Antioxidants: Characterization, natural sources, extraction and analysis

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Review

Antioxidants: Characterization, natural sources, extraction and analysis

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ABSTRACT

Recently many review papers regarding antioxidants from different sources and different extraction and quantification procedures have been published. However none of them has all the information regarding antioxidants (chemistry, sources, extraction and quantification). This article tries to take a different perspective on antioxidants for the new researcher involved in this field. Antioxidants from fruit, vegetables and beverages play an important role in human health, for example preventing cancer and cardiovascular diseases, and lowering the incidence of different diseases. In this paper the main classes of antioxidants are presented: vitamins, carotenoids and polyphenols. Recently, many analytical methodologies involving diverse instrumental techniques have been developed for the extraction, separation, identification and quantification of these compounds. Antioxidants have been quantified by different researchers using one or more of these methods: in vivo, in vitro, electrochemical, chemiluminescent, electron spin resonance, chromatography, capillary electrophoresis, nuclear magnetic resonance, near infrared spectroscopy and mass spectrometry methods.

Contents

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1. Introduction

Antioxidants found in food are a heterogeneous category of molecules (Tuberoso, Boban, Bifulco, Budimir, & Pirisi, 2013). Antioxidants are compounds or systems that can safely interact with free radicals and terminate the chain reaction before vital molecules are damaged. They can use several mechanisms: (i) scavenging species that initiate peroxidation, (ii) chelating metal ions so that they are unable to generate reactive species or decompose peroxides, (iii) quenching $^*O_2^-$ preventing formation of peroxides, (iv) breaking the auto-oxidative chain reaction, and/or (v) reducing localized O_2 concentrations (Asimi, Sahu, & Pal, 2013).

The anti-oxidative effectiveness of these compounds depends on their chemical characteristics and physical location within a food (proximity to membrane phospholipids, emulsion interfaces, or in the aqueous phase) (Watanabe et al., 2000). Antioxidants (e.g., flavonoids, phenolic acids, tannins, vitamin C, vitamin E) have diverse biological properties, such as anti-inflammatory, anti-carcinogenic and anti-atherosclerotic effects, reduce the incidence of coronary diseases and contribute to the maintenance of gut health by the modulation of the gut microbial balance (Bartoszek & Polak, 2012; Boffetta et al., 2010; Cardona, Andrés-Lacueva, Tulipani, Tinahones, & Queipo-Ortuño, 2013; Díaz et al., 2012; Fernández-Marín et al., 2012; Fu et al., 2011; Hamrouni-Sellami et al., 2013; Li & Beta, 2011; Machmudah et al., 2012; Ratnasooriya & Rupasinghe, 2012; Strati & Oreopoulou, 2011; Toro-Funes et al., 2012).

The aim of this study is to describe: the main classes of antioxidants existing in fruit, beverages, vegetables and herbs; the different procedures to determine total antioxidant activity; and the different extraction, separation and quantification procedures used to evaluate their presence in food. The article tries to take a different perspective on antioxidants for the new researcher involved in this field, collecting important knowledge related to this topic.

2. Classification of antioxidants

Antioxidants cover different classes of compounds which can interfere with oxidative cycles to inhibit or retard the oxidative damage of biomolecules. The major classes of compounds with antioxidant activity are: vitamins (vitamin C and vitamin E), carotenoids (carotenes and xanthophylls) and polyphenols (flavonoids, phenolic acids, lignans and stilbenes).

2.1. Vitamins

2.1.1. Vitamin C

Vitamin C (L-ascorbic acid; here after, 'ascorbic acid' and 'ascorbate' refer to 'L-( )-ascorbic acid' and 'L-ascorbate' Fig. 1a) is unique among vitamins for several reasons. It is believed to be the most important hydrophilic antioxidant (Lykkesfeldt, 2000) being effective in scavenging superoxide radical anions, hydroxyl radicals, hydrogen peroxide, reactive nitrogen species and singlet oxygen. Vitamin C can acts as a reactive oxygen species (ROS) scavenger (>1000 mg/kg) and inhibits oxidation, however, at low levels, vitamin C (<100 mg/kg) can catalyze oxidation (in muscle tissue) (Ahn, Grün, & Mustapha, 2007).

Vitamin C has, at a structural level, 4 –OH groups which can donate hydrogen to an oxidizing system (Brewer, 2011). Resonance forms can also be written for the form of vitamin C that has lost one electron, making the radical semidehydroascorbate (SDA) much more stable, and thus much less reactive, than most other free radicals (Buettner, 1993).

The antioxidant mechanism of vitamin C was proposed by Bendich, Machlin, Scandurra, Burton, and Wayner (1986). At pH 7, the ascorbate anion (AH^-) is the predominant form present, due to the acidic nature of ascorbic acid (AH_2). This compound can undergo a reversible oxidation process and form dehydroascorbic acid (A), with ascorbyl radical formation ($A^{-\cdot}$). The ascorbyl radical is relatively unreactive and may react with other free radicals and the propagation of free radical reactions may be stopped (Eq. (1)):

$$2A^{-\cdot} + H^+ \rightarrow AH^- + A^{\cdot} \quad (1)$$

The reaction between the peroxyl radicals and ascorbate has been proposed as (Bendich et al., 1986):

$$ROO^{\cdot} + AH^- \rightarrow ROOH + A^{-\cdot} \quad (2)$$

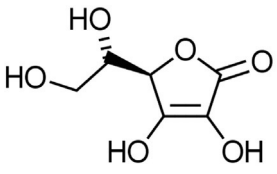
$$A^{-\cdot} + O_2 \rightarrow A + O_2^{-\cdot} \quad (3)$$

$$O_2^{-\cdot} + ROO^{\cdot} + H^+ \rightarrow O_2 + ROOH \quad (4)$$

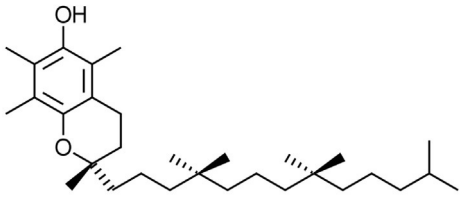
$$O_2^{-\cdot} + AH^- + H^+ \rightarrow H_2O_2 + A^{+\cdot} \quad (5)$$

$$A^{-\cdot} + ROO^{\cdot} + H^+ \rightarrow A + ROOH \quad (6)$$

In the case of in vivo cellular assays, ascorbate efficiency, is higher at low concentrations (one molecule of ascorbate can trap 2 molecules of peroxyl radical), while at high concentrations the efficiency decreases exponentially to 0 (Bendich et al., 1986). The superoxide anion (reaction 4) or the ascorbyl radical (reaction 6) reacts with a peroxyl radical at very low concentrations of ascorbate. At higher concentrations of ascorbate, reaction 4 propagation competes with the chain termination



a) Vitamin C



b) α - tocopherol

Fig. 1. a. Vitamin C. b. α-Tocopherol.

reactions 4 and 6. This "wastes" the ascorbate, and lowers its efficiency (Bendich et al., 1986). The European Food Safety Authoriy (EFSA, 2013) recommends a nutrient intake of vitamin C between 25 and 45 mg/day, depending on age. The main sources of vitamin C and its health benefits are presented in Table 1.

2.1.2. Vitamin E

The term vitamin E refers to a group of chemical compounds (tocopherols and tocotrienols). Vitamin E (Fig. 1b) is generally accepted to be the primary lipid-soluble antioxidant in humans and acts as an antioxidant via two primary mechanisms: (i) a chain-breaking electron donor (CB-D) mechanism and (ii) a chain-breaking acceptor (CB-A) mechanism. The antioxidant capacity of α-tocopherol has been studied (Thoo et al., 2013), observing that its activity depends on parboiling, storage and cooking (Pascual et al., 2013) and genotype (Beltrán et al., 2010).

Vitamin E is formed by four tocopherols and four tocotrienols, which exhibit chain-breaking antioxidant activity. The tocopherols group exhibit the antioxidant activity (Van Acker, Koymans, & Bast, 1993). Burton and Ingold (1981) proposed that the self-initiated autooxidation depends on the number of the phenol (ArOH) toward ($ROO^{\cdot}$), on the number of radicals trapped per phenol (n), and on the occurrence of chain transfer:

$$ArO^{\cdot} + RH \rightarrow ArOH + R^{\cdot} \quad (7)$$

The peroxyl radicals are being trapped:

$$ROO^{\cdot} + ArOH \xrightarrow{k_1} ROOH + ArO^{\cdot} \quad (8)$$

The phenoxyl radicals ($ArO^{\cdot}$) are resonance stabilized and do not continue the chain. In some cases the phenoxyl radicals may react with a second peroxyl radical:

$$ROO^{\cdot} + ArO^{\cdot} \xrightarrow{k_2} \text{molecular products} \quad (9)$$

k_1 and k_2—reaction rate constant.

The European Food Safety Authority (EFSA, 2010) indicates the recommended nutrient intake of vitamin E ranges from 8 to 25 mg/day, depending on age.

The main sources of vitamin E and its health benefits are presented in Table 1.

2.2. Carotenoids

At least 60 carotenoids occur in fruit and vegetables consumed by humans. The main carotenoids present in the daily diet are: α-, β-carotene and lycopene (as carotenes) and the hydroxy carotenoids (xanthophylls—zeaxanthin and lutein). Carotenoids are important not only for their provitamin A activity, but also for a spectrum of other actions in biological systems. Like tocopherols (Nowicka & Kruk, 2012), carotenes and xanthophylls are effective $^1O_2$ (singlet oxygen) quenchers (Ramel et al., 2012) and free radical (reactive oxygen species) scavengers (Böhm, Edge, & Truscott, 2012).

The singlet oxygen quencher mechanism of carotenes involves the conversion of singlet oxygen into heat via the carotene lowest excited triplet state (^{3}CAR) (Schmidt, 2004). While the reactions of carotenes with free radicals are much more complex and depend mostly on the nature of the free radical rather than the carotene. The mechanism involves three different reactions, as follows: electron transfer, adduct formation and hydrogen abstraction (Böhm et al., 2012).

The main sources of carotenoids and itshealth benefits are presented in Table 1.

2.2.1. Carotenes

2.2.1.1. β-carotene. β-carotene, a lipid-soluble provitamin, (Fig. 2a) is composed of two retinyl groups, and is broken down in the mucosa of the human small intestine to retinal, a form of vitamin A (Condron, Lemenager, Claeys, Lipkie, & Schoonmaker, 2014; Weber & Grune, 2012). It is one of the most powerful antioxidants, being capable of quenching singlet oxygen and inhibiting lipid oxidation (Samaniego-Sánchez, Quesada-Granados, de la Serrana, & López-Martínez, 2010).

The main sources of β-carotene and its health benefits are presented in Table 1.

2.2.1.2. Lycopene. Lycopene (Fig. 2b) with eleven conjugated and two non-conjugated double bonds is the most efficient singlet oxygen quencher of the natural carotenoids (Perretti et al., 2013). The many conjugated double bonds of lycopene make it a potentially powerful antioxidant (de Cortes Sanchez-Mata, 2013), a characteristic believed to be responsible for its beneficial effects. The antioxidant activity of lycopene is highlighted by its ability to trap peroxyl radicals (Chan & Hung, 2014). The main sources of lycopene and its health benefits are presented in Table 1.

2.2.2. Hydroxy-carotenoids (xanthophylls)

Xanthophylls are oxygenated carotenoids that are synthesized within the plastids and are commonly found as the yellow pigments of leaves. Lutein and zeaxanthin are structural isomers differing only in the configuration in one of the cyclohexene moieties that flank both terminal ends of both compounds. Lutein is chemically designated as β, ε-carotene-3, 3′-diol, while zeaxanthin is designated as β, β-carotene-3, 3′-diol (Pasaporte, Rabayam, Toleco, & Flores, 2014). The main sources of xanthophylls and its health benefits are presented in Table 1.

2.3. Polyphenols

Polyphenolic compounds are ubiquitous in all plant organs and are, therefore, an integral part of the human diet. In excess of 8000 phenolic structures have been reported and they are widely dispersed throughout the plant kingdom—many occur in food. Phenolics range from simple, low molecular weight, single aromatic ring compounds to the large complex tannins and derived polyphenols (Crozier, Jaganath, & Clifford, 2009). They are synthesized by the shikimate, polyketide and mevalonate pathways or mixed pathways, which produce the large variety of plant phenols. In the last part of 20th century, the interest in food phenolics has increased due to their antioxidant and free radical-scavenging abilities (Ahmed et al., 2015), anti-inflammation, modulation of signal transduction, anti-microbial and anti-proliferation activities (Velderrain-Rodríguez et al., 2014). Polyphenols may exert an indirect antioxidant effect, by protecting endogenous antioxidant enzymes in the human body (Pradeep & Sreerama, 2015; Zhang et al., 2015a, 2015b). Stevenson and Hurst (2007) suggest in their review that it appears that polyphenols can provide significant protection from oxidative stress in vitro at concentrations much lower than would be required for chemical antioxidant protection (Weichselbaum & Buttriss, 2010). The main mechanism by which dietary phenolic compounds play a role in preventing degenerative diseases are: NF-κB (nuclear factor kappa B) signaling pathway, activator protein-1 (AP-1—a redox sensitive transcriptional factor), Phase II enzyme activation and Nrf2 and mitogen-activated protein kinase (MAPK) signaling pathway (Crozier et al., 2009). The main groups of polyphenols are flavonoids, phenolic acids, phenolic alcohols, stilbenes and lignans (Oliveira, Carvalho, & Melo, 2014); their chemical structures are presented in Figs. 3–12.

