated that the high sugar content of the grapes/raisins may have affected the antioxidant capacity of blood by causing postprandial oxidative stress [41]. A more recent study found that serum antioxidant capacity was modestly increased by daily consumption of raisin, but this did not alter fasted or postprandial inflammatory response in these relatively healthy but overweight individuals [80].

Foods high in phenolic antioxidants can protect against DNA damage during intense physical activity by counteracting oxidative stress. Presence of 8-hydroxy-2-deoxyguanosine (8OHdG) in urine or in leukocytes is an indication of free radical oxidative damage to DNA [81]. Feeding 170 g of sun-dried raisins prior to and during a triathlon to trained athletes significantly lowered the level of 8OHdG in urine compared to feeding of a glucose drink with the same amount of calories. This suggests that raisins can protect against DNA damage caused by oxidative stress during strenuous exercise [82]. Thus, raisins exhibit excellent antioxidant activity in both *in vitro* and *in vivo* tests.

## 20.6.2 Cardioprotection

Cardiovascular disease (CVD) is a main cause of mortality and morbidity in the world and ranks first in this respect. In Canada, CVD is the leading cause of death and accounts for at least 36% of all deaths [83]. The cause of most CVD is atherosclerosis. High levels of total and LDL cholesterol concentrations are the major atherogenic components of plasma.

Raisins are a significant source of dietary fiber and other phytochemicals which may reduce the risk of CVD by affecting lipoprotein metabolism and inflammation. Phytochemicals, especially phenolics, can protect from atherosclerosis because of their antioxidant potential and through their anti-inflammatory activity [84]. The antioxidant activity of raisins has been discussed in the previous section. The effect of diets containing raisins alone or together with other plant material on blood lipids has been reported by different research groups. In adults with hypercholesterolemia, consumption of Mediterranean-style diets high in whole grains, nuts, and 84 g raisins daily, for 4 weeks, lowered the total and LDL cholesterol concentrations by 9 and 15%, respectively, but there was no significant change in high-density lipoprotein (HDL) cholesterol [85]. A similar result was reported in a crossover study [86] in which hyperlipidemic volunteers were fed a diet with unrefined food, which contained 126 g raisins daily. By the end of the study, total and LDL cholesterol concentrations were lowered by 13 and 16%, respectively, compared to the baselines.

More recently, Puglisi *et al.* [87] indicated that simple lifestyle modifications such as adding raisins to the diet or increasing walking steps have distinct beneficial effects on CVD risk. Volunteers were assigned to consume 160 g raisins per day, increase the number of walking steps per day, or a combination of both interventions for 6 weeks. Results indicated that the total and LDL cholesterol concentrations were decreased by 9.4 and 13.7%, respectively, for all subjects. Subjects in the raisin group had significantly lower levels of  $\alpha$ -tumor necrosis factor (TNF- $\alpha$ ) and soluble intercellular adhesion molecule-1 (sICAM-1). TNF- $\alpha$  is a powerful pro-inflammatory cytokine. Reducing TNF- $\alpha$  could potentially prevent progression of inflammatory damage. Lower levels of sICAM-1 could potentially prevent progression of atherosclerosis by decreasing adhesion of monocytes to the vascular endothelium.

Addition of raisins to the daily diet could reduce the risk of CVD by increasing the plasma antioxidant capacity, lowering the total and LDL cholesterol concentrations, and reducing inflammation.

### 20.6.3 Diabetes

Diabetes is a chronic disease marked by high levels of sugar in the blood. It not only increases the risk of death, but also results in a variety of complications including heart disease, kidney disease, eye disease, problems with erection (impotence), and nerve damage [88]. Controlling blood glucose levels closer to normal values through different strategies may lower the risk of diseases and death from these complications.

Potential concerns about raisins causing a high postprandial glycemic response, especially in diabetic or prediabetic individuals, may arise as raisins are a concentrated source of natural sugars. However, except the absolute amount of carbohydrate, other factors in foods may also play important roles in influencing the postprandial glycemic response, such as the glycemic index (GI) of a carbohydrate source and the presence of other antidiabetic bioactive compounds [89]. Although raisins are a concentrated source of carbohydrates, roughly half of their available carbohydrates is fructose, which has a low GI value of 19 (glucose = 100) [90]. The GI values for raisins in healthy adults and women with gestational diabetes were 64 and 65.7, respectively [91, 92]. More recently, GI of raisin from 49.4 to 69 with corresponding insulin index of 47.3–54.4 has also been reported [89].

In addition to its low GI and high dietary fiber content, the high content of antioxidants, especially phenolics such as flavonoids, may also serve as important factors in the management of diabetes. It has been hypothesized that flavonoids, functioning as free radical scavengers and metal chelator, may preserve  $\beta$ -cell function by reducing oxidative stress-induced tissue damage and protect against the progression of insulin resistance to type-2 diabetes. However, results from the available epidemiological studies on the relationship between dietary flavonoids and development of type-2 diabetes are controversial [93–95]. More research is needed to confidently conclude the role of dietary flavonoids in the control of type-2 diabetes.

### 20.6.4 Anticancer activities

Cancer is the second leading cause of death in the world after heart disease. Epidemiological studies have consistently shown that diets rich in fruits and vegetables help prevent many

types of cancer [96]. Although there is no study on the anticancer effect of raisin-containing diets, raisins could serve as important ingredients of a healthy diet to help prevent cancer due to their high content of fiber (fructans) and phenolics (flavonols). The cancer-protective effect of fructans and flavonols is well documented. Animal model studies indicated that fructans possessed anticarcinogenic properties. For example, dietary fructans inhibit the formation of chemically induced aberrant crypt foci in rats. These are neoplastic lesions in the colon from which adenomas and carcinoma may develop [97–99]. High intakes of selected flavonoids, including flavonols, have been found to reduce the risk of developing several types of cancer, such as ovarian cancer [100], breast cancer [101], oral and pharyngeal cancers [102], colorectal cancer [103], and pancreatic cancer [104]. More research is needed to explore the cancer-protective effects of raisins.

### 20.6.5 Dental health

Traditionally, raisins have been thought of as cariogenic foods because of their high content of sugar and sticky texture. However, studies demonstrated that the perceived “stickiness” bears little relationship to the retention of food particles on tooth surface. Actually, raisins are one of the least retentive foods among the 21 tested commercial snack foods due to their rapid clearing rates after consumption [105]. The sugar composition of raisins may also benefit the dental health. Compared with most commercial sweets, raisins contain a high amount of fructose and glucose instead of sucrose. Sucrose normally induces the most smooth-surface-type and fissure-type caries among the five tested sugars, namely, sucrose, maltose, lactose, fructose, and glucose [74].

Triterpenoids from raisins such as oleanolic acid, oleanolic aldehyde, betulin, and betulinic acid have been shown to inhibit the growth of two species of oral bacteria, *Streptococcus mutans* and *Porphyromonas gingivitis*, which can cause tooth cavities and periodontal disease, respectively [66]. Oleanolic acid also blocks the adherence of *S. mutans* to experimental surfaces, which reduces the risk of forming dental plaque [67]. Thus, raisins may protect teeth and gums through different means as mentioned above.

## 20.7 Conclusions

Raisins are important dried fruits that enhance diet quality due to their pleasing flavor (taste and aroma) as well as offering nutrition and physiological benefits. They are a rich source of phytochemicals, including phenolics, prebiotics, tartaric acid, and other minor components, which contribute to the different bioactivities and health benefits of raisins.

Although various drying techniques for raisin production have been developed, more research is needed to further refine and optimize the drying process. Pretreatment with chemicals such as sulfur dioxide should be avoided. The undesirable changes in color, flavor, and composition of raisins should also be minimized. In addition, the development of new raisin grape cultivars with high contents of total phenolics and low polyphenol oxidase activity would be valuable to growers and consumers.

More research is particularly needed in the areas related to raisin phytochemicals and in the extraction and analyses of minor phytochemicals and composition of flavonoids other than flavonols as well as the bioavailability of certain raisins phytochemicals, especially the absorption and metabolism of tartaric acid esters.

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## **Part 3**

### Tropical Dried Fruits

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# **21 Açaí fruits: potent antioxidant and anti-inflammatory superfruits with potential health benefits**

Alexander G. Schauss

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## **21.1 Introduction**

The terms “superfood” and “superfruit” first appeared in food advertising at the beginning of the twenty-first century to describe a food that possessed functional health properties beyond its nutritive value. Familiar foods such as blueberries [1], strawberries [2, 3], cranberries [4, 5], walnuts [6], and pomegranates [7] were the first to be categorized as superfoods, which resulted in a significant increase in their consumption based on the assumption that food sources containing exogenous nutrient and/or phytochemical antioxidants could protect the body from damage arising from chronic oxidative stress—caused by excessive production of free radicals. However, initial clinical evidence for any potential health benefits of superfoods was open to question based on clinical trial outcomes. For example, a walnut consumption randomized crossover trial did not see a significant change in plasma antioxidant capacity in healthy, well-nourished older adults [8], while a cranberry juice randomized, double-blind, and placebo-controlled trial of female subjects with metabolic syndrome observed a significant reduction in lipid oxidation and an increase in plasma antioxidant capacity [9]. Evidence is accumulating that certain superfoods, such as the subject of this chapter, not only have antioxidant bioactivity but also possess anti-inflammatory properties.

There is a growing consensus in the medical community that chronic non-resolved inflammation contributes to numerous diseases including atherosclerosis [10–12], ischemic heart disease [13, 14], hypertension [15], cancer [16–18], obesity [19], inflammatory bowel disease [20, 21], Crohn’s disease [19, 22], type 2 diabetes [23, 24], end-stage renal disease [25], and autoimmune disorders [26], among others.

Of all fruits that quickly became identified as superfruits based on growing and increased year-to-year consumer interest through 2010, none captured as much attention and interest among food scientists as that of a small Amazonian palm fruit known as “açaí” (pronounced, “ah-sigh-ee”) [27]. From virtual obscurity in the 1990s to superfruit status a decade later [28], this small and tasteless nutritionally dense fruit with remarkable antioxidant and anti-inflammatory properties *in vitro* and *in vivo* came to define what a superfruit is.

### 21.1.1 Açaí palm trees

Palms belong to the plant family known as Arecaceae, which consists of nearly 4000 species that grow primarily in the tropics and subtropics. Within the palm family there are more than 200 genera. Nearly 220 different palm species have been identified as growing in the Amazon, of which only 40 species of palms are within the genera *Euterpe*. Three commercial species of açaí fruits, *Euterpe oleracea*, *Euterpe precatoria*, and *Euterpe edulis*, are only found growing at various altitudes in the southern hemisphere within a geographical area commonly referred to as the Amazon.

The origin of the word, *Euterpe*, comes from the Greek words, “forest grace,” owing to its elegant appearance. Its drooping leaflets give the long pendulous fronds the appearance that rain just fell on them. Among the three açaí palms of interest, *E. edulis* is primarily harvested for its heart-of-palm, not its fruit. Of the remaining two *Euterpe* species, *E. oleracea* has received the most research attention due to its ample availability and documented traditional use as a food in and between the Amazon River and its tributaries and estuaries in the Amazon floodplains of Brazil. In the State of Para, Brazil, during any 8-month açaí fruits harvest season, more than 35,000 people are employed at various occupations in the state’s largest city, Belem, gathering, wholesaling, retailing or processing the fruit into frozen pulp or either spray-dried or freeze-dried powders for domestic consumption and/or export. More recently, *E. precatoria* has drawn attention with the discovery of remarkably stronger antioxidant and anti-inflammatory activity than even *E. oleracea*, which had already gained recognition for having the highest antioxidant activity on the oxygen radical absorbance capacity (ORAC) assay of almost any food tested by the US Department of Agriculture (USDA) [29].

## 21.2 Compositional and nutrition characteristics of açaí fruits

### 21.2.1 *Euterpe oleracea* fruits

*Euterpe oleracea* fruits have been found to have a remarkable range of nutrients, including unusually high content of mono- and polyunsaturated fatty acids (MUFA and PUFA) approximating that of olives and avocados, phytosterols, amino acids, soluble and insoluble fibers, vitamins, minerals, and trace elements, among others [30, 31]. The compositional and nutritional characteristics of freeze-dried açaí fruits are shown in Table 21.1.

The phytochemistry of *E. oleracea* fruits has proven to have similarities to other antioxidant-rich berries. Anthocyanins are believed to be the major compounds that contribute to the *E. oleracea*’s antioxidant activity. *E. oleracea* fruits contain two major anthocyanins, namely cyanidin 3-glucoside and cyanidin 3-rutinoside, and three minor anthocyanins, cyanidin 3-sambubioside, peonidin 3-glucoside, and peonidin 3-rutinoside [30]. However, quantitatively, total anthocyanin content is lower than other dark-colored berries, such as blackberries, blueberries, and cranberries, which suggest that açaí fruits’ extraordinary antioxidant activity may be due to other compounds or a combination of anthocyanins and other compounds. Proanthocyanidin content has also been characterized and quantified, as proanthocyanidin have been found to possess strong antioxidant capacity. Açaí fruits contain monomers (catechin and epicatechin) and B type procyanidins from dimers to polymers,

**Table 21.1** Compositional and nutritional characteristics of freeze-dried açai fruits

Nutrient	Units	Freeze-dried <sup>a</sup> [31]
<b>Proximate composition</b>		
Water	g	3.4
Energy	kcal	534
Protein	g	8.1
Lipid	g	32.5
Ash	g	3.8
Carbohydrate	g	52.2
Dietary fiber	g	44.2
Sugars	g	1.3
<b>Minerals</b>		
Calcium	mg	260
Iron	mg	4.4
Potassium	mg	na
Sodium	mg	30.4
<b>Vitamins</b>		
β-Carotene	IU	<5.0
Vitamin A	IU	1002
Vitamin C	mg	<0.1
Vitamin E (ATE)	mg	na
<b>Amino acids</b>		
Alanine	g	0.46
Arginine	g	0.42
Aspartic acid	g	0.83
Cystine	g	0.18
Glutamic acid	g	0.80
Glycine	g	0.39
Histidine <sup>b</sup>	g	0.17
Hydroxyproline	g	<0.01
Isoleucine <sup>b</sup>	g	0.38
Leucine <sup>b</sup>	g	0.65
Lysine <sup>b</sup>	g	0.66
Methionine <sup>b</sup>	g	0.12
Phenylalanine <sup>b</sup>	g	0.43
Proline	g	0.53
Serine	g	0.32
Threonine <sup>b</sup>	g	0.31
Tryptophan <sup>b</sup>	g	0.13
Tyrosine	g	0.29
Valine <sup>b</sup>	g	0.51
<b>Fatty acids</b>		
SFA	g/100 g oil	26.1
MUFA	g/100 g oil	60.6
PUFA	g/100 g oil	13.3
<b>Phytosterols</b>		
β-Sitosterol	mg/g	0.44
Campesterol	mg/g	<0.03
Stigmasterol	mg/g	0.04

Note: Some numbers are rounded to the second digit after decimal point.

ATE, alpha-tocopherol equivalents; na, not available; SFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids.

<sup>a</sup>Values per 100 g in dry weight unless otherwise stated.

<sup>b</sup>Indispensable amino acids.

with the latter being the major proanthocyanidins accounting for 12.89 mg/g dry weight (DW) [30]. Interestingly, the proanthocyanidin profiles of açai fruits are similar to that of blueberries.

## 21.3 Antioxidant and anti-inflammatory activities of açai fruits

The ORAC assay was initially developed to measure antioxidant inhibition of hydrophilic and lipophilic compounds and components in foods against peroxyl radical-induced oxidation [32]. Over time, a series of additional assays have been developed based on the original ORAC peroxyl radical scavenging assay that measures antioxidant inhibition against other reactive oxygen species/reactive nitrogen species (ROS/RNS) moieties, including  $\cdot\text{OH}$ ,  $\text{O}_2^{\bullet-}$ ,  $\text{ONOO}^-$ , and  ${}^1\text{O}_2$  [33], and which have been given the corresponding names of hydroxyl-ORAC (HORAC), superoxide-ORAC (SORAC), peroxy nitrite-ORAC (NORAC), and singlet-oxygen-ORAC (SOAC) to distinguish them, as there are various reactive nitrogen or oxygen free radical species involved in the pathophysiology of human diseases. The antioxidant and anti-inflammatory activities of açai fruits have been evaluated by numerous assays. Besides the ORAC assay, 2,2'-diphenyl-1-picrylhydrazyl (DPPH) assay has also been widely employed [34].

Characterization of *E. precatoria* fruits has only recently focused on their phytochemical compositions. As was the case with *E. oleracea* fruits, anthocyanins were the predominant polyphenolics. Various flavones, flavanol derivatives including procyanidin dimers and trimers, and phenolic acids are present in *E. precatoria* fruits, leading to the conclusion that both açai species are characterized by similar polyphenolic profiles and antioxidant activities [35]. However, later investigations found significantly higher antioxidant activity in *E. precatoria* fruits than *E. oleracea* fruits [36]. As shown in Table 21.2, where the combination of hydrophilic ORAC ( $\text{ORAC}_{\text{hydro}}$ ) and lipophilic ORAC ( $\text{ORAC}_{\text{lipo}}$ ) scavenging capacity yields an ORAC value of 1027  $\mu\text{mol}$  trolox equivalents (TE)/g for *E. oleracea* fruits, the combined ORAC result for *E. precatoria* fruits yield a value of 1824  $\mu\text{mol}$  TE/g, a significant difference in scavenging capacity. The antioxidant activity of *E. precatoria* fruits in scavenging the peroxyl radical is superior to *E. oleracea* fruits, and far superior to other antioxidant-rich fruits and berries, nuts, vegetables, and grains, with the exception of sumac bran, based on USDA database of ORAC values for foods [29].

A further comparison between *E. oleracea* and *E. precatoria* fruits' free radical scavenging activities that include the ORAC, HORAC, SORAC, NORAC, and SOAC assays, to provide a more comprehensive understanding of each açai fruits' radical scavenging activities, has been carried out, given the complexity of the body's antioxidant defense system. This is now becoming the standard method of *in vitro* antioxidant scavenging assessment since a single antioxidant assay cannot reflect all aspects of scavenging activities of foods otherwise. As seen in Table 21.3, *E. precatoria* fruits have nearly three-fold higher total ORAC value against multiple radicals of *E. oleracea* fruits *in vitro*.

In evaluating the antioxidant activities of a given food or natural product, combining both chemical and cell-based assays provides a useful approach toward understanding the antioxidant effects of antioxidants found in food and their biological relevance to any health benefits that may be observed *in vivo* [37]. The advantages of a cell-based assay over current

**Table 21.2** ORAC values of açai species' pulp compared to other antioxidant-rich foods

Food	$\mu\text{mol TE/g DW}$	Reference
Sumac, bran	3124	[29]
Açaí pulp ( <i>E. precatoria</i> )	1824	[38]
Açaí pulp ( <i>E. edulis</i> )	1193	<sup>a</sup>
Açaí pulp ( <i>E. oleracea</i> )	1027	[29, 30]
Sorghum, bran, black	1008	[29]
Cocoa, dry powder, unsweetened	557	[29]
Chocolate, unsweetened	499	[29]
Black raspberry	192	[29]
Pecan	179	[29]
Chokeberry	160	[29]
Elderberry	147	[29]
Walnut	135	[29]
Cranberry	91	[29]
Blueberry (wild)	96	[29]
Plums	76	[29]
Blackberries	59	[29]
Pomegranate	45	[29]
Strawberry	43	[29]

DW, dry weight; TE, trolox equivalents.

<sup>a</sup>Unpublished data.

chemical assays such as the ORAC and DPPH assays are numerous. Whereas chemical assays depend on chemical reactions using a limited number of reagents, cell-based assays take into consideration complex enzymatic reactions in biological systems, providing qualitative rather than just quantitative assessment. In this way, cell-based assays incorporate those enzymes involved in redox reactions that are occurring in red blood cells (RBCs) as well as polymorphonuclear (PMN) cells or other living cells.

**Table 21.3** ORAC values of two different freeze-dried açai fruit species (*E. precatoria* and *E. oleracea*)

ORAC-based assays	<i>E. precatoria</i> ( $\mu\text{mol of TE/g DW}$ )	<i>E. oleracea</i> ( $\mu\text{mol of TE/g DW}$ )
ORAC (against peroxyl radical)	1828	1014
H-ORAC (hydrophilic fraction)	1792 $\pm$ 90	986 $\pm$ 57
L-ORAC (lipophilic fraction)	36 $\pm$ 2.6	28 $\pm$ 2.1
HORAC (against hydroxyl radical)	4114 $\pm$ 313	1357 $\pm$ 68
SORAC (against superoxide anion radical)	1040 $\pm$ 55	169 $\pm$ 12
NORAC (against peroxy nitrite anion)	87 $\pm$ 5.9	37.2 $\pm$ 2.6
SOAC (against singlet oxygen)	629 $\pm$ 33.4	71.6 $\pm$ 8.8
Total ORAC	7698	2649

Source: Adapted with permission from Kang *et al.* [38].

Note: Some numbers are rounded to the second digit after decimal point.

DW, dry weight; TE, trolox equivalents.

The comparison of the antioxidant activities of *E. oleracea* and *E. precatoria* fruits has been evaluated by multiple assays, including ORAC, DPPH, and cell-based antioxidant protection in erythrocyte (CAP-e). The CAP-e assay showed that both *E. oleracea* and *E. precatoria* fruits protect human cells from oxidative damage [38]. In addition, potential anti-inflammatory activity was evaluated by the lipopolysaccharide (LPS)-induced secreted embryonic alkaline phosphatase (SEAP) reporter assay, designed to measure nuclear factor-kappa B (NF- $\kappa$ B) activation [39, 40]. *E. precatoria* fruits contained much stronger water-soluble antioxidants that can enter live cells and effectively inhibit ROS formation compared to those from *E. oleracea* fruits. *E. precatoria* fruits, but not *E. oleracea* fruits, inhibited NF- $\kappa$ B activation as assessed by the SEAP reporter assay, suggesting that *E. precatoria* fruits have potential anti-inflammatory effects. NF- $\kappa$ B is a major mechanism for induction of inflammatory and immune responses.

Considering the extremely high SOAC value observed (Table 21.3), carotenoids were analyzed in *E. precatoria* fruits and five carotenoids, namely  $\beta$ -carotene, lycopene, astaxanthin, lutein, and zeaxanthin, were detected and quantified. Their levels ranged from 18.7  $\mu$ g/g DW of astaxanthin to 483.0  $\mu$ g/g DW of lutein for *E. precatoria* fruits; total carotenoid in *E. precatoria* fruits was calculated as 963.7  $\mu$ g/g DW. Only  $\beta$ -carotene reached a detectable level, quantified at 10.8  $\mu$ g/g DW in *E. oleracea* fruits [38]. These differences may explain in part the significant difference in SOAC values between both açai fruit species and the role that carotenoids play in singlet-oxygen scavenging.

Açai fruits have been shown to improve the lifespan and survival of *Drosophila melanogaster* females fed a high-fat diet through activation of stress response pathways and the suppression of phosphoenolpyruvate carboxykinase (*Pepck*) expression, increased transcription of a small heat-shock-related protein (*I(2)efl*), and two detoxification genes, while decreasing the transcript level of *Pepck* [41]. The study demonstrated a potential benefit in alleviating the effect of oxidative stress on aging, as oxidative damage that accumulates in cells with advancing age is thought to be one of the causative contributions to aging [42].

Studies on the cardioprotective properties of açai fruits have been demonstrated. Animals were fed high-fat hypercholesterolemic diets, while controls were fed standard diets. De Souza *et al.* [43] fed rats a hypercholesterolemic diet for 6 weeks. Serum levels of carbonyl proteins and total, free, and protein sulphydryl groups, and superoxide dismutase activity, at the end of the period were reduced. Feio *et al.* [44] hypothesized that feeding of açai fruits to New Zealand rabbits on a cholesterol-enriched diet for 12 weeks followed by 12 weeks of a diet containing an açai fruit extract would attenuate the development of atherosclerosis by decreasing cholesterol absorption and synthesis. Rabbits fed açai fruits in the last half of the feeding study had marked improvement in their lipid profile, smaller atherosclerotic plaque area in aortas, smaller intima/media ratio, and differences in plaque composition, than controls. The attenuation of atherosclerosis was marked. These improvements in cardiovascular status may partially be due to the endothelial anti-inflammatory effects of açai fruit polyphenolics seen during oxidative stress in another study as açai fruits inhibited gene expression of adhesion molecules and NF- $\kappa$ B activation [45].

An açai-enriched fruit/berry juice attenuated atherosclerosis in apolipoprotein E deficient (apoE $^{-}$ ) mice through antioxidant and anti-inflammatory activities [46]. The treatment group fed the juice experienced a reduction in mean lesion area of 58% in the aorta compared to the controls ( $P < 0.001$ ). Treated mice also had higher high-density lipoprotein (HDL)-cholesterol and significantly lower levels of lipid peroxidation, including F<sub>2</sub>-isoprostanes and isomers of hydroxyoctadecadienoic acids (HODEs), and hydroxyeicosatetraenoic acids

(HETEs) in serum and in liver. The expression of two antioxidant enzyme genes was significantly upregulated in the aorta, while glutathione peroxidase (GPX), glutathione reductase (GSR), and serum paraoxonase-1 (PON1) activity was increased in serum and/or liver of animals fed the açai juice. Tumor necrosis factor-alpha (TNF- $\alpha$ ) and interleukin-6 (IL-6) levels were lower in resident macrophages with or without LPS stimulation, as well. The açai-enriched juice has assembled a body of experimental evidence of safety [47], allowing for future studies on the juice's impact on various disease processes and their progression.

A number of studies have also examined the effect of açai fruits fractions on brain cells *in vitro*. Poulose *et al.* [48] carried out experiments to assess the effects of ethanol, methanol, acetone, and ethyl acetate fractions of açai fruits on dopamine-induced changes in recovery, reactive ROS production, and viability, in primary rat hippocampal cells. The results indicate that a 1-hour pretreatment of hippocampal cells with ethanol (50  $\mu$ g/mL) and acetone (10  $\mu$ g/mL) fractions were effective in preventing decreases in calcium recovery. In BV-2 microglial cells, all of the fractions were effective in preventing LPS-induced increases in nitrite. The protection of microglial cells by ethanol, methanol, and acetone açai fruit fractions was accompanied by a significant concentration-dependent reduction in NF- $\kappa$ B, TNF- $\alpha$ , cyclooxygenase-2 (COX-2), and p38 mitogen-activated protein kinase (p38-MAPK). These results suggest that açai fruits might contribute to mitigating the adverse effects of aging brain cells by combating the inflammatory and oxidative mediators of aging at the cellular level.