The mechanism for the antioxidant activity of the polyphenols has been proposed by Leopoldini, Russo, and Toscano (2011). Firstly, the polyphenol molecule inactivates free radicals according to hydrogen atom transfer and to single electron transfer mechanisms.

Table 1
Natural sources of antioxidants and their health benefits.

Antioxidant		Natural sources	Health benefits
Vitamin C		• Apple (Bosch et al., 2013) • Banana (Bosch et al., 2013) • Bayberry (Yu, Lin, Zhan, He, & Zhu, 2013) • Broccoli (Rybarczyk-Plonska et al., 2014) • Citrus peel (de Moraes Barros et al., 2012) • Garlic (Di Cagno, Coda, de Angelis, & Gobbetti, 2013). • Orange juice (Remini et al., 2015) • Pear (Bosch et al., 2013) • Strawberry (Sapei & Hwa, 2014) • Tangerine (Bosch et al., 2013) • Peppermint (Curutchet, Dellacassa, Ringuelet, Chaves, & Vina, 2014) • Spearmint (Curutchet et al., 2014)	Vitamin C is of great interest due to the possibility of increasing the resistance of plasma to lipid peroxidation in the case of short and long term supplementation (Shahkar et al., 2015), in lowering serum uric acid levels, resulting in a correspondingly lower incidence of gout (Roddy & Choi, 2014), significantly decreases the risk of having a stroke (Yamagata & Tagami, 2015), and reduces the incidence of chronic and degenerative diseases (Wojcik, Burzynska-Pedziwiatr, & Wozniak, 2010)
Vitamin E		• Dabai (Azlan et al., 2010) • Grains (Gerstenmeyer et al., 2013; Okarter, Liu, Sorrells, & Liu, 2010) • Green tea (Yin, Becker, Andersen, & Skibsted, 2012) • Olives and olive oil (Azlan et al., 2010; Beltrán et al., 2010) • Palm oil (Azlan et al., 2010) • Pumpkin seeds (Butinar, Bučar-Miklavčič, Mariani, & Raspor, 2011) • Sunflower seeds and sunflower oil (Aladedunye & Przybylski, 2013)	Vitamin E is believed to be the primary components of the antioxidant system of the spermatozoa (Anel-López et al., 2012), and is one of the major membrane protectants against reactive oxygen species and lipid peroxidation (Yousef, 2010).
Carotenoids		• Grains (Gerstenmeyer et al., 2013; Mellado-Ortega & Dámaso, 2015) • Orange juice (Wibowo et al., 2015) • Parsley, celery, basil, coriander, dill (Pokorny & Panek, 2012) • Peppermint (Curutchet et al., 2014) • Spearmint (Curutchet et al., 2014)	Carotenoids have been shown to play a range of roles in the prevention against various health disorders, including cancer,metabolic disease and possibly cardiovascular disease (Jomova & Valko, 2013)
Carotenoids	β-carotene	• Amaranth (Gautam, Platel, & Srinivasan, 2010) • Dark green leafy vegetables (Lemmens et al., 2013) • Gac (*Momordica cochinchinensis* Spreng) (Kubola, Meeso, & Siriamornpun, 2013) • Olive oil (Samaniego-Sánchez et al., 2010) • Red carrots (Gautam et al., 2010; Lemmens et al., 2013; Zaccari, Cabrera, Ramos, & Saadoun, 2015) • Sweet potato (Laurie, van Jaarsveld, Faber, Philpott, & Labuschange, 2012).	It has been reported that β-carotene is associated with positive influence on certain types of cancer (Greenlee, 2012) and cardiovascular diseases (Key, 2011).
	Lycopene	• Apricots, grapefruit, guava, watermelon, papaya and carrots (Zuknik, Norulaini, & Omar, 2012) • Tomatoes (Ilahy, Hdider, Lenucci, Tlili, & Dalessandro, 2011; Lavelli & Torresani, 2011; Choi et al., 2014)—the peel contains five times more lycopene than tomato pulp (Machmudah et al., 2012) • Gac (*Momordica cochinchinensis* Spreng) (Kubola et al., 2013)	Lycopene prevents several pathologies, such as: cardiovascular disease (Riccioni et al., 2012), obesity (Kim et al., 2012) and some cancer types (de Groot & Munden, 2012).
Carotenoids–xanthophylls		• Spinach (Pasaporte et al., 2014) • Kale (Arnold, Jentsch, Dawczynski, & Böhm, 2013) • Zea mays (Pasaporte et al., 2014) • Carrot (Pasaporte et al., 2014)	Lutein and zeaxanthin are strongly associated with visual health and are also involved in reducing the risk of developing cardiovascular diseases (Pasaporte et al., 2014)
Polyphenols			
Flavonoids		• Grains (Gerstenmeyer et al., 2013; Okarter et al., 2010; Taleon, Dykes, Rooney, & Rooney, 2014) • Honey (Alvarez-Suarez et al., 2012; Oroian, 2012) • Orange juice (da Silva et al., 2013) • Tsaoko amomum fruit (Lu, Yuan, Zeng, & Chen, 2011) • Drumstick (*Moringa oleifera*) (Moyo, Oyedemi, Masika, & Muchenje, 2012) • *Stevia rebaudiana* leaves (Periche, Castelló, Heredia, & Escriche, 2015)	The intake of flavonoids is inversely associated with subsequent cancer (Chen & Chen, 2013; Kurzawa-Zegota, Najafzadeh, Baumgartner, & Anderson, 2012).
Flavonols		• *Vitis vinifera* grape berry skins (Alcalde-Eon et al., 2014; Liang et al., 2014a, 2014b) • Green tea (Bae, Ham, Jeong, Kim, & Kim, 2015; Song et al., 2011; Yin et al., 2012) • Wine (Liang et al., 2014a, 2014b) • Green prickleyash (Lu et al., 2011) • Sichuan pepper (Lu et al., 2011) • Fennel (Lu et al., 2011) • Onion (Kühn, Wollseifen, Galensa, Schulze-Kaysers, & Kunz, 2014) • Drumstick (*Moringa oleifera*) (Moyo et al., 2012)	Studies have shown that quercetin, which is the major flavonol present in onions, exhibits anti-cancer, anti-inflammatory, anti-viral activity, and may also prevent cardiovascular disease in humans (Caridi et al., 2007; Santos et al., 2014).
Flavones		• Citrus peel (de Moraes Barros, de Castro Ferreira, & Genovese, 2012) • Trollflowers (Sun et al., 2013) • Onion (Rehman et al., 2013) • Parsley (Kaiser, Carle, & Kammerer, 2013) • Corn silk (*Zea mays* L.) (Liu et al., 2011a, 2011b)	The flavones have antioxidant (Voicescu, Nistor, & Meghea, 2015), anti-cancer (Yuan et al., 2012), anti-inflammation (Hou & Kumamoto, 2010), neuroprotective (Yu, He, & Du, 2012), anti-diabetes (Singh et al., 2014), anti-ulcer (Sumbul, Ahmad, Mohd, & Mohd, 2011) and anti-microbial effects (Sagrera, Bertucci, Vazquez, & Seoane, 2011)
Flavanones		• Lemons, limes, sweet oranges, tangerine and tangor species of citrus fruits (Khan & Dangles, 2014) • Black sorghums (Dykes, Rooney, & Rooney, 2013) • Deffated olive (Alu'datt, Rababah, Ereifej, & Alli, 2013) • Deffated soybean (Alu'datt et al., 2013)	As a flavanone, naringenin exhibits antioxidant and antidiabetic activity (Kapoor & Kakkar, 2014) as well as demonstrating antiproliferative properties in cervical cancer (Ramesh & Alshatwi, 2013). Naringenin inhibits gastrointestinal smooth muscle contractility in isolated animal tissues (Yang, Pan, Zuo, Guo & Zhou, 2014), and chloride secretion in isolated colonic epithelia (Collins et al., 2011). This compound has a wide spectrum of pharmacological properties such as anti-inflammatory, anticarcinogenic, antihypertensive and anti-atherogenic (Rodrigo, Gil, Miranda-Merchak, & Kalantzidis, 2012)

(Continued on next page)

Table 1 (*continued*)

Antioxidant	Natural sources	Health benefits
		and also exhibits antioxidant properties (Shagirtha & Pari, 2011).
Flavanols (flavan-3-ols)	• Green tea (Song et al., 2015) • Human milk (Song, Jouni, & Ferruzzi, 2013) • Quince liquors (Carbonell-Barrachina, Szychowski, Vásquez, Hernández, & Wojdyło, 2015) • Partridgeberry (Bhullar & Rupasinghe, 2015)	Flavanols poses antioxidant, anti-thombotic, anti-inflammatory and anti-proliferative activities, as well as inhibition of pathogenic bacteria and modulation of lipid metabolism (Monagas et al., 2010; Sánchez-Patán et al., 2012).
Anthocyanins	• Berries (Ferrari et al., 2011; Kubota et al., 2012; Ramirez, Zambrano, Sepúlveda, Kennelly, & Simirgiotis, 2015) • Grapes, tomatoes, pomegranates and purple carrots (Can, Arli, & Atkosar, 2012) • Green coffee beans (Cheong et al., 2013) • Red cabbage (Chandrasekhar et al., 2012; Wiczkowski, Szawara-Nowak, & Topolska, 2015) • Sweet potatoes (Truong, Hu, Thompson, Yencho, & Pecota, 2012) • Wine (Can et al., 2012; Chen et al., 2015; Mulero, Pardo, & Zafrilla, 2010) • Drumstick (*Moringa oleifera*) (Moyo et al., 2012)	Anthocyanins exert beneficial effects on humans; they exhibit antioxidant, and anticarcinogenic activity (Hui et al., 2010), plays a vital role in the prevention of neuronal and cardiovascular illnesses, cancer and diabetes (Castañeda-Ovando et al., 2009; Konczak & Zhang, 2004; Santos-Buelga, Mateus, & De Freitas, 2014; Tomas-Barberan & Andres-Lacueva, 2012). It is proved that the administration of anthocyanins for 4 weeks decreases myopia, apoptosis, diabetes and obesity symptoms (Tsuda, 2012). The antioxidant potential of anthocyanins depends on the chemical structure of the molecule, the phenolic structure giving antioxidant properties (Pojer et al., 2013).
Isoflavones	• Soybean (Lee, Chung, Kim, & Jung, 2015; Toro-Funes et al., 2012) • Green, yellow and red lentils, red kidney beans, haricot beans and chickpeas (Konar, Poyrazoğlu, Demir, & Artik, 2012).	Isoflavones have a large spectrum of functional benefits on the human body, such as reduction of cardiovascular risk (Liu, Ho, Chen, & Ho, 2012), postmenopausal symptoms (Virk-Baker, Barnes, Krontiras, & Nagy, 2014) or cancer (He & Chen, 2013).
Phenolic alcohols	• Olives and olive oil (Franco et al., 2014) • Olive mill wastewater (Rahmanian, Jafari & Galanakis, 2014) Greek white wines from *Vitis vinifera* L cv. Malagousia (Tourtoglou, Nenadis, & Paraskevopoulou, 2014)	The hydroxytyrosol remarkable antioxidation activity makes it a highly promising alternative to synthetic antioxidants such as 2,6-di-*tert*-butyl-4-hydroxytoluene (BHT), 2- and 3-*tert*-butyl-*4*-hydroxyanisoles (BHA), or ethoxyquin, which are still commonly used as food and/or feed preservatives in spite of their confirmed toxicity (Kulawik, Ozogul, Glew, & Ozogul, 2013). Hydroxytyrosol and tyrosol exert an in vitro protective effect against low-density lipoprotein (LDL) oxidation and at low concentration have been found to protect human erythrocytes and DNA against oxidative damages (Ilavarasi, Kiruthiga, Pandian, & Devi, 2011). Hydroxytyrosol is one of the few nutraceuticals approved by the E. F. S. A. (2011) for its ability to maintain healthy LDL cholesterol levels and lipid antioxidation.
Phenolic acids	• Dried ginger (Lu et al., 2011) • Fennel (Lu et al., 2011) • grains (Gerstenmeyer et al., 2013) • Green coffee beans (Cheong et al., 2013) • Green prickleyash (Lu et al., 2011) • Mustard (Lu et al., 2011) • Orange juice (Agcam, Akyıldız, & Akdemir Evrendilek, 2014) • Sichuan pepper (Lu et al., 2011) • Spices (thyme, sage, rosemary, oregano, basil, marjoram) (Pokorny & Panek, 2012) • Tsaoko amomum fruit (Lu et al., 2011) • Wine (Mulero et al., 2010)	The phenolic acids are powerful antioxidants and have been reported to demonstrate antibacterial, antiviral, anticarcinogenic, anti-inflammatory and vasodilatory actions (Lima et al., 2014; Mudnic et al., 2010).
Tannins	• Condensed tannins are present in bean seed coats (Díaz, Caldas, & Blair, 2010), persimmons (Tian et al., 2012), mangosteens (Zhou, Lin, Wei, & Tam, 2011) and canola (Khattab, Goldberg, Lin, & Thiyam, 2010). • Green coffee beans (Cheong et al., 2013) • Hydrolysable gallotannins can be present in wine from oak, and could be added as oenotannins during winemaking (traditionally to remove undesirable proteins) (Harbertson, Parpinello, Heymann, & Downey, 2012). • Mango kernels (Luo et al., 2014) • Pomegranates (Li et al., 2015) • Strawberries (Álvarez-Fernández, Hornedo-Ortega, Cerezo, Troncoso & García-Parrilla, 2014) • Walnuts (Slatnar, Mikulic-Petkovsek, Stampar, Veberic, & Solar, 2015) • Whisky (Maitin, 2014)	Tannins have been reported to have anti-thrombotic, anti-atherogenic (Ntchapda et al. 2015), anti-mutagenic, anti-diabetic and anti-proliferative effects (Landete, 2011; Larrosa, García-Conesa, Espín, & Tomás-Barberán, 2010), anti-carcinogenic (Tikoo, Sane, & Gupta, 2011), anti-inflammatory (Piwowarski, Kiss, & Kozłowska-Wojciechowska, 2011), antiviral (Kwon et al., 2010) and antibacterial properties (Chan, Ng, Tan, & Low, 2011).
Stilbenes	• Almonds (Xie & Bolling, 2014) • Chocolate and cocoa (Crozier & Hurst, 2014). • Seeds and skins of grapes, red wine (Mulero et al., 2010)	The stilbenes have: antioxidant and antimicrobial efficiency prevent cardiovascular disease, arteriosclerosis and cancer acting and act as anti-inflammatory and antiviral agents (Frombaum, Le Clanche, Bonnefont-Rousselot, & Borderie, 2012; Galindo et al., 2011).
Lignans	• Roots, leaves, seeds, fruits and woody parts of vascular plants, vegetables, non-alcoholic beverages, alcoholic beverages and cereals (Fang et al., 2014; Su, Wang, Wang, & Wu, 2015). • Spices (Mukhija, Lal Dhar, & Nath Kalia, 2014)	Lignans are antioxidants and they play a role in normal colon functioning, and inhibit/delay the growth of experimental mammary cancer (Landete, 2012).

The hydrogen atom transfer mechanism supposes that the antioxidant, ArOH, reacts with the free radical, R, with hydrogen atom transfer:

$$ArOH + R^{\cdot} \rightarrow ArO^{\cdot} + RH \quad (10)$$

The other mechanism, single electron transfer, supposes that the oxidant donates an electron to the antioxidant molecule:

$$ArOH + R^{\cdot} \rightarrow ArOH^{\cdot +} + R^{-} \quad (11)$$

The reaction products of the two mechanisms are: a harmless species (RH), an oxidized radical ($ArO^{\cdot}$), a cation radical ($ArOH^{\cdot +}$) and an energetically stable species (R^{-}).

2.3.1. Flavonoids

Flavonoids (Fig. 3), many of which are plant pigments, are abundant in nature (Majer, Neugart, Krumbein, Schreiner, & Hideg, 2014). Flavonoids can be further divided into several subclasses, of

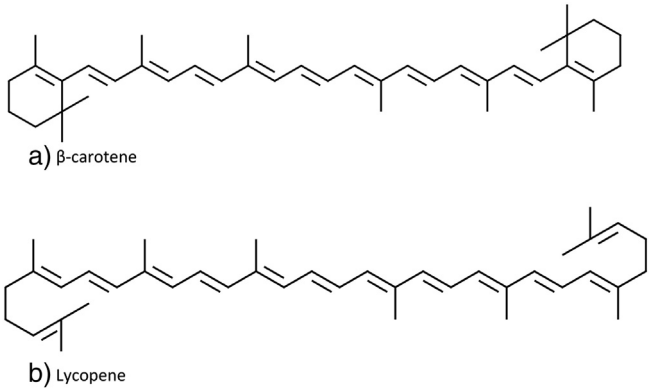


Fig. 2. a. β-Carotene. b. Lycopene.

which the most representative are: flavones, flavanones, flavonols, flavanols (also called flavan-3-ols or catechins), anthocyanidins and isoflavones (Spencer, Abd El Mohsen, Minihane & Mathers 2008; Ziberna, Fornasaro, Čvorović, Tramer, & Passamonti, 2014). The general structure of flavonoids includes a C15 (C6–C3–C6) skeleton (Andersen & Jordheim, 2010).

The flavonoids can be classified in several subgroups which are mainly indicated either by (i) hydroxylation, (ii) *O*-methylation, (iii) *C*-methylation, (iv) isoprenylation, or (v) methylenedioxy substitution. The main sources of flavonoids and their health benefits are presented in Table 1.

2.3.1.1. Flavonols. Flavonols make up the most abundant class in *Vitis vinifera* grape berry skins (Alcalde-Eon, García-Estévez, Martín-Baz, Rivas-Gonzalo, & Escribano-Bailón, 2014; Liang et al., 2014a).

Flavonols (Fig. 4) are identified by the location of the alcohol group on the C ring. In general, the frequent sugar moieties in flavonols are glucose, rhamnose, galactose and arabinose (Rahman, 2012). The principal dietary flavonols are quercetin, myricetin, rutin, isorhamnetin and kaempferol.

One of the most important flavonols is quercetin. Quercetin, 3,3′,4′,5,7-pentahydroxyflavone, is present in fruit and vegetables. It occurs mainly in leaves and in the other parts of the plants as aglycones and glycosides, in which one or more sugar groups is bound to phenolic groups by a glycosidic bond. Glucose is the most common sugar, with galactose and rhamnose also frequently found in combination with flavonoids. In general, quercetin glycosides contain a sugar group at the 3-position (Wach, Pyrzyńska, & Biesaga, 2007).

The main sources of flavonols and their health benefits are presented in Table 1.

2.3.1.2. Flavones. Chemically, flavones (Fig. 5) lack a 3-hydroxygroup. The major part of the flavones is synthesis from two flavanones (naringenin and pinocembrin). These two flavones are synthesized from the condensation of one molecule of hydroxycinnamoyl—Coenzyme A and three

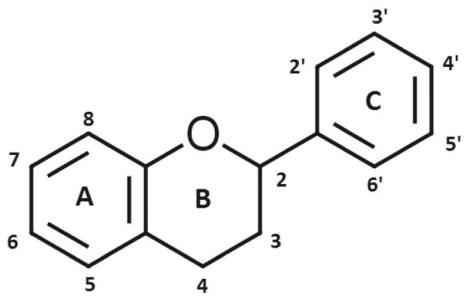


Fig. 3. Flavonoid chemical structure.

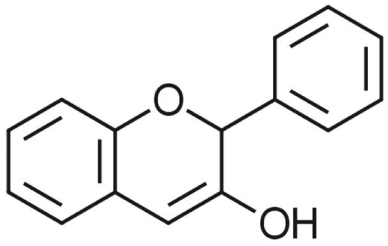


Fig. 4. Flavan-3-ols.

molecules of malonyl-Coenzyme A. The flavones can be transformed into flavones by flavones synthetases I and II (Austin & Noel, 2003; Winkel-Shirley, 2001). As combinations of various modifications can occur, the number of different flavones is enormous. Flavones can be found in all parts of plants, above and below ground, in vegetative and generative organs: stem, leaves, buds, bark, heartwood, thorns, roots, rhizomes, flowers, fruit, seeds, and also in root and leaf exudates or resin (Singh, Kaur, & Silakari, 2014). The main sources of flavones and their health benefits are presented in Table 1.

2.3.1.3. Flavanones. Flavanones (Fig. 6) also can occur as *O*-or *C*-glycosides and are especially abundant in citrus fruit and prunes (Khan & Dangles, 2014). Naringenin (4′,5,7-trihydroxyflavanone) is a flavanone found predominantly in citrus fruit such as oranges and grapefruit. The main sources of flavanones and their health benefits are presented in Table 1.

2.3.1.4. Flavanols (flavan-3-ols)/procyanidins. The flavanols are vulnerable to several dedragative reactions accelerated by heat, food ingredients, elevated pH (>5) conditions, and presence of dissolved oxygen or other reactive oxygen species (Song, Manganais, & Ferruzzi, 2015). The auto-oxidation of flavan-3-ols occurs by the formation of a radical semiquinone structure and is stabilized via multiple resonance structures available to the flavan-3-ol (Song et al., 2015).

2.3.1.5. Anthocyanins. Anthocyanins, the largest group of pigments in nature, are one of the pigment groups responsible for color in some fruits and flowers (Cavalcanti, Santos, & Meireles, 2011; Zhang et al., 2015a, 2015b). They are a class of natural bioactives whose presence in food and beverages can be visually appreciated, this facilitates the transfer of information from the nutritional and pharmacological research into practical advice to health-concerned consumers (Pojer, Mattivi, Johnson, & Stockley, 2013). Anthocyanidins when linked to one or more glycosidic units are named anthocyanins.

Anthocyanidins are linked to one or more glycosidic units, being glycosylated polyhydroxy and polymethoxyderivates of 2-phenylbenzopyrylium salts (flavylium). The glycosidic units may be linked to the anthocyanidin by α or β linkage, and always in position 3 of the aglycon (Fig. 7). When additional sugars are present in the anthocyanin molecule, they are linked to positions 5 and 7, and less frequently to 3′ and 5′. The sugars encountered in anthocyanins

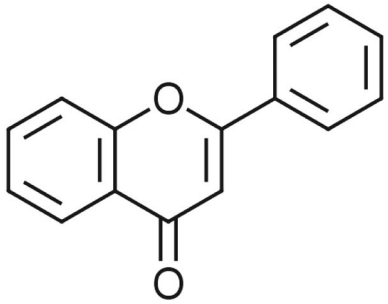


Fig. 5. Flavones.

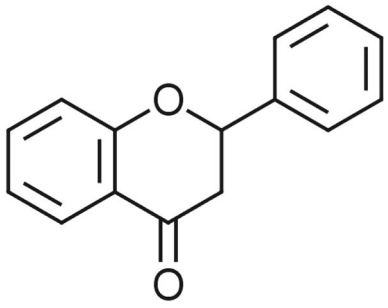


Fig. 6. Flavanones.

can be hexoses (glucose and galactose) and pentoses (xylose, arabinose) (Osorio et al., 2012). The isolated anthocyanins are highly instable and very suspectible to degradation (Castañeda-Ovando, de Lourdes Pacheco-Hernández, Páez-Hernández, Rodríguez, & Galán-Vidal, 2009). Anthocyanin molecules are unstable and easily degraded (Reque et al., 2014) by temperature, pH, light, oxygen, solvents, metallic ions, ascorbic acid, sulphite and enzymes (Castañeda-Ovando et al., 2009; Cavalcanti et al., 2011).

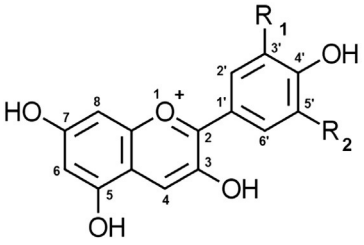
The main sources of anthocyanins and their health benefits are presented in Table 1.

2.3.1.6. Isoflavones. Isoflavones (Fig. 8) are a group of oxygen heterocycle compounds that belong to the family of phytoestrogens (Xiao, Cao, Wang, Zhao, & Wei, 2009). The most common isoflavones are daidzein, genistein and glycitein (Kassem, 2015) which occur in legumes, especially in soybean (Balisteiro, Rombaldi, & Genovese, 2013). The main forms of isoflavones in plants are glycosides with a sugar (e.g., glucose, malonylglucose, acetylglucose, galactose, rhamnose, etc.). The main sources of isoflavones and their health benefits are presented in Table 1.

2.3.1.7. Phenolic alcohols. The phenolic alcohols (Fig. 9) are 2-phenylethanol, (3,4-dihydrozyphenyl) ethanol, also called hydroxytyrosol, (*p*-hydroxyphenyl) ethanol, also named tyrosol and (3,4-dihidrophenyl) ethanol-glucodise. Tyrosol and hydroxytyrosol, two important *o*-diphenols present in olives, olive oil and olive mill wastewater (Franco et al., 2014; Rahmanian, Jafari, & Galanakis, 2014).

The main sources of phenolic acids and their health benefits are presented in Table 1.

2.3.1.8. Phenolic acids. Phenolic acids (Fig. 10) can be divided into two categories depending on their structure: derivates of benzoic acid and derivates of cinnamic acid. These compounds consist of a benzene ring bonded to a carboxylic group (benzoic acids) or to a propenoic acid (cinnamic acids). In many fruits and vegetables, cinnamic acids (especially caffeic acid) is present as ester derivates (chlorogenic acid, other cinnamoyl quinic acids, phenylethanoic glycosides) which show a high potential as antioxidants (Sova, 2012). Hydroxybenzoic acids include gallic, *p*-hydroxy-benzoic, protocatechuic, vanilic and syringic acids. The most important hydroxycinnamic acids are caffeic, ferulic,



	R_1	R_2
Pelargonidin	H	H
Cyanidin	OH	H
Delphinidin	OH	OH
Paeonidin	OCH_3	H
Petunidin	OCH_3	OH

Fig. 7. Anthocyanidins.

p-coumaric and sinapic acids (Abramovič, 2015). The main sources of phenolic acids and their health benefits are presented in Table 1.

2.3.1.9. Tannins. Tannins (Fig. 11), with a molecular mass of up to 30,000 Da, are produced by plants as secondary metabolites (Saric et al., 2015). According to their structure, tannins can be broadly divided into two classes of macromolecules, termed hydrolysable tannins and condensed tannins.

Hydrolysable tannins have a molecular mass ranging between 500 and 5000 Da (Arapitsas, 2012). In addition to their astringent character (Shahat & Marzouk, 2013), they have important antioxidant activity (Figueroa-Espinoza, Zafimahova, Alvarado, Dubreucq, & Poncet-Legrand, 2015; Hosu, Cristea, & Cimpoiu, 2014).

Condensed tannins or proanthocyanidins are high-molecular-weight polymers with a molecular mass up to 30000 Da. The monomeric form is a flavan-3-ol (catechin, epicatechin, etc.), with a flavan-3, 4-diol or aleucoanthocyanidin molecule as its precursor. Oxidative condensation occurs between carbon C-4 of the heterocycle and carbons C-6 or C-8 of adjacent units.