In another study by Poulose *et al.* [48], the effects of açai fruit fractions on autophagy in BV-2 microglial and HT-22 hippocampal cells were examined. Autophagy is critical for intracellular degradation or recycling of toxic proteins and cellular debris. As the brain ages, this function declines leading to accumulation of toxic debris, a known contributor to age-related neurodegenerative diseases. Cells were pretreated with 6-hydroxydopamine (HDA) causing substantial accumulation of ubiquinated protein aggregates. Açai fruit fractions induced activation of neuronal housekeeping (autophagy) and inhibited the action of a protein that shuts down the autophagic process in both microglial and hippocampal cells. Microglial cells can be activated during chronic inflammation and lead cells to leak toxic proteins. During activation inflammatory gene production is stimulated which increased oxidative stress and promotes cell death.

The findings from these studies offer valuable insight into the neuroprotective effects of açai fruit fractions on certain brain cells, which could have implications for the mitigation of neurodegenerative diseases as well as maintenance of cognitive and motor functions.

Components other than anthocyanins in açai fruits have been shown to have "remarkably suppressive" antiproliferative activity against C-6 rat brain glioma cells (C-6) [49]. The antioxidant and antiproliferative activity of an anthocyanin-rich açai fruit extract against C-6 was studied leading to the discovery that only an açai fruit extract exhibited antiproliferative activity against C-6 in a dose-dependent manner with a half-maximal inhibitory concentration ( $IC_{50}$ ) of 121  $\mu$ g/mL, whereas other anthocyanin-rich extracts, including blueberry, strawberry, raspberry, blackberry, and wolfberry, did not exhibit any antiproliferative activity. This suggested that the active antiproliferative components in the extract were not due to anthocyanins. The contributive moieties' chemical structures remain to be characterized, as does the apoptotic pathways, warranting additional research.

A comprehensive review of all research on açai fruits is not within the scope of this chapter. One area worth adding to the discussion is recent reports on potential benefit of açai's seeds that fits well within the concept of novel foods.

### 21.3.1 Antioxidant and anti-inflammatory properties of açai seeds

There is anticipation that interest in the commercial value of açai seeds, currently considered a “waste product” by açai fruit producers, will change given recent studies that demonstrate surprising evidence that a hydroalcoholic extract of açai seeds can attenuate damage in the lungs of mice exposed to short-term or chronic cigarette smoking.

De Moura *et al.* [50] have described experiments conducted in Brazil medical school laboratories in which short-term (5 days) inhalation of tobacco smoke by mice orally administered a hydroalcoholic açai seed extract reduced the inflammatory and pro-oxidant damage associated with cigarette smoking. It has been shown that short-term inhalation of tobacco smoke leads to acute lung inflammation due to oxidative stress [51].

In a 60-day chronic inhalation of tobacco smoke study, oral administration of the açai seed extract resulted in a protective effect against the development of emphysema in mice [52]. Oxidative stress based on differences in antioxidant enzyme activities, and the observed reduction in macrophage and neutrophil elastase levels, provided mechanisms that partially explain the protective effect of the extract against the damage from tobacco seen in control mice not fed the extract. The possibility that compounds in the seed of açai might reduce the harmful effects associated with cigarette smoking and possibly other tobacco products, and possibly prevent the development of such tobacco-related diseases as chronic obstructive pulmonary disease (COPD), warrants further research and independent confirmation.

## 21.4 Phytochemicals in açai fruits

Numerous analytical efforts have been made to identify and quantify the anthocyanins and other flavonoids in açai fruits. Early attempts disagreed on what the major anthocyanins were in the fruit. While Bobbio *et al.* [53] reported that the major anthocyanins were cyanidin 3-arabinoside and cyanidin 3-arabinosylarabinoside, Lichtenthaler *et al.* [54] reported cyanidin 3-glucoside and cyanidin 3-rutinoside as the main anthocyanins. These disagreements mirrored much of the literature related to açai's nutritional composition up to 2005; hence, we attempted not only to elucidate the fruits' nutritional composition but also to establish definitively what the major and minor anthocyanins were in the fruits, a project that began in 2000 to identify and elucidate all of the bioactive compounds in the fruit.

Over a span of several years, characterization of açai fruits determined that açai mesocarp/epicarp contain numerous phytochemicals, including the following:

- Homoorientin, taxifolin deoxyhexose, isovitexin, cyanidin 3-glucoside, and cyanidin 3-rutinoside [55, 56]
- Cyanidin 3-sambubioside, peonidin 3-glucoside, peonidin 3-rutinoside, trans-resveratrol, hydroxybenzoic acids, isoquercitin, apigenin, eriodictyol, eriodictyol 7-glucoside, luteolin 4'-glucoside, eupatorin, catechin, protocatechuic acid, quercitin-3-arabinoside, kaempferol, and chrysoeriol [30]
- Luteolin, quercitin, orientin, vitexin, and dihydrokaempferol [57]
- The novel dihydroflavone glucoside, (2S,3S)-dihydrokaempferol 3-O- $\beta$ -D-glucoside, and its isomer (2R,3R)-dihydrokaempferol 3-O- $\beta$ -D-glucoside, velutin, and 5,4'-dihydroxy-7,3',5'-trimethoxyflavone [58]

**Table 21.4** ORAC antioxidant activities of açai (*E. oleracea*) fruit flavones

Compound	ORAC ( $\mu\text{mol of TE/g}$ ) [57, 58]
Isovitexin	22,404 $\pm$ 1322
(2S,3S)-dihydrokaempferol 3-O- $\beta$ -D-glucoside	15,199 $\pm$ 503
(2R,3R)-dihydrokaempferol 3-O- $\beta$ -D-glucoside	11,219 $\pm$ 433
Vitexin	14,800 $\pm$ 451
Velutin	13,643 $\pm$ 1119
Quercetin	12,300 $\pm$ 1070
Dihydrokaempferol	8390 $\pm$ 94
Luteolin	7870 $\pm$ 350
5,4'-dihydroxy-7,3',5'-trimethoxyflavone	4458 $\pm$ 409
Chrysoeriol	4400 $\pm$ 189
Orientin	1700 $\pm$ 79
Homoorientin	1420 $\pm$ 63

Note: Some numbers are rounded to the second digit after decimal point.  
TE, trolox equivalents.

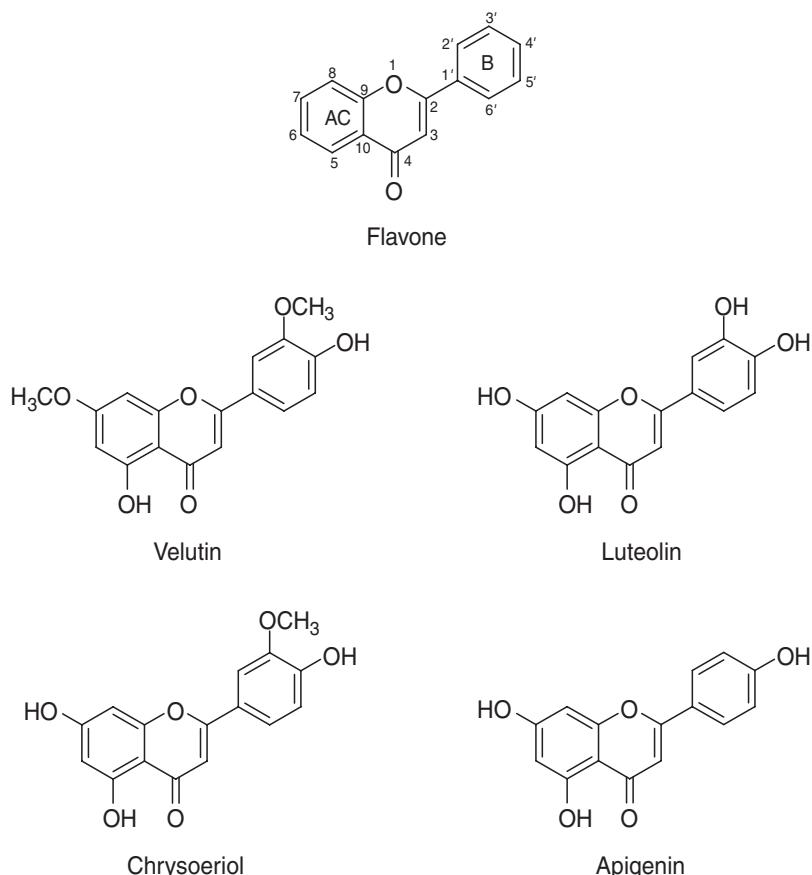
Agawa *et al.* [59] determined the concentration of various anthocyanins in the mesocarp, epicarp, and endocarp, of fresh açai, and had each component's antioxidant activities measured, using the ORAC, DPPH, 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), ferric reducing antioxidant power (FRAP), and superoxide dismutase (SOD) assays. Açai mesocarp/epicarp extracts were found to have potent antioxidant activity compared to blueberry extract on every assay. The major anthocyanins, namely cyanidin 3-glucoside and cyanidin 3-rutinoside, were found to provide strong antioxidant potency if derived from the mesocarp/epicarp portion. These findings, in general, support previous work reported on the polyphenolic constituents of the *E. oleracea* açai fruit [55].

Isolation and structure identification studies by Kang *et al.* [57, 58] confirmed that flavonoids are the major polyphenols in açai fruits. The antioxidant activities, bioactivities, and bioavailability of these flavonoids were evaluated by ORAC, CAP-e, ROS, and PMN assays. The assays determined that the antioxidant activities of the flavonoid compounds in açai fruits varied significantly; aglycones had much higher antioxidant activities than their corresponding C-glycosides. The position of the methoxy group exerted a significant effect on antioxidant activity, while the CAP-e assay demonstrated that the polyphenols were able to penetrate into living cells.

The difference in ORAC antioxidant activities between the pure flavones is shown in Table 21.4. The difference in antioxidant activities is based on the number and position of the hydroxyl groups and/or other substitute groups. For example, in terms of the difference in ORAC values between chrysoeriol and luteolin, the *O*-methylation of the hydroxyl groups reduced the ORAC value of chrysoeriol by nearly 50%.

The CAP-e assays of the flavones revealed that of the compounds able to get into RBCs all were aglycones, with the exception of chrysoeriol, which bears a methoxy group, possibly due to its structural properties.

The isolation and identification of velutin in açai fruits is particularly significant since it exhibits the most potent anti-inflammatory bioactivity of any flavonoid so far reported in the literature ( $\text{IC}_{50}$  calculated at 2.0  $\mu\text{M}$ ) [36]. In addition, four other flavones identified in the fruits were found to exhibit strong anti-inflammatory properties, including



**Figure 21.1** Major flavones found in açai fruits.

luteolin (12.4  $\mu\text{M}$ ), whose only difference compared to velutin is in the position of the hydroxy/methoxy groups. Velutin bears two methoxy groups at the 7'- and 3'-positions, whereas luteolin has two hydroxy groups at the 7'- and 3'-positions. It was determined that the substitution of the methoxy groups is the significant difference that contributes to its more pronounced antioxidant activity and anti-inflammatory properties. Isovitexin also exhibited anti-inflammatory bioactivity ( $\text{IC}_{50}$  calculated at 58.5  $\mu\text{M}$ ). Isovitexin has been shown to inhibit the translocation of NF- $\kappa\text{B}$  from the cytoplasm to the nucleus [60]. Velutin's potent anti-inflammatory bioactivity has been shown to reduce NF- $\kappa\text{B}$  activation. NF- $\kappa\text{B}$  plays a crucial role as a transcription factor in regulating many pro-inflammatory cytokine genes [61, 62]. It is likely that the combination of the açai flavone's antioxidant and anti-inflammatory properties work synergistically, a theory being researched to determine whether they act synergistically or are additive in nature. Exactly to what extent the methoxy groups and stereo configurations modulate the inhibitory properties of the flavone compounds has not been determined. Figure 21.1 shows the chemical structures of flavones found in açai fruits.

The results seen for velutin and other flavones found in açai fruits as observed in the SEAP reporter gene assays implicate potential protective actions of these compounds in

**Table 21.5** Content of proanthocyanidins in freeze-dried açai fruits

Proanthocyanidins	mg/g DW
Monomers	0.21
Dimers	0.30
Trimers	0.25
Tetramers	0.32
Pentamers	0.31
Hexamers	0.52
Heptamers	0.32
Octamers	0.39
Nonamers	0.64
Decamers	0.34
Polymers	9.28
Total	12.98

Source: Adapted with permission from Schauss *et al.* [31].  
DW, dry weight.

attenuating the progression of atherosclerosis. As part of the study, the inhibitory effect of velutin in oxidized low-density lipoprotein (oxLDL) induction of NF-κB activation was examined. Velutin was found to inhibit NF-κB activation induced by oxLDL. It is known that oxLDL plays a crucial role in the initiation and progression of atherosclerosis [63]. These findings, combined with the growing body of *in vivo* evidence in animals fed a high-fat/high-cholesterol diet with açai fruits, suggest that the flavones in açai fruits may play an important role in attenuating the progressive development of atherosclerosis.

Besides anthocyanins, other polyphenols in açai fruits also contain proanthocyanidins that have strong antioxidant properties [31], such as flavan-3-ol (epicatechin), as shown by the concentration of proanthocyanidins in Table 21.5. They have also been shown to counteract the negative effects of high-fat diets on the arteries [64].

Polyphenols in açai fruits are associated with enhanced antioxidant protection in cells and generalized vascular protection. In a pharmacokinetic study in humans, anthocyanins from açai fruit were shown to be bioavailable in healthy volunteers [65]. Açai fruits caused a significant increase in antioxidant activity of plasma, in peripheral blood mononuclear cells (PBMC) collected from patients hourly for 4 hours. However, the investigators used an açai juice drink that contained frozen açai fruits imported from Brazil. The beverage was sweetened with sucrose. Although the antioxidant activity in PBMC increased, the concentration of antioxidant polyphenolics in plasmas did not rise sufficiently to reduce the hydrogen peroxide-induced generation of ROS in any of the volunteers, which may be due to the use of frozen fruits and added sugar. Stress situations, where soluble sugars are involved such as chilling, are related to important changes in ROS balance [66]. A high-sucrose diet has been shown to increase ROS generation [67]. In contrast, in two studies using another açai-rich beverage fed to volunteers placed under oxidative stress, an increase in antioxidant activity of both plasma in RBCs and PMN cells was observed [68, 69], as determined by the antioxidant protection in erythrocytes (CAP-e) bioassay and evaluation in PMN cells of the inhibition of ROS production [37]. The difference between the two studied beverages was that the MonaVie açai beverage contained a combination

of freeze-dried and frozen açai fruits, containing more of the antioxidant polyphenolics needed either to inhibit ROS production or to indirectly increase endogenous antioxidant activity. The practical benefit of incorporating such a juice in the diet was seen in both the randomized, double-blind, placebo-controlled, and crossover clinical trial, as well as in the range of motion (ROM) study involving 48- to 84-year-old adults, who started the study with limited ROM affecting the quality of life, and who within weeks and through to the end of a 12-week study had significant improvements in mobility and reduction of pain in key joints [68].

Given how many compounds are found in foods, many of which exhibit bioactivity and contribute to health benefits, their identification and characterization can determine which foods may play the greatest role in the prevention, mitigation, and treatment of diseases. It is also important to know how many compounds are there in the açai fruits, besides their contents of vitamins, minerals, protein, fat, carbohydrates, and soluble and insoluble fibers. This is because any number of compounds in a food, such as açai fruits, might be of therapeutic value, depending on the degree of evidence. For example, proteins in açai fruits have been found to show high-antitryptic activity, while some may inhibit human salivary  $\alpha$ -amylase overproduction [70]. The effect of an açai extract on the antiproliferation and induction of apoptosis in human leukemia-60 (HL-60) cells has been reported [56].

To determine the phytochemical compounds in açai fruits, a semiquantitative matrix-assisted laser desorption time-of-flight mass spectrometry (MALDI-TOF MS) analysis was performed at the University of Wisconsin–Madison (unpublished data). MALDI-TOF MS characterizes complex mixtures of oligomeric polyphenolic compounds in various foods, including fruits, berries, and grains [71]. MS does not distinguish between isomers (although various stereoisomers and structural isomers can be described of dimers and trimers). The number of possible structures significantly increases by isomerization of each of the masses detected by MALDI-TOF MS. Analysis of açai fruits by MALDI-TOF MS determined that classical proanthocyanidins (homopolymers of repeating catechin/epicatechin units) were not present in appreciable levels. The açai spectra showed more than 3000 compounds, indicating that açai is far more complex than fruits such as cranberries and blueberries, also suggesting that there is greater structural heterogeneity in the fruits' polyphenols waiting to be elucidated [72].

## 21.5 Processing of açai fruits for value-added products

Açai palm trees are found in dense grooves and virtually every island among the Amazon River's estuaries and riverines. In Para state, it is estimated that more than 11 million hectares of the floodplains contain dense groves of açai palm trees. Each hectare can have 2000 to more than 7000 such palms. Government agricultural surveys have estimated that a palm tree can produce more than 1000 kg in a 5- to 7-year period (depending on rain levels) upon reaching maturity. In essence, there is a seemingly limitless quantity of açai fruits available in the floodplains. Harvesting occurs over an 8-month period as the trees produce up to four crops of fruit during the "drier" months, even though some rain may fall nearly every day during the dry season that runs from June to late December. Hence, most natives have access to the fruits as açai palm trees abound, allowing for daily harvesting of the fruits that ends when the rainy season begins in January.

### 21.5.1 Traditional preparation

Açaí fruits are obtained from mature infructescences containing from 200 to 500 fruits removed from near the crown of the palm tree. The fruits are then stripped from the infructescence and sorted. Once filled, the basket is taken to one's home where it is placed in a large bowl. Warm water is added and the fruits soaked for half an hour to an hour. This softens the exocarp, epicarp, and mesocarp and removes dirt or debris that either sinks to the bottom of the bowl or floats to the top. In the most remote areas of the Amazon floodplains, a square device called a *caroceiro* is used which is made from strips of the Aruma tree. Fruit is pressed against the interweaving strips that force the seed to drop through weaving. The remaining pulp and skin is then rubbed repeatedly against a large mesh sieve under which is a finer screen that separates approximately 80–90% of the solid matter from the juice. In recent years, families have acquired mechanically handheld devices that far more easily remove the seed. The seeds are either thrown into the garden to turn into mulch within 2–3 months, to provide a soil amendment in the garden, or fed to pigs.

Most families consume the juice within 2 hours of harvesting to produce a soup eaten at breakfast with a spoon, or as a beverage, much like one would drink unfiltered pulp-rich orange juice. Some prefer the açai fruit to be more viscous. It is estimated that in cities and towns in açai tree-rich areas in the floodplains people consume an average of 2 L of fresh açai juice a day during the harvest season. Açaí forms a major part of the diet of inhabitants of the Amazon floodplains along with farinha and whatever other food sources are available. Açaí and farinha constitute approximately 65% of the diet of natives [27, 73], which confirms its nutritional density, as determined by nutrient composition analysis [30].

If produced for local consumption, only the fruits are sold at wholesale markets to local retail vendors or residents who take them home to make a beverage according to traditional methods of preparation.

### 21.5.2 Commercial production for value-added products

Large processing operations, located in larger cities in the Amazon floodplains, purchase açai fruits from large wholesalers. Fruits are ranked according to a quality scale. To produce pulp for sale in tonnage quantities, the fruits are sorted, washed, and softened by immersion in large tanks filled with water. After removing any debris, damaged fruits, or unripe or green fruits, the fruits are placed into mechanical mills that strip the seed and some of the exocarp, leaving the remaining mesocarp (pulp) with some skin segments for further processing. Ultraviolet (UV) sterilized water is added to the pulp, homogenized, during which time citric acid is added to stabilize acidity and inhibit microbial growth (usually, the pulp is standardized to 10–12% total solids, depending on customer's preference). Thereafter, the pulp is pasteurized at around 85°C for approximately 1 minute then transferred into polypropylene bags that line steel drums with removable lids. The drums are then frozen in a chamber, where after moved into refrigerated cold storage, maintained at around 17°C. Facilities producing açai pulp for export must be government certified, meet hazard analysis critical control point (HACCP), sanitation operating procedures, guided by good manufacturing practice (GMP) procedures and practices.

Frozen pulp can be spray- or freeze-dried into a powder that is stored in sealed aseptic polypropylene to prevent reabsorption of moisture. Spray-dried or freeze-dried powders are used to primarily produce açai juice beverages. Because of the relatively bland taste of

the fruits, other fruits or berries are typically mixed with the pulp powder to produce an organoleptically acceptable beverage for consumers. Almost all of the research on açai has been performed on freeze-dried açai or beverages that include freeze-dried açai due to the powders' shelf life and retention of the pulp's nutritional composition and bioactivities. ORAC assays have shown that freeze-dried açai powders are superior in terms of antioxidant activity compared to the spray-dried powders [31].

Nindo *et al.* [74] have studied the rheology of fruit pulps and have pointed out that extended application of heat coupled with continuous shearing during component fruit separation and processing can cause irreversible structural breakdown of the products. Tonon *et al.* [75] have shown that at a temperature range of 10–70°C, açai pulp shows shear-thinning behavior with yield stress in the steady-shear measurements and other characteristics unlike that of most fruit pulps. This rheological information about açai pulp is partially due to the unusual chemical composition of the fruits, such as their high levels of lipids, proteins, and fibers.

## 21.6 Conclusions

Research interest in the fruits of the Amazonian açai has been of relatively recent but intensive interest following the discovery of the fruit's pronounced potent antioxidant and anti-inflammatory properties. Two of the species that have earned particular interest due to their superior antioxidant activities compared to almost all other foods and commercial availability are that of *E. precatoria* and *E. oleracea*, both of which are commonly called "açai" by natives living in the Amazon.

Years of characterization of the fruits has lead to a much better qualitative and quantitative understanding of their chemistry and bioactive properties. The three species of açai fruits occupy the top four out of five ORAC assay values of all foods assayed for the peroxyl radical scavenging capacity *in vitro*. The fruits contain a class of flavones that includes the most potent anti-inflammatory flavonoid found. Most of these flavones are not only bioavailable and protect cells from oxidative damage and chronic inflammation, but they may act synergistically, suggesting that the fruits as a whole may have therapeutic benefits beyond their considerable nutritive values. It also suggests that there may be a synergy between many compounds in the fruits, from anthocyanins, proanthocyanidins, fatty acids (to facilitate gut absorption), to numerous polyphenolics, some unique to the fruits.

Preliminary evidence shows açai fruits decrease production or signaling of pro-inflammatory cytokines and/or inflammatory mediators. Isolation of all the compounds in açai that may act to inhibit or reduce inflammation and oxidative stress and/or enhance protective mechanisms such as has been shown by the induction of autophagy will take time.

The evidence in support of a protective effect of açai compounds in providing cardiovascular protection is more compelling based on a number of well-controlled animal studies that compared the effect of feeding hypercholesterolemic and/or high-fat diets. Downregulation of pro-inflammatory moieties such as NF-κB has been consistently seen in each experiment. Given the prevalence and incidence of atherosclerosis, it seems warranted at this time to include açai fruits in the diet.

An intriguing finding has been the unexpected emergence of evidence that what was once considered a waste product, namely, the seeds of the açai fruits, may have potential benefit in mitigating the harmful effects of cigarette smoking. Considerable funding should be committed toward a greater understanding of the mechanisms of action to account for the

observed protection seen in animal lung tissue following short-term and long-term inhalation of cigarettes either laced with a hydroalcoholic extract of the seed or fed orally to rodents unable to prevent the inhalation of the smoke.

Fortunately, there are ample year-to-year supplies of açai fruits available to support worldwide interest and consumption. Millions of hectares of açai palms can be found throughout the floodplains of the Amazon, in addition to the availability of equally as much of the other açai species at higher elevations, including the Bolivian Amazon.

The rate of publications on açai fruits related to its potential health benefits is mirrored by the exponential growth of papers appearing in databases such as PubMed [managed by the US National Library of Medicine, National Institutes of Health (NIH)]. Whereas in 2005, there were only two papers on açai in PubMed, by early 2012 there were more than 100 published papers, including a 2012 report that in hypercholesterolemic zebrafish fed for 4 weeks to evaluate the fruit's hypolipidemic activity, açai inhibited cholesteryl ester transfer protein (CETP) production [76]. The fish fed açai demonstrated lower serum triglycerides levels, total cholesterol, attenuation of fatty liver, reduced content of oxidized species, and significantly less hepatic inflammation. This study as well as others discussed earlier providing the growing body of data showing açai to have antioxidant, anti-inflammatory, and anti-atherosclerotic activity in cellular assays as well as *in vivo* models. The pace of research is continuing given the interest in açai generated by scientists studying their properties and attributes at the NIH's National Institute on Aging, various USDA research centers including the USDA Human Nutrition Research Center on Aging at Tufts University, USDA Arkansas Children's Nutrition Center, FDA's Center for Biologics Evaluation and Research, and numerous universities and research foundations.

Given the exponential research interest in the attributes, properties, and applications of each species of açai fruits, consumer interest would be expected to continue to support their status as one of the true "superfoods" worth considering as part of a nutritious human diet; a diet that should include foods that promote healthy aging and is able to mitigate damage associated with acute and/or chronic oxidative stress.

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## **22 Bananas, dried bananas, and banana chips: nutritional characteristics, phytochemicals, and health effects**

Arianna Carughi

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### **22.1 Introduction**

The word “banana” encompasses a variety of species or hybrids derived from two wild species of *Musa acuminata* and *Musa balbisiana*. Bananas are often categorized as “dessert” sweet bananas, which are ripened and eaten raw, and starchy or “cooking” bananas and plantains intended for cooking or processing, but also edible when fully ripe. Bananas have their origin in the Asia Pacific region and are now cultivated throughout the humid tropical and subtropical areas of the world [1]. They are perennial, giant herbs, seedless and parthenocarpic—the fruit develops without fertilization or pollination—and produce fruit throughout the year [2]. More than 300 types of bananas are cultivated, but little is known about the variation in nutrient content among them and their contribution to dietary requirements of different populations. Part of the reason for this may be the commercial popularity of only a few varieties, exports almost exclusively dominated by the Cavendish banana. Yet this variety accounts for little more than about 13% of the world’s banana and plantain production. The other 87% is made up of a broad range of varieties adapted to specific climate/growing conditions and selected for specific eating/cooking qualities [3]. This chapter is an overview of the nutritional properties of fresh bananas, dried bananas, and banana chips highlighting characteristic phytochemicals in the fresh fruit as a potential source in dried fruit products.

### **22.2 Production and consumption**

Bananas and plantains represent the fourth most important crop in the world after rice, wheat, and maize. They are grown in more than 130 countries worldwide and harvested over approximately 11 million hectares, with an annual production that surpassed 132 million tonnes in 2009 [4]. Table 22.1 shows banana and plantain production data. These figures are an approximation since most of the world’s banana production comes from small plots and home gardens and so may have escaped reporting.

Bananas have been a staple food for centuries and one of the most important sources of energy in the diet of millions of people, in regions in Africa, Asia, Central and South America,

**Table 22.1** Top banana and plantain producers and production in 2009

<b>Rank</b>	<b>Country</b>	<b>(MT × 1000)</b>
<b>Bananas</b>		
1	India	26,470
2	Philippines	9013
3	China	9006
4	Ecuador	7637
5	Brazil	6783
6	Indonesia	6374
7	United Republic of Tanzania	3219
8	Guatemala	2544
9	Mexico	2232
10	Colombia	2020
<b>Plantains</b>		
1	Uganda	9512
2	Ghana	3563
3	Colombia	3012
4	Rwanda	2993
5	Nigeria	2911
6	Cameroon	2450
7	Peru	1867
8	Côte d'Ivoire	1497
9	Democratic Republic of the Congo	1200
10	Kenya	843

Source: Adapted from FAO [4].

MT, metric tonnes.

and the Pacific. Today, in addition to being a major cash crop around the world, more than 85% of bananas are produced for local consumption by small scale farmers growing the crop either for home consumption or for trading at local markets. They are, therefore, very important for income and food security. Bananas are the most popular fresh fruit in the United States where per annual capita consumption is about 11 kg [5], slightly above the European average of about 9 kg in 2009 [6].

Most bananas are eaten raw or cooked (baked, boiled, roasted, or fried) and only a very minor proportion is processed (5% dessert bananas and 24% plantains) or dried [7]. This is true both at the village level and in the international trade of “dessert” bananas. Barriers to processing include a susceptibility to enzymatic browning, discoloration, flavor deterioration, and lack of demand since the fresh fruit is available year round [8]. However, high volumes of banana that is lost after harvest, and those that are rejected for the export market has stimulated finding solutions to these problems [9]. Also, in many areas dried bananas are important in periods where food is scarce [10].

## 22.3 Dried bananas or banana figs

Banana figs are dried or dehydrated bananas, usually whole, but sometimes sliced lengthwise. They are very sweet and have a sticky, fig-like consistency. Traditionally, sun drying was the

most widespread method of producing banana figs but now hot-air circulation in tunnel or cabinet dryers are more popular. Banana figs are made from fully ripe fruits from varieties with high total solid content and a sugar content of about 19.5%. They are peeled, sulfured either by dipping in sulfuric acid solution or by burning sulfur in an enclosed room and dried at temperatures ranging from 50 to 80°C for 5–24 hours, depending if bananas are whole or sliced, to reach a final moisture content of 20–25% [8]. Bananas can also be dipped in a boiling sugar solution before drying. Osmotic dehydration has recently gained popularity. It requires less energy and the nutrient loss is minimized. In this process, banana slices are dipped into an isotonic sugar solution and a sweeter, stable banana fig of intermediate moisture content is produced [11]. Ecuador is one of the main producers of banana figs, but India, Brazil, Philippines, and Costa Rica also produce considerable amounts of it. Europe is the main importer, especially France and Germany [12].

## 22.4 Dried and fried banana chips (crisps)

Typically green (unripe) bananas are used for producing dehydrated chips. They are thinly sliced, blanched in hot water or steam, or dipped in a solution of a browning inhibitor ( $\text{SO}_2$  and citric acid) and dried by different methods to a very low moisture content (2.5–9%) [8]. For banana crisps, the slices are deep-fried in cooking oil (usually coconut, palm or cottonseed oil, depending on the location) at 180–200°C and dusted with salt and occasionally an antioxidant [12]. Sometimes, the slices are partially dried or dipped in salt or sugar solutions before frying. In Philippines, they are fried to intermediate moisture content, soaked in a sugar solution, and fried again in hot oil [9]. Many variations of banana chips exist with a concomitant variation in caloric content and nutrient composition. Philippines is the main exporting country of banana chips [12].

## 22.5 Nutritional content of bananas, dried bananas, and banana chips

Tables 22.2 and 22.3 show compositional and nutritional characteristics of fresh bananas, plantains, chips, and banana figs [13–17]. Table 22.4 depicts the contributions that one serving of these foods makes toward meeting daily requirements of essential nutrients, expressed as percentage of the Daily Value (DV) [18]. It is important to note that these tables reflect the fruit and dried fruit products available in the United States and Europe. They represent only a fraction of the varieties and products consumed by people in tropical and subtropical areas of the world. Significant compositional differences exist among banana varieties/cultivars particularly in provitamin A activity, but also in fat, iron, calcium, and zinc contents, among others [19]. Data on nutritional content of locally consumed dried banana figs/chips are lacking or are incomplete.

Bananas are a major source of carbohydrate in the diet of people worldwide. In the green fruit, they provide 12–30 g/100 g of starch, and as low as 1% in some fully ripe varieties [20]. The ripe Dwarf Cavendish has 5% starch and provides 12 g/100 g sugar (glucose, fructose, and sucrose). Bananas and plantains are a particularly good source of fiber, one cup (about one fruit) providing 16 and 14%, respectively, of the Dietary Reference Value (DRV). They

**Table 22.2** Compositional and nutritional characteristics of bananas and plantains, and their chips (values in per 100 g edible portion)

Nutrient	Unit	Fresh bananas	Fresh plantains	Banana chips (snacks)	Plantain chips (salted snacks)
<b>Proximate composition</b>					
Water	g	74.91	65.28	4.30	2.09
Energy	kcal	89	122	519	531
Protein	g	1.09	1.30	2.30	2.28
Lipid	g	0.33	0.37	33.60	29.59
Ash	g	0.82	1.19	1.4	2.19
Carbohydrate	g	22.84	31.89	58.40	63.84
Dietary fiber	g	2.6	2.3	7.7	3.5
Sugars	g	12.23	15.00	35.34	0.92
<b>Minerals</b>					
Calcium	mg	5	3	18	9
Copper	mg	0.08	0.081	0.21	0.20
Fluoride	µg	2.2	na	na	na
Iron	mg	0.26	0.60	1.25	0.97
Magnesium	mg	27	37	76	71
Manganese	mg	0.27	na	1.56	0.28
Phosphorus	mg	22	34	56	78
Potassium	mg	358	499	536	786
Selenium	µg	1.0	1.5	1.5	0.4
Sodium	mg	1.0	4	6	202
Zinc	mg	0.15	0.14	0.75	0.37
<b>Vitamins</b>					
Choline	mg	9.8	13.5	21.3	na
Folate	µg	20	22	14	35
Niacin	mg	0.67	0.69	0.71	0.80
Pantothenic acid	mg	0.33	0.26	0.62	1.1
Pyridoxine	mg	0.37	0.30	0.26	0.46
Riboflavin	mg	0.07	0.05	0.02	0.04
Thiamine	mg	0.03	0.05	0.09	0.07
Vitamin A (RAE)	µg	3.0	56	4.0	69
Vitamin C	mg	8.7	18.4	6.3	32.1
Vitamin E (ATE)	mg	0.10	0.14	0.24	5.1
Vitamin K	µg	0.5	0.7	1.3	28.6
<b>Amino acids</b>					
Alanine	g	0.040	0.051	na	na
Arginine	g	0.049	0.108	na	na
Aspartic acid	g	0.124	0.645	na	na
Cystine	g	0.009	0.108	na	na
Glutamic acid	g	0.152	0.116	na	na
Glycine	g	0.038	0.045	na	na
Histidine <sup>a</sup>	g	0.077	0.064	na	na
Isoleucine <sup>a</sup>	g	0.028	0.036	na	na
Leucine <sup>a</sup>	g	0.068	0.059	na	na
Lysine <sup>a</sup>	g	0.050	0.060	na	na
Methionine <sup>a</sup>	g	0.008	0.017	na	na

(continued)

**Table 22.2** (Continued)

Nutrient	Unit	Fresh bananas	Fresh plantains	Banana chips (snacks)	Plantain chips (salted snacks)
Phenylalanine <sup>a</sup>	g	0.049	0.044	na	na
Proline	g	0.028	0.050	na	na
Serine	g	0.040	0.014	na	na
Threonine <sup>a</sup>	g	0.028	0.034	na	na
Tryptophan <sup>a</sup>	g	0.009	0.015	na	na
Tyrosine	g	0.009	0.032	na	na
Valine <sup>a</sup>	g	0.047	0.046	na	na
<b>Lipids</b>					
SFA	g	0.11	0.14	28.97	8.34
MUFA	g	0.03	0.03	1.95	5.63
PUFA	g	0.07	0.07	0.63	11.74

Source: Adapted from USDA [13].

Note: Some numbers are rounded to the second digit after decimal point.

RAE, retinol activity equivalents; ATE, alpha-tocopherol equivalents; na, not available; SFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids.

<sup>a</sup>Indispensable amino acids.

are excellent sources of potassium and also provide 10 and 14% of the recommended intake of magnesium and 20% of that of manganese. Bananas and plantains are rich in vitamins C and pyridoxine. They also provide significant amounts of the daily requirement of folic acid, niacin, riboflavin, and copper. The yellow- and orange-fleshed bananas are rich in vitamin A, providing as much as 45% of the daily requirement [21]. As is the case of most fruits, they are low in sodium and fat.

Banana figs have comparable proximate compositions to other dried fruits. They are an excellent source of sugar (57–79 g/100 g) and provide fair amounts of fiber (2.1–3.0 g/100 g) [14]. Since drying concentrates the minerals, dried banana and plantain chips are excellent sources of potassium, magnesium, manganese, and copper and provide a significant amount of iron (Table 22.3). Depending on the drying method and the variety of the fruit, they can provide appreciable amounts of the daily intake of pyridoxine, niacin, thiamine, vitamin C, and vitamin A. Dried bananas and banana chips could play an important role in alleviating micronutrient deficiencies particularly in tropical and subtropical areas where they are most severe and where bananas are a staple component of the diet.

Fried banana and plantain chips or crisps, in terms of their composition, could be more accurately compared to potato chips than dried fruits. In addition to being high in carbohydrate, they provide more than 50% of the calories from fat. Since they are highly caloric, vitamin and mineral content is diluted and consequently is lower than that of their fresh counterparts. Nonetheless, in populations at risk of micronutrient deficiency, banana crisps can be a source of essential minerals and vitamin A, if high β-carotene varieties are used [22]. Techniques are being investigated to reduce the oil uptake and preserve nutritional properties [23]. Vitamin C is particularly susceptible to drying and deep frying [24, 25].

**Table 22.3** Compositional and nutritional characteristics of dried bananas, plantains, and banana figs (values in per 100 g edible portion)

Nutrient	Unit	Dried bananas (banana figs) [14]	Smoked/ dried (banana figs) [15]	Hawaiian dried bananas [16]	Dried plantains (green) <sup>a</sup> [14]	Dried bananas (ripe) <sup>a</sup> [17]
<b>Proximate composition</b>						
Moisture	g	19.5–27.7	12.5	29.2	9.0	4
Energy	kcal	300	337	—	359	346
Protein	g	2.8–3.5	5.1	5.3	3.3	4
Lipid	g	0.8–3.5	0.2	2.3	1.4	2
Ash	g	2.1–2.8	—	5.3	2.4	—
Carbohydrate	g	60–69	79	57.9	83.9	88
Dietary fiber	g	2.1–3.0	—	—	1 (4%)	10 (40%)
<b>Other nutrients</b>						
Calcium	mg	—	—	50 (5%)	22 (2%)	—
Copper	mg	—	—	—	0.4 (20%)	—
Iron	mg	—	—	—	1.2 (6%)	—
Magnesium	mg	—	—	—	1.1 (6%)	—
Manganese	mg	—	—	—	108 (27%)	—
Phosphorus	mg	—	—	—	0.6 (29%)	—
Potassium	mg	—	—	—	74 (7%)	—
Vitamin C	mg	—	—	—	1491 (43%)	—
β-Carotene	µg	—	—	—	7 (12%)	—
Niacin	mg	—	—	—	45 (2%)	—
Riboflavin	mg	—	—	—	1.9 (10%)	—
Thiamin	mg	—	—	—	0.16 (9%)	—
Folic acid	µg	—	—	—	0.10 (7%)	—
					0.2 (8%)	—
					14 (3%)	—

<sup>a</sup>Value (Percentage RDI for vitamins and minerals; percentage DRV for fiber and potassium).

**Table 22.4** Percentage of the daily value for fiber, vitamins, and minerals met by a serving of fresh bananas and plantains, and their chips

Nutrient	DV <sup>a</sup> [18]	Unit	Bananas (1 cup sliced serving basis or 150 g) <sup>b</sup>	Plantains (1 cup sliced serving basis or 148 g) <sup>c</sup>	Fried banana chips (1 oz or 28.5 g serving basis) <sup>d</sup>	Fried plantain chips (1 oz or 28.5 g serving basis) <sup>d</sup>
<b>Fiber</b>	25 g/day	g	9	16	14	8
<b>Vitamins</b>						
Folate	400 µg/day	µg	8	8	1	2
Niacin	20 mg/day	mg	5	5	1	1
Pantothenic acid	10 mg/day	mg	5	4	2	3
Pyridoxine	2.0 mg/day	mg	28	22	4	7
Riboflavin	1.7 mg/day	mg	6	5	0	1
Thiamine	1.5 mg/day	mg	3	5	1	1
Vitamin A (RAE)	1500 µg/day	µg	2	33	0	8
Vitamin C	60 mg/day	mg	22	45	3	15
Vitamin E (ATE)	20 mg/day	mg	1	1	0	7
Vitamin K	80 µg/day	µg	0	1	0	10
<b>Minerals</b>						
Calcium	1000 mg/day	mg	1	0	1	0
Copper	2 mg/day	mg	6	6	3	3
Iron	18 mg/day	mg	2	5	2	2
Magnesium	400 mg/day	mg	10	14	5	5
Manganese	2 mg/day	mg	20	na	22	4
Phosphorus	1000 mg/day	mg	3	5	2	2
Potassium	3500 mg/day	mg	15	21	4	5
Selenium	70 µg/day	µg	2	3	1	0
Sodium	2500 mg/day	mg	0	0	0	2
Zinc	15 mg/day	mg	2	1	1	1

DV, Daily Value; RAE, retinol activity equivalents; ATE, alpha-tocopherol equivalents; na, not available.  
<sup>a</sup>DV is derived from the Daily Reference Values and Reference Daily Intakes and is based on a caloric intake of 2000 calories, for adults and children 4 or more years of age.

<sup>b</sup>Serving size is about one large banana.

<sup>c</sup>Serving size is about one small plantain.

<sup>d</sup>Serving size is defined by USDA.

## 22.6 Phytochemicals in bananas and dried fruit products

Phytochemicals are bioactive compounds in plants that appear to play a role in health and longevity and have been associated with a reduction in the risk of major chronic degenerative diseases. Like other fruits, bananas have a characteristic array of phytonutrients (Table 22.5). Those that have received most attention in the raw fruit are carotenoids, flavonoids, and phenolic acids. Phytosterols, particularly  $\beta$ -sitosterol, have been found at low levels in banana pulp (530 mg/kg dry weight) and peel and are being investigated as a means to utilize banana refuse [26].

### 22.6.1 Phenolics in fresh and dried bananas

Phenolic compounds are ubiquitous in plants. They not only contribute to the taste and color of plant-derived foods and beverages but also to the health benefits associated with consumption of diets high in fruits and vegetables. Phenolic acids and flavonoids are major classes of phenolic compounds. They are considered to be potent antioxidants and exhibit a wide range of beneficial physiological properties. Many studies have measured total phenolic content of different varieties of banana using the Folin–Ciocalteu colorimetric method (Table 22.5). Values range from 14 to 518 mg of gallic acid equivalents (GAE)/100 g [27–32]. The wide variation of total phenolics not only reflects the intrinsic (e.g., cultivar and degree of ripeness) and extrinsic factors (e.g., agronomic and storage), but also the method of extraction. Phenolic compounds in plants occur in both bound and free forms. As the former may be excluded from the analysis, total phenolic content is sometimes underestimated.

Literature on flavonoid profiles of bananas is scarce and inconsistent. Most data available come from studies surveying flavonoid content in a range of fruits/vegetables (Table 22.5). The main classes of flavonoids detected in bananas are flavan-3-ols and flavones. High levels of +(-catechin) have been found in two varieties of bananas from Tenerife and one from Ecuador [33]. Epicatechin, epigallocatechin, and gallicatechin have been detected in Dwarf Cavendish bananas [34–36] as well the flavonols quercetin, myricetin, and kaempferol [27, 32]. The only anthocyanin that has been detected is delphinidin at 7.4 mg/100 g edible portion [34] and in banana pulp cell walls [37].

Total content of phenolic acids in bananas has been reported at 7 mg/100 g fresh weight [38]. Phenolic acids bound to other plant components such as polysaccharides and lignin in cell walls, predominate. Ferulic acid is particularly high in bananas accounting for 69% of the total [39]. Ferulic, gallic, hydroxybenzoic, *p*-coumaric, protocatechuic, salicylic, sinapic, syringic, and vanillic acids have all been detected in bananas (Table 22.5).

No data are yet available on the flavonoid and phenolic content of dried bananas. It is known that there is a loss and modification of phenolic acids of up to 90% and approximately 60% loss of flavonols due to sun drying [40]. However, total phenolic content remains relatively unchanged, which implies that many of these modified compounds are yet to be identified and could include oligomeric or polymeric products that are difficult to categorize. Treatment with sulfiting agents inactivates polyphenol oxidase and inhibits non-enzymatic browning and so pre-treated dried bananas would better retain the phenolic compounds than their fresh counterparts [40].

**Table 22.5** Major phytochemicals detected in fresh bananas

	<b>Unit</b>	<b>Fresh bananas</b>	<b>Reference</b>
<b>Total phenolics</b>	mg of GAE/100 g fw	155	[27]
	mg of GAE/100 g fw	14	[27]
	mg of GAE/100 g fw	51	[28]
	mg of GAE/100 g fw	321–518	[29]
	mg of GAE/100 g fw	68–263	[30]
	mg of GAE/100 g fw	90.4	[31]
	mg of CAE/100 g fw	475	[32]
<b>Flavan-3-ols</b>			
+(-catechin)	mg/100 g fw	6.23–6.30	[33]
	mg/100 g fw	nd	[34]
	mg/100 g fw	10.29	[33]
Epicatechin	mg/100 g fw	0.03–0.2	[34, 35]
Epigallocatechin	mg/100 g fw	0.01	[35]
Gallocatechin	mg/100 g fw	29.6	[36]
<b>Anthocyanins</b>	mg/100 g fw	nd	[32]
Delphinidin	mg/100 g fw	7.4	[34]
<b>Flavonols (aglycones)</b>			
Kaempferol	mg/100 g fw	0.012–0.11	[27, 32]
Quercetin	mg/100 g fw	0.06–0.292	[27, 32]
Myricetin	mg/100 g fw	0.01–0.143	[27, 32]
<b>Flavones</b>	mg/100 g fw	nd	[34]
<b>Flavanols</b>	mg/100 g fw	nd	[34]
<b>Phenolic acids</b>	mg/100 g fw	7	[38]
Gallic acid (aglycones)	mg/100 g fw	0.87–1.06	[33]
<b>Bound</b>			
Ferulic	mg/100 g dw	40.07	[39]
Gallic acid	mg/100 g dw	3.22	[39]
Hydroxybenzoic	mg/100 g dw	1.64	[39]
p-Coumaric	mg/100 g dw	3.47	[39]
Salicylic	mg/100 g dw	6.73	[39]
Sinapic	mg/100 g dw	0.27	[39]
Syringic	mg/100 g dw	3.54	[39]
Vanillic	mg/100 g dw	1.04	[39]
<b>Free</b>			
Protocatechuic	mg/100 g dw	0.16	[39]
Syringic	mg/100 g dw	0.21	[39]
Vanillic	mg/100 g dw	0.30	[39]
<b>Fructooligosaccharides</b>	g/100 g fw	nd–0.7	[42, 43]
Fructans 1-kestose, nystose and 1-β-fructofuranosyl-nystose measured only	g/100 g fw	0.02	[44]
	g/100 g fw	0.04–0.13	[46]
<b>Carotenoids</b>			
β-Carotene	μg/100 g fw	25.2–58.8	[51]
	μg/100 g fw	26–457	[13]
	μg/100 g fw	50.6–61.6	[52]
	μg/100 g fw	42.8–131.4	[53]
α-Carotene	μg/100 g fw	25–438	[13]
	μg/100 g fw	61–1055	[21]
	μg/100 g fw	67.9–155.6	[53]
Lutein	μg/100 g fw	22–30	[13]
	μg/100 g fw	86.3–192.2	[53]
Cryptoxanthin	μg/100 g fw	nd	[13, 53]
Lycopene	μg/100 g fw	nd	[51]

nd, not detected; dw, dry weight; fw, fresh weight; GAE, gallic acid equivalents; CAE, chlorogenic acid equivalents.

### **22.6.2 Fructooligosaccharides (FOS)**

FOS are oligosaccharides consisting of short chains of fructose units linked by beta (2–1) bonds. They occur naturally in plant foods or are added to foods as functional ingredients. Since they are not digested in the human small intestine, they are considered dietary fibers. Fructans have important physiological effects. They appear to promote the growth of beneficial intestinal flora and suppress the growth of potential pathogens in the colon. They increase stool-bulking capacity, enhance mineral absorption, maintain the integrity of the intestinal mucosal barrier, and may stimulate the gastrointestinal immune system [41]. Bananas are among the few fruits where FOS have been detected (Table 22.5) at levels ranging from 0.02 [42] to 0.7 mg/100 g [43, 44]. Levels of FOS in dried bananas have not been measured, but it is possible that they are present and become concentrated. Raisins have relatively high levels of fructans while they are absent in the grapes they are made from [45]. It is possible that fructans are formed from the sugars in the grapes during sun drying. There are no detectable levels of FOS in banana chips [46].

### **22.6.3 Carotenoids**

Other than the provitamin A activity of a number of carotenoids, these compounds may have a protective effect against heart disease and certain types of cancer. In addition, epidemiological studies suggest that diets rich in lutein and zeaxanthin may prevent age-related macular degeneration and cataracts [47]. A broad survey of banana varieties indicate that many have very high levels of provitamin A and total carotenoids [21, 48, 49]. More than 90% of the carotenes in bananas consist of all trans  $\beta$ -carotene and  $\alpha$ -carotene with only very small amounts of the 13-cis-isomer of  $\mu\text{g}/100\text{ g}$  [5, 50–53]. Levels for  $\beta$ - and  $\alpha$ -carotene range from 25  $\mu\text{g}/100\text{ g}$  in creamy fleshed bananas to more than 1000  $\mu\text{g}/100\text{ g}$  in deep orange- or yellow-fleshed fruits (Table 22.5). The only other major carotenoid present is lutein, detected at levels ranging from 22 to 192  $\mu\text{g}/100\text{ g}$  [5, 53]. Proportion of carotenoids in bananas is characteristic of the variety [50].

Dried bananas, banana figs, and banana chips do retain part of the carotenoid content of the fresh fruit, the proportion that is retained depends mostly on the duration and the severity of the drying process [22, 54]. While sun drying is the most affordable method, it is slow and can lead to considerable losses. With hot-air drying, significantly higher retention of carotenoids is achieved in the final product. Other than destruction by oxidation, drying causes isomerization of all-trans carotenoids into the cis-form, thus affecting provitamin A activity, bioavailability, and antioxidant activity [23]. Pre-treatments such as dipping in a salt or ascorbic acid solution, sodium sulfiting increase carotenoid retention during drying [54]. Conventional deep frying also leads to significant losses which can range from 20 to 50% of total carotenoids and 16 to 60% of  $\beta$ -carotene, depending on the duration, temperature, type, and freshness of the oil [25, 55]. Double frying of plantain chips leads to further degradation of carotenoids [24].

## **22.7 Potential health benefits of dried bananas**

Dried bananas, banana figs, and banana chips (non-fried) are low in fat and sodium and high in potassium, magnesium, and fiber. This makes them desirable snacks for a diet aimed at

cardiovascular health. It is recognized that increasing dietary potassium intake can lower blood pressure and attenuates the adverse effects of sodium [56]. Potassium intake is low among both adults and children and has become a public health concern [57]. High fiber diets are recommended to reduce the risk of developing cardiovascular disease (CVD) and various other conditions including constipation, diverticulitis, diabetes, and colon cancer.

Dried bananas are also a rich source of carbohydrate and depending on the drying process and the variety of the fruit; they can provide appreciable amounts of the daily intake of pyridoxine, niacin, thiamine, vitamin C, and vitamin A. They could play an important role in alleviating micronutrient deficiency, particularly in tropical and subtropical areas where they are most severe and where bananas are a staple component of the diet. Green banana starch has a low glycemic index (GI) as it resists digestive enzyme's catalytic hydrolysis [58]. Green bananas have been found to have a protective effect against experimentally induced gastric mucosal lesions [59]. It is not clear how these effects would transfer to dried chips made with green bananas.

Total antioxidant capacity of bananas, as measured by the oxygen radical absorbance capacity (ORAC), has been reported as 879 µmol of trolox equivalents (TE)/100 g, which is intermediate among fruits but equal or higher than most vegetables [60]. This is due to the presence of micronutrients such as vitamin C and phytonutrients such as phenolic acids, flavonoids, and carotenoids with high antioxidant activity. Current scientific thought regards oxidative stress as an important contributing factor in the development of chronic diseases such as heart disease, diabetes, cancer, neurodegenerative diseases such as in Alzheimer's and Parkinson's disease as well as in the aging process itself. Dietary antioxidants are part of the body's antioxidant defence system. Epidemiological, case-control, and dietary intervention studies suggest or show the importance of plant foods rich in antioxidants in the prevention against chronic disease. Depending on the processing method, it is possible that dried bananas retain their antioxidant potential as other dried fruits do.

## 22.8 Conclusions

While fresh bananas are very nutritious, high in fiber and potassium, excellent sources of many micronutrients and phytonutrients, more nutritional information is needed to fully appreciate the potential health benefits of dried bananas.

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## **23 Nutritional composition, phytochemicals, and health benefits of dates**

Cesarettin Alasalvar and Fereidoon Shahidi

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### **23.1 Introduction**

Dates are produced largely in the hot desert regions of the Middle East and North Africa and are marketed worldwide as a high-value crop. The world production of dates has increased from 4,600,000 metric tonnes (MT) in 1994 to 7,321,090 MT in 2009 [1]. Egypt is the largest producer of dates, contributing 17.4% to the total global production, followed by Iran (14.0%), Saudi Arabia (13.5%), United Arab Emirates (10.4%), and Pakistan (10.0%). Other countries (Algeria, Iraq, Sudan, Oman, Tunisia, Libya, China, Morocco, Yemen, Niger, Turkey, Israel, the United States, and Mauritania) contribute 34.7% to the total global production [1]. There are more than 600 known date varieties [2].