The main sources of tannins and their health benefits are presented in Table 1.

2.3.1.10. Stilbenes. Stilbenes are phenolic compounds (Kostadinović et al., 2012) displaying two aromatic rings linked by an ethane bridge, and exist in monomeric (resveratrol, oxyresveratrol) and oligomeric form as oligomers of stilbenes (dimmers, trimers or polymers of resveratrol) or other stilbenes (e.g., epsilon–viniferin, pallidol, etc.) (Charles, 2013).

They are important because of their health effects, which occur in lower concentrations compared to other phenolic compounds. Resveratrol, an important stilbene (Fig. 12), is produced by vines in response to *Botrytis* infection and other fungal attacks (Adrian & Jeandet, 2012). Resveratrol occurs in two isomeric forms, the *trans*- and *cis*-configured isomers; light influences the *cis*/*trans* isomerization. The glucosilated forms of resveratrol are *trans*-piceid and *cis*-piceid.

The main sources of stilbenes and their health benefits are presented in Table 1.

2.3.1.11. Lignans. Lignans (Fig. 13) are a group of phenolic compounds, which occur in high concentrations in flaxseed and other seeds (Landete, 2012), roots, leaves, fruits and woody parts of vascular plants (Ekiert, Szopa, Ekiert, Krzek, & Dzik, 2013) and grains (Gerstenmeyer, Reimer, Berghofer, Schwartz, & Sontag, 2013). The lignans' structures are built on C6–C3 units (a propylbenzene skeleton) derived from cinnamyl units.

The main sources of lignans and their health benefits are presented in Table 1.

3. Analysis of antioxidants in food

In recent decades many methods have been developed for the analysis of antioxidants. These methods involve the evaluation of total antioxidant activity and the individual identification and quantification of different antioxidant substances. However, before quantification, extraction of the different compounds from the food matrix is required. This involves using organic solvents, supercritical fluids, microwave procedures, subcritical water extraction, high hydrostatic pressure, pulsed electric fields, ultrasonics or subcritical water.

3.1. Extraction

The extraction yield of antioxidant compounds from plant material is influenced mainly by the conditions under which the process of liquid–solid extraction is carried out. As each plant material has unique properties in terms of structure and composition, the behavior of the resulting material–solvent system is unpredictable when they are combined with solvents (González-Montelongo, Lobo, & González, 2010).

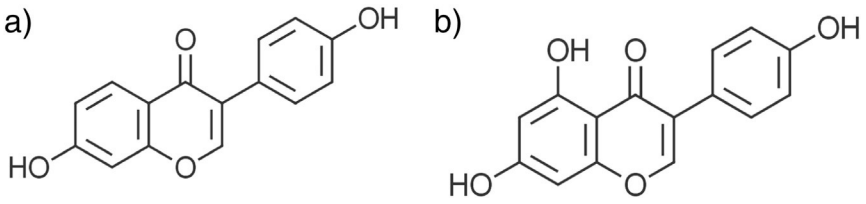


Fig. 8. Isoflavones: a—daidzein, b—genistein.

3.1.1. Extraction with solvents

Solvent extraction is a separation operation which applies a solvent to extract/separate a desired component (the solute) from solid food. The separation factor for solvent extraction is the chemical equilibrium of the component between solid and solvent phases and the driving force for solvent extraction is the concentration difference of the component between the two phases. In principle, an ideal solvent should have the following desirable features: it should have a high capacity for the solute being separated into it, it should be selective, dissolving the specific component to a large extent while having a minimum capacity for the other components, it should be chemically stable (no irreversible reactions with contacting components), it should be regenerable, and it should have low viscosity for easy pumping and transportation. Its polarity is manifested by a permanent electric dipole in their molecules, since its atoms have differing electronegativities. When nonpolar liquids are placed in an electric field, only the electrons in its atoms respond to the external electric forces, resulting in some atomic polarization. This produces a relative permittivity, which is approximately equal to the square of the refractive index, or about 2. Polar molecules, however, further respond to the external electric field by reorienting themselves, which results in a considerably larger relative permittivity. The attractive forces between charges (such as those on ions) of opposite sign are inversely proportional to the relative permittivity of the liquid medium in which they find themselves (Rydberg, Cox, Musikas, & Choppin, 2004). The intermolecular interaction between solvent and solute molecules determines the mutual solubility. Murphy et al. (1999) found that the adding a certain amount of water (5–10 mL depending on the matrix) to different organic solvents optimized the total extraction efficiency.

Anthocyanins are polar molecules, thus the most common efficient solvents used in the extractions are aqueous mixtures of acetone, methanol and ethanol (Boulekbache-Makhlouf, Medouni, Medouni-Adrar, Arkoub, & Madani, 2013). Among the most common methods are those which use acidified methanol or ethanol as extraction solvents (Chandrasekhar, Madhusudhan, & Raqhavarao, 2012). The acid in the solvents acts to rupture cell membranes and to release anthocyanins, however this harsh chemical treatment may break down the innate anthocyanin structure. It is therefore important to acidify the solvents with organic acids (formic or acetic acid) rather than mineral acids such as 0.1% HCl (Castañeda-Ovando et al., 2009).

Ethanol is one of the most used solvents for antioxidant extraction, because it is: cheap, reusable, nontoxic and the extracts can be used in the food industry (Chew et al., 2011). The extraction of phenols with different concentrations of aqueous ethanol can fractionate phenolics on the basis of polarity (Durling et al., 2007). Aqueous solutions of ethanol offer many advantages as: hydrophilic and lipophilic active compounds are recovered together in different proportions and synergistic interactions occur inside the medium (McDonald, Prenzler, Antonolovich, & Robards, 2001). In the case of phenolic content extracted with different concentrations of ethanol (20, 50, 70 and 100 ml/100 ml) from olives, it seems that the concentration of 70 ml/100 ml ethanol reaches the highest yields for total phenolic compounds (at 725 nm and 280 nm), hydroxycinnamic acids, flavonols and *o*-diphenols (Tsakona, Galanakis & Gekas, 2012). Among the variety of alcohols, ethanol is most preferable because it is rather cheap, possesses "GRAS" status (Generally-Recognized-As-Safe according to American Food and Drug Administration) and the extracts can be used in the food industry. Methanol is cheaper than ethanol but due to its toxicity it is not favored in the food industry. On the other hand, carotenoids such as tomato lycopene are more liposoluble and thereby polar aprotic or non-polar solvents (i.e., acetone or ethyl acetate, respectively) are preferred (Strati & Oreopoulou, 2011). In this case, the solvent should be removed completely from the extract prior to its re-utilization in food products. The extraction of phenols, carotenoids and flavorings sometimes occurs in combination with pressurized and distillation processes, which accelerate the process and extract volatile compounds, respectively (Galanakis, 2012). Galanakis, Goulas, Tsakona, Manganaris, and Gekas (2013a) have analyzed activity coefficients of fifteen natural phenols in seven solvents and three extraction temperatures. They observed that the preference of the phenols for methanol and ethanol may be caused by their non polar part and the aliphatic fragment of alcohols. The bigger molecules (i.e., oleuropein, rosmarinic acid, *p*-hydrobenzoic, *p*-hydroxyphenil acetic acid, tyrosol and hydroxytyrosol) preferred ethanol, as it could better "cover" the gaps between the hydrogen bonds. Tyrosol and hydroxytyrosol are recovered better with polar aprotic ethyl acetate than with non polar solvents, while extraction yield is enhanced with the increase in the medium polarity.

Do et al. (2014) observed that in the case of phenol extraction from *Limnophila aromatica*, the yields of extraction with various solvents decreased in the following order: 50% aqueous acetone > 50% aqueous ethanol > 75% aqueous methanol > 50% aqueous ethanol > 75% aqueous ethanol > 100% methanol > water > 100% ethanol > 100% acetone. It can be seen that the extraction yield of pure methanol is higher than that of pure ethanol and pure acetone. This shows that the extraction yield increases with increasing polarity of the solvent used in extraction. The results obtained indicate that increasing the water concentration in the solvent enhances extraction yield. The combined use of water and organic solvent may facilitate the extraction of chemicals that are soluble in water and/or organic solvent.

The extraction of anthocyanins from red cabbage with 1% (v/v) HCl in methanol is better than the extraction with acidified ethanol (50%, v/v) (Chandrasekhar et al., 2012). Nevertheless, in the food industry ethanol is preferred due to the toxicity of methanol (Castañeda-Ovando et al., 2009).

The solvent extraction of antioxidants can be improved increasing the solvent temperature. Higher temperatures favor extraction since the diffusion coefficient is higher. Galanakis, Tornberg, and Gekas (2010a) have analyzed the influence of the temperature on the total phenol and anthocyanin extraction from olive waste using ethanolic

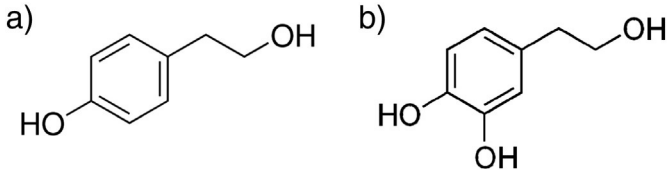


Fig. 9. Phenolic alcohols: a—tyrosol, b—hydroxytyrosol.

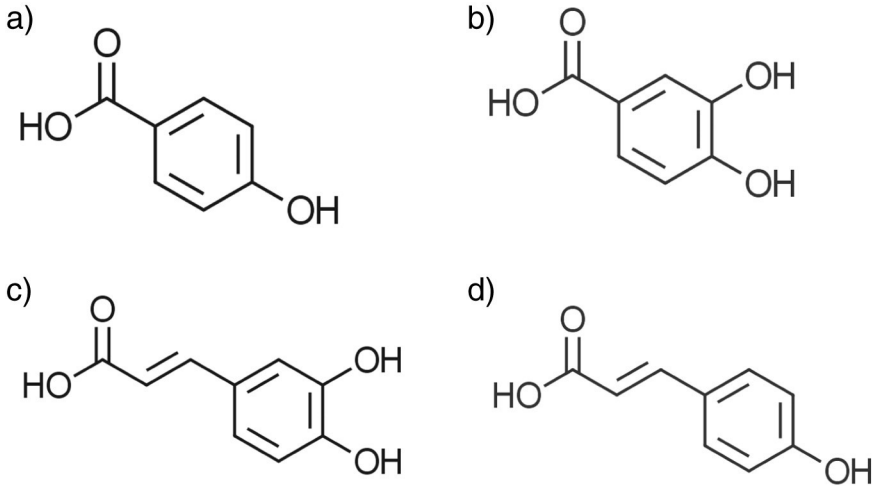


Fig. 10. Phenolic acids: a—p-hydroxybenzoic acid, b—3, 4-dihydroxybenzoic acid, c—caffeic acid, d—p-coumaric acid.

extraction at four different temperatures (25, 50, 60 and 85 °C). They observed that in the case of total phenol extracts (at 725 nm), the yield decreases in the following order: 25 > 80 > 60 > 50 °C, while the anthocyanin concentration decreased as follows: 50 > 25 > 60 > 80 °C. Hydroxycinamic acids and flavonols concentration of the extracts decreased with increasing temperature although the differences were not always significant.

One of the major problems of the antioxidant extracts is their preservation. Galanakis et al. (2010a) reported that the content of total phenol (at 725 nm) from olive waste remained constant over a period of 18 weeks, while in the case of total phenols (at 280 nm) concentration treated at room temperature showed a significant reduction in total phenols in contrast with those treated at 50, 60 and 80 °C. The high temperature treatment (80 °C) has an important role on the preservation of hydroxycinnamic acid and flavonol.

3.1.2. Extraction with supercritical fluids

Extraction with supercritical fluids (SCF) has become increasingly popular in biomaterial processing. Unlike normal solvent extraction, supercritical fluid extractions use fluids in their supercritical states. Supercritical fluids exhibit desirable transport properties that enhance their adaptability as solvents for extraction processes. The extraction efficiency of polar compounds with CO_2 can be improved by the addition of small quantities of polar organic solvents used as modifiers. CO_2 is non-toxic, non-flammable, and requires a minimum amount of solvent (5–10 ml). Extraction is fast (10–60 min), selective, requires no additional clean-up and can be carried out with small amounts of sample (Said et al., 2015).

CO_2 cannot extract compounds with high molecular weight (e.g., anthocyanins) because of their lipophilic and nonpolar nature. To eliminate these drawbacks co-solvents are used to enhance the solubility of target compounds and to increase the extraction selectivity. Another way to eliminate this drawback is the use of enhanced solvent extraction (ESE). ESE consists of using CO_2, organic solvents and/or water at temperatures higher than the ambient temperature (40–200 °C) and pressures between 3.3 and 20.3 MPa. The ESE technique has been used with success for the extraction of polar compounds (Adil, Yener, & Bayindirh, 2008) including anthocyanins from elderberry pomace (Serra et al., 2010). The extraction efficiency of supercritical fluids can be improved using ethanol as a modifier (Veggi, Cavalcanti & Meireles, 2011).

Supercritical CO_2 has been applied for the extraction of polyphenols from grapes (Boussetta, Vorobiev, Le, Cordin-Falcimaigne & Lanoiselle, 2012; Ghafoor, Park, & Choi, 2010; Wijngaard, Hossain, Rai, & Brunton, 2012) rosemary (Visentin, Rodriguez-Rojo, Navarrette, Maestri, & Cocero, 2012) and wine.