Sun drying is the common method of drying dates; taking around 7–10 days depending on the daytime temperature which varies from 30 to 50°C and the humidity (60–85%) [3, 4]. Several factors affect the quality of dates during sun drying. These include insect infestation, microbial infestation, and browning by enzymatic and non-enzymatic reactions [5]. The drying of dates can also be achieved by artificial heat treatment in circumstances where early rains threaten to damage the crop. The process requires rooms in which temperature, humidity, and air ventilation can be controlled. Drying rate is a function of temperature, relative humidity, and velocity of the air. For drying of soft dates, a temperature of 65°C is recommended, which ensures a reasonable drying rate with a minimal effect on the basic qualities. Relative humidity should be maintained at over 40%, but should not exceed 60% to avoid case-hardening and also for fuel economy [5].

Dates are considered to be an important component of daily diet in the Middle East and North Africa. They are consumed either fresh (30–40%) or sun-dried (60–70%). Sun-dried dates are consumed throughout the year, but their use reaches peak during the month of Ramadan, for breaking the fast before eating. The average daily consumption of dates per capita was estimated in Oman and United Arab Emirates at 164 and 114 g, respectively [6, 7]. Socio-economic changes have reduced date consumption due to improvement in living standards, changes in eating habits, continued urban drift, and the tendency toward a smaller sized family. The year round availability of alternative competitive confectioneries and other fruits have aggravated the problem [4].

Because of their nutritional value and potential health promoting activities, dates may be considered as an emerging and potential candidate for the development of foods with disease risk reduction potential [2]. This chapter reviews the latest research on fresh and dried dates' nutrition, phytochemicals, and their roles in antioxidant status and other human health potentials. Factors affecting the phytochemical composition and antioxidant activity during drying/processing are also discussed. Readers who are interested in detailed information and in-depth discussions about the specific nutritional, phytochemicals or functions of dates, are referred to comprehensive reviews by others [2, 4]. In addition, final section of a recent book entitled "*Dates: Production, Processing, Food, and Medicinal Values*" focuses on the potential medicinal values of dates along with the latest research findings [8].

## **23.2 Compositional and nutritional characteristics of fresh and dried dates**

Dates have provided nutrition to millions of people around the world for thousands of years. Therefore, it is worthwhile to assess their nutritional significance as a food for regular consumption and as a good source of nutritional components for maintaining health and for reducing the risk of various diseases [2]. Dates contain many nutrients, at 3–10-fold higher than the other commonly consumed fruits (such as apples, grapes, oranges, cranberries, and blueberries), and may be considered as one of the highly nutritious fruits available on earth for human consumption [2]. Vinson *et al.* [9] have indicated that fresh dates have the best nutrient score among the fresh apricots, cranberries, figs, green grapes, and plums.

### **23.2.1 Proximate composition**

The average proximate composition and caloric value of fresh and dried dates are summarized in Table 23.1. The detailed information on nutritional and functional properties of 10 fresh and 16 dried date varieties have been extensively reviewed by Al-Farsi and Lee [4]. In addition, Table 1.2 (see Chapter 1) compares compositional and nutritional characteristics of some dried fruits (apples, apricots, dates, figs, peaches, pears, prunes, and raisins). Here, comparison between fresh and dried dates is discussed briefly. Carbohydrate is the predominant component in both fresh and dried dates, ranging in concentration from 54.9 g/100 g (in fresh dates) to 80.6 g/100 g (in dried dates), followed by moisture (42.4 g/100 g in fresh dates and 15.2 g/100 g in dried dates), along with small amounts of protein, lipid, and ash (Table 23.1). The significant reduction in the moisture content of dried dates is mainly due to sun drying, which is a traditional way of preserving dates. The energy values range from 213 kcal/100 g in fresh dates to 314 kcal/100 g in dried dates, due to their high sugar content.

### **23.2.2 Dietary fiber**

Table 23.1 presents the content of dietary fiber in fresh and dried dates. Dietary fiber is divided into water-soluble (pectin and hydrocolloids) and water-insoluble (cellulose, hemicellulose, and lignin). Dietary fiber plays an important role in human health as its low intake has been linked to several diseases in the industrialized nations [2]. The average total fiber content in fresh and dried dates ranges from 7.5 to 8.0 g/100 g, respectively; due to moisture reduction

**Table 23.1** Compositional and nutritional characteristics of fresh and dried dates (average values in per 100 g edible portion)

<b>Nutrient</b>	<b>Units</b>	<b>Fresh dates</b>	<b>Dried dates</b>
<b>Proximate composition</b>			
Water	g	42.4	15.2
Energy	kcal	213	314
Protein	g	1.5	2.14
Lipid	g	0.14	0.38
Ash	g	1.16	1.67
Carbohydrate	g	54.9	80.6
Dietary fiber	g	7.5	8.00
Soluble	g	0.96	0.84
Insoluble	g	5.89	5.76
Sugars	g	43.4	64.1
Fructose	g	19.4	29.4
Glucose	g	22.8	30.4
Sucrose	g	4.03	11.6
<b>Minerals</b>			
Calcium	mg	20.2	70.7
Copper	mg	0.21	0.24
Iron	mg	0.64	0.83
Magnesium	mg	43.3	64.2
Manganese	mg	0.29	0.27
Phosphorus	mg	41.0	58.1
Potassium	mg	486	713
Selenium	mg	0.24	0.31
Sodium	mg	90.9	32.9
Zinc	mg	0.24	0.27
<b>Vitamins</b>			
Folate	µg	na	53.75
Niacin	µg	na	1442
Pyridoxine	µg	na	207
Riboflavin	µg	na	116.5
Thiamin	µg	na	78.67
Vitamin A (RAE)	µg	na	23.85
Vitamin C	µg	na	3900
<b>Amino acids</b>			
Alanine	mg	50.0	93.2
Arginine	mg	52.0	80.9
Aspartic acid	mg	118	152
Cystine	mg	27.3	46.0
Glutamic acid	mg	147	244
Glycine	mg	60.3	107
Histidine <sup>a</sup>	mg	23.7	27.7
Isoleucine <sup>a</sup>	mg	21.3	46.2
Leucine <sup>a</sup>	mg	68.0	98.7
Lysine <sup>a</sup>	mg	86.3	66.9
Methionine <sup>a</sup>	mg	7.7	22.9
Phenylalanine <sup>a</sup>	mg	37.0	53.2
Proline	mg	54.0	105
Serine	mg	48.7	67.4
Threonine <sup>a</sup>	mg	39.3	52.6
Tryptophan <sup>a</sup>	mg	nd	40.6
Tyrosine	mg	26.3	41.2
Valine <sup>a</sup>	mg	na	na

Source: Adapted with permission from Al-Farsi and Lee [4].

Average values are composed of between three and ten date varieties.

RAE, retinol activity equivalents; na, not available; nd, not detected

<sup>a</sup>Indispensable amino acids.

and to the ripening process in which enzymes gradually break down these substances to the more soluble compounds which soften the fruit [10]. It is important to note that high content of dietary fiber in dates helps meeting dietary recommendations (14 g of fiber for every 1000 calories of food consumed each day). This becomes 25–38 g of fiber per day depending on the age and gender [11]. On a per serving basis (40 g), fresh and dried dates deliver between 7.9 and 12.8% of the daily required value of fiber [12]. The high content of the insoluble fiber induces satiety and has a laxative effect due to increased stool weight. It, therefore, may reduce the risk of serious conditions such as bowel cancer and diverticular disease [13, 14]. In comparison with other dried fruits (see Table 1.2 in Chapter 1), dried dates are a good source of dietary fiber.

Based on the published reports, the total fiber content in dates varies from 1.7 to 11.4% (w/w) depending on the date variety and the method of analysis [15]. However, in a recent study [16], *Deglet Noor* and *Allig* cultivars were analyzed and their total dietary fiber content was reported as 14.4 and 18.4% of the dry matter, respectively.

### **23.2.3 Sugars**

The predominant sugars in dates are simple reducing sugars such as fructose and glucose, and small amounts of non-reducing sugar sucrose, depending on the stage of the fruit development and the date palm varieties [2]. The average content of fructose, glucose, and sucrose in fresh dates are 19.4, 22.8, and 4.03 g/100 g, respectively, with an average total of 43.4 g/100 g. The content of sugars in dried dates increases to 29.4, 30.4, and 11.6 g/100 g for fructose, glucose, and sucrose, respectively, with a total of 64.1 g/100 g [4]. Both fructose and glucose are the major sugars in most date varieties and are present almost in equal amounts [3]. *Deglet Noor* variety of dates, however, presented an exception, where sucrose constituted 38% of the total carbohydrates in the fruit, possibly due to a lower invertase activity compared to other varieties [2, 17].

Fully ripened dates contain more than twice the amount of fructose compared to any other commonly consumed fruits (such as apples, grapes, oranges, cranberries, and blueberries). Occurrence of high amount of fructose in dates may provide several beneficial effects on human health and delay or prevent the development of chronic diseases [2, 18–20].

### **23.2.4 Minerals**

Fresh and dried dates, in general, serve as a reasonable source of copper, iron, magnesium, manganese, phosphorus, and potassium (Table 23.1). Based on daily 40 g consumption of dried dates (on a per serving basis), recommended dietary allowances (RDA) or adequate intake (AI) of minerals for adult males and females are given in Table 1.3 (see Chapter 1). Consuming 40 g of dried dates (Table 1.3, see Chapter 1) supplies 1.6% of calcium, 9.3% of copper, 2.3–5.1% of iron, 4.2–5.5% of magnesium, 4.5–5.8% of manganese, 3.5% of phosphorus, and 5.6% of potassium for RDA or AI for adults [12, 21–23]. The values in Table 23.1 are within the range of the above given RDA or AI. The high potassium and low sodium content in dates are desirable for individuals suffering from hypertension [24]. Dates contain the highest amount of selenium among eight dried fruits (Tables 1.2 and 1.3, see Chapter 1) [12].

### 23.2.5 Vitamins

Dried fruits, in general, contain a small amount of vitamins (Table 23.1). With regard to RDA or AI of vitamins, 40 g of dried dates provide 5.4% of folate, 3.6–4.1% of niacin, 6.4% of pyridoxine, 3.6–4.2% of riboflavin, 2.6–2.9% of thiamine, 1.1–1.4% of vitamin A, and 1.7–2.1% of vitamin C [4, 22, 25, 26]. Among eight dried fruits, dates contain higher amount of folate and pantothenic acid than other dried fruits based on USDA database (Tables 1.2 and 1.4, see Chapter 1) [12].

### 23.2.6 Amino acids

Despite the fact that fresh and dried dates contain all indispensable amino acids (except tryptophan in fresh and valine in both fresh and dried dates), in general, they are not good sources of amino acids due to their low content of protein (Table 23.1). Glutamic acid, aspartic acid, lysine, leucine, and glycine are the predominant amino acids in fresh dates, whereas glutamic acid, aspartic acid, glycine, proline, and leucine are the predominant amino acids in dried dates [4, 27]. Among indispensable amino acids, only lysine was lost as a result of drying.

## 23.3 Phytochemicals in fresh and dried dates

Phytochemicals (non-nutritive bioactive compounds) have gained increased interest due to their antioxidant activity, cholesterol-lowering properties, and other potential health benefits such as cancer chemoprevention, prevention of diabetes, and cardiovascular diseases (CVD). Dates are renowned for the presence of many classes of phytochemicals such as phenolics (phenolic acids, tannins, and certain flavonoids such as flavonols, flavones, anthocyanins, and phytoestrogens) and carotenoids [2, 4, 28, 29]. These phytochemicals together with other minor components and certain antioxidant vitamins render antioxidant properties to dates. However, studies pertaining to the detailed identification, characterization, and quantification of phytochemicals in different date varieties at different stages of fruit ripening and processing are still insufficient. The effect of sun drying on antioxidant status and phytochemicals of dates are discussed below.

### 23.3.1 Antioxidant activity

The antioxidant activity of dates has been evaluated *in vitro* by different methods, such as oxygen radical absorbance capacity (ORAC), trolox equivalent antioxidant capacity (TEAC), ferric-reducing ability of plasma (FRAP), and 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging assays [9, 30–38]. The antioxidant activities of dates using these methods have been discussed extensively by Vayalil [2]. Therefore, the effect of sun drying on antioxidant activity of dates is discussed here.

Most available data on antioxidants in dates are reported using the ORAC assay. Significant differences ( $P < 0.05$ ) in ORAC values exist among fresh and sun-dried date varieties (Table 23.2). Comparison of ORAC values of some dried fruits, including dates, is given in Table 1.5 (see Chapter 1).

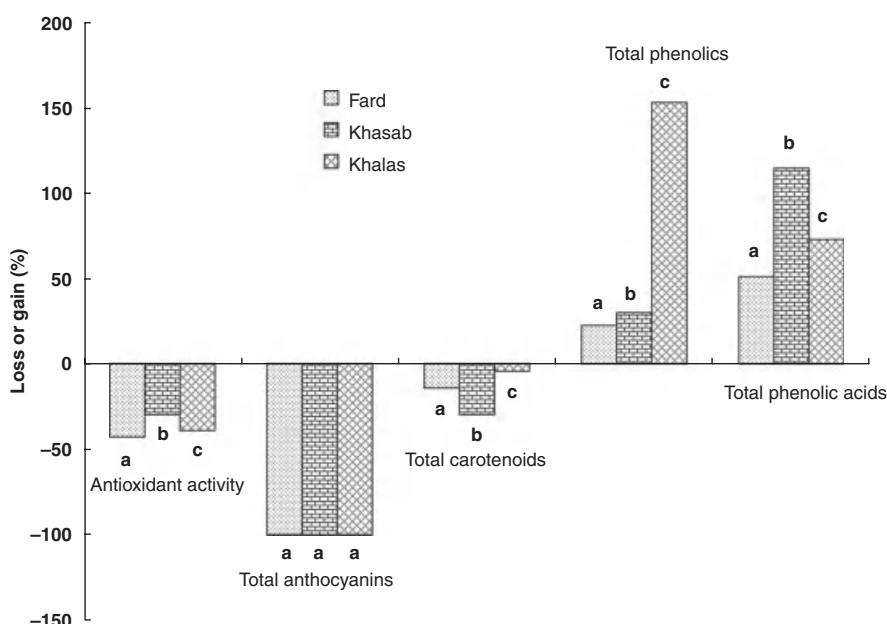
**Table 23.2** Antioxidant activities and phenolics of fresh and dried dates

	Fresh dates	Dried dates	Reference
ORAC values ( $\mu\text{mol of TE}/100 \text{ g}$ )	11,687–20,604	2387–12,543	[35, 36]
Total phenolics (mg of GAE/100 g)	134–280	172–661	[35, 36, 66]
Total anthocyanins (mg of C3GE/100 g)	0.24–1.52	nd	[36]
Total carotenoids (mg/100 g)	1.31–3.03	0.92–2.91	[36]
Total phytoestrogens ( $\mu\text{g}/100 \text{ g}$ )	na	329.5	[58]

The values are given as a range from minimum to maximum (three varieties of fresh dates and eight varieties of dried dates).

ORAC, oxygen radical absorbance capacity; TE, trolox equivalents; GAE, gallic acid equivalents; C3GE, cyanidin-3-glucoside equivalents; na, not available; nd, not detected.

Al-Farsi *et al.* [36] found that sun drying caused a significant loss (ranging from 29.7 to 42.5%) of antioxidant activity in date varieties (Figure 23.1). This loss could be due to the decomposition of natural antioxidants in dates after drying. The reduction in antioxidant activity after drying has also been reported for other fruits. Larrauri *et al.* [39] reported decreases of 28 and 50% in the antioxidant activity of red grape pomace peel after drying at temperatures of 100 and 140°C, respectively. The antioxidant activity of blueberry decreased after drying (52%) and canning (65%) [40]. The difference between antioxidants in fresh and sun-dried dates observed by Al-Farsi *et al.* [36] was of similar magnitude. In contrast, there is only a few studies in which either an increase in antioxidant activity or no change



**Figure 23.1** Effect of sun drying on different varieties of date antioxidants. Different letters in the same column (Fard, Khasab, and Khalas) indicate significant differences ( $P < 0.05$ ). (Adapted with permission from Al-Farsi *et al.* [36].)

after drying has been observed. Piga *et al.* [41] reported an increase in antioxidant activity in plums and prunes after drying at 85°C for 40 hours. They explained that this increase was due to the formation of Maillard reaction products during drying process. Thus, chemical and biochemical changes that affect the antioxidant activity may occur during drying.

### 23.3.2 Total phenolics

The average content of total phenolics ranges from 134 to 280 mg of gallic acid equivalents (GAE)/100 g and from 172 to 661 mg of GAE/100 g in fresh and dried date varieties, respectively (Table 23.2) [35, 36]. Vinson *et al.* [9] compared the amount and quality of phenolic antioxidants among dried and fresh fruits. Among seven fresh and dried fruits studied (apricots, cranberries, dates, figs, green grapes, and plums), it was observed that dates contained the highest concentration of total phenolics in both fresh and dried states when compared to other fruits.

Al-Farsi *et al.* [36] found that total phenolic contents of sun-dried dates were significantly ( $P < 0.05$ ) higher than those of fresh dates in Fard, Khasab, and Khalas by 22.5, 29.9, and 153%, respectively (Figure 23.1). It was also observed that drying increased the amount of total phenols in dates which was statistically significant in Iranian dates [34] and not significant in California dates [9]. Shahidi and Naczk [42] reported that drying, in general, is regarded as being unfavorable due to the possibility of inducing oxidative decomposition either enzymatically by polyphenol oxidase and glycosidase or by thermal degradation of phenolic compounds. However, total phenolic content in dates showed increases after sun drying, possibly due to the release of phenolic compounds [43]. Thus, the linkages between *p*-coumaric acid and lignin, and between ferulic acid and arabinoxylans could be broken down at high temperatures.

### 23.3.3 Anthocyanins

Anthocyanins are a group of phenolic phytochemicals that are found in small amounts in fresh dates. Their presence has been reported only in red- and dark-colored fresh dates, from 0.24 to 1.52 mg of cyanidin-3-glucoside equivalents (C3GE)/100 g in three fresh date varieties (Fard, Khasab, and Khalas) (Table 23.2). These differences are related to the color of these varieties (both Khasab and Fard varieties are red, whereas Khalas variety is yellow due to the presence of carotenoids).

The absence of anthocyanins in sun-dried dates is probably due to their destruction upon drying (Figure 23.1) [36, 42, 44]. In a previous study by Alasalvar *et al.* [45], a significant loss of anthocyanins (92.5%) during heat processing was reported in the production of pekmez. Raynal [46] found that only 14.6% of the initial anthocyanins in plums remained after 1 hour of drying at 95°C, whereas 45.6% remained upon drying at 55°C. Studies have shown that anthocyanins are readily destroyed by heat during food processing [44, 47]. Apart from heat, many other factors such as light, temperature, agronomics, and storage conditions, among other variables, are also responsible for the degradation of anthocyanins during drying and processing of fruits [42, 47]. Wrolstad [48] stated that the degradation of anthocyanins during drying and storage is due to enzymatic and non-enzymatic browning reactions. Several enzymes have been found to be involved in the degradation of anthocyanins; these include glycosidase and polyphenol oxidase [42].

**Table 23.3** Carotenoid content of fresh and dried dates ( $\mu\text{g}/100\text{ g}$ )

Carotenoid	Fresh dates	Dried dates
$\alpha$ -Carotene	3.0	nd
$\beta$ -Carotene	34.4	59.8
Zeaxanthin	33.0	nd
$\beta$ -Zeaxanthin	9.0	nd
Lutein	244	289
Neoxanthin	306	252
Total	913	973

Source: Adapted with permission from Al-Farsi and Lee [4].

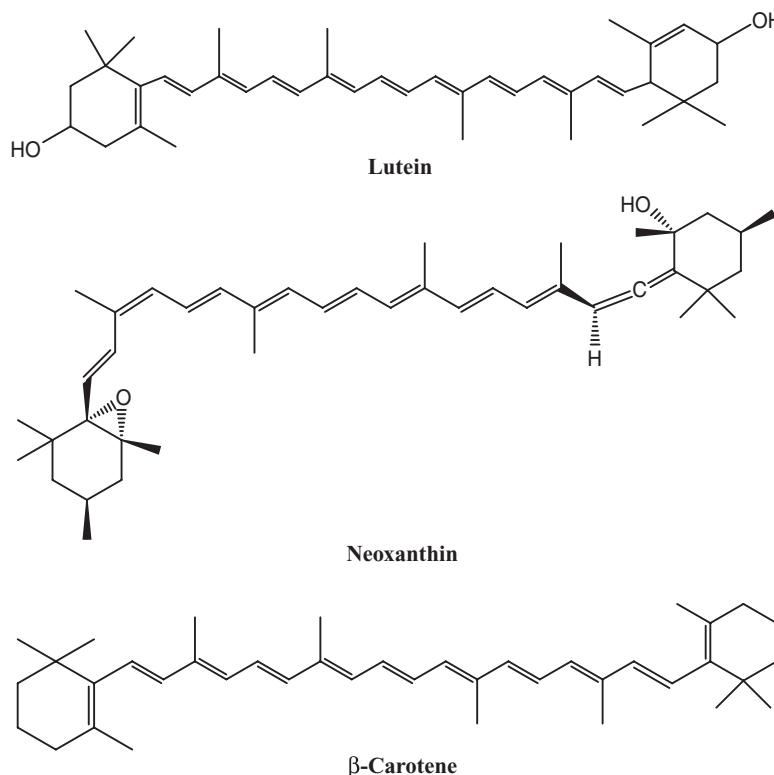
Average values are composed of nine date varieties.

nd, not detected.

### 23.3.4 Carotenoids

The major class of phytochemicals found in the lipid fractions of dates is carotenoids [2]. Six carotenoids, namely  $\alpha$ -carotene,  $\beta$ -carotene, lutein, neoxanthin, zeaxanthin, and  $\beta$ -zeaxanthin, are present, albeit at different levels, in both fresh and dried dates (Table 23.3). The average total carotenoids content of fresh and dried dates are 913 and 973  $\mu\text{g}/100\text{ g}$ , respectively. Of these, lutein, neoxanthin, and  $\beta$ -carotene were the major carotenoids (Figure 23.2) among nine fresh (244, 306, and 34.4  $\mu\text{g}/100\text{ g}$ , respectively) and dried dates (289, 252, and 59.8  $\mu\text{g}/100\text{ g}$ , respectively) [4]. The total carotenoid content in date varieties differs between yellow and red colors. The high content of carotenoids is expected to be in the yellow variety. Al-Farsi *et al.* [36] measured total carotenoid content in three date varieties (Fard, Khasab, and Khalas) of fresh (ranged from 1.31 to 3.03 mg/100 g fresh weight) and dried (ranged from 0.92 to 2.91 mg/100 g fresh weight) products (Table 23.2). The highest total carotenoids were expected in Khalas, as this variety has a yellow color, whereas the other two varieties are red. A detailed analysis of total carotenoids in few varieties of Algerian dates has shown that lutein (89–94%) and  $\beta$ -carotene (3–10%) were the major carotenoids present in dates and another 2–8% consisted of unidentified minor carotenoids [49]. Ben-Amotz and Fishier [50] analyzed different carotenoids in freeze-dried dates. They estimated 220  $\mu\text{g}/100\text{ g}$  of total carotenoids as dry weight and the major carotenoids identified were cis-violaxanthin (10  $\mu\text{g}/100\text{ g}$ ), zeaxanthine (110  $\mu\text{g}/100\text{ g}$ ),  $\beta$ -zeacarotene (30  $\mu\text{g}/100\text{ g}$ ),  $\alpha$ -carotene (10  $\mu\text{g}/100\text{ g}$ ), and  $\beta$ -carotene (60  $\mu\text{g}/100\text{ g}$ ). However, details of the dates used for the analysis are unavailable. Among eight dried fruits (apples, apricots, dates, figs, peaches, pears, prunes, and raisins), dates are the fourth richest source of carotenoids after apricots, peaches, and prunes [12] (Figure 1.2, see Chapter 1). Therefore, dates can be considered a moderate source of carotenoids.

Similar to anthocyanins and antioxidant activity, commercial sun drying caused a significant ( $P < 0.05$ ) loss (ranging from 4 to 29.8%) of carotenoids in date varieties except in Khalas, which was insignificant ( $P > 0.05$ ) (Figure 23.1). Several studies reported the loss of carotenoids in carrot and orange juices during processing and storage [51, 52]. Mahanom *et al.* [53] reported that 64% of carotenoids were lost after drying (at 50°C for 9 hours) in the herbal preparation of eight medicinal plant leaves. In addition, lycopene losses during processing of tomato paste varied from 9 to 28% [54]. A number of mechanisms for the



**Figure 23.2** Structures of major carotenoids in dates.

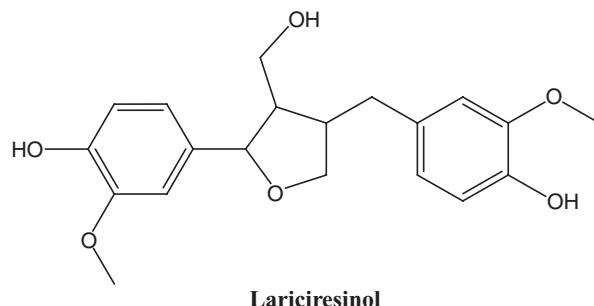
reaction and decomposition of carotenoids in plant materials have been reported. These include enzymatic processes, autoxidation, and thermal degradation [55–57].

### 23.3.5 Phytoestrogens

There are three major classes of phytoestrogens such as isoflavones, coumestans, and lignans that occur in plants, fruits, and their byproducts. Total phytoestrogens in dried dates has been reported to be 329.5  $\mu\text{g}/100\text{ g}$  (Table 23.2), lariciresinol being a major one (Figure 23.3) [58]. Among five dried fruits (apricots, currants, dates, prunes, and raisins), dates rank the second richest source of phytoestrogens after apricots (444.5  $\mu\text{g}/100\text{ g}$ ) (Table 1.7, see Chapter 1). Despite being complex, detailed quantitative analysis on the different classes of phytoestrogens present in different forms and varieties of dates at different stages of ripening remains unexplored [2].

### 23.3.6 Phenolic acids

Based on the available data [3, 28, 59], dates may be considered as a rich source of phenolic acids when compared with other fruits and berries [60]. Al-Farsi *et al.* [36] identified a total



**Figure 23.3** Structure of major phytoestrogen (lignan) in dates.

of nine phenolic acids (caffeic, ferulic, gallic, *o*-coumaric, *p*-coumaric, *p*-hydroxybenzoic, protocatechuic, syringic, and vanillic) in fresh and sun-dried dates (Table 23.4). Four free phenolic acids (protocatechuic, ferulic, syringic, vanillic) were present in dates, with total concentrations varying between 2.61 and 12.27 mg/100 g in fresh dates, and between 6.06 and 14.77 mg/100 g in their sun-dried counterparts (Table 23.4). The total bound phenolic contents were in the range of 6.84–30.25 mg/100 g in fresh dates and 14.18–49.67 mg/100 g in sun-dried dates. Ferulic and *p*-coumaric were major phenolic acids in the bound form in dried dates (Figure 23.4). Sun drying significantly ( $P < 0.05$ ) increased the total concentration of bound phenolic acids in all date varieties (Figure 23.1). This was probably due to degradation of complex, high molecular weight polymers such as tannins [4, 36].

Detailed phenolics profile of dates was first published in the late 1980s by Regnault-Roger *et al.* [28]. They identified eight phenolic acids in dried Tunisian dates (namely caffeic, ferulic, gallic, *p*-coumaric, *p*-hydroxybenzoic, protocatechuic, syringic, and vanillic). In

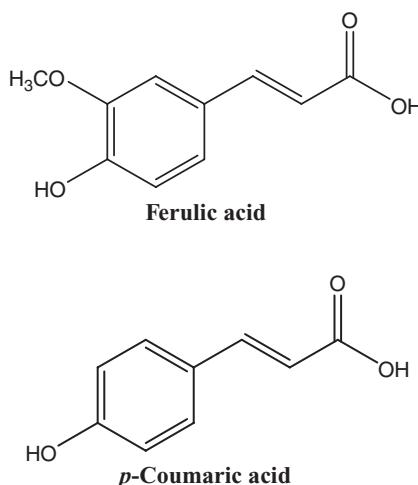
**Table 23.4** Composition of free and bound phenolic acids (mg/100 g) in fresh and sun-dried dates

<b>Phenolic acids</b>	<b>Free</b>		<b>Bound</b>	
	<b>Fresh</b>	<b>Dried</b>	<b>Fresh</b>	<b>Dried</b>
<b>Benzoic acids</b>				
Gallic	nd	nd	nd–0.48	nd–3.09
<i>p</i> -Hydroxybenzoic	nd	nd	nd–0.49	nd
Protocatechuic	nd	nd–2.04	nd–4.49	nd–8.34
Syringic	nd–5.49	nd–6.02	nd–1.70	nd–3.22
Vanillic	1.45–2.13	2.18–4.14	nd	nd–2.26
<b>Cinnamic acids</b>				
Caffeic	nd	nd	nd–10.10	nd–7.57
<i>o</i> -Coumaric	nd	nd	nd–1.46	nd–6.71
<i>p</i> -Coumaric	nd	nd	0.49–6.25	1.41–14.19
Ferulic	1.16–4.71	1.84–5.08	2.06–12.27	6.08–13.28
Total	2.61–12.27	6.06–14.77	6.84–30.25	14.18–49.67

Source: Adapted with permission from Al-Farsi *et al.* [36].

The values are given as a range from minimum to maximum (three varieties of dried dates).

nd, not detected.



**Figure 23.4** Structures of major phenolic acids in dates.

addition to these phenolic acids, recent studies have demonstrated the presence of sinapic acid, 5-*o*-caffeoyleshikimic acid and its three isomers, xantoxylan, hydrocaffeic acid, and coumaroylquinic acid in seven varieties of ripe Algerian dates [59].

It has been reported that caffeic, sinapic, ferulic, and *p*-coumaric acids are more antioxidative than protocatechuic, syringic, vanillic, and protocatechuic acids [61]. Since dates are a good source of the more active phenolic acids, they may be considered as good sources of natural antioxidant. Besides their naturally occurring antioxidant properties, phenolic acids can also influence product flavor and color.

### 23.3.7 Other phenolics

Some flavonoids including flavonols and proanthocyanidins, especially procyanidins and flavanoid glycosides, have been reported [29, 37, 59, 62–64]. Gu *et al.* [37] demonstrated that *Deglet Noor* contained proanthocyanidins of type B consisting exclusively of (epi) catechin while in *Medjool* proanthocyanidins were not detected. Mansouri *et al.* [59] indicated the presence of flavonoid glycosides in many Algerian dates. Hong *et al.* [63] identified that procyanidins in dates are homogeneous B type oligomers and these oligomers were identified through decamers. Higher molecular weight polymers were also well documented and composed mainly of undecamers through heptadecamers. Moreover, in their study, 19 flavonoid glycosides of luteolin, quercetin, and apigenin were identified together with their isomeric forms. Luteolin, quercetin, and apigenin glycosides also existed as methylated and sulfated forms in dates [2].

## 23.4 Health benefits of dates

A recent review article on *date fruits: an emerging medicinal foods* has been published by Vayalil [2]. This review provides an account of health benefits of dates, hence only a

summary of health effects of dates is given here. Dates are considered to have several health benefits due to their compositional and nutritional characteristics as well as their non-nutritive phytochemicals. In certain countries (such as the Middle East and North Africa), dates and their byproducts are used as folk medicine (such as diabetes and hypertension) for centuries [65]. Although both fresh and dried dates are sugar-packed fruits, consumption of certain varieties of dates do not induce any metabolic and inflammatory markers that are associated with metabolic syndrome and related diseases and the effect is comparable to that of other fruits. The main health benefits of date consumption are detailed by Vayalil [2], as shown below:

- a potential medical nutritional therapy for the prevention and control of diabetes mellitus,
- a potential medical nutritional therapy for cardio-and cerebrovascular diseases,
- a potential cancer preventive diet,
- a potential medicinal food against bacterial and fungal infections,
- other potential health benefits (laxative, anti-inflammatory activity in adjuvant arthritis model, protective effects against chemical-induced toxicity, neuro-protective effects, anti-ulcer effect, and dates for deficiency diseases, among others).

### 23.5 Food application of dates, syrups, and their byproducts

Limited data is available regarding the compositional and functional characteristics of date syrups and byproducts (such as press cakes and seeds) [66]. Table 23.5 shows the nutritional composition, total phenolics, and antioxidant activity of date flesh, syrup, press cake, and seed. Date seeds contain a relatively high amount of protein (2.29–5.40 g/100 g) as compared

**Table 23.5** Nutritional composition, total phenolics, and antioxidant activity of date flesh, syrup, and their byproducts

	Byproducts			
	Date flesh	Syrup	Press cake	Seed
<b>Proximate composition</b>				
Protein	1.10–1.79	0.95–1.09	3.62–5.23	2.29–5.40
Fat	2.04–3.25	0.62–2.84	1.40–2.20	5.02–5.90
Moisture	9.73–17.52	20.56–34.33	8.30–10.59	3.14–5.19
Ash	1.41–1.99	1.23–1.76	1.68–2.46	0.89–1.16
Carbohydrates	77.34–84.45	62.73–74.24	81.86–83.33	83.14–86.89
Dietary fiber	5.94–8.72	0.01–0.18	25.39–33.81	77.75–80.15
<b>Total phenolics</b>	172–246	96–162	165–435	3102–4430
<b>Total antioxidant activity</b>	14,600–16,200	8400–17,400	13,400–35,700	58,000–92,900

Source: Adapted with permission from Al-Farsi *et al.* [66].

The values are given as a range from minimum to maximum (three varieties of dried dates).

Proximate composition is expressed as g/100 g fruits.

Total phenolics are expressed as milligrams of gallic acid equivalents (GAE) per 100 g.

Total antioxidant activities are expressed as micromoles of trolox equivalents (TE) per 100 g.

to date flesh (1.10–1.79 g/100 g), syrups (0.95–1.09 g/100 g), and press cakes (3.62–5.23 g/100 g). Date seeds are also the richest sources of dietary fiber (77.75–80.15 g/100 g), total phenolics (3102–4430 mg of GAE/100 g), and antioxidant activity (58,000–92,900 µmol of TE/100 g) among date flesh and byproducts (Table 23.5).

At present, date seeds are used mainly for animal feed, whereas most is regarded as waste. Utilization of such waste is very important to date cultivation and to increase the income to this sector. Date byproducts (particularly seeds) can be used in a variety of food and specialty products, including functional foods and ingredients in nutraceuticals, pharmaceuticals, and medicinal products. In addition, date seeds could potentially be considered as an inexpensive source of dietary fiber and natural antioxidants. Date seeds, roasted and ground into powder make a beverage like coffee, called “date coffee.” Date syrup is a popular product world-wide and can be used for several purposes, including a sweetener in tea and hot-chocolate, topping on ice creams, breadmaking, spreading in breads, and mixing with cold and hot milk, among others.

## 23.6 Conclusions

Dates can be stored for months after harvest without need for using preservatives. They are an energy-dense food containing high concentrations of carbohydrates (up to 80% in dried dates), several essential nutrients (minerals, amino acids, and vitamins), and health-promoting phytochemicals (such as phenolic acids, tannins, flavonols, flavones, anthocyanins, phytoestrogens, and carotenoids) in maintaining human health. They serve as a good source of natural antioxidants and could potentially be considered as a functional food or functional food ingredient.

Date consumption would be a good alternative for the malnourished infants and adults for their basic nutritional requirements and to fight against nutrient deficiency-related diseases and infections which is an endemic in the poor nations of the world. Therefore, dates may be considered as a gift of nature to the people not only for those living in the hot arid regions, but also other parts of the world for general nutrition and a potential emerging functional food [2].

A significant ( $P < 0.05$ ) amount of antioxidants, anthocyanins, and carotenoids is lost during sun drying of dates. This is an important issue that needs to be addressed in order to maximize their retention during the drying process, perhaps by devising innovative and alternative techniques.

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## **24 Neutraceutical properties of dried tropical fruits: guavas and papayas**

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### **24.1 Introduction**

Fruits and vegetables are of increasing economic importance due to their contribution to health promotion as “functional” foods. Thus, they are capable of not only providing basic nutritional requirements, but also an array of phytochemicals that may prevent or delay onset of chronic diseases [1, 2]. Inadequate intake of fruits and vegetables in the diet has now been recognized as one of the top 10 leading global disease burden risk factors [3]. Epidemiological studies have shown that a high intake of fruits can lower the occurrence of cardiovascular diseases (CVD), stroke, and cancer [4].

Fruits are broadly classified as temperate, Mediterranean-subtropical, and tropical. Tropical fruits originate from the warm climate of the tropics where the temperatures remain relatively constant throughout the year. It is predicted that world production of tropical fruits is likely to expand over the next 10 years. More than 3000 types of tropical fruits with production of approximately 140 million tonnes are produced annually worldwide [5]. Amongst them, avocados, bananas, mangos, papayas, and pineapples have the largest global production. Worldwide tropical fruit utilization per capita has improved by 33% in the last two decades [6].

Many of the tropical fruits have high moisture content ( $>80\%$ ) with short storage life, leading to their easy spoilage and infection [7]. It is estimated that about 40% of fruit production is wasted due to poor post-harvest management [8, 9]. To overcome this wastage, processing of fruits to increase their shelf life is an alternative. Worldwide markets of processed fruits have constantly increased due to the improved quality, convenience of ready-to-serve products, and availability of seasonal commodities, which has been expanded by processing [10].

Drying is the most common, cost effective, and viable processing method. It provides an alternative to expensive preservation methods such as cold storage. It is the oldest method to preserve fruits by selectively removing water, thus preventing microbial spoilage and quality deterioration due to undesirable biochemical reactions [11]. Dried fruits are being used traditionally and appreciated for their convenience and usefulness [12]. Dried fruits

also have wider application as they are included in many breakfast cereal-based packages to offer more nutritious products besides providing an appealing color. In addition, dried fruits have been regarded as alternative fat-free snacks for health conscious consumers. Among popular dried fruits, raisins, currants, plums, figs, and prunes may be included. Dried fruits are more concentrated with nutrients and are easily available throughout the year, retain the characteristics as natural products, easy to handle and stored with reduced transportation cost [10, 11]. Moreover, drying reduces fruit wastes and post-harvest losses, and allows the whole fruit to be used in production by the food industry. The dried fruit industry maintains the potential to contribute to the well-being of the country through substituting a natural product in place of the highly refined foods [13].

During drying, increase in solid concentration due to the removal of water and partial inversion of sucrose occurs in fruits having a high acid content. This leads to more hygroscopic dried fruits with altered texture, taste, and appearance. Reaction of reducing sugars with nitrogen compounds (Millard reaction) imparts a brown color and caramel-like flavor to the dehydrated products. In addition, due to loss in some volatile compounds, a difference in flavor between fresh and dried fruits is noticed [10]. However, the existing literature has focused more on fresh products, their nutritional qualities and health benefits than their dried counterparts. Therefore, information on some dried fruits is scarce. Hence, in the present chapter we have focused to review the nutritional qualities, bioactive compounds, and health benefits of dried tropical fruits with special emphasis on dried guavas and papayas. This information will be useful for researchers, food industries, and nutritionists. A comparison with fresh fruits is also provided, when possible.

## 24.2 Guavas

Guavas (*Psidium guajava* L.) belong to the family *Myrtaceae*. The tree is indigenous to Central America, South America, Mexico, India, and Caribbean. Guava pulps are sweet and have a white or deep pink color with many seeds of variable number and their texture depends on the species [14, 15]. Guavas are commercially used in the production of juice, jam, puree, marmalade, ice cream, cookies, and several bakery products, among others.

### 24.2.1 Nutritional composition of dried guavas

Nutritional compositions of dried guavas are given in Table 24.1. Osorio *et al.* [16] developed a guava powder by hot-air drying and freeze drying. Both powders were rich in pectin and had a good retention of guava aroma. Guava powders obtained from hot-air drying had moisture and crude fiber content of 5.3 and 47%, respectively. In addition, guava powders obtained by freeze drying had lower moisture (2.75%), but a higher crude fiber (54.5%) content. Munhoz *et al.* [17] extracted pectin from dried pulp and peel of guavas. They developed an optimized method for extraction of pectin using 5% citric acid, 60 minute extraction time, and a temperature of 97°C. Under these conditions, the yield of pectin was more than 11%. Pectins from dried guava slices were analyzed by Tsai *et al.* [18]. Dried guavas were rich in total pectin (6108 ppm), cold water soluble pectin (3384 ppm), hot water soluble pectin (841 ppm), and hot acid soluble pectin (111 ppm).

Nutritional composition of sun dried by-product of guavas, consisting of seed, pulp, and fruits, was analyzed by El-Deek *et al.* [19]. The products had a moisture content of 6.94%,

**Table 24.1** Nutritional composition of dried guavas

Nutritional composition	Product	g/100 g	Reference
Moisture	Guava powder	2.7–5.3	[16]
	Dried fruit	6.9	[19]
	Dried guavas	13.8	[21]
	Freeze-dried pulp	7.0	[10]
Protein	Dried fruit	9.7	[19]
Carbohydrate	Dried fruit	33.0	[19]
Fat	Dried fruit	4.5	[19]
Crude fiber	Guava powder	47.0–54.5	[16]
	Dried fruit	40.0	[19]
Ash	Dried fruit	5.6	[19]
Pectin	Dried pulp and peel	11.0	[17]
	Guava slices	61.0	[18]
Vitamin C	Freeze-dried pulp	3.0	[10]

while their crude protein, carbohydrate, and lipid were at 9.78, 33, and 4.52%, respectively. Meanwhile, their crude fiber, ash, and calcium were 40, 5.62, and 0.37%, respectively. Chemical characteristics such as pH, soluble solids, total acidity, protein, lipids, fiber, ash, moisture, and total and reducing sugars of cookies enriched with guava fibers were evaluated by Matias *et al.* [20]. Marques *et al.* [10] estimated some nutritional content (moisture, vitamin C, phosphorus, and calcium) of fresh and freeze-dried guavas pulps. The nutritional quality of freeze-dried guava pulps was reported as follows: moisture (7%), vitamin C (30 mg/100 g), phosphorus (9.69 mg/100 g), and calcium (12.49 mg/100g). Dried guavas had a moisture content of 13.8%, total sugar (16%), and titratable total acidity (5.7%), as reported by Sanjinez-Argandona *et al.* [21].

Queiroz *et al.* [22] reported the loss of vitamin C and other minerals (sodium, potassium, calcium, magnesium, zinc, and manganese) during the dehydration process of dried guavas. A reduction in mineral content (20–64%) and vitamin C (32–68%) was noticed. Retention of vitamin C in freeze-dried guavas was more (63%) than air-dried (25%) and vacuum-dried (58%) products [23]. Degradation of ascorbic acid and carotenoids in osmotic pre-treated and convective-dried guavas was investigated by Sanjinez-Argandona *et al.* [21]. The results showed that the degradation values for carotenoid varied from 66 to 70% and ascorbic acid from 20 to 35% of the original values in osmotic pre-treated and dried guavas, respectively. Effects of cyclic air temperature on moisture and ascorbic acid content of dried guava pieces were also evaluated by Chua *et al.* [24].

The color change of dried guavas during blanching increased with increasing temperature and immersion time. For a 90 second immersion, the total color change increased by 400% between 80 and 95°C. Red color of guavas was also deepened after air drying when osmotic dehydration was applied as pre-treatment. The *L* and *a* values were increased during vacuum drying while no significant changes were noticed for the *b* value compared to the fresh samples. This could probably be due to the browning reaction and pigment destruction [14]. Chemical [total soluble solids (TSS), acidity, color, pH, aroma, appearance, flavor, and

texture] and sensory properties of fresh and osmotically dehydrated guavas were analyzed by Queiroz *et al.* [25]. Dried samples showed alteration in color values compared to the osmotic dehydration. Sensory qualities of osmotically dehydrated samples were also most preferred to those of air-dried guavas. Guava tea sample was found to have a higher color retention (*L*, *a*, *b*) as investigated by Lee *et al.* [26].

With regard to texture, penetration tests show that osmotically dehydrated guavas require 109% more force than air-dried guavas. Blanching prior to osmotic dehydration could decrease the penetration force by 15%, while ascorbic acid and calcium lactate increased the penetration force by 14.6 and 87.9%, respectively [14]. Dried guava slices treated with phenolic compounds such as gallic acid, ferulic acid, and caffeic acid retained a better hardness (1.25–1.60 folds) when compared to the control [18]. Sensory analysis of osmotically dehydrated guavas was more acceptable by consumers than air-dried guavas. Rating for osmotically dehydrated guavas was more than double that of the air-dried guavas for appearance, flavor, and texture [14].

### 24.2.2 Phytochemicals in dried guavas

Research on phytochemicals from dried guavas is very limited. Tea prepared from guavas was shown to have the highest phenolic (144.7 mg/g) and flavonoid contents (3.02 mg/g) [26] which was higher than that of the dried fruit. Gallic acid was the predominant phenolic acid present in guava tea (Table 24.2).

### 24.2.3 Antioxidant activity of dried guavas

Guava tea prepared from dried guavas exhibited a weaker antioxidant activity when compared to the extract of guava leaves [27, 28]. However, dried guava tea still exhibited a stronger antioxidant activity than the other commercial products, as evaluated by the linoleic acid method, especially at higher concentrations (Table 24.3). Although the exact mechanism of action as an antioxidant is not clear, it is believed that dried guava fruits may possess strong free-radical scavenging ability [28]. Table 24.4 summarizes the scavenging effects of dried guava fruits as compared to guava leaves and commercial tea. The inhibitory effect of dried guava on peroxyl radicals was increased with increase in the concentration, reaching 91% at higher concentrations.

**Table 24.2** Total phenolic and phenolic acid content of extracts from guava tea and guava dried fruit

<b>Samples</b>	<b>Total phenolic (mg/g)</b>		<b>Phenolic acid (μg/g)</b>	
	<b>Catechin equivalent</b>	<b>Gallic acid equivalent</b>	<b>Gallic acid</b>	<b>Ferulic acid</b>
Guava tea	177 ± 9.2	279 ± 14.0	1278 ± 92.7	234 ± 27.5
Guava dried fruit	69.6 ± 2.8	115 ± 4.2	266 ± 15.4	–
Tea polyphenon 60	643 ± 8.5	985 ± 12.8	–	–

Source: Adapted with permission from Chen and Yen [28].

Data expressed as means ± standard deviation (*n* = 3) on an extract.

**Table 24.3** Antioxidant activity (by linoleic acid method) of extracts from guava tea and guava dried fruit

Sample concentration ( $\mu\text{g/mL}$ )	Peroxidation (%) <sup>a</sup>		
	Guava tea	Guava dried fruit	Tea polyphenon 60
50	17.8 $\pm$ 2.6	49.9 $\pm$ 2.7	17.8 $\pm$ 1.8
100	4.7 $\pm$ 0.2	11.6 $\pm$ 0.8	10.1 $\pm$ 1.1
150	3.7 $\pm$ 0.2	7.3 $\pm$ 0.3	11.3 $\pm$ 0.4
200	4.5 $\pm$ 0.1	4.8 $\pm$ 0.2	13.1 $\pm$ 0.4
500	6.2 $\pm$ 0.2	0.7 $\pm$ 0.1	19.5 $\pm$ 1.2

Source: Adapted with permission from Chen and Yen [28].

Data expressed as means  $\pm$  standard deviation ( $n = 3$ ) on an extract.

<sup>a</sup>A lower peroxidation indicates higher antioxidant activity.

#### 24.2.4 Health benefits of dried guavas

There is a growing interest in guavas and their effects on human health. They have been used in traditional medicine around the world. They are claimed to be beneficial in the treatment of hypertension and diabetes, act as anti-inflammatory, pain relieving, and wound-healing agents and improve diarrhea, and reduce fever [27]. Other parts of guava that have been extensively studied are dried leaves, root barks, fresh ripe fruits or extracts of the whole fruits, or plants, but limited studies have been carried out on dried fruit components [27].

Much of the health benefits of guavas in any form of the plant have been attributed to their phytochemical components such as flavonoids and phenolics that possess strong antioxidant activity [28]. This is also governed by the content of phytochemicals present.

Increased production of free radicals causes oxidation in the cells which play a key role in CVD, cancer initiation, cataract formation, aging process, inflammatory diseases, and a variety of neurological disorders [29]. The antioxidant defence system in dried guavas may potentially protect against oxidative damage by preventing radical formation, repair oxidative damage, eliminate damaged molecules, and prevent mutation [30].

The hypothetical protective effect of dried guavas against oxidation is consistent with an experimental study conducted in healthy young adults [31] and in an animal model [32].

**Table 24.4** Scavenging effects (by peroxy radicals) of extracts from guava tea and guava dried fruit

Sample concentration ( $\mu\text{g/mL}$ )	Scavenging effects (%)		
	Guava tea	Guava dried fruit	Tea polyphenon 60
2.5	37.9 $\pm$ 2.4	16.6 $\pm$ 7.3	90.6 $\pm$ 6.7
5	66.8 $\pm$ 1.7	44.0 $\pm$ 4.3	89.2 $\pm$ 4.0
10	90.5 $\pm$ 3.3	79.3 $\pm$ 6.6	79.0 $\pm$ 4.6
25	89.0 $\pm$ 4.9	89.2 $\pm$ 2.3	62.9 $\pm$ 5.7
50	78.7 $\pm$ 8.0	91.2 $\pm$ 4.2	39.8 $\pm$ 5.7

Source: Adapted with permission from Chen and Yen [28].

Data expressed as means  $\pm$  standard deviation ( $n = 3$ ) on an extract.

using either fresh guava fruits or guava purees. In both studies, consumption of fresh guavas [31] or guava purees [32] resulted in a significant increase in the plasma antioxidant levels and reduced oxidative stress as indicated by decreased level of glutathione peroxidase and glutathione reductase [31].

Aside from their phytochemical properties, dried guavas are also high in fiber. Isolated dietary fiber, particularly pectins in fresh guavas have been shown to have hypocholesterolemic effect in humans [33]. However, the contribution of dried guava fibers in their specific hypolipidemic effect has not yet been studied.

Fresh guavas are also potassium-rich fruits and their consumption has benefited patients with hypertension [33]. As the drying process of dried guavas promotes loss of vitamins and minerals [22], their potential hypotensive role has yet to be elucidated.

### **24.2.5 Commercial products from dried guavas**

Dried guava slices are available in the markets in Southeast Asia [5, 14]. Osorio *et al.* [16] developed two types of guava powders by hot-air drying and freeze drying. Both powders were rich in pectin and had a good retention of guava aroma. These two guava powders can be used as value-added food products and as alternatives to fresh guavas. Dry guava by-products can be used in poultry feed and also as value-added products [19]. Krasaekoopt and Suthanwong [34] developed probiotic food by fortifying probiotics (*Lactobacillus casei*,  $10^8$ – $10^9$  log cfu/g) in partially dried guava pieces. Ready to use dehydrated products such as slices and leather was developed by Sagar and Kumar [35]. Osmotic drying considerably increased the sugar content and reduced the acidity without causing any significant changes in color, texture, and original flavor of the slices. Guava leather was also prepared from guava pulp [35].

Tea prepared from guavas can be consumed as a safe drink as well as a chemopreventing agent [26]. Cookies enriched with guava fibers are developed with a high rate of acceptability in flavor relation [20]. A clarified guava juice powder was obtained using different drying methods such as freeze drying, spray drying, and tunnel drying. The freeze-dried product had a superior quality; however, the spray-dried product was more stable and may be economical for industrial exploitation [36].

## **24.3 Papayas**

Papayas (*Carica papaya L.*) belong to the family of *Caricaceae*. They are an important fruit crop grown in the tropical and subtropical regions of the world. Their production is next to mangos, bananas, citrus fruits, and pineapples at a global level [37]. The fruits are very nutritious (rich in vitamins and carotenoids) and have good taste, color, and aroma. They are usually eaten fresh, or are processed into juice, jam, jellies, fruit salad, ice cream, canned, or frozen forms [38–40].

### **24.3.1 Nutritional composition of dried papayas**

Effect of osmotic pre-treatment on vitamin C, texture, and color of osmotically dehydrated papayas was studied by Lemus-Mondaca *et al.* [41]. Treatment with a 40–50% sucrose solution enhanced retention of vitamin C with improved color and texture quality. The

**Table 24.5** Nutritional composition of fresh, sliced, and dried papaya fruits (values in per 100 grams edible portion)

Samples	Units	Juice	Fresh slices	Dried slices
Energy	kJ	836	867	163
Fat	g	0.51	0.53	0.10
Fiber	g	1.8	1.6	2.6
Vitamin A (RAE)	μg	85.6	380	8.8

Source: Adapted with permission from Gouado *et al.* [43].

Data expressed as means ( $n = 3$ ) on a fresh weight basis.

RAE, retinol activity equivalents.

nutritional quality of dried cereal flakes containing ripe papayas is as follows: moisture (1.08%), acidity (0.34), total sugars (60%), reducing sugars (56%), ascorbic acid (241 mg/100 g), and carotenoids (7.3 mg/100 g) [42]. Nutritional composition of fresh, sliced, and dried papayas are presented in Table 24.5 [43]. Dried papaya slices had higher fiber content than fresh slices.

Vitamin C content has been reported to be higher in freeze-dried (88%), vacuum-dried (86%), carbon dioxide-dried (82%), and nitrogen-dried (80%) than fresh papaya fruits [23]. The nutritional qualities of freeze-dried papayas have been found to be lower than fresh ones (Table 24.6) [10]. Kamaruzzman *et al.* [44] investigated the nutritional composition of dried papaya skin and found that protein (25.2%) and sugars (65%) were dominant components. Aspartic acid and glycine were the major amino acids found in dried papaya skin (Table 24.7). Proximate composition of dried papaya skin was also evaluated by Fouzder *et al.* [45]. Effect of drying on vitamin A, vitamin C, total sugars, and moisture content of dried papaya powders was studied by Mugula *et al.* [39]. A significant loss in vitamin A (97%), vitamin C (98%), total sugars (86.8%), and moisture content (84.2%) was noticed in dried papaya powders when compared to those of fresh papayas (Table 24.8).