3.1.3. Microwave-assisted extraction

Microwave-assisted extraction (MAE) has become very popular in the last decade due to the reduction of extraction time and solvent used. This technique involves extraction with controlled pressure and temperature. The use of closed vessels shortens the extraction time and increases the extraction efficiency. This method has been applied for the extraction of phenolic compounds from plant material (Ballards, Mallikarjunan, Zhou, & O'Keefe, 2010; Tsubaki, Sakamoto, & Azuma, 2010). MAE can be used with or without the addition of any solvent.

Solvent-free microwave extraction (SFME) and microwave hydrodiffusion and gravity (MHG) are both types of solvent free MAE performed at atmospheric pressure. SFME is based on a combination of microwave heating and dry distillation which does not need any addition of solvent (Michel, Destandau, & Elfakir, 2011). Microwave hydrodiffusion and gravity (MHG) is a novel, green technology, which has been used for the extraction of polyphenols from onion (Zill-e-Huma, Fabiano-Tixier, Elmaataoui, Dankgles, & Chemat, 2011). The diffusion of secondary metabolites by microwaves is the result of an increase in permeability and tissue softening. During microwave extraction the mass transfer increases due to higher penetration capacity following cell disruption. MHG is an economical, efficient and environmentally-friendly extraction method; this method requires less energy and no solvent, combining microwaves and the earth's

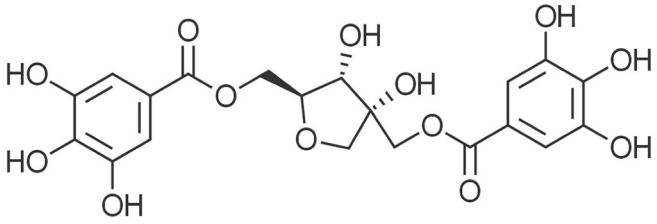


Fig. 11. Tannins—Hamamelitannin.

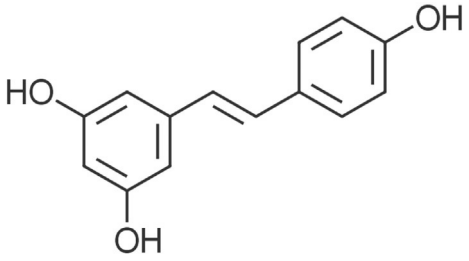


Fig. 12. Stilbenes–Trans resveratrol.

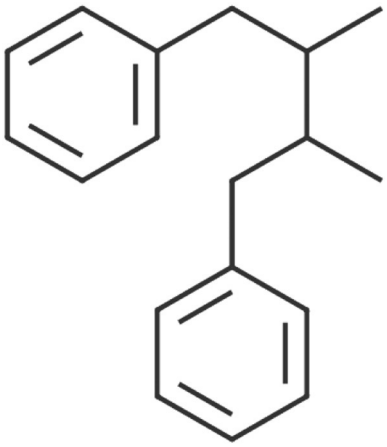


Fig. 13. Lignans.

gravity at atmospheric pressure (Chemat, Abert-Vian, & Visinoni, 2008; Zill-e-Huma et al., 2011).

Subcritical water extraction (SWE) is increasingly used in the preparation of environmental samples, and the extraction of natural products from herbs, plants and foodstuffs (Plaza, Amigo-Benavent, del Castillo, Ibanez, & Herrero, 2012). Subcritical water, also called pressurized (hot) water refers to water at a temperature between 100 and 374 °C and a pressure which is high enough to maintain the liquid state (below the critical pressure of 22 MPa) (Karakama, 2011). An important feature of subcritical water is a reduction in polarity, expressed as a dielectric constant with increasing temperature.

SWE is a highly efficient method for the extraction of phenolic compounds from pomegranate (*Punicagranatum* L.) seed residues (He et al., 2012), anthocyanins and other phenolic compounds from dried red grape skin (Ju & Howard, 2005) and potato peel (Singh & Saldaña, 2011) and flavanones from citrus peel (Cheigh, Chung, & Chung, 2012).

Ultrasonics is one of the most used techniques in industry to enhance the mass transfer phenomena. The mass transfer rate is increased in ultrasonic extraction by cavitation forces, in this case the bubbles in the liquid/solid extraction can explosively collapse and generate localized pressure causing plant tissue rupture and improving the release of intracellular substances into the solvent (Goula, 2013). Ultrasonic extraction is applied in the case of anthocyanin extraction from grapes (González-Centeno et al., 2014), flavonoids from *Prunella vulgaris* L. (Zhang, Fu, & Zhang, 2011) and polyphenols from orange peel (Khan, Abert-Vian, Fabiano-Tixier, Dangles, & Chemat, 2010).

Pulsed electric fields (PEF) are being developed as a non-thermal emerging technology for the preservation of food. PEF enhances mass transfer rates by cell membranes improving tissue softness, influencing textural properties and the electroporation of plants. PEF increases the content of valuable components when applied to juice production and can replace the enzymatic maceration of the process (Corrales, Toepfl, Butz, Knorr, & Tauscher, 2008). PEF was applied in the case of anthocyanin extraction from grapes (Delsart et al., 2014) as well as phenolics (Parniakov, Barba, Grimi, Lebovka, & Vorobiev, 2014)

3.1.4. High hydrostatic pressure (HHP)

The use of HHP improves mass transfer rates increasing cell permeability as well as increasing secondary metabolite diffusion according to changes in phase transitions (Sadus, 2012). During HHP extraction the liquid partially fills the air gaps present in fruit tissues. When the pressure is released subsequently, the occluded air in the pores exits causing plant cell membrane damage (Fernandez Garcia, Butz, & Tauscher, 2001). HHP was applied in the case of anthocyanin extraction from grapes (Morata et al., 2014), polyphenols and anthocyanins from red fruits (Ferrari, Maresca, & Ciccarone, 2011) and anthocyanins from grape skins (Corrales, García, Butz, & Tauscher, 2009).

High voltage electrical discharges (HVED) have electrical and mechanical effects on the product caused by shock waves. This technique introduces energy directly into an aqueous solution through a plasma channel formed by a high-current/high-voltage electrical discharge between two submerged electrodes. The phenomen of HVED is based on the electrical breakdown in water. Water vapor bubbles that are initially present in water formed due to local heating are involved in this phenomenon and accelerate the process. If the electrical field is intense enough, the avalanche of electrons becomes a starting point of streamer propagation from the high voltage needle electrode to the grounded one. The electrical breakdown is accompanied by a number of secondary phenomena (high-amplitude pressure shock waves, bubble cavitation, creation of liquid turbulence, etc.). These secondary phenomena cause particle fragmentation and cell structure damage (Boussetta & Vorobiev, 2014). This technique includes a large range of current (10^3–10^4 A), voltage (10^3–10^4 V) and frequency (10^{-2}–10^{-3} Hz) (Chang, Looy, Urashima, Bryden, & Yoshimura, 1998). The HVED method requires short treatment times (a few ms) and low energy consumption (10–50 kJ/kg) (Gros, Lanoisellé, & Vorobiev, 2003). The temperature elevation after treatment is low (<5 °C). HVED was applied in the case of oil extraction from linseed (Gros et al., 2003), polyphenols from wine by-products (Boussetta, Lanoiselle, Bedel-Cloutour & Vorobiev, 2009), grape pomace (Boussetta et al., 2011) and grape seed (Liu, Vorobiev, Savoire, & Lanoiselle, 2011a).

Enzyme-assisted extraction (EAE) is an efficient procedure to enhance the release and recovery of bioactive compounds from plants and algae. These methods are gaining more attention because of the need for eco-friendly extraction technologies. Enzymes can effectively catalyze the degradation of vegetable cell walls, favoring the release of bioactive components contained inside the cells. The targeted use of enzymes can increase the effect of solvent pre-treatment, and either reduces the amount of solvent needed for extraction, or increase the yield of extracable compounds. The primary cell wall of plants is mainly composed of cellulose, hemicelluloses (xyloglucans), pectin and proteins (Jordan et al. 2012). Besides, phenolic compounds have been reported to be linked to cell wall polysaccharides by hydrophobic interactions and hydrogen bonds. Therefore, cellulases, hemicelullases, pectinases as well as other enzymes can be used to disrupt the cell wall structure, break down complex interior storage materials, thereby facilitating the release of intracellular bioactive compounds (Wang et al., 2010). Cell-wall degrading enzymes have been used successfully to increase the release of a variety of components including anthocyanin, lycopene, β-carotene and carotenoids from vegetable tissues (Ranveer, Patil, & Sahoo, 2013). When the biological materials are pretreated with enzymes the yield of bioactive compounds increases. Enzyme pretreatment followed by a solvent extraction process is referred to as enzyme-assisted extraction (Özkan & Bilek, 2015).

EAE has been applied for the extraction of antioxidant compounds from lemon balm (*Melissa officinalis*) (Miron, Herrero, & Ibanez, 2013), red algae (*Palmaria palmate*) (Wang et al., 2010) *Agaricus blazei Murrilli* (Jia et al., 2013), alfalfa (Wang, Dong, & Tong, 2013) and pumpkin (*Cucurbita moschata*) (Wu, Zhu, Diao, & Wang, 2014).

The endogenous enzymes of fruit/vegetables can play an important role in the antioxidant activity. The hydrolysis of the fruit phenolic glycosides during the olive oil extraction process is mainly carried out by an endogenous β-glucosidase that exhibits the highest substrate affinity toward oleuropein (Romero-Segura, García-Rodríguez, Sanz, & Pérez, 2010). On the other hand, endogenous oxidoreductases are also suggested to play an important role during the milling and kneading steps in the olive oil extraction process by promoting phenolic oxidation (Servili et al., 2008). Thus, Ghanbari, Anwar, Alkharfy, Gilani, and Saari (2012) found that slow kneading of olive pastes in the presence of oxygen may reduce the concentration of or the *o*-diphenols in oils by half. Besides free radicals, the main oxidizing agents of phenols in plant products are oxidoreductase activities such as polyphenol oxidase (PPO) and peroxidase (POX). Garcia-Rodriguez, Romero-Segura, Sanz, Sanchez-Ortiz, and Perez (2011) observed that POX and PPO activities in olive fruit at

ripening stages selected for olive oil extraction are able to oxidize both main phenolic glucosides found in the olive fruit, and phenolic compounds arising during the industrial process to obtain the oil, especially those derivatives of hydroxytyrosol such as decarboxymethyl oleuropein and aldehydic forms of oleuropein. Given that hydroxytyrosol derived compounds possess such high antioxidant activity and sensory influence compared to the tyrosol group (Pérez et al., 2014), modulation of olive POX and PPO, either by modifying technological conditions or through varietal selection, could have a great effect on nutritional and organoleptic quality of virgin olive oil.

The endogenous enzymes (PPO and POX) can cause the degradation of anthocyanins and other polyphenols in strawberry products, leading to discoloration and loss of antioxidant activity. Several studies have shown that the activities of polyphenol oxidase (Lopez-Serrano & Barcelo, 2002) and to a lesser extent peroxidase (Chisari, Barbagallo, & Spagna, 2007) are responsible for the degradation of anthocyanins and other polyphenols in strawberries. To reduce this effect Terefe, Yang, Knoerzer, Buckow, and Versteeg (2010) proposed a thermal and high pressure inactivation of strawberry polyphenol oxidase and peroxidase procedure. They observed that neither thermal processing nor combined high pressure-thermal processing could effectively inactivate polyphenol oxidase in strawberry puree.

To improve the enzyme assisted extraction it can be combined with ultrasound extraction (UAEE). This method has been shown to enhance the juice yield and reduce processing time. Tchabo, Ma, Engmann, and Zhang (2015) applied the UAEE to enhance the total phenolic, total flavonoids and total anthocyanins from mulberry must. They observed that UAEE reduce the time of processing during the maceration of juice and wine.

Another combination used is enzyme assisted extraction with microwaves (MAEE). The extraction yield of total polyphenols using the MAEE method is higher than other extraction methods including heat-refluxing extraction, ultrasonic-assisted extraction and enzyme-assisted extraction (Zhang et al., 2013a, 2013b; Liu et al., 2011a. Zhang et al. (2013a, 2013b) observed that the MAEE is an efficient and environmental friendly method, and the polyphenols from waste peanut shells have significant antioxidant and antibacterial activities, which can be used as a source of potential antioxidant and preservatives.

Wu et al. (2015) used a simultaneous microwave/ultrasonic assisted enzymatic extraction (SMU–AEE) method of antioxidant ingredients from *Nitraria tangutorum* juice by-products. In this study, the chemical composition assay showed that the concentents of phenols, flavonoids and anthocyanins were, respectively, 25.06%–141.48%, 8.86%–133.52%, and 9.81%–92.42% higher than those by traditional extraction methods.

The advantages and disadvantages of each type of extraction are presented in Table 2.

3.2. Isolation, purification, recovery and fractionation

The classical methods used for the isolation of antioxidants from complex extracts are time-consuming, labor intensive, expensive and sometimes have many errors in isolation and purification due to dilution effects or decomposition effects on antioxidants (Dai et al., 2013). HPLC is a good method for antioxidant isolation and purification based on online post-column free radical assays (Nuengchamnong, Krittaship, & Ingkaninan, 2011); however this method needs technical skills, special equipment and has lower resolution and sensitivity (Li et al., 2012). A suitable method for isolation and purification might be high-speed counter-current chromatography (HSCCC). HSCCC is a liquid–liquid partition chromatography based on two immiscible phases without support matrix, a low risk of sample denaturation, no irreversible adsorption, total sample recovery, large load capacity and low cost (Dai et al., 2013).

HSCCC was applied with success for many bioactive compounds (e.g., phenolics) from natural products (Dai et al., 2013; Li et al., 2013). Trabelsi et al. (2012) purified phenolic compounds from *Limoniastrum guyonianum* using a preparative HPLC equipped with a 2-way binary high-pressure gradient pump.