### 24.3.2 Phytochemicals in dried papayas

Dried papaya in cereal flakes are rich in ascorbic acid (241 mg/100 g) and low in carotenoids (7.3 mg/100 g) [42]. Carotenoid composition of fresh, sliced, and dried papayas is given

**Table 24.6** Nutritional characteristics of fresh and freeze-dried papaya pulps

Samples	Nutritional composition		Mineral composition	
	Moisture (g/100 g)	Vitamin C (mg/100 g)	Phosphorus (mg/100 g)	Calcium (mg/100 g)
Fresh papayas	89.8	87.2	9.3	13.8
Freeze-dried papayas	0.8	66.1	6.6	13.9

Source: Adapted from Marques *et al.* [10].

Data expressed as means ( $n = 3$ ) on a fresh weight basis.

**Table 24.7** Nutritional characteristics of dried papaya skin

Nutrient	(g/100 g)
<b>Proximate composition</b>	
Moisture	91.0
Crude protein	25.2
Crude fiber	6.7
Lipids	2.1
Ash	1.0
Nitrogen free extract	65.0
<b>Amino acids</b>	
Alanine	0.62
Arginine	0.48
Aspartic acid	2.60
Glutamic acid	1.50
Glycine	3.00
Isoleucine <sup>a</sup>	0.41
Leucine <sup>a</sup>	0.77
Lysine <sup>a</sup>	0.79
Phenylalanine <sup>a</sup>	0.39
Serine	0.60
Threonine <sup>a</sup>	0.36
Tryptophan <sup>a</sup>	0.02
Tyrosine	0.29
Valine <sup>a</sup>	0.52

Source: Adapted with permission from Kamaruzzaman *et al.* [44].

Data expressed as means ( $n = 3$ ) on a dry weight basis.

<sup>a</sup>Indispensable amino acids.

in Table 24.9. Among them, lycopene is the predominant one followed by  $\beta$ -carotene, cryptoxanthin,  $\alpha$ -carotene, and zeaxanthin [43]. Sian and Ishak [46] studied carotenoid concentration of dried papayas at various blanching temperatures and found that they decreased with increase in blanching temperature. The carotenoid concentration ranged from 99.4 to 85.8  $\mu\text{g/g}$  dry weight. In addition, anthocyanin content was also reduced from 9.2 to 6.7  $\mu\text{g/g}$ , with increase in blanching temperature.

**Table 24.8** Effect of drying on nutritional characteristics of fresh and dried papaya powders

Samples	Units	Fresh papaya	Sun dried	Oven dried
Moisture	g/100 g	93.8	15.24 (83.8)	14.85 (84.2)
Total sugar	g/100 g	171.7	22.7 (86.8)	22.9 (86.9)
Vitamin A (RAE)	mg/100 g	13.39	0.41 (97)	0.93 (92)
Vitamin C	mg/100 g	812.9	20.3 (97.5)	5.1 (98.1)

Source: Adapted with permission from Mugula *et al.* [39].

Numbers in parentheses represent percentage nutrient loss compared to fresh sample.

Data expressed as means ( $n = 3$ ) on a dry weight basis.

RAE, retinol activity equivalents.

**Table 24.9** Carotenoid compositions of fresh, sliced, and dried papaya fruits

Samples	Units	Juice	Fresh slices	Dried slices
α-Carotene	µg/100 g	368	83	nd
β-Carotene	µg/100 g	3427	668	93.7
Lycopene	µg/100 g	5081	581	188
Cryptoxanthin	µg/100 g	1885	635	24
Zeaxanthin	µg/100 g	83	99	tr

Source: Adapted with permission from Gouado *et al.* [43].

Data expressed as means ( $n = 3$ ) on a fresh weight basis.

nd, not detected; tr, trace.

### 24.3.3 Antioxidant activity of dried papayas

Antioxidant activity (*in vitro* and *in vivo*) of dried papaya juices was also evaluated by Mehdipour *et al.* [47]. Dried papaya juices exhibited excellent 1,1-diphenyl-2-picrylhydrazyl (DPPH) scavenging activity in a dose-dependent manner. The highest inhibition was 80% at a concentration of 17.6 mg/mL. In addition, using animal models, lipid peroxidation was reduced by 35, 39, and 40% at dosages of 100, 200, and 400 mg/kg per day, respectively. Furthermore, total antioxidant power in the blood was also significantly improved (11–24%) as compared to the control and vitamin E (18%) groups [47].

### 24.3.4 Health benefits of dried papayas

Similar to the guava fruits, papayas have also been widely used in traditional medicine to improve digestion problems, as a wound-healing agent and as a folk remedy for contraception and abortion. In a survey conducted by Adebisi and Bello [48], they found that dried papayas have been the primary herbs used as a traditional male contraception method in South-West Nigeria.

Aqueous and ethanolic extracts of dried papaya fruits have some hepatoprotective capability in animal models [49]. These extracts inhibited harmful effects of carbon tetrachloride that may induce hepatotoxicity [49]. This protection effect could be due to the decreasing levels of serum bilirubin and several liver-related enzymes such as serum alanine aminotransferase, aspartate aminotransferase, and alkaline phosphatase. Interestingly, consumption of dried papaya extracts showed remarkable reduction in necrosis and degeneration of liver cells, when compared with the control in histopathological studies on rat liver [49, 50].

Indeed, combined mixtures of dried papayas and dried kales at a ratio of 40:60% produced a positive prebiotic and intestinal anti-inflammatory effect in a rat colitis model [51]. The prebiotic effect was achieved by increasing the colony count of *Lactobacillus* and *Bifidobacterium*. On the other hand, intestinal anti-inflammatory activity of the same mixture played a significant role for necrosis reduction in colitis of rats [51].

In addition to the above, regular consumption of papayas and their products (in the form of either juices or dried fruits) would improve vitamin A status of human beings. Gouado *et al.* [43] demonstrated that frequent consumption of fresh, juice, and dried papayas increased serum retinol levels in the Cameroon population. However, as compared to dried papayas, fresh fruits and juice forms were found to be more beneficial and this could be due to the bioavailability of carotenoids which was better in the fresh forms than in the dried products.

The anti-ulcer activity of alcoholic extracts of dried papayas has been investigated in an animal model [52]. In this study, improvement in ulcer was assessed by measuring the volume of gastric secretion, free acidity, total acidity, and ulcer index. This study showed that dried papaya extracts had anti-ulcer effect as indicated by decreasing the volume of gastric acid secretion, free acidity, total acidity, and ulcer index with respect to the control group [52].

### **24.3.5 Commercial products from dried papayas**

Cereal flakes were developed from ripe papayas [42]. They had a good shelf life of 60 days (at refrigerated storage) with good sensory qualities. Dried pickles were developed by Trongpanich *et al.* [53]. Fernandes *et al.* [54] used ultrasonic pre-treatment to remove sugars for production of dehydrated papayas. Krasaekoopt and Suthanwong [34] developed probiotic food by fortifying probiotics (*Lactobacillus casei*,  $10^8$ – $10^9$  log cfu/g) in partially dried papaya pieces. Sulfur dioxide and glycerin-treated dried papayas were developed by Buenz and Fuatai [13] and these have the potential to be profitable value-added agricultural products. Restructured fruit was made from concentrated papaya pulps, with the addition of other ingredients such as sugar, sodium alginate, pectin, and glycerol. They were cut in a solid cylindrical form, dehydrated, and covered with icing sugar [55]. In addition, papaya cubes [56] and papaya powders [39] have been developed. The powder can be used as a beverage drink with acceptable sensory qualities. Dry papaya skins can also be used as a dietary ingredient for broiler chickens [45].

## **24.4 Conclusions**

Dried fruits help in reduction of fruit wastage and improve their shelf life. They are handy when needed and are packed with nutrients, specifically fiber and vitamin C, which could play a role to overcome nutrient deficiency. Since many of the dried fruits appear wrinkled with loss of valuable nutrients during the drying process, further studies are warranted to determine the most novel food processing method in minimizing nutrient loss while at the same time retaining their phytochemicals. Health claims of dried guavas and papayas have been extensively documented; however, proper studies either in animals or humans using these dried fruits in comparison with their fresh counterparts for the prevention and the management of chronic diseases are needed.

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## **25 Dried mangoes: phytochemicals, antioxidant properties, and health benefits**

Fouad Abdulrahman Hassan, Sadeq Hasan Al-Sheraji, and Amin Ismail

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### **25.1 Introduction**

Mangoes are one of the most popular tropical fruits in the world. They ranked fifth in total world production among the major fruit crops with world's annual production of 33.5 million metric tonnes (MT) in 2009 [1] and have been listed at the top of the superfruit list because of their health-promoting properties [2]. India is the world's largest mango producer followed by China, Thailand, Indonesia, Pakistan, Mexico, and Brazil. Most mangoes are consumed uncooked as a dessert fruit, the rest of them being processed into various products, such as nectar, juice powder, dried mangoes, canned mango slices in syrup, chutneys, and pickles, among others [3].

The majority of the mango species are indigenous and underutilized and have the potential to be further exploited and utilized commercially. Among the edible species are *Mangifera indica*, *M. caesia*, *M. foetida*, *M. odorata*, and *M. pajang*. Most of the fruit commonly known as mango belongs to the species *M. indica*. Other species such as *M. pajang*, an underutilized fruit, are found in Malaysia, Brunei, and Indonesia with size three times larger than commercial mangoes (*M. indica*). The physical characteristics of mangoes are almost similar. Several studies have reported that *Mangifera* species are rich in dietary fiber and phytochemicals in all their parts [4–8] and play an important role as antioxidants [9, 10].

It has been widely accepted that increased consumption of fruits, such as mangoes, could reduce the risk of cardiovascular diseases (CVD) and certain cancers, thus preserving the quality of life [11, 12]. In general, most of the fresh fruits contain more than 80% water that limits their shelf life and hence are more susceptible to deterioration. As such, preservation technique such as drying is most suitable to remove the water content of the fruits. The appearance of such dehydrated fruits has continually grown in national and international markets due to improved quality characteristics such as retention of the natural health-promoting compounds, prevention of the growth of microorganisms, and reduction of storage and transportation costs. This chapter reviews nutritional characteristics, antioxidant capacity, and health-promoting properties of dried mangoes (pulp and peels).

## 25.2 Compositional and nutritional characteristics of dried mangoes

### 25.2.1 Compositional characteristics

Table 25.1 shows the compositional characteristics of fresh and dried mango varieties. The average moisture content of *M. indica* powder has been reported to be 1% [13] and 4% [14]. *M. pajang* fibrous powder prepared from fibrous pulp contains less than 5% moisture [7]. For every 100 g edible portion *M. foetida* flesh contains 78 g moisture [15]. *M. pajang* peel powder has a relatively low moisture content of 4% [8]. The differences observed in the moisture content may be due to different drying methods used, variety/cultivar, and treatment processing for preparation of the powder.

Ash content of *M. indica* L. fiber (2.8%) [5] was higher than *M. pajang* fiber pulp of 0.84% [7]. Meanwhile the ash content of *M. pajang* juice powder was 3.3% [16], which is three times higher than *M. indica* juice powder [13]. This indicates that the intake of dried mango products will provide a good source of minerals.

Fresh mangoes contain about 2 g protein/100 g edible portion. Protein content of *M. pajang* juice powder (3.8%) [16] was higher than *M. indica* juice powder [13]. Furthermore, protein contents in *M. pajang* fiber and peel powder were 3.7% [7] and 4.6% [8], respectively. Edible portion of *M. foetida* flesh contained 0.8% protein [15].

Mangoes are one of the tropical fruits that contain relatively very low amounts of fat and are generally low in calories. Fat contents of *M. pajang* pulp, *M. pajang* juice powder, and *M. pajang* fibrous pulp are 1.98, 1.75, and 0.79% of dry sample, respectively. The fat content of *M. pajang* peel powder (2.9%) [8] was similar to those reported previously for *M. indica* peels [4, 5, 9].

The carbohydrate of *M. indica* L. (32.6% of dry sample) [5] was higher than 0.18% reported for *M. foetida* flesh [15], 4.1% for *M. pajang* pulp [7], 7.3% for *M. pajang* peel powder [8], and 29% for Indian mango peels [9]. Among fruits, *M. indica* had the highest amount of carbohydrate as compared to grape skins (3%) [20], citrus peel fiber (27%), and guava fiber (28%) [21].

**Table 25.1** Chemical composition (%) of fresh and dried mango varieties

Proximate composition	<i>M. indica</i> (fresh) [17, 18]	<i>M. indica</i> (powder) [13]	<i>M. pajang</i> (fresh) [16]	<i>M. pajang</i> (powder) [16]	<i>M. indica</i> (edible portion) [19]	<i>M. pajang</i> (peel powder) [8]	<i>M. pajang</i> (fibrous) [7]
Moisture	79.1	0.8	86.8	10.0	88.2	3.9	4.65
Protein	0.98	1.3	1.13	3.78	0.7	4.6	3.37
Fat	0.32	0.1	1.98	1.75	0.1	2.9	0.79
Ash	0.5	0.7	0.43	3.3	nd	2.7	0.84
Carbohydrate	15.6	95.8	21.0	76.1	11.6	7.3	4.02
SDF	1.0	nd	0.42	0.68	nd	33.4	9.05
IDF	1.0	nd	4.84	0.12	nd	38.8	78.5
Energy (kcal/100 g)	nd	389	429	335	nd	nd	nd

SDF, soluble dietary fiber; IDF, insoluble dietary fiber; nd, not detected.

**Table 25.2** Dietary fiber content of mango varieties and their valuable findings

Variety	Part	Valuable findings	Dietary fiber	Reference
<i>M. indica</i>	Peel	Rich source of dietary fiber	70.1	[4]
<i>M. indica</i>	Peel with pulp	Antiradical efficiency	28.1	[5]
<i>M. indica</i>	Peel	Improved antioxidant properties	51.2	[6]
<i>M. indica</i>	Whole fruit	Equal ratio of SDF/IDF	7.9	[22]
<i>M. indica</i>	Whole fruit	Rich source of soluble fiber	10.0	[18]
<i>M. indica</i>	Unripe, ripe peel	Highest DF found in ripe peel	45–78	[23]
<i>M. pajang</i>	Powdered juice	Rich in SDF	0.8	[16]
<i>M. indica</i>	Powdered juice	High content of fiber	1.4	[13]
<i>M. pajang</i>	Fibrous pulp	Rich source of insoluble fiber	88.0	[7]
<i>M. pajang</i>	Peel	Balance ratio of SDF/IDF		[8]
<i>M. indica</i>	Pulp	High content of crude fiber	3.7	[24]
<i>M. indica</i>	Peel	High pectin (SDF)	11–21	[25]
<i>M. indica</i>	Green, ripe fruit	Green rich in fiber	10.7	[26]

SDF, soluble dietary fiber; IDF, insoluble dietary fiber; DF, dietary fiber.

Ripe and unripe mangoes represent good sources of dietary fiber for consumers and the food industry. Table 25.2 lists the dietary fiber content in different parts of mangoes with their valuable finding. Dietary fiber fractions, neutral sugars (monosaccharides), uronic acids, and Klason lignin of *M. pajang* fiber pulp and powdered peel are shown in Table 25.3. The presence of uronic acids together with monosaccharides reported in mangoes indicated the presence of hemicelluloses (arabinoxylans, glucuronoxylans, and xyloglucans) and pectic substances associated with the cell wall matrix in *M. pajang* fibrous and peel powders.

**Table 25.3** Monosaccharide compositions of SDF and IDF in dried products prepared from mangoes of *M. pajang*

Monosaccharide	<i>M. pajang</i> fibrous pulp (% dry weight)		<i>M. pajang</i> peel (% dry weight)	
	SDF	IDF	SDF	IDF
Erythrose	0.14 ± 0.01	nd	nd	nd
Glucose	0.39 ± 0.01	4.46 ± 0.11	2.49 ± 0.23	1.15 ± 0.15
Galactose	0.05 ± 0.01	1.20 ± 0.06	0.80 ± 0.06	0.17 ± 0.01
Rhamnose	0.16 ± 0.01	1.65 ± 0.04	0.44 ± 0.02	0.20 ± 0.02
Arabinose	0.72 ± 0.02	18.47 ± 0.19	4.89 ± 0.28	3.05 ± 0.13
Mannose	1.51 ± 0.03	3.15 ± 0.12	12.49 ± 0.56	4.87 ± 0.22
Xylose	0.04 ± 0.01	0.99 ± 0.02	0.40 ± 0.14	0.09 ± 0.01
Fructose	nd	nd	0.15 ± 0.01	0.10 ± 0.01
Fucose	0.01 ± 0.01	0.26 ± 0.02	nd	nd
Neutral sugars	3.02 ± 0.11	30.18 ± 0.56	21.66 ± 0.32	9.63 ± 0.53
Uronic acids	5.83 ± 0.13	15.51 ± 0.17	11.75 ± 0.23	7.60 ± 0.11
Klason lignin	nd	33.11 ± 0.72	nd	21.51 ± 0.47
Total NSP	8.85 ± 0.24	78.80 ± 0.96	33.41 ± 0.32	17.26 ± 0.52

Source: Adapted from Al-sheraji *et al.* [7] and Hassan *et al.* [8].

Data expressed as means ( $n = 3$ ) on a dry weight basis.

SDF, soluble dietary fiber; IDF, insoluble dietary fiber; NSP, non-starch polysaccharide (neutral sugars + uronic acid); nd, not detected.

**Table 25.4** Mineral and vitamin contents of *M. indica* (values per 100 g edible portion)

Nutrient	Unit	Fresh mangoes [27]	Dried mangoes [13, 23]
<b>Minerals</b>			
Calcium	mg	11	48.4
Copper	mg	0.11	0.3
Iron	mg	0.16	2.2
Magnesium	mg	10	16.7
Manganese	mg	0.06	nd
Phosphorus	mg	14	nd
Potassium	mg	168	486
Selenium	µg	0.6	nd
Sodium	mg	1	732
Zinc	mg	0.09	0.12
<b>Vitamins</b>			
Vitamin C	mg	36.4	31.5
Vitamin E (ATE)	mg	0.90	33.7

ATE,  $\alpha$ -tocopherol equivalents; nd, not detected.

In addition, these dried mangoes have considerable amounts of mannose, arabinose, and galactose, which may be suggestive of the presence of arabinomannose, galactomannas, or other pectic monosaccharides.

### 25.2.2 Nutritional characteristics

The mineral and vitamin compositions of fresh and dried mangoes are listed in Table 25.4. Mangoes serve as a good source of potassium, phosphorus, calcium, magnesium, sodium, copper, iron, zinc, manganese, and selenium. Dried mangoes are rich in sodium, potassium, calcium, magnesium, sodium, copper, iron, and zinc [13].

Ascorbic acid content of *M. pajang* juice powder (132 mg/100 g) was higher than that of *M. pajang* pulp (46 mg/100 g) [16], *M. foetida* (47 mg/100 g) [15], *M. indica* pulp (18–65 mg/100 g), and *M. indica* pulp powder (63 mg/100 g) [14, 28]. Ascorbic acid content in *M. pajang* pulp and juice powder was similar to that previously reported for *M. indica* pulp [29]. During the drying process of fruits, several factors can affect the degradation of ascorbic acid such as pH, temperature, light, oxygen, metal catalysts, presence of enzymes, and drying methods [30]. Conventional drying method affects the quantity of ascorbic acid more than that of the freeze drying method [31].

## 25.3 Phytochemicals and antioxidant activity of dried mangoes

### 25.3.1 Antioxidant activity

Antioxidant components that include polyphenols, carotenoids, and ascorbic acid possess bioactivities. The antioxidant activity of *M. pajang* peel powder as determined by the 1,1-diphenyl-2-picrylhydrazyl (DPPH) and ferric-reducing antioxidant power (FRAP) assays

**Table 25.5** Antioxidant compounds of fresh and freeze-dried mangoes

	<b>Phenolic content (mg of GAE/100 g)</b>	<b>Ascorbic acid (mg/100 g)</b>	<b>β-Carotene (μg/100 g)</b>	<b>Reference</b>
Fresh	99.7 ± 8.7	8.36 ± 2.33	660 ± 61	[23]
Freeze-dried	76.6 ± 8.1	8.34 ± 1.74	487 ± 29	[35]

GAE, gallic acid equivalents.

exhibited a strong potency corresponding to that of butylated hydroxytoluene (BHT) and ascorbic acid. The antioxidant power of *M. pajang* peel powder was 1248 μg/mL compared to ascorbic acid (1318 μg/mL) [32], and the DPPH scavenging activity determined as IC<sub>50</sub> was 44 μg/mL [8]. Gorinstein *et al.* [33] found that commercial mango (*M. indica*) had higher antioxidant properties compared to other fruits. Fresh *M. foetida* fruit exhibited the highest antioxidant activity based on the FRAP and trolox equivalent antioxidant capacity (TEAC) assays followed by its fiber and powder [34]. Freeze-dried mangoes have low antioxidant activity as compared to the fresh pulp [35]. In contrast, Soong and Barlow [36] reported that freeze-dried mango flesh (*M. indica*) had a higher antioxidant activity as compared to that of its fresh counterpart. This could be due to differences in applying antioxidant assays, maturity of the fruit, and sample preparation. Mohamad Shofian *et al.* [35] have reported a comparison of antioxidant compounds (phenolic content, ascorbic acid, and β-carotene) between fresh and freeze-dried mangoes as shown in Table 25.5. They found no significant change ( $P > 0.05$ ) in ascorbic acid content of the fresh and dried mangoes.

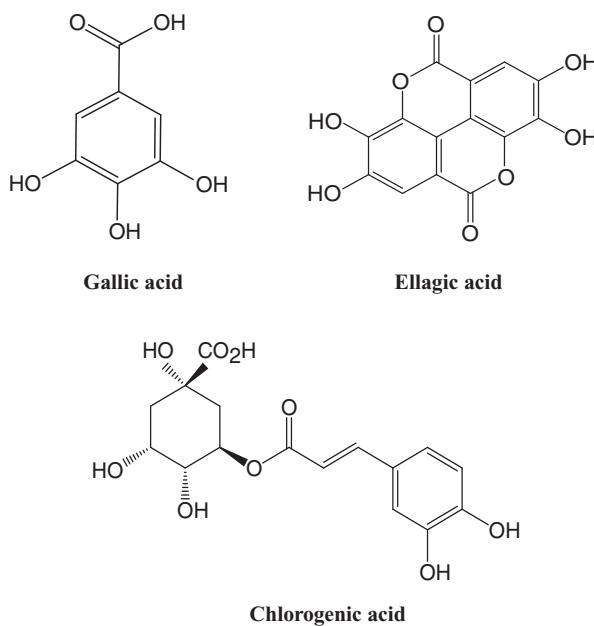
Mangoes exhibited strong antioxidant activity due to the presence of associated total phenolics. Total phenol content (16.1 mg of gallic acid equivalents (GAE)/g) in *M. indica* L. [5] was lower than that reported for *M. pajang* fibrous (30 mg of GAE/g). *M. indica* had a lower amount of total phenolics than those in Mexican lime (10.55 and 19.9 mg of GAE/g) [37] and guava (58.7 mg of GAE/g) [38], but higher than that of apple (3 mg of GAE/g) [4]. Total phenol content was different among the Ubá, Palmer, Haden, and Tommy Atkins cultivars grown in Brazil, being higher in Ubá mango pulp at 220 mg of GAE/g compared with the Palmer, Haden, and Tommy Atkins cultivars (130, 60, and 50 mg of GAE/g, respectively) [28]. The mango cultivars contained total phenol content that may contribute to increased antioxidant intake in the human diet, since the intake of polyphenolic compounds in the diet is estimated to range between 0.15 and 1.0 g/day [39, 40]. Total phenol content of *M. pajang* juice powder (0.19 mg of GAE/g) was lower than that of *M. pajang* pulp (0.26 mg of GAE/g) [16]. *M. pajang* pulp had a low phenolic content (48–87%) as compared to *M. indica* reported by Ribeiro *et al.* [28]. As reported earlier, the total phenol content for *M. pajang* was higher in peels and kernel fractions [10].

The total extractable polyphenol (TEP) content in the *M. pajang* peel powder was 98 mg of GAE/g [8], which is higher than that of Haden mango peel fiber (70 mg of GAE/g) [4], Mexican lime peels (19 mg of GAE/g) [37], guava peels (59 mg of GAE/g) [38], grape skins (37.6–52.2 mg of GAE/g) [20], and unripe *M. pajang* fruit peels (24 mg of GAE/g) [10], but similar to the TEP content of Indian mango peels (96.2 mg of GAE/g) [9]. The high level of TEP, which is distinct to *M. pajang* peel, had potential antioxidant activity. Freeze-dried mangoes had 23% lower TEP content compared to the fresh ones [35].

### 25.3.2 Phenolic acids

Plant foods are rich in phenolic acids. Hassan *et al.* [32] reported that phenolic acids, such as gallic acid and methyl gallate, have antimicrobial activity, controlling dental caries and periodontal disease. Other studies have reported that ellagic acid exhibits antimutagenic, antiviral, antitumor, and antioxidant properties, along with the ability to whiten the skin [32]. Among those identified in mangoes are gallic acid, benzoic acid, 3,4-dihydroxybenzoic acid, gallic acid methyl ester, gallic acid propyl ester, and benzoic acid propyl ester [41]. In mango pulp, gallic acid, *m*-digallic acid, gallotannin, mangiferin, and an unknown hydrolyzable tannin were detected [42]. During all stages of mango ripening, total phenolic acids were higher in the peels than in the pulp [43]. El-sissi *et al.* [44] identified some major components of phenolic acids (hydrolyzable tannins) in mango parts (pulp, peels, seeds, leaf, and stem bark extracts) which included gallic acid, methyl gallate, digallic acid, ellagic acid,  $\beta$ -glucogallin and  $\alpha$ -gallotannin at a low concentration.

Mangoes are a rich source of various phenolic acids [45]. The major polyphenols identified in mango (*M. indica*) pulp are mangiferin, gallic acids (*m*-digallic and *m*-trigallic acids), ellagic acid, and  $\beta$ -glucogallin derivative [42]. Gallic acid has been identified as the major polyphenol present in mango fruit pulp [46]. *M. pajang* peels had numerous phenolic acids such as gallic acid, ellagic acid, protocatechuic acid, 4-hydroxybenzoic acid, chlorogenic acid, vanillic acid, *p*-coumaric acid, ferulic acid, methyl gallate, and ethyl gallate [8]. Gallic acid was the major polyphenol in mango fruits [8, 47], with the highest amount in ripe mangoes as compared with other fruits [33]. The main phenolic acids found in mangoes are shown in Figure 25.1.



**Figure 25.1** Chemical structures of major phenolic acids detected in mangoes.

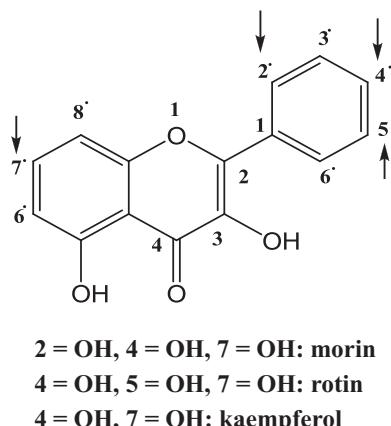
### 25.3.3 Flavonoids and xanthones

Flavonoids can be divided into several classes according to the degree of oxidation of the oxygen heterocycle: flavones, flavanones, flavonols, flavanols, isoflavones, anthocyanins, and proanthocyanidins. The flavonoids identified in mangoes are reported by Schieber *et al.* [42], who demonstrated the presence of quercetin and related glycosides in mango pulps, with the predominant flavonol glycoside, namely quercetin 3-galactoside, at 22.1 mg/kg, followed by quercetin 3-glucoside (16.0 mg/kg) and quercetin 3-arabinoside (5.0 mg/kg). The amount of quercetin aglycone was 3.5 mg/kg. Other flavonol glycosides, such as kaempferol, were also present in trace amounts.

Mangoes are a rich source of flavonoids and xanthones such as mangiferin, catechins, quercetin, kaempferol, and rhamnetin [45], flavonol, and xanthone [48]. Quercetin and isoquercetin are reported in *M. indica* pulp [42]. While quercetin, kaempferol, rhamnetin, mangiferin, mangiferin gallate, isomangiferin, and isomangiferin gallate can be found in *M. indica* peels [46], in *M. pajang* peels, flavonoids such as (+)-catechin, rutin, morin, daidzein, kaempferol, and xanthone mangiferin are present [8].

A study on mangoes by Berardini *et al.* [48] demonstrated that peels of the cultivar Tommy Atkins contained a large number of flavonol *O*- and xanthone *C*-glycosides including isomangiferin, mangiferin gallate, isomangiferin gallate, quercetin 3-*O*-diglycoside, quercetin 3-*O*-galactoside, quercetin 3-*O*-glucoside, quercetin 3-*O*-xyloside, quercetin 3-*O*-arabinopyranoside, quercetin 3-*O*-arabinofuranoside, quercetin 3-*O*-rhamnoside, kaempferol 3-*O*-glucoside, rhamnetin 3-*O*-galactoside, rhamnetin 3-*O*-glucoside, quercetin (aglycone), mangiferin, isomangiferin, mangiferin gallate, and isomangiferin gallate. Ribeiro *et al.* [49] identified some flavonol and xanthone compounds, including mangiferin, isomangiferin, mangiferin gallate, kaempferol, quercetin, and their related glycosides. Structures of some flavonoids present in mangoes are shown in Figure 25.2.

Catechins are also reported in some varieties of mangoes such as (+)-catechin, (−)-epicatechin, (−)-epigallocatechin, (−)-epicatechin gallate, and (+)-gallocatechin. The *M. indica* extract was rich mainly in catechin and epicatechin [41, 46, 50].



**Figure 25.2** Chemical structures of flavonoids found in dried mangoes.

The most prominent flavonoids present were anthocyanins which are universal plant colorants responsible for the red, purple, and blue color in many foods with over 600 structures identified [51]. In mango peels, anthocyanins have been estimated at 203–565 mg/100 g dry matter depending on the variety and stage of maturity [52].

### 25.3.4 Carotenoids

Carotenoids are classified into two main groups:

- (1) Carotene which are hydrocarbon molecules comprising only carbon and hydrogen atoms; this group includes  $\beta$ -carotene and lycopene [53].
- (2) Xanthophylls which are oxygenated derivatives of the carotenes and include lutein, zeaxanthin, isozeaxanthin, capsanthin, capsorubin, cryptoxanthin, astaxanthin, 3-epilutein, and canthaxanthin [53].

Mangoes are rich in carotenoids which are responsible for the yellow to orange color of ripe mango pulp and provide a high provitamin A and antioxidant activity. As shown in Table 25.6,  $\beta$ -carotene is generally the predominant carotenoid in mango pulps, comprising 48–84% of the total carotenoids [57]. Among the wide variety of carotenoids in mangoes, *all-trans*-violaxanthin is the predominant carotenoid followed by *all-trans*- $\beta$ -carotene [58]. The Haden variety had a total carotenoid significantly lower than that of the Tommy Atkins and Palmer varieties [28].  $\beta$ -Carotene content of Haden mangoes is similar to the one described in studies with the same variety cultivated in Brazil (494  $\mu\text{g}/100 \text{ g}$ ) [57].  $\beta$ -Carotene content of the evaluated mango pulps was higher than those described for other mangoes (49.8  $\mu\text{g}/100 \text{ g}$ ) [59]. Values obtained for total carotenoids for varieties of Tommy Atkins and Palmer were lower than those reported previously with the same mango cultivars obtained under experimental field conditions in Brazil [60].

Considering the vitamin A value expressed in retinol activity equivalents (RAE) [61], mangoes serve as a very good source of provitamin A. The RAE values for Haden, Tommy

**Table 25.6** Carotenoids found in mangoes and their byproducts

Variety	Type of carotene	Part	Content (mg/100 g)	Reference
<i>M. indica</i>	Total carotenoids	Edible portion	0.13	[54]
<i>M. indica</i>	Total provitamin	Edible portion	0.63	[54]
<i>M. indica</i>	Total carotenoids	Powdered peel	309	[6]
<i>M. indica</i>	Total carotenoids	Powdered peel	334	[9]
<i>M. indica</i>	Total carotenoids	Ripe powdered peel	395	[55]
<i>M. indica</i>	Total carotenoids	Unripe powdered peel	140	[55]
<i>M. foetida</i>	Total carotenoids	Edible portion	0.26	[15]
<i>M. pajang</i>	$\beta$ -Carotene	Powdered pulp	42.21	[16]
<i>M. pajang</i>	$\beta$ -Carotene	Powdered juice	35.60	[16]
<i>M. pajang</i>	$\alpha$ - and $\beta$ -carotenes	Powdered pulp	8 and 20	[56]
<i>M. pajang</i>	$\alpha$ - and $\beta$ -carotenes	Powdered peel	4 and 13	[56]
<i>M. indica</i>	$\beta$ -Carotene	Pulp	0.66–2.29	[28]
<i>M. indica</i>	Total carotenoids	Pulp	1.91–2.63	[28]
<i>M. indica</i>	$\beta$ -Carotene	Pulp	0.49	[57]

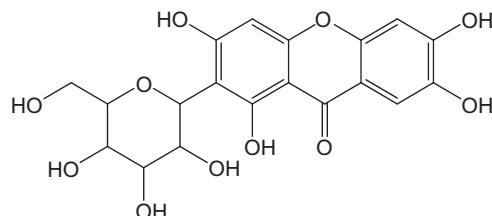
Atkins, Palmer, and Ubá cultivars were 74, 51, 55, and 185 µg/100 g, respectively. Mangoes of *M. foetida* contained 255 µg carotenes/100 g. β-Carotene content of *M. pajang* pulp, juice, and peel powder [16] was relatively high when compared to that reported for *M. indica* by El-sissi *et al.* [44]. A previous report showed that β-carotene was relatively unstable and often degraded during processing and storage [14]. α- and β-carotenes in *M. pajang* pulp were 8 and 20 mg/100 g, and 4 and 13 mg/100 g in its peels, respectively (Table 25.6). In adult men, the daily intake of one serving of pulp equivalent to 150 g of Haden, Tommy Atkins, Palmer, and Ubá varieties supplies 12, 6, 6, and 21%, respectively, of the recommended dietary allowance (RDA) of vitamin A [61].

## 25.4 Health benefits of dried mangoes

The dried mango fruits are generally stored for periods between 1 and 18 months [62, 63]. Fruits and vegetables consumption is associated with a reduced risk of heart disease and certain cancers [64, 65]. Mangoes have been reported to be rich in dietary fiber [4, 7–9] with associated antioxidants such as carotenoids and phenolic compounds [32, 42, 56]. The dietary fibers of mangoes are of interest to the food industry because of their health-promoting properties. It has been shown that high consumption of dietary fiber is associated with reduced incidence of disorders and diseases that are common in developed nations such as chronic bowel disorders, obesity, diabetes, CVD, and cancer [64]. Several studies reported that dietary fiber and naturally occurring antioxidants (obtained from fruits) are dietary factors involved in CVD risk reduction [66, 67]. Polyphenols are bioactive compounds that have protective effect against diseases such as coronary heart disease (CHD), cancer, and neurodegenerative disorders, mostly through their antioxidant properties [68]. The presence of mangiferin in mangoes has a wide range of pharmacological effects including hypolipidemic, antidiabetic, anti-HIV, antitumor, immunomodulatory, and antioxidant activities [32]. The chemical structure of mangiferin is presented in Figure 25.3.

### 25.4.1 Anticancer

Dietary fiber of mangoes has been associated with a number of health benefits. Soluble and insoluble dietary fibers are reported to have positive effects in reducing the incidence and severity of gastrointestinal disease and cancer [69]. Data on 25 plants including mangoes indicated strong antimutagenic properties in the plants [70]. The presence of polyphenols,



**Figure 25.3** Chemical structure of xanthone (mangiferin) detected in dried mango pulp, peels, and seeds.

carotenoids, and antimutagens in the mangoes suggests their potential anticancer activity. Whole mango juice and its extract demonstrate anticancer activity by inhibiting the growth cycle in an immortal cancer cell line. The 50% methanolic extract of mangoes was the only fraction that significantly arrested cells in the G0/G1 phase of the cell cycle [65].

### **25.4.2 Cardiovascular protective**

Ascorbic acid presented in mangoes provides protection against oxidative stress-related diseases such as CVD and in respiratory infection [71]. Among different food varieties,  $\beta$ -carotene in mangoes provides the highest vitamin A activity [28], which contributes to the protection against free radical-induced diseases. A study found that  $\beta$ -carotene inhibits the progression of atherosclerosis and cancer [72]. Flavonoids from *M. indica* successfully reduced lipid levels in serum and tissues of induced hyperlipidemia models. In addition, the plasma lecithin cholesterol acyltransferase (LCAT) level was elevated [73]. The activities of free radical-scavenging enzymes were significantly elevated and products of lipid oxidation significantly decreased in flavonoid-treated hypercholesterolemic rats [74].

It has been reported that *M. indica* L. (Vimang) increased extracellular superoxide dismutase activity and serum total antioxidant status. It also decreased serum thiobarbituric acid-reactive substances (TBARS). Components of the mango extract could be utilized by blood and endothelial cells [75].

Mangiferin extracted from *M. indica* decreased plasma total cholesterol triacylglycerols (TAG) and low-density lipoprotein (LDL) cholesterol and elevated high-density lipoprotein (HDL) cholesterol [76]. It has been found that mangiferin and epigallocatechin gallate (EGCG) isolated from *M. indica* protect erythrocytes from reactive oxygen species (ROS) production, contributing to the decrease in TBARS production [77]. The protective effect might be related to the strong radical-scavenging ability of mangiferin and EGCG. In addition, *M. indica* elevated bile acids in fecal excretion that reduced total cholesterol and LDL due to its mangiferin [78].

## **25.5 Conclusions**

Dried mangoes have valuable nutritional, antioxidant, and health-promoting properties comparable to their fresh counterparts. The dried products prepared from mangoes are of interest to the food industry as a food supplement, including prospective applications as functional food ingredients in cookies, crackers, confectioneries, and low-calorie products. Besides fresh mangoes, the dried forms could also serve as a rich source of nutrients and antioxidants. These health-promoting compounds present in dried mangoes could help managing and reducing the risk factors of degenerative diseases.

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## **26 Phytochemicals and health applications of dried passion and pineapple fruits**

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### **26.1 Introduction**

Passion flower, a vine species in the *Passifloraceae* family, is native to Paraguay, Brazil, and northern Argentina, which is now cultivated in most tropical and subtropical areas of the world as well as in a few temperate zones [1]. Eight countries (United States, Australia, Papua New Guinea, Fiji, South Africa, Kenya, Colombia, and Sri Lanka) account for 80–90% of the world production of passion fruits [2]. Passion fruit is round or ovaloid and apricot-sized (4–6 cm in diameter) at maturity, with a soft to firm, juicy, and aromatic interior filled with numerous seeds [1, 3, 4]. There are two recognized varieties, purple (*Passiflora edulis* Sims.) and yellow (*Passiflora edulis* Sims. f. *flavicarpa* Degener). Passion fruits are usually used for the processing of pulp and juice, and sometimes they are produced into dried fruit powder and dried fruit bar [5–12].

Pineapples (*Ananas comosus* (L.) Merr.) are another tropical and subtropical plant widely cultivated in many places including Hawaii, Philippines, Thailand, Malaysia, Mexico, South Africa, and China [13]. This plant is indigenous to South America and is by far the most economically important one in the *Bromeliaceae* family. Its juicy and aromatic fruit is oval to cylindrical-shaped, developing from many small fruits fused together. Pineapples are well known for their nutritive and health-promoting properties [14]. The fruit can be consumed fresh, but most of the production is used in processing. Canned slices, juices, concentrates, salads, and jams are common commercial products of pineapples in many countries [15, 16]. Some dried fruit products such as dried fruit pieces (chunks or dices) are also widely available in the market [17, 18].

This chapter reviews compositional and nutritional characteristics, phytochemicals, health benefits, commercial products, and industrial applications of the dried passion and pineapple fruits.

## 26.2 Compositional and nutritional characteristics of dried passion and pineapple fruits

Although dried passion fruits are not so frequently found in the market as are dried pineapples, they are good sources of nutrients. The basic nutritional compositions have been detected by several research groups (Table 26.1). Elmadfa *et al.* [19] determined the contents of proteins, fats, total sugars, fiber, vitamin C, some minerals (Fe, K, and Na), and phosphates in lyophilized passion fruits from Spain. Romero-Rodriguez *et al.* [4] further comprehensively analyzed nutritional compositions of lyophilized passion fruits from northwest of Spain. They reported that this lyophilized fruit contained proteins, fats, sugars (sucrose, glucose, and fructose), fiber, organic acids, vitamin C, and some minerals (Ca, Cu, Fe, K, Mg, Mn, Na, and Zn), and phosphates. From their investigation, passion fruits possessed relatively high content of dietary fiber with known health benefits. In the seeds of passion fruits, dietary fiber was especially high [20]. Twenty minerals in passion fruits (obtained from northeast China) after heated drying were also determined by Wang *et al.* [21] using inductively coupled plasma-emission spectroscopy (ICP-ES). Amongst them, Na (100 µg/g), K (10,810 µg/g), Ca (1410 µg/g), Mg (3160 µg/g), Zn (37.65 µg/g), Fe (93.96 µg/g), and Ge (82.12 µg/g) were abundant, while five common toxic elements, Cd, Hg, As, Cr, and Pb, were not detected.

**Table 26.1** The nutritional composition of lyophilized passion fruits

<b>Composition</b>	<b>Unit</b>	<b>References</b>	
		[19]	[4] <sup>a</sup>
Proteins	%	2.80	3.0
Fats	%	0.40	0.12
<b>Total sugars</b>	%	13.4	–
Glucose	%	–	2.1
Fructose	%	–	2.1
Sucrose	%	–	2.9
Fiber	%	1.50	12.8
Ash	%	–	0.5
<b>Organic acids</b>			
Citric acid	%	–	3.0
Malic acid	%	–	0.3
Vitamin C	mg/100 g	20.0	23.3
Phosphates	mg/100 g	54.0	63.8
<b>Minerals</b>			
Na	mg/100 g	28.0	8.0
K	mg/100 g	350	208
Ca	mg/100 g	–	6.8
Mg	mg/100 g	–	27.9
Fe	mg/100 g	1.1	0.6
Cu	mg/100 g	–	0.2
Zn	mg/100 g	–	0.5
Mn	mg/100 g	–	0.2

<sup>a</sup>Results are mean values of replicated determinations of six samples.

In the processing of pineapple fruits, osmotic dehydration (OD) is a common method for producing dried fruit products, because other drying techniques such as sun drying, heated air drying, or mechanical drying often influence sensory attributes (e.g., color, flavor, and texture) and even compromise the nutritional value of these products [22–24]. OD is widely used for the partial removal of water from plant tissues by immersion in a hypertonic (osmotic) solution. The driving force for the diffusion of water from the tissue into the solution is provided by the higher osmotic pressure of the hypertonic solution. The diffusion of water is accompanied by simultaneous counter diffusion of solute from the osmotic solution into the tissue [22, 25–27]. A most commonly used hypertonic solution is sucrose syrup during OD. Zheng [28] reported that fresh pineapple fruits contained approximately 13% sugars, 0.6% proteins, 0.6% organic acids, 0.3% fiber, 0.02% Ca, 0.9% Fe, and 0.01% P. The contents of vitamin A (60 IU), vitamin B<sub>2</sub> (120 mg/100 g), vitamin C (63 mg/100 g), Ca, Fe, and P are relatively high in passion fruits [28]. Additionally, pineapple fruits are also rich in a commercially important enzyme, bromelain, which possesses potent anticancer effects [29, 30]. After drying by OD, some nutritional substances can be lost from pineapple fruit. Peiró-Mena *et al.* [31] studied some compositional changes after 15 successive OD cycles and found that citric acid, majority of minerals (Ca, Mg, K, P, Na), and galacturonic acid (AGU) (related to pectin) in pineapple fruits decreased after each cycle (Table 26.2). Pineapple fruit bromelain is a cysteine endopeptidase which is unstable and prone to loss of activity after drying treatment [29].

### **26.3 Phytochemicals in dried passion and pineapple fruits**

There is an absence of report on phytochemicals in dried passion and pineapple fruits. However, some important chemical constituents in the two fresh fruits, such as carbohydrates, carotenoids, phenolic compounds, and other phytochemicals, have already been isolated, identified, and quantified. These chemical constituents may exist in the dried form as well.

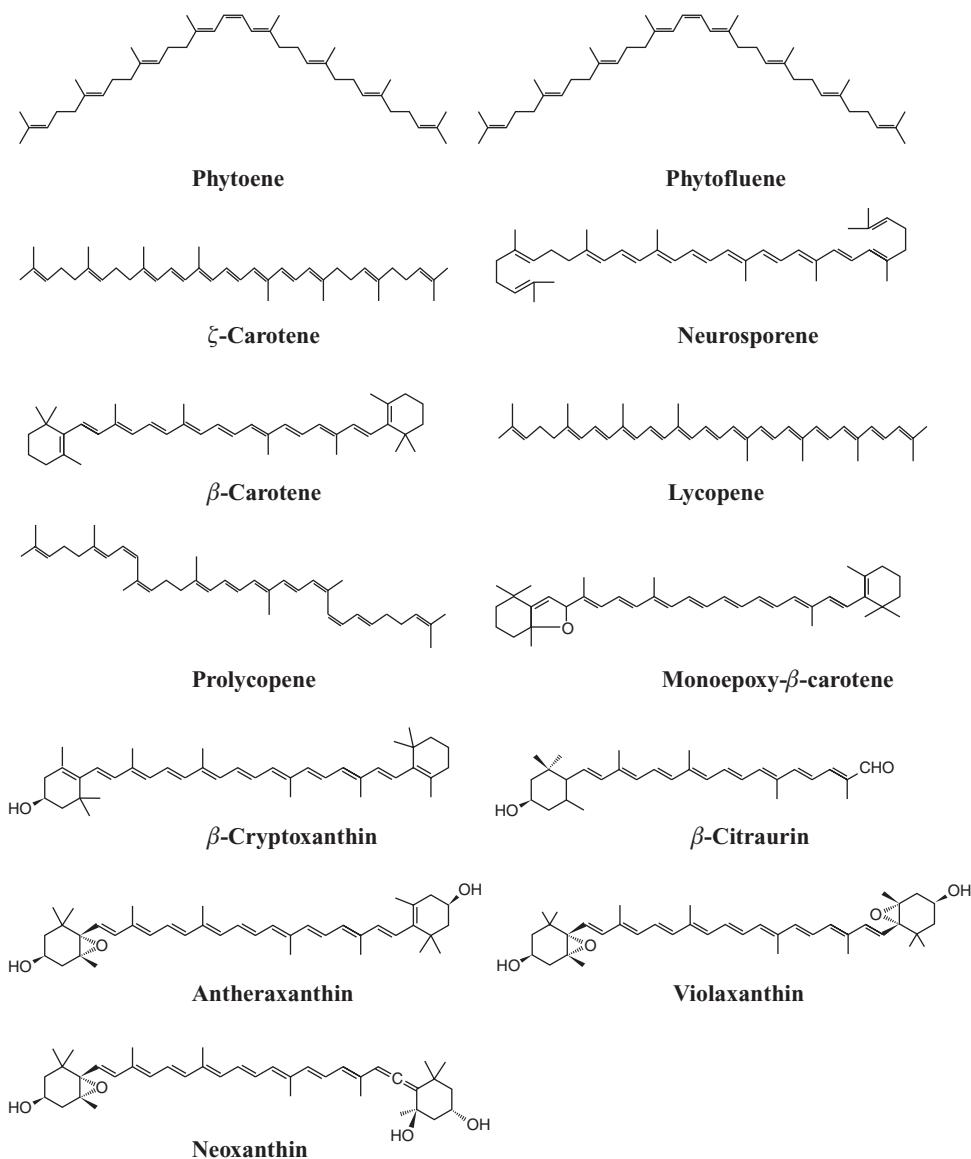
Carbohydrates constitute a major group of nutrients in passion fruits. Pruthi and Lal [32] reported that three sugars (glucose, fructose, and sucrose) together composed approximately 86.3% of the total carbohydrate makeup, the rest being starch. Cillie and Joubert [33] established that the passion fruit starch, belonging to the waxy type, was rather unusual in that it contained only 1–2% amylose and as such was almost a pure amylopectin in which the side chains had an average length of 17 glucose residues. Pectins mostly exist in passion fruit rinds and their chemical constituents mainly include D-galacturonic acid, L-arabinose, and D-galactose, among others [34]. Passion fruits have an orange-yellow color of juice which is due mostly to a complex mixture of carotenoid pigments [35]. Pruthi and Lal [36] reported variation range of the major groups of carotenoid pigments in purple passion fruits: free xanthophylls at 10.3–21.5%, xanthophyll esters at 11.1–34.6%, and epiphatic nonsaponifiables (mostly carotenes) at 45.7–76.3% of the total carotenoid pigments. No material difference was noticed in the carotenoid makeup of yellow and purple passion fruits except that total carotenoids and xanthophyll esters are usually higher in the former [37]. Mercadante *et al.* [38] further identified 13 carotenoids (phytoene, phytofluene,  $\zeta$ -carotene, neurosporene,  $\beta$ -carotene, lycopene, prolycopene, monoepoxy- $\beta$ -carotene,  $\beta$ -cryptoxanthin,  $\beta$ -citraurin, antheraxanthin, violaxanthin, and neoxanthin) from yellow passion fruits. Their chemical

**Table 26.2** Organic acids and mineral content of fresh pineapples [FP] and osmodehydrated pineapples (ODP)

Sample	Citric acid	Galacturonic acid	Ca	Mg	K	P	Na
FP <sub>1</sub> <sup>a</sup>	1016 ± 144	746 ± 5	26 ± 2	17 ± 1	167 ± 5	8.1 ± 0.4	3.4 ± 0.3
ODP <sub>1</sub> <sup>a</sup>	698 ± 28	542 ± 35	5 ± 1	11 ± 1	111 ± 14	5.4 ± 0.3	1.6 ± 0.2
ODP <sub>1</sub> <sup>b</sup>	790 ± 32	614 ± 40	6 ± 1	13 ± 1	126 ± 16	6.1 ± 0.4	1.8 ± 0.2
Loss <sub>1</sub> <sup>c</sup>	30 ± 13	27 ± 5	81 ± 6	32 ± 10	33 ± 8	33 ± 5	51 ± 8
FP <sub>3</sub> <sup>a</sup>	994 ± 50	857 ± 53	28 ± 2	19.5 ± 0.4	168 ± 7	6.8 ± 0.1	3.2 ± 0.5
ODP <sub>3</sub> <sup>a</sup>	674 ± 94	618 ± 66	18 ± 4	14.8 ± 0.2	71 ± 7	5.1 ± 0.3	2.4 ± 0.2
ODP <sub>3</sub> <sup>b</sup>	741 ± 103	699 ± 75	20 ± 5	16.3 ± 0.2	78 ± 8	5.6 ± 0.4	2.7 ± 0.2
Loss <sub>3</sub> <sup>c</sup>	32 ± 9	26 ± 3	36 ± 15	24 ± 1	58 ± 3	24 ± 5	23 ± 16
FP <sub>5</sub> <sup>a</sup>	1342 ± 59	751 ± 19	35 ± 3	20 ± 1	198 ± 5	9.8 ± 0.3	3.7 ± 0.5
ODP <sub>5</sub> <sup>a</sup>	884 ± 38	655 ± 45	6 ± 1	11.7 ± 0.3	93 ± 13	6.2 ± 0.2	1.9 ± 0.1
ODP <sub>5</sub> <sup>b</sup>	988 ± 42	741 ± 51	7 ± 1	13.4 ± 0.4	107 ± 15	7.1 ± 0.3	2.2 ± 0.1
Loss <sub>5</sub> <sup>c</sup>	34 ± 3	14 ± 7	82 ± 3	42 ± 3	53 ± 7	37 ± 3	48 ± 8
FP <sub>7</sub> <sup>a</sup>	1043 ± 148	804 ± 39	22.4 ± 0.2	18.5 ± 0.4	184 ± 11	6.1 ± 0.2	2.8 ± 0.4
ODP <sub>7</sub> <sup>a</sup>	684 ± 108	679 ± 49	9 ± 2	15 ± 1	142 ± 1	5.4 ± 0.4	1.8 ± 0.2
ODP <sub>7</sub> <sup>b</sup>	770 ± 118	768 ± 56	10 ± 2	17 ± 1	156 ± 2	5.9 ± 0.4	2.0 ± 0.2
Loss <sub>7</sub> <sup>c</sup>	34 ± 8	13 ± 10	61 ± 8	18 ± 3	23 ± 4	12 ± 9	36 ± 5
FP <sub>9</sub> <sup>a</sup>	942 ± 33	888 ± 62	29 ± 3	18 ± 1	195 ± 2	9.9 ± 0.3	3.0 ± 0.4
ODP <sub>9</sub> <sup>a</sup>	638 ± 39	662 ± 50	12 ± 1	12.8 ± 0.3	98 ± 9	5.9 ± 0.4	1.9 ± 0.1
ODP <sub>9</sub> <sup>b</sup>	729 ± 45	749 ± 57	13 ± 1	14.5 ± 0.3	112 ± 10	6.7 ± 0.4	2.2 ± 0.2
Loss <sub>9</sub> <sup>c</sup>	32 ± 2	26 ± 3	60 ± 9	29 ± 3	47 ± 3	40 ± 3	35 ± 13
FP <sub>12</sub> <sup>a</sup>	970 ± 27	932 ± 35	23 ± 1	17.3 ± 0.4	161 ± 3	7 ± 1	3.2 ± 0.2
ODP <sub>12</sub> <sup>a</sup>	660 ± 64	722 ± 37	16 ± 1	13 ± 2	92 ± 6	5.7 ± 0.3	1.9 ± 0.2
ODP <sub>12</sub> <sup>b</sup>	750 ± 73	817 ± 42	18 ± 1	14 ± 2	105 ± 7	6.4 ± 0.4	2.1 ± 0.2
Loss <sub>12</sub> <sup>c</sup>	32 ± 9	23 ± 1	28 ± 4	28 ± 10	43 ± 3	15 ± 6	41 ± 5
FP <sub>15</sub> <sup>a</sup>	994 ± 133	630 ± 50	25 ± 1	17 ± 1	151 ± 4	7.4 ± 0.3	3 ± 1
ODP <sub>15</sub> <sup>a</sup>	559 ± 44	571 ± 65	13 ± 3	15 ± 1	61 ± 8	4.3 ± 0.2	1.4 ± 0.1
ODP <sub>15</sub> <sup>b</sup>	634 ± 50	646 ± 73	15 ± 3	17 ± 1	69 ± 9	4.9 ± 0.3	1.5 ± 0.1
Loss <sub>15</sub> <sup>c</sup>	44 ± 4	10 ± 4	46 ± 12	11 ± 3	60 ± 4	42 ± 6	57 ± 11
Mean FP <sub>a</sub>	1043 ± 158	780 ± 112	27 ± 4	18 ± 1	174 ± 17	8 ± 1	3.2 ± 0.2
Mean ODP <sub>a</sub>	685 ± 112	615 ± 83	11 ± 5	13 ± 2	96 ± 25	5 ± 1	1.9 ± 0.3
Mean ODP <sub>b</sub>	772 ± 112	696 ± 93	12 ± 5	16 ± 2	108 ± 27	6 ± 1	2.1 ± 0.3
Mean loss <sup>c</sup>	34 ± 8	21 ± 9	59 ± 21	26 ± 10	44 ± 13	30 ± 12	41 ± 13

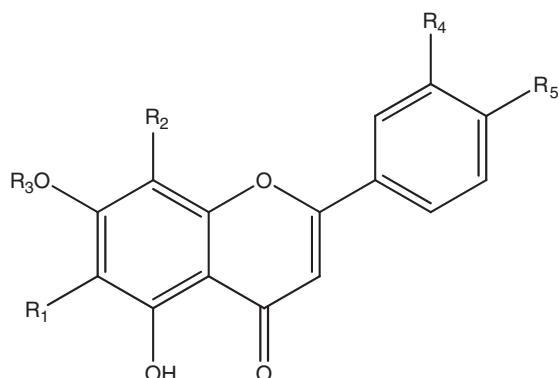
Source: Adapted with permission from Peiró-Mena et al. [31].