Other methods used for antioxidant isolation and purification are: butanol fraction extraction (involves silica gel column separation) (Pukalskas, Venskutonis, Salido, de Waard, & van Beek, 2012), ultrafiltration, gel filtration chromatography and reversed-phase high-performance liquid chromatography (RP-HPLC) (Chen, Ma, Liu, Liao, & Zhao, 2012), diethylaminoethyl-Cellulose (DEAE-C) (Al-Sheraji et al., 2012) and ion exchange chromatography (Lapsongphon & Yongsawatdigul, 2013).

Macroporous adsoption resins were used in the purification of bioactive constituents from natural extracts due to their high efficiency (Dahui, Zaigui, & Yunhua, 2011). The macroporous adsorption resins exhibit higher adsorption capacity not only because of their similar polarity with the target compounds, but also because of their surface area and larger average pore diameter. Macroporous resins (MARs) are durable polar, non-polar or slightly hydrophilic polymers with high adsorption capacity. Compared to the conventional matrices, MARs have some advantages, such as mechanical strength, diverse structures, good performance, low costs and environmental friendliness (Sun et al., 2013). This method is time-consuming, laborious and requires large volumes of solvents (Ma et al., 2013). Phenolics possessing benzene rings and hydrogen groups, could be adsorbed by polar or weak-polar resins with proper surface area and average pore diameter (Lin, Zhao, Dong, Yang, & Zhao, 2012). The macroporous resins have been used for the purification and separation of bioactive substances from trollflowers (Sun et al., 2013), brown seaweed *Ecklonia cava* (Kim et al., 2014), *Glycyrrhiza glabra* L. leaf (Dong et al., 2015) and *Dalbergia odorifera* T. Chen leaves (Ma et al., 2013). The isolation and purification of *Grifola fandosa* antioxidant was reported by Chen et al. (2012). They used an anion-exchange chromatography for isolation reaching a total yield of 3.13%. The elution peaks obtained were collected, concentrated and purified by a gel filtration chromatography, reaching recovery levels between 21.5 and 33.3%.

The anthocyanins can be isolated with the following procedure: extraction (80% methanol containing sodium sulfate or acetone–water solution, petroleum ether (Chai et al., 2012) followed by purification (using an Amberlite XAD-16 ion exchange gel or macroporous resins) (Wiczkowski, Szawara-Nowak, & Topolska, 2013; Zhang et al., 2013a, 2013b) and initial separation of anthocyanins on ion-exchange gel. The isolation was made up on a C18 semi-preparative column (Wiczkowski et al., 2013).

The food industry generates huge amounts of by-products from the processing of foods of plant origin. The disposal of these by-products represents both a cost to the food processor and a potential negative impact on the environment. Research over the past 20 years has revealed that many of these by-products could serve as a source of potentially valuable bio-active compounds (Wijngaard et al., 2012). The recovery of antioxidants reflects not only the need for biofunctional compounds, which may also be interesting from a technological point of view as valuable components of nutraceuticals in food and pharmaceutical preparations or in the cosmetics industry, but can also exploit the food production chain (Schieber, Stintzing, & Carle, 2001).

Galanakis (2012, 2013, 2014) proposed a so called "5-Stages universal recovery processing" for the recovery of antioxidants from natural sources. These "5-stages" are: 1. Macroscopic pre-treatment, which implies: a. wet milling, thermal and/or vacuum concentration, b. mechanical pressing, freeze drying, centrifugation and microfiltration, 2. Macro- and micro-molecules separation–alcohol precipitation, ultrafiltration, isoelectric solubilization–precipitation and extrusion, 3. Extraction—solvent, acid, alkali, microwave-assisted, steam diffusion, hydrodystillation, supercritical fluids, 4. Isolation and purification—adsorption, chromatography, nanofiltration and electrodialysis, and 5. Product formation—spray- and freeze–drying emulsions.

Recently, many scientists have paid attention to antioxidant recovery from food by products. One of the sources exploited for antioxidant recovery is olive mill waste (Ena, Pintucci, & Carlozzi, 2012, Galanakis et al., 2010a; Rahmanian et al., 2014), olive stones (Lama-Munoz,

Table 2
Extraction procedure advantages and disadvantages.

Techniques	Advantages	Disadvantages
Extraction with solvents	Inexpensive Can be performed with simple equipment and can be automated. The solvent can be reused (Wang et al., 2010)	Low selectivity, low extraction efficiency, solvent residue, multiple extractions might be required and environmental pollution (Wang et al., 2010) Time consuming, high temperature (Wang et al., 2013) Multiple extractions might be necessary
Extraction with supercritical fluids	Non-toxic, environmentally friendly, non-flammable The fluids are easily removed from the product It has a convenient critical temperature (31.04 °C). This enables extractions to be carried out at comparatively low temperature (often as low as 40 or 50 °C), decreasing the risk of damage of thermalabile compounds The number of solvents possible to be used on supercritical extraction is superior to classic organic solvents Supercritical fluids have a superior selectivity although they have an inferior solvent power than classic organic solvents Supercritical extraction can be connected directly to a chromatograph, allowing analysis immediately after extraction (McHugh & Krukonis, 2013)	An important drawback of supercritical extraction and most of the other supercritical fluids is that predominantly, a non-polar extraction fluid, such as CO_2, is used (Darani & Reza Mozafari, 2010)
Microwave-assisted extraction	Less solvent and energy, not time consuming High efficiency (Ballards et al., 2010), reduced extraction time, reduced solvent consumption, and less environmental pollution as a result of increased efficiency and clean transfer of energy to the matrix; improved extraction yield and product quality, because materials can be rapidly heated, and often processed at lower temperatures; up to 70% energy saving compared to conventional energy forms from the high energy densities and the direct absorption of energy by the materials; compact systems, as small as 20% of the size of conventional systems; and selective energy absorption resulting from the dielectric properties of the material and applicator design (Michel et al., 2011; Yuan et al., 2012, Veggi, Martinez & Meireles, 2013)	Additional filtration or centrifugation is necessary to remove the solid residue after the process; the efficiency of microwaves can be poor when the target compounds or solvents are nonpolar, or when they are volatile; and the use of high temperatures that can lead to degradation of heat-sensitive bioactive compounds (Veggi et al., 2013)
Subcritical water extraction (SWE)	Less expensive operation, environmentally friendly, lower working temperatures (thus avoiding losses and degradation of volatile and thermostabile compounds), it is a selective method, because by means of kinetic experiments, it is possible to manipulate the extract composition under given working conditions and higher quality of the extracts (He et al., 2012).	More laborious and time-consuming method (He et al., 2012).
Ultrasonics (US)	Ultrasonic extraction is a simple, efficient and inexpensive alternative to conventional extraction techniques. Moreover, there is no chemical involvement in the ultrasonic extraction, which can prevent possible chemical degradation of target compounds (Chemat & Khan, 2011). Ultrasonic-assisted extraction can be carried out at lower temperatures, avoiding thermal damage to the extracts and the loss of volatile components on boiling (Ormeno, Goldstein, & Niinemets, 2011). Environmentally friendly (Wu et al., 2014)	Need to be applied for a long time (1 h) at a high temperature (70 °C) to significantly increase the yield of polyphenols (Corrales et al., 2008)
Pulsed electric fields (PEF)	Replace the enzymatic maceration of the plant tissue, works on an entire mash flow, keeps the product temperature almost unchanged cost-effective because uses the latest advances in pulsed power technology (Corrales et al., 2008)	It's effectiveness is 50% of the HVED (in the case of polyphenols yields) (Boussetta et al., 2013)
High hydrostatic pressure (HHP)	It can obtain a single component of high purity. Strong, weak and non-polar compounds can all be extracted. Energy saving method (Rendueles et al., 2011)	Complex material handling, little flexiblility in choice of container, greater dead time in use of pressure (Mathavi, Slujatha, Ramaya, & Devi, 2013)
High voltage electrical discharges (HVED)	Short times of treatment (a few ms) and low energy consumption (10–50 kJ/kg) High extraction yields of polyphenols compared with PEF and US (Rajha, Boussetta, Louka, Maroun, & Vorobiev, 2014)	Slow rate of material removal, The addition time and cost for creating electrodes Reducing sharp corners on the work piece is difficult due to electrode wear (Rajha et al., 2014) The method could be too sophisticated (in terms of high capital cost and energy consumption) for their application in nutraceuticals recovery from by-products (Galanakis, 2013)
Enzyme-assisted extraction	High extraction yield enhances the release of secondary plant metabolites and preserves the bioactive properties of the extracts and energy—saving (Wang et al., 2013) Environmentally friendly (Wu et al., 2014)	Long time required and the high cost of enzymes that makes this strategy uneconomical (Martínez-Maqueda, Hernández-Ledesma, Amigo, Miralles, & Gómez-Ruiz, 2013)

Romero-Garcia, Cara, Moya, & Castro, 2014), brewers's spent grains (Meneses, Martins, Teixeira, & Mussatto, 2013), *Citrus limon* residues (Dahmoune et al., 2013), winery sludge (Galanakis, Markouli, & Gekas, 2013b), blackberry bagasse (Reategui, Machado, Barbero, Rezende, & Martinez, 2014), rice hull (Nenadis, Kyriakoudi, & Tsimidou, 2014), grape pomace (González-Centeno, Comas-Serra, Femenia, Rosselló, & Simal, 2015) and apple pomace (Reis, Rai, & Abu-Ghannam, 2012).

In the last years many methods for phenolic compound recovery from plant processing and their purification and fractionation have been proposed (Kammerer, Carle, Stanley, & Saleh, 2010). The fractionation steps may enhance antioxidant properties of phenolic mixtures by reducing antagonistic effects (Iacopini, Baldi, Storchi, & Sebastiani, 2008). Furthermore, extract components, such as peptides, proteins and sugars, may also interact with the phenolic compounds, thus

affecting their antioxidant activity or causing color and flavor changes (Teixeira, Eiras-Dias, Castellarin, & Gerós, 2013), which renders selective polyphenol enrichment and fractionation worthwhile (Kammerer, Schweizer, Carle, & Kammerer, 2011).

One method used for the polyphenol fractionation involves column chromatography of Sephadex LH 20 or reversed C18 phase, where the phytochemicals are fractioned into several fractions according to the phenolic properties (weight, solubility and polarity) and much easily identified and quantified using modern methods. Fractionation facilitates the study of the secondary metabolite activities (Falleh et al., 2013; Martinez-Correa et al., 2011).

Falleh et al. (2013) used a column containing C18 resin for the polyphenol content fractionation from *Mesembryanthemum edule* organs and they observed that the best biological activities were found in 40 and 60% methanol/water stem and root fractions.

Juadjur and Winterhalter (2012) proposed an adsorptive membrane chromatographic method for the fractionation of polyphenols from bilberries. The membrane consists of two types of strongly acidic membrane adsorbers: 1. Sartobind S 75 with a membrane area of 75 cm^2 and 2. Sartobind SIEX 150 ml with a membrane area of 0.55 m^2.

Galanakis et al. (2013b) proposed an ultrafiltration method for the recovery and fractionation of different phenolic classes from winery sludge. Ultrafiltration is among the conventional technologies that are utilized prior or after extraction process because it is able to separate macromolecules (i.e., soluble dietary fibers or polysaccharides) from smaller compounds (i.e., phenols, sugars or ions) in a physicochemical and non-destructive way (Galanakis, Tornberg, & Gekas, 2010b). These scientists observed that the application of a non-polar fluoropolymer membrane in the border of ultrafiltration and nanofiltration (1 kDa), provided a successful methodology to separate different phenolic classes like hydroxycinnamic acids, flavonols and anthocyanins on the basis of polarity, but not in terms of membrane adsorption. Galanakis et al. (2010a) applied ultrafiltration for the fractionation of different phenolic classes from olive mill wastewater, the 100 kDa membrane can be utilized for the clarification of the phenol containing beverage. This type of membrane was able to partially remove the heavier fragments of hydroxycinnamic acid derivatives and flavonols in the concentrate stream and at the same time to sustain the antioxidant properties of the beverage in the permeate stream.

3.3. Evaluation of total antioxidant activity

3.3.1. In vitro methods

The in vitro methods widely used for achieving the antioxidant activity are: DPPH (1, 1-diphenyl-2-picrylhydrazyl) scavenging activity, the determination of Trolox equivalent antioxidant capacity (TEAC), the determination of ferric reducing/antioxidant power (FRAP), oxygen radical absorbance capacity (ORAC) and hydroxyl radical-scavenging capacity assay (HRSCA). All the methods used in the quantification of total antioxidant activity involve the reactions of the reactive oxygen species with some reagents and the complex formed is VIS spectrometrically detected at a different wavelength (520 nm in the case of DPPH assay (Molyneux, 2004), 660, 734 and 820 nm respectively in the case of TEAC (Gan et al., 2010), 593 nm in the case of FRAP assay (Pérez-Jiménez et al., 2008) and 530 nm in the case of HRSCA, respectively (Li, 2013; Lu et al., 2014)) in the case of color complex or is measured using a flourometrical detection (at an excitation wavelength at 540 nm and an emission at 565 nm) in the case of ORAC assay (Huang, Majumder, & Wu, 2010).

A special combination of an in vitro method is represented by the combination of DPPH assay with High performance liquid chromatography (DPPH–HPLC). On-line DPPH–HPLC (High Performance Liquid Chromatography) methods could be used for a rapid screening of antioxidants from complex mixtures, particularly for natural products with a minimum of sample preparation (Dai et al., 2013). The DPPH–HPLC method was been developed for the determination of DPPH scavenging activity, due to the drawbacks of the DPPH assay. The DPPH assay is a typical off-line detection method, where the antioxidant activity is measured colorimetrically. However, the DPPH and anthocyanins showed strong absorption at 500–550 nm and so the weak changes in DPPH absorbance could not be observed and quantified (Sun et al., 2012).

The on-line DPPH–HPLC method involves the post-column extract reaction with DPPH according to the colorimetric assay (at 517 nm) and then the mixture is passed to the HPLC detection (Zhang et al., 2013a, 2013b). The peak areas of compounds with potential antioxidant activities will be reduced or disappear in the HPLC chromatogram after their reaction with DPPH, and for those without antioxidant activities, the peak areas have almost no change (Dai et al., 2013).

Free radical scavenging activity can be evaluated by comparison with the water-soluble synthetic vitamin E derivate 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox). This method permits a rapid, selective and relatively simple detection of free radicals in complex mixtures and a quantitative analysis of individual antioxidants in complex mixtures (Zhang et al., 2013a, 2013b). The On-line HPLC with DPPH radical scavenging assay has disadvantages that these targets of anti-oxidative activity could not be purified for the identification and/or evaluation of unknown compounds by NMR, in vivo, and in vitro assays (Liang, Yang, Cao, Wu, & Wu, 2011). Another drawback is that it needs special equipment, technical skill for analysis and lower sensistivity and resolution (Li et al., 2011).

Qiu et al. (2012) applied for the screening of the natural antioxidants in peanut shell a DPPH–HPLC–DAD–TOF/MS method. The method is based on the hypothesis that upon reaction with 1, 1-diphenyl-2-picrylhydrazyl (DPPH), the peak areas of compounds with potential antioxidant activities in the HPLC chromatogram will be significantly reduced or disappeared, and the identity confirmation could be achieved by HPLC–DAD–TOF/MS technique.

The DPPH–HPLC method can be followed by the HSCCC experiments for the fast screening and purification of potent antioxidants from differents fraction in solvents. The best advantage of this method is that the active compounds can be screened from a chromatographic separation, and the then target-guided purifications can be operated by HSCCC. The method has a broad applicability and is rapid, robust and suitable for fast screening and preparing antioxidants from crude plant extracts. Shi et al. (2012) used this method for the separation and purification of 18 antioxidants from *Pueraria lobata* flower.

The on-line DPPH–HPLC method has been applied for antioxidant screening from rabbit eye blueberry (Sun et al., 2012), *Eucommia ulmoides* leaves (Dai et al., 2013), peanut shells (Qiu et al., 2012), *Teucrium polium* (Goulas et al., 2012), pomegranate (Romani, Campo, & Pinelli, 2012), *P. lobata* (Shi et al., 2012), *Selaginella sinensis* (Zhang et al., 2011), fruit wine (Nuengchamnong & Ingkaninan, 2010), and koji (Giri, Osako, Okamoto, Okazaki, & Ohshima, 2012). For the identification of the antioxidant compound HPLC–DPPH coupled with HSCCC (Dai et al., 2013; Shi et al., 2012; Zhang et al., 2011), TOF/MS (Qiu et al., 2012), SPE-NMR (Goulas et al., 2012), DAD (Zhang et al., 2013a, 2013b), MS (Nuengchamnong & Ingkaninan, 2010) has been used.

3.3.2. In vivo methods

The in vivo action of antioxidants is due to the inhibition generation of the reactive oxygen species or by direct scavenging of free radicals (Aruoma, 2003). In the case of in vivo methods, the antioxidants should be absorbed, transported, distributed and retained properly in the biological fluids, cells and tissues. The in vivo methods involve testing the antioxidant administration to animals at a specified dosage regimen. After a period of time, the animal blood or tissues are used for the assay. During the animal treatment for the antioxidant capacity measurement many transformations could occur (e.g., biotransformation during enzymatic conjugation), and for these reasons the experiments should be treated with caution (Niki, 2010).

The in vivo antioxidant capacity may be measured using biological fluids and tissues (erythrocytes, urine, plasma, cerebrospinal fluids, saliva or tear) from humans or animals (Liu, Jia, Kan, & Jin, 2013b).

The most used methods for the evaluation of antioxidant activity in vivo are: Total radical-trapping parameter (TRAP), Reduced glutathione (GSH) estimation, Superoxide dismutase (SOD), Glutathione peroxidase (GSH-Px), Catalase (CAT) and Lipid peroxidation (LP).

3.3.3. Electrochemical methods

3.3.3.1. Voltammetric procedures. The cyclic voltammetry procedure is an affordable, rapid and sensitive enough method for the determination of antioxidants. Cyclic voltammetry involves three electrodes: the working electrode (e.g., glassy carbon), the reference electrode (Ag–AgCl), and the auxiliary electrode (platinum wire). The working electrode is subjected to a constant potential rate of 100 mV/s and records the evolution curve named cyclic voltammogram. The two parameters of reducing power of a sample are: the peak potential [$E_{p(a)}$], which may be correlated with individual compounds, and the anodic current ($I_{p(a)}$), which may be correlated with the antioxidant concentration (Cadenas & Parker, 2001).

Cyclic voltammetry proved to be a useful technique for the rapid determination of antioxidant capacity in fruit tea beverages. Piljac-Žegarac, Valek, Stipčević, and Martinez (2010) observed that the high degree of positive correlation with the other antioxidant capacity measures indicate that the results derived from cyclic voltammetry are reliable and comparable to the results of commonly used methods for antioxidant capacity.

Cyclic voltammetry has been applied with success in the case of seaweed (Keyrouz et al., 2011), green, oolong and black teas (Kilmartin & Hsu, 2003), wine (Aguirre et al., 2010), fruit juice (Piljac-Žegarac et al., 2010) and wild plants (Barros, Cabrita, Boas, Carvalho, & Ferreira, 2011a; Barros, Nunes, Gonçalves, Bennet, & Silva, 2011b).

Differential pulse voltammetry has been applied to measure the antioxidant activity of wine (Aguirre et al., 2010; Šeruga, Novak, & Jakobek, 2011), raspberries (Aguirre et al., 2010) and wild plants (Barros et al., 2011a, 2011b).

3.3.3.2. Bionsensors. Campanella, Bonanni, Finotti, and Tomassetti (2004) developed a superoxide dismutase (SOD) biosensor for the determination of the total and natural antioxidant capacity of red and white wines. The biosensor was obtained by coupling a transducer (an amperometric electrode for hydrogen peroxide, with a platinum anode maintained at a constant potential of 650 mV with respect to an Ag/AgCl/Cl^- cathode) and the superoxide dismutase enzyme immobilized in a gel-like kappa-carrageenan membrane. They observed that the correlation between total antioxidant activity measured by various spectroscopic methods for white and red wines, respectively, has a relatively strong correlation with the bionsensor method.

The SOD biosensor method is a valid method for measuring the capacity of algae (Campanella, Martini, & Tomassetti, 2005). This method permits the measurement of the antioxidant capacity in the case of both cultivated and powdered algae, and also when the algae sample is tested in its whole form or after homogenization and centrifugation (Campanella et al., 2005).

The purine-based biosensor (adenine or guanine) for antioxidant activity is based on the interaction of adenine or guanine immobilized on the glassy carbon electrode (GCE) surface with the hydroxyl radical. Vitamin C presents the highest antioxidant activity values and seems to be the most sensitive standard antioxidant. The purine-based biosensor is disposable, and requires very easy, rapid, reproducible preparation and can be combined with portable equipment (Barroso, Delerue-Matos, & Oliveira, 2012).

Han et al. (2012) developed a novel amperometric biosensor based on immobilizing tyrosinase on the surface of an Mg–Al–CO_3HTLc modified electrode for the detection of polyphenols. The fabricated biosensor showed a low detection limit, satisfactory linear concentration range, excellent stability, high reproducibility and effective application to real samples (different types of tea).

Gil and Rebelo (2010) have developed a laccase-based biosensor to evaluate the antioxidant activity of wine. They observed a good correlation between the antioxidant properties determined using the ABTS assay and the bio electrochemical polyphenol index obtained at pH 3.5 with the biosensor, taking caffeic acid as reference solution. The immobilization of the enzyme on the derivated polyethersulfone membranes is rapid.

Other approach used for antioxidant biosensor involves the printing techniques, which are used in the fabrication of organic devices. Pavinatto, Paschoal, and Arias (2014) reported the fabrication of an allprinted and flexible biosensor for antioxidants. Gold interdigitated electrodes with sub-100 μm features were directly inkjet-printed on plastic substrates using a nanoparticle-based ink. This kind of biosensor is compatible with roll-to-roll processes and it is believed that it has a great potential for the development of a technological product for the analysis of dietary products.

The DNA-based electrochemical biosensors have proved to be one of the most efficient methods for measuring the antioxidants capacity. These biosensors are based on the immobilized double stranded (ds)-DNA on the surface of electrodes and the protective effect of the antioxidants induced by •OH generated via a Fenton-type rection. Silver is used to achieve the ds-DNA immobilization due to its excellent conductivity, good electrocatalytic activity and chemical stability (Wang, Jiao, & Yu, 2014). When silver is modified on the electrode, highly reactive silver oxides are generated and alter the conductivity of the immobilized ds-DNA molecules. Conducting polymer incorporated with metallic particles provides an exciting system and is a potential application in sensors (Tsai, Lin, & Chen, 2011). Wang et al. (2014) developed a biosensor using a poly L-glutamic acid and Ag and an outside layer of chitosan/double stranded DNA for measuring the total antioxidant capacity of orange juice beverage. The method produces results comparable with the UV–VIS spectroscopy method, exhibiting a good stability and reproductibility.

Barberis et al. (2015) have used four fullerenes- or nanotubes-modified sensor-biosensor systems, coupled with a dual-channel telemetric device, based on ascorbate oxidase biosensor, for the on line simultaneous amperometric detection of ascorbic acid and antioxidant activity in blueberry, kiwi and orange juice. Biosensors register lower ascorbic acid currents than the sensors due to the enzyme capability to oxidize ascorbic acid before it reached the transductor surface. Phenols currents registered by sensors and biosensors did not differ. The biosensor makes possible an effective rapid screening of ascorbic acid and antioxidant capacity at any moment of the productive chain. However it has two main limits, the fragility of graphite rods and the laborious realization.

The laccases enzyme can be used to create an amperometric biosensor for phenolic compounds determination. Laccase are multicopper oxidoreductases, capable of oxidizing several phenolic and non-phenolic compounds. Touloupakis, Chatzipetrou, Boutopoulos, Gkouzou, and Zergioti (2014) have immobilized with success laccase in active form onto nonfunctionalized screen printed electrodes by using the laser printing technology. This type of immobilization established efficient electrochemical contact between the enzyme and the electrodes surface. The biosensor has a good sensitivity for catechol.

3.3.4. Chemiluminescent methods

Chemilumiscences (CL) is a sensitive and fast method for screening antioxidant activity. A suitable reagent for CL is luminol, due to its ability to scavenge the free radicals involved in the sequence leading to an excited electron (3-aminophtalatedianion (3-APA*)), which emits light on return to its ground state (Barni, Lewis, Berti, Miskelly, & Lago, 2007).

Nalewajko-Sieliwoniuk, Nazaruk, Antypiuk, and Kojło (2008) reported a new flow injection analysis-CL detection method useful for the detection and quantification of phenolic compounds (6′-caffeoylerigeroside and caffeic acid) from *Erigeron acris* L. extracts based on the phenolic compound-inhibited luminol-I_2 CL in a sodium

hydroxide medium. CL-detection is advantageous due to its high sensitivity in comparison with the spectrophotometric assays (DPPH), moreover, the luminol-I_2 detection system is simple and based on stable and easy-to-handle reagents.

3.3.5. Electron spin resonance

Electron spin resonance (ESR) also called Electron Paramagnetic Resonance (EPR) spectroscopy is the most comprehensive technique for detecting and monitoring processes involving radicals. ESR spectroscopy provides both qualitative and quantitative information about paramagnetic species having one or more unpaired electrons. Since hydroxyl radicals ($OH^{\cdot}$) have a very short life-time, spin-trapping techniques with DMPO (5, 5-dimethyl-1-pyrroline-1-oxide) are used for its detection (Elia, Azoulay, & Zeiri, 2012). This method is the only one that detects free radicals involved in autoxidation.

The identity of the radical can be deduced from the obtained ESR spectrum, since the hyperfine coupling pattern and hyperfine coupling constants are characteristic for the different adducts of trapped radical and spin traps. Moreover, the intensity of the ESR signal provides an estimate of the amount of radicals formed under various conditions (Hougaard, Arneborg, Andersen, & Skibsted, 2013).

Ludwig et al. (2012) measured the antioxidant activity of coffee using two stabilized radicals: potassium nitrosodisulfonate (Fremy's salt) and 2, 2, 6, 6-tetramethyl-1-piperidin-1-oxyl (TEMPO). Mainly phenolic compounds can be detected when Fremy's salt is used as the stabilized radical, whereas TEMPO is mainly scavenged by Maillard reaction products (MRP), such as melanoidins. The results obtained with ESR spectroscopy showed that Fremy's salt scavenging capacity was almost four times higher than TEMPO (Ludwig et al., 2012).

Kohri et al. (2009) developed an ORAC-electron spin resonance (ESR) assay using a spin-trapping method for the determination of the 2, 2′-Azobis (2-anidinopropane) dihydrochloride (AAPH)-derived free radical. The ORAC-ESR assay is based on the competitive reaction between spin-trapping of the 2, 2′-Azobis (2-anidinopropane) dihydrochloride-derived free radical, mainly $RO^{\cdot}$, and its elimination by particular substrate.

The ORAC-ESR assay, being based on the competitive elimination of the alkoxyl radical by substrate and spin trap, is far superior to the ORAC-FL assay and should yield accurate ORAC values. The reaction scheme of the AAPH decomposition follows three steps: (1) the formation of an alkyl radical ($Ra^{\cdot}$) by the UV irradiation of AAPH, (2) transfer of the alkyl radical to the peroxyl radical ($RaOO^{\cdot}$) with O_2, and (3) decomposition of the peroxyl radical to an alkoxyl radical ($RaO^{\cdot}$) [$Ra = C(CH_3)_2$–$C(NH_2\,Cl^{-}\bullet)NH_2$] (Nakajima et al., in press). This assay has very good reproducibility, and is conducted under stoichiometric experimental conditions (Nakajima et al., in press).

The ESR method was applied to measure antioxidant activity of coffee (Ludwig et al., 2012), aqueous and aroma extracts of squid miso prepared with *Aspergillus oryzae*-inoculated koji (Giri, Osako, Okamoto, Okazaki, & Ohshima, 2011) and fermented fish paste (Giri, Osako, Okamoto, & Ohshima, 2010).

3.4. Methods for the determination of the different compounds in the antioxidant fraction

3.4.1. Chromatographic methods

Due to its precision and versatility, High Performance Liquid Chromatography (HPLC) is used to analyze carotenoids and phenolic compounds. In general, reversed-phase C18 columns are used. The mobile phase consists of a two solvent system containing a polar organic solvent (methanol or acetonitrile) and acidified water. A UV–VIS and PDA (Photodiode array) detectors are normally coupled to HPLC for the analysis of carotenoids and phenolic compounds (Irakli, Samanidou, Biliaderis, & Papadoyannis, 2012; Luthria, 2012, Šeruga et al., 2011; Zhang et al., 2013a, 2013b).

One of the disadvantages of the HPLC method is the detection limit and sensitivity in complex matrices, such as crude plant extracts. Thus, an initial pre-concentration and purification of polyphenols from complex matrix is crucial prior to the instrumental analysis by HPLC. The recovery of polyphenols using polymeric resins is approved for food processing by the Food and Drug Administration and the council of Europe (Scordino, Di Mauro Passerini & Maccarone 2003). Gu et al. (2008) developed a method which involves macroporous adsorption resin (AB-8 macroporous resin) combined with ultra-filtration; this method was successfully employed to isolate and purify high molecular weight and low molecular weight phenolic compounds from crude extracts of persimmon. The absorption of flavonoids and phenolic acids on different resins has been studied (Escriche, Kadar, Juan-Borrás, & Domenech, 2014). Ginger polyphenol adsorption has been studied using an anion exchange resin, AmberliteIR-400 (Datta, Dutta, Dutta, & Chaudhuri, 2011).

Thin-layer chromatography (TLC) is a good method for screening plant extracts for the presence of antioxidants (Waksmundzka-Hajnos, Sherma, & Kowalska, 2008). TLC is a simple, inexpensive technique which is particularly suitable for analyzing a large number of samples (Simões-Pires, Hmicha, Marston, & Hostettmann, 2009). TLC has been applied for the detection of lignin in Oriental medicinal plants (Slanina & Glatz, 2004). In some cases, the fractions analyzed using TLC may be identified by HPLC-MS or GC–MS. All lignans absorb UV light and for this reason they can be detected at 254 nm (Willför et al., 2005).

Gas chromatography (GC) is a good method for the identification of lignans due to its excellent resolution, although it requires the derivatisation of the compounds. This derivatisation leads to an increase in the thermal stability of lignans and enhances the detection selectivity. One group of lignans (podophyllotoxintypelignans), which does not have free hydroxyl groups does not need derivatisation for identification (Willför et al., 2005). Bonzanini, Bruni, Palla, Serlataite, and Caligiani (2009) reported the presence of six lignans in *Punicagranatum* L fruit endocarp, pulp, seeds, wood knots and commercial juices.

HSCCC is a support-free liquid–liquid chromatographic technique, which allows complete recovery of the sample and is suitable for separations in large quantities (Cheng et al., 2012). HSCCC is used for the separation and isolation of tannins (Liu, Su, Wang, Gu, & Xing, 2010), flavonoids (Liang et al., 2011) and anthocyanins (Inoue, Baba, Hino & Oka 2012). This method works without any solid stationary phase and separation is solely based on the partition of compounds between two immiscible liquid phases. Advantages are high sample input and mild separation conditions (Köhler, Wray, & Winterhalter, 2008). The HSCCC techniques use immiscible liquid two-phase solvent systems, and the distribution effects caused by column rotation, and the fast changing centrifugal force-fields result in a very effective partition process for isolation of bioactive natural products (Rodríguez-Rivera, Lugo-Cervantes, Winterhalter, & Jerz, 2014).

The ion pair—HSCCC was applied by Jerz et al. (2014) for the separation of amaranthine-type betacyanins. They obtained a better reolution between polat betacyanins, and identified eighteen betacyanins/isobetacyanins with a wide range of polarities in the *Iresinii lindenii* Van Houtte leaves extract. In addition to the well known pigments (amaranthine, betanin and iresini I) they observed three new acylated (feruloylated and sinapoylated) betacyanins.

Regalado et al. (2011) used HSCCC coupled with HPLC–DAD–ESI-MS^n for the isolation and identification of phenolic compounds from rum aged in oak barrels for screening the antioxidant activity. They observed that coupling HSCCC with HPLC–DAD–ESI-MS^n obtained lower detection limits for electrospray mass-spectrometry and revealed eighty-five compounds.

Mass spectrometry has a very important role for research and quality control, and its analytical power is relevant for structural studies on aroma and polyphenolic compounds (Willoughby, Sheehan, & Mitrovich, 1998). Mass spectrometers are instruments that separate ionized atoms or molecules according to their difference in mass to charge ratio (m/z). Mass spectrometry is therefore useful for the quantification of atoms or molecules and, since molecules have distinctive

fragmentation patterns, to provide structural information for the identification of structural components (Watson & Sparkman, 2007).

The main components of a mass spectrometer are: ion source, a mass-selective analyzer and the detector. Separation devices are used to increase the sensitivity, dynamic range and selectivity of the MS (e.g., gas chromatographic separation which can be made up before the mass spectrometric analysis, in online or offline mode).

3.4.1.1. The ionization methods. Prior to analysis in a mass spectrometer, molecules need to be ionized. Various ionization methods exist but the most standardized and one of the most common forms of ionization is electron ionization (EI), also called electron impact. Another method is chemical ionization (CI) (Gad, 2012). The main ionization methods are presented in Table 3.

3.4.1.2. Mass analyzers. Mass analyzers are another one of the basic components of a mass spectrometer. After ionization occurs, the charged molecules enter another region of the mass spectrometer in which separation of the ion mixture occurs. Nowadays, there are many mass analyzer designs and variations that accomplish this task. Some analyzers not only separate charged ions from each other but also store and filter the ions. In other words, one analyzer can function in several modes. This multifunctioning ability often makes it advantageous to design mass spectrometers that utilize more than one type of analyzer in a single instrument. Mass analyzers measure the *m/z* ratio. This becomes especially important when compounds take on several charges (*z*) because the *m/z* will be much less than the actual mass (*m*) of the compound (Gad, 2012). The main types of mass analyzer, advantages, disadvantages and their application are described in Table 4.

Liquid Chromatography–Mass Spectrometry (LC–MS) techniques are nowadays the best analytical approach to study polyphenols in grape extracts and wine, and are the most effective tool in the study of the structure of anthocyanins. LC–MS allows the characterization of complex structures of grape polyphenols, such as procyanidins, proanthocyanidins, prodelphinidins, and tannins, and provides experimental evidence for structures that were previously only hypothesized (Flamini, 2003). LC–MS/MS has been applied for the identification and quantification of ferulic, caffeic and syringic acids, quercetin, pyrogallol, α-tocopherol, vanillin, *p*-coumaric, *p*-hydroxybenzoic, ascorbic and gallic acid in cherry stems (*Cerasusavium* L) (Bursal, Köksal, Gülçin, Bilsel, & Gören, 2013). Jaitz et al. (2010) have quantified gallic acid, caffeic acid, catechin, epicatehin, *cis p*-coumaric acid, *transp*-coumaric acid, myricetin, *cis*-resveratrol, *trans*-resveratrol and quercitin using LC–MS/MS in red wine, obtaining excellent detention limits.

HPLC-MS/MS is used for the identification and quantification of minor components at mg/kg and μg/kg levels (Zhang, Rose, & Trenerry, 2009). HPLC-MS/MS has been used for the determination and quantification of vitamin A and E (Plozza, Trenerry, & Caridi, 2012), β-carotene (Plozza et al., 2012) and phenolic profile (Perestrelo et al., 2012).

Ultra performance liquid chromatography (UPLC) has a sensitivity and separation power greater than HPLC so the time and the cost of analysis are lower. The UPLC method is faster, more sensitive, consumes less eluant and it is more eco-friendly than the conventional HPLC method. Klimczak and Gliszczyńska-Świgło (2015) have compared the UPLC and HPLC as methods for the ascorbic acid and total ascorbic acid (as the sum of ascorbic acid and dehydroascorbic acid after its reduction to ascorbic acid) determination in fruit beverages and in pharmaceutical preparations. In terms of limits of detection and quantification, the UPLC is that of HPLC. Wong et al. (2014) used UPLC for the detection of vitamin E in vegetable oils, margarines and supplement capsules. The method exhibited considerable advantages as it is not only simpler, faster (aprox. 9.5 min) and sensitive (especially with FL detection) but also managed to overcome the pressure build-ups that are inherent of the conventional RP-HPLC systems.

Ultra-performance liquid chromatography coupled with tandem mass spectrometry (UPLC-MS) is recognized as a powerful tool for the quantitative determination of the active compound in biological samples due to the selectivity, sensitivity, robustness, sample throughput (Sun et al., 2015), better speed and precision can assist the rapid identification of secondary metabolites from antioxidant extracts (Kenny, Smyth, Hewage & Brunton, 2013). Ortega et al. (2010) compared UPLC-MS/MS with HPLC-MS/MS to determine procyanidins in cocoa samples. The two methods have been compared in terms of speed, sensitivity, selectivity, peak efficiency, linearity, reproductibility, detection limits and quantification limits. The UPLC-MS/MS method allowed the determination of procyanidins up to nonamers at low-concentration levels in a short analysis time. The analysis time was reduced from 80 min (in the case of HPLC-MS/MS) to 12.5 min (in the case of UPLC-MS/MS).

Prokudina et al. (2012) used an UPLC–ESI-MS/MS method for the quantitative determination of 26 compounds in plant extracts including 15 isoflavonoids. Using this method, a typical experimental run was completed in about 17 min, which, coupled with the relatively low flow rate of 0.2 ml/min, resulted in a noticeable reduction in solvent consumption, and thus environmental impact compared to conventional HPLC systems. This kind of method can be applied for the metabolites detection and quantification. The UPLC–ESI-MS/MS was applied for the metabolites related to polyphenol gut microbial metabolism in biological samples detection. Gasperotti, Masuero, Guella, Mattivi, and Vrhovsek (2014) determined the polyphenol microbial metabolites in urine, plasma, tissues and blood. They determined 23 polyphenol metabolites in all matrixes applied. No interference was observed any in the different biological matrices.

Mass spectrometry coupled to gas chromatography (GC–MS) is a powerful method used to separate, identify and quantify *cis*- and *trans*-resveratrol in red wine (Cai, Koziel, Dharmadhikari, & van Leeuwen, 2009). Rodríguez-Cabo, Rodríguez & Cela (2012) developed a method for the identification of pterostilbene, resveratrol and piceatannol from wine using GC–MS.

High Performance Liquid Chromatography–electrospray tandem mass spectrometry (HPLC–ESI-MS) is a versatile technique used recently for individual antioxidant analysis. Chai et al. (2012), used HPLC–ESI-MS for the identification of condensed tannins from leaf, fruit and stem bark of *Delonix regia*, these compounds were identified by degradation of tannins using hydrolysis in the presence of benzyl mercaptan. Stalmach, Edwards, Wightman, and Crozier (2011) used HPLC–ESI for identification of anthocyanins, flavan-3-ols, flavonols, hydroxycinnamic acids, hydroxybenzoic acids, and stilbenes in grape juice.

3.4.2. Capillary electrophoresis

Capillary electrophoresis (CE) methods, much used in recent years (Lee, Boyce, & Breadmore, 2011a), are suitable for the analysis of anionic and cationic compounds and hydrophobic molecules from complex natural matrices (Başkan, Öztekin, & Erim, 2007).

In the case of CE, a sample, which usually contains charged species, is introduced into the end of a capillary that has been filled with a buffer solution (or electrolyte). Under the influence of an electric field, the analytes migrate away from the injection end of the capillary toward the detector end, where they are visualized. Three distinct mechanisms have been developed for the separation of analytes by CE: 1. The first mechanism is based on the mobility differences of the analytes in an electric field (these differences are dependent on the size and charge-to-mass ratio of the analyte ion), 2. The second separation mechanism is found in capillary isoelectric focusing, where analytes are separated on the basis of isoelectric points and 3. The third mechanism is found in capillary isotachophoresis, where all the solutes travel at the same velocity through the capillary but are separated on the basis of differences in their mobility (Weston, Brown, & Foret, 1998).

The advantages of CE are: a rapid and an economical methodology (Ballus, Meinhart, de Oliveira, & Godoy, 2012), they do not require a pre-separation process, the consumption of reagents is low, they generate less toxic waste compared with other separation techniques and could be applicable to the quality