Data are expressed as means ± standard deviation ( $n = 3$ ).<sup>a</sup>mg component/100 g FP.<sup>b</sup>mg component/100 g ODP.<sup>c</sup>mg component loss/100 mg initial component.



**Figure 26.1** Chemical structures of carotenoids from yellow passion fruits.

structures are shown in Figure 26.1. A previous report [39] has described the presence of flavonoids as one of the major constituents in passion fruits, mainly *C*-glycosylflavones. The flavonoids schaftoside, isoschaftoside, isoorientin, orientin, isovitexin, luteolin-6-*C*-chinovoside, and luteolin-6-*C*-fucoside (Figure 26.2) have been identified from passion fruits. Polyphenols (Figure 26.3) mainly exist in passion fruit rinds (e.g., anthocyanins in purple passion fruit rinds: cyanidin-3-glucoside, quercetin-3-glucoside, pelargonidin-3,5-diglucoside, cyanidin-3-6''-malonyl glucoside, cyanidin-3-*O*- $\beta$ -glucopyranoside, and



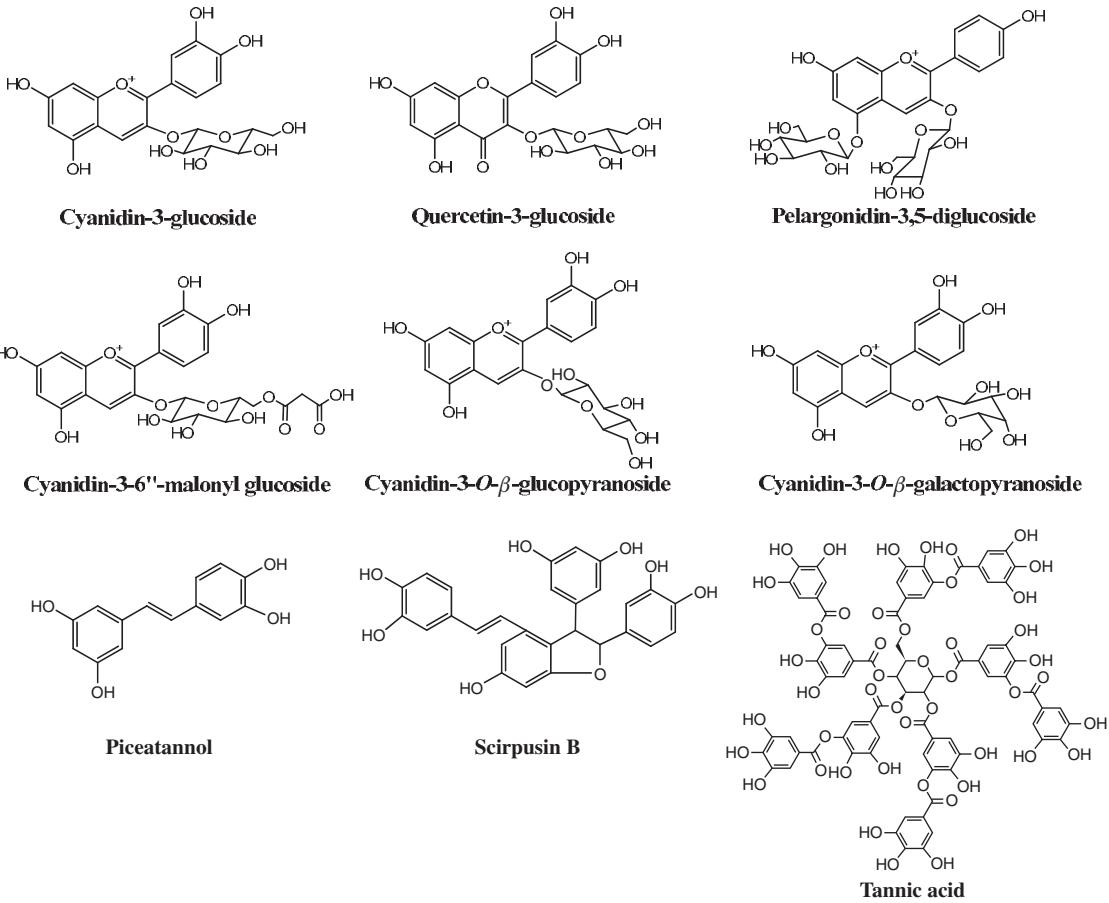
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>
<b>Schaftoside</b>	glc	ara	H	H	OH
<b>Isoschaftoside</b>	ara	glc	H	H	OH
<b>Isoorientin</b>	glc	H	H	OH	OH
<b>Orientin</b>	glc	H	H	OH	OH
<b>Isovitexin</b>	glc	H	H	H	OH
<b>Luteolin-6-C-chinovoside</b>	chinovose	H	H	OH	OH
<b>Luteolin-6-C-fucoside</b>	fucose	H	H	OH	OH

glc =  $\beta$ -D-glucopyranosyl; ara =  $\alpha$ -L-arabinopyranosyl

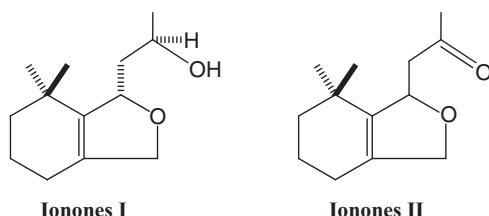
**Figure 26.2** Flavonoids identified from passion fruits.

cyanidin-3- $O$ - $\beta$ -galactopyranoside) and seeds (e.g., piceatannol and scirpusin B) [40, 41]. Fruit pulps only contain a few polyphenols, of which tannic acid has been found to be the major constituent [34]. In addition to the above-mentioned chemical constituents, there are other important phytochemicals in passion fruits. Two ionones I and II (Figure 26.4) have been isolated from passion fruits [41]. Additionally, Winterhalter [42] has identified a wide range of terpenoids (Figure 26.5) in purple passion fruits, including linalool, 4-hydroxy- $\beta$ -ionol, 4-oxo- $\beta$ -ionol, 4-hydroxy-7,8-dihydro- $\beta$ -ionol, 4-oxo-7,8-dihydro- $\beta$ -ionol, 3-oxo- $\alpha$ -ionol, isomeric 3-oxoretro- $\alpha$ -ionols, 3-oxo-7,8-dihydro- $\alpha$ -ionol, 3-hydroxy-1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene, vomifoliol, dehydrovomifoliol, and some monoterpenoids, among others.

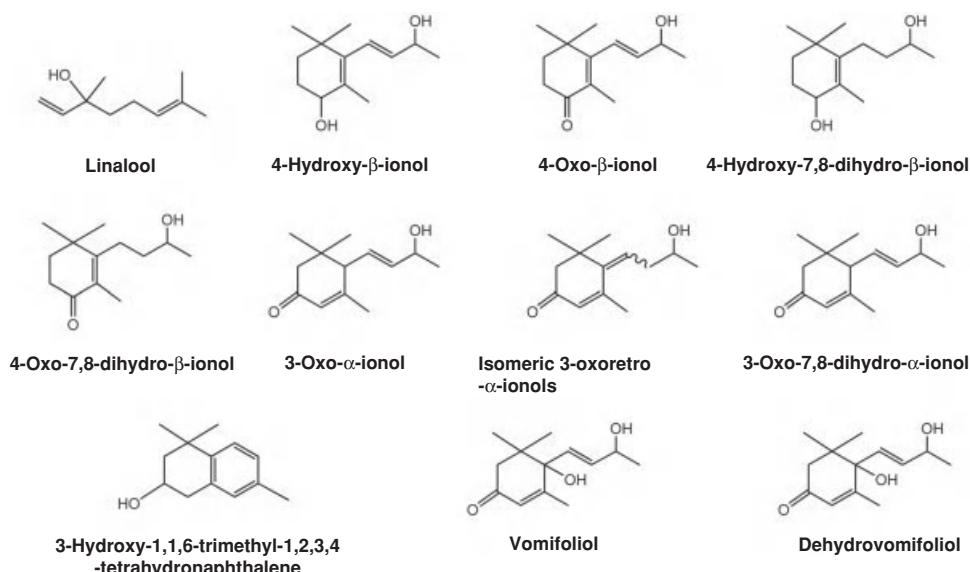
Pineapples contain unusual fiber components with specific physiological properties. Vidal-Valverde *et al.* [43] reported contents of dietary fiber, cellulose, hemicellulose, lignin, and pectic substances of pineapples, describing that they are very rich in hemicelluloses (41.8%). Polysaccharides isolated from pineapple flesh were chemically analyzed by Smith and Harris [44]. Glucuronoarabinoxylans were the major noncellulosic polysaccharides in pineapples. Xyloglucans were also present, together with small amounts of

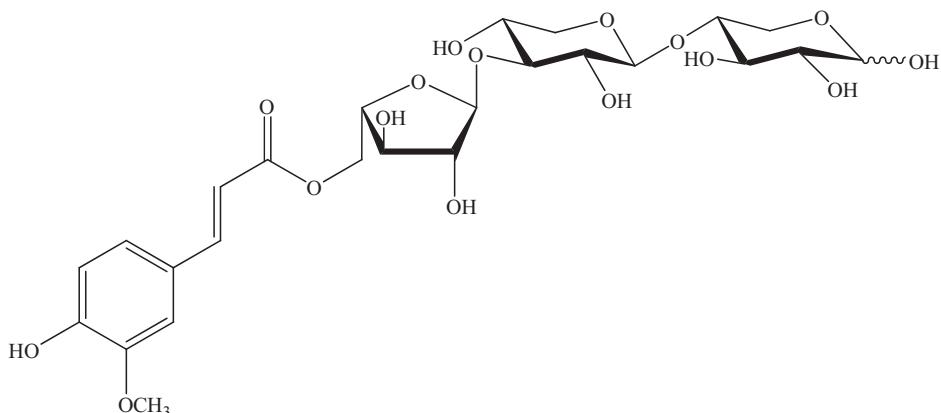


**Figure 26.3** Chemical structures of polyphenols from passion fruits.

**Figure 26.4** Chemical structures of ionones I and II from passion fruits.

pectic polysaccharides and glucomannans (or galactoglucomannans). They further indicated that ferulic acid was ester-linked to glucuronoarabinoxylans, and the most abundant feruloyl oligosaccharide released was *O*-[5-*O*-(E-feruloyl)- $\alpha$ -L-arabinofuranosyl](1 $\rightarrow$ 3)-*O*- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-D-xylopyranose (FAXX) (Figure 26.6) [45]. A “neutral” polysaccharide and an “acidic” one were also isolated by Bartolomé and Rupérez [46] from pineapples. The “neutral” fraction was composed of xylose, arabinose, glucose, galactose, and minor quantities of mannose. Yapo [47] reported that pectic polysaccharides in pineapple flesh consisted of homogalacturonans as well as type I and II arabinogalactan side chain-containing rhamnogalacturonan I. From pineapples, Zheng *et al.* [13] isolated and identified many phenolic compounds (Figure 26.7), such as (*S*)-2-amino-5-((*R*)-1-carboxy-2-((*E*)-3-(4-hydroxy-3-methoxyphenyl)allylthio)ethylamino)-5-oxopentanoic acid (compound 1), and (*S*)-2-amino-5-((*R*)-1-(carboxymethylamino)-3-((*E*)-3-(4-hydroxyphenyl)allylthio)-1-oxopropan-2-ylamino)-5-oxopentanoic acid (compound 2), *N*-[*N*-L- $\gamma$ -glutamyl-*S*-(3-(4-hydroxy-3-methoxyphenyl)-2-propenyl)-L-cysteinyl]-glycine (compound 3), *N*-L- $\gamma$ -glutamyl-*S*-sinapyl-L-cysteine (compound 4), *S*-sinapylglutathione (compound 5), *S*-sinapyl-L-cysteine (compound 6), sinapoylgucose (compound 7), 3-(4 $\beta$ -D-glucopyranosyloxy-3,

**Figure 26.5** Chemical structures of terpenoids from purple passion fruits.



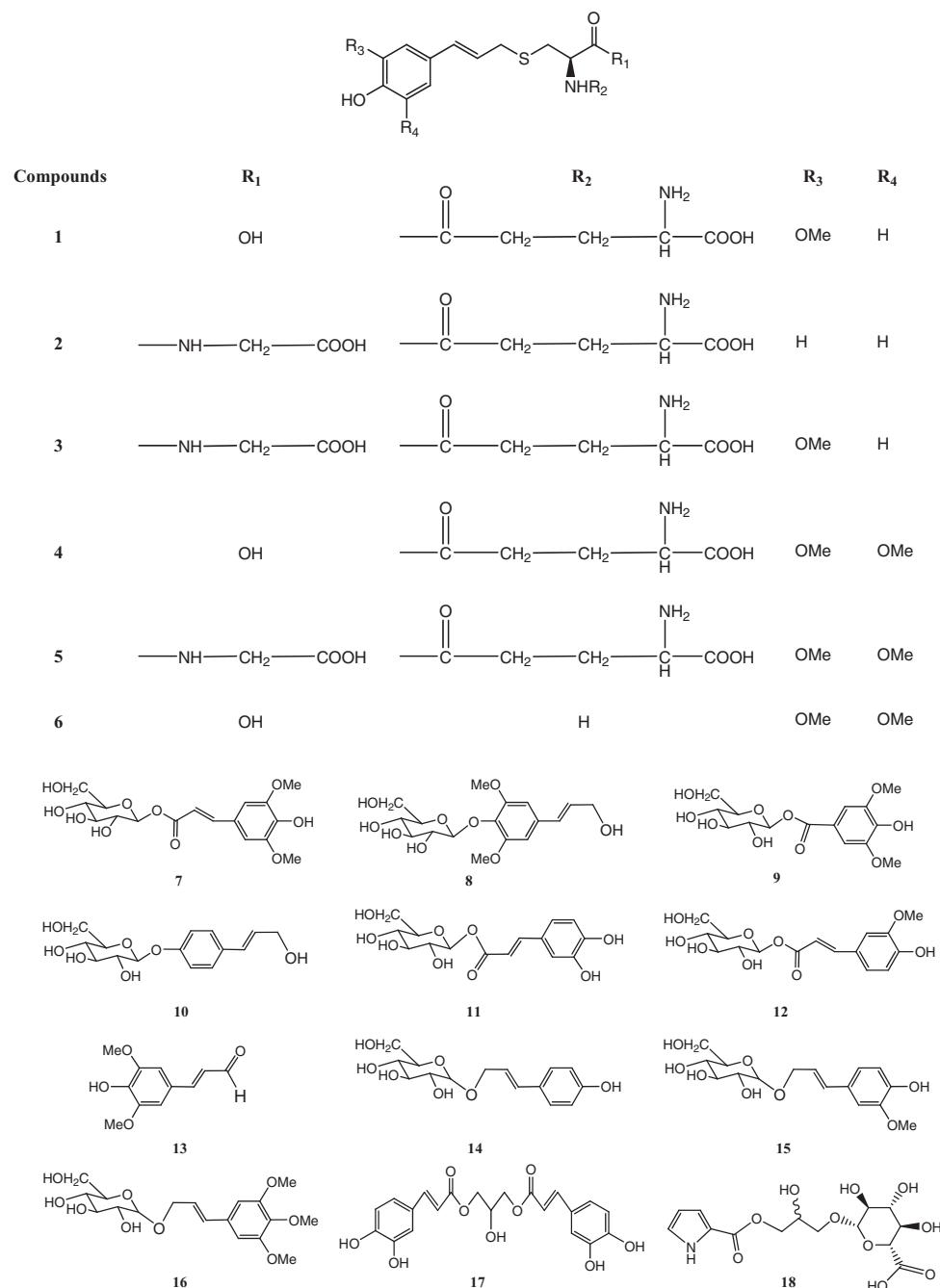
**Figure 26.6** Chemical structures of FAXX from pineapples.

5-dimethoxy)-phenyl-2*E*-propenol (compound **8**), erigeside C (compound **9**), *p*-coumaryl alcohol  $\beta$ -D-glucopyranoside (compound **10**), caffeoyl glucose (compound **11**), 1-*O*-feruloyl- $\beta$ -D-glucose (compound **12**), sinapyl aldehyde (compound **13**), triandrin (compound **14**), citrusin D (compound **15**), icariside H1 (compound **16**), ananasate (compound **17**) and so on, as well as one 1*H*-pyrrole-2-carboxylic acid derivative, 6-(3-(1*H*-pyrrole-2-carbonyloxy)-2-hydroxypropoxy)-3,4,5-trihydroxy-tetrahydro-2*H*-pyran-2-carboxylic acid (compound **18**). In addition, pure bromelain from pineapples is needed for the preparation of health-care products. Li and Lee [48] isolated and purified  $\alpha$ - and  $\beta$ -D-mannopyranosidases from crude pineapple bromelain.

## 26.4 Health benefits of dried passion and pineapple fruits

Dried passion and pineapple fruits are good natural sources for human health. Epidemiological and medical anthropological investigations have suggested that these two fruits have positive effects in the prevention or treatment of many diseases.

Passion fruits are known for many ethno-pharmacological properties. Dhawan *et al.* [41] summarized the research status of the genus *Passiflora* and described that passion fruits were regarded as digestive stimulant and were used as remedy for gastric carcinoma in Madeira, while this fruit was eaten for relief from constipation in Nagaland (India). Bezerra *et al.* [49] reported that the pulps of yellow passion fruits were commonly used as sedative, pain killer, and anti-inflammatory agent and also for the treatment of skin wounds and the healing of colonic anastomoses. Puricellia *et al.* [50] found that the decoction of purple passion fruits inhibited the activity of gelatinase matrix metalloproteinase-2 (MMP-2) and matrix metalloproteinase-9 (MMP-9), two metalloproteases involved in tumor invasion, metastasis, and angiogenesis. Additionally, a series of investigations have revealed that oral administration of purple passion fruit rind extracts (a mixture of bioflavonoids, phenolic acids, and anthocyanins) can attenuate blood pressure in hypertensive patients [51], reduce wheeze and cough and improve shortness of breath in adults with asthma [52], and reduce pain and

**Figure 26.7** Chemical structures of phenolic compounds from pineapples.

stiffness and improve physical function in adult patients with knee osteoarthritis [53]. On the other hand, Rebello *et al.* [54] reviewed the health benefits of yellow passion fruit rind extracts (containing pectin, tryptophan, grax acid, and amino acids) and reported that the studies in human beings suggested an effect of pectin on gastric emptying, protein metabolism in the digestive tract, reduction of cholesterol, glucose blood levels, and intestinal glucose absorption. Wen *et al.* [55] found that passion fruit rind extracts exhibited strong antioxidant capacity, which could effectively scavenge 1,1-diphenyl-2-picryl hydrazyl (DPPH) radical and hydroxyl radical. Besides pulps and rinds, the seeds in dried passion fruits also exhibit a good bioactivity. An antifungal protein, passiflin, was isolated from seeds by Lam and Ng [56], which impeded mycelial growth in *Rhizoctonia solani* and potently inhibited proliferation of Michigan Cancer Foundation-7 (MCF-7) breast cancer cells. Pelegrini *et al.* [57] also purified an antifungal peptide, *Passiflora edulis* antifungal peptide-1 (Pe-AFP1), from seed. *In vitro* assays indicated that Pe-AFP1 was able of inhibiting the development of the filamentous fungi *Trichoderma harzianum*, *Fusarium oxysporum*, and *Aspergillus fumigatus*.

In dried pineapples, polysaccharides, phenolic substances, and bromelain are important bioactive constituents. Guo [58] found that pineapple polysaccharides were good natural antioxidants which had the ability to scavenge hydroxyl radical and superoxide anion. Furthermore, he studied multiplication effects of pineapple polysaccharides on active *Bacillus bifidus* and found that these polysaccharides could adjust intestinal flora and improve intestinal environment. Dried pineapples contain dietary fiber which possesses some medical functions such as intestinal disease prevention, coronary heart disease (CHD) prevention, blood sugar level regulation, and cholesterol reduction, among others [59]. Binding of bile acids and increasing their fecal excretion has been hypothesized as a possible mechanism by which dietary fiber lowers cholesterol. Kahlon and Smith [60] indicated that pineapples presented a high bile acid binding and therefore possessed health-promoting potential. Phenolic substances in pineapples are known to promote human health, mainly due to their antioxidant activity. Mhatre *et al.* [61] revealed that pineapple core/pulp extracts exhibited strong antioxidant activity as evidenced by DPPH radical-scavenging, oxygen radical absorbance capacity (ORAC), and lipid peroxidation assays. Hossain and Rahman [62] also reported that flavonoids and other phenolics from pineapples exhibited high radical-scavenging activity. Table 26.3 shows total phenolic content and antioxidant activities of passion fruits and pineapples. Bromelain from pineapples is an especially important bioactive constituent which

**Table 26.3** Total phenolic content and antioxidant activities of passion fruits and pineapples

Samples	Total phenolic	DPPH radical (%)	References
<b>Passion fruits<sup>a</sup></b>			
Rind	28.11 ± 0.22	91.62 ± 1.60	[55]
Pulp	41.20 ± 4.20	89.51 ± 5.00	[63, 64]
<b>Pineapples<sup>b</sup></b>			
Rind	0.95 ± 0.01	87.60 ± 6.90	[65, 66]
Pulp	0.42 ± 0.00	93.70 ± 0.58	[65, 67]

DPPH, 1,1-diphenyl-2-picryl hydrazyl.

<sup>a</sup>Total phenolics are expressed as milligrams of gallic acid equivalents (GAE) per gram.

<sup>b</sup>Total phenolics are expressed as milligrams of tannic acid equivalents (TAE) per gram.

has diverse biological properties. Fruit bromelain can be used in various medical applications including prevention of diarrhea, as digestive aids, as antithrombotic, treatment of edema and osteoarthritis, and promotion of absorption of antibiotic drugs, and additionally it also regulates and activates various immune cells and their cytokine production [68, 69]. Existing evidence indicates that bromelain serves as a promising candidate for the development of future oral enzyme therapies for oncology patients [70].

## **26.5 Commercial products and industrial applications of dried passion and pineapple fruits**

Some commercial products of the dried passion fruits, such as freeze-dried fruits, dehydrated fruits, dried fruit powders, or dried fruit bars, have been found in markets in the United States, Brazil, India, China, Thailand, Colombia, and South Africa, among others. These products can be used by the food industry to produce functional foods and beverages, snack foods, sport drinks, as well as additives or flavorings for fruit jellies, sauces, candies, desserts, breakfast cereals, and yogurts, among others. The common commercial products of the dried pineapples in international markets include dried fruit pieces (chunks or dices), dried fruit rings, dried fruit powders, honey-dipped dried fruit slices, freeze-dried fruits, sweetened pineapple titbits, and chocolate-covered pineapples, among others. The major applications of these dried pineapple products are for healthy snacks, additives in breakfast cereals, trail mix, beverages, pancakes, and breads, as well as ingredients in recipes. Sometimes, they are added to leafy salads or for baking. Otherwise, there is currently an increasing interest on dried passion and pineapple fruits in pharmaceutical industry because of the health benefits arising from their phytochemicals.

## **26.6 Conclusions**

The consumption of dried tropical fruits is on the rise due to not only their good taste and aroma, but also the health benefits from their bioactive components. The investigations on nutritional compositions and phytochemicals have indicated that dried passion and pineapple fruits contain certain nutritional ingredients and bioactive constituents which are of great benefits to human health. Many compounds have been isolated and identified from these two fruits. Epidemiological and pharmacological evaluations have confirmed their positive effects on the prevention or treatment of some diseases. Several commercial products of both dried fruits have been sold in markets or used in food industry as additives and flavorings. Both dried fruits may also be potentially used by the pharmaceutical industry and beyond.

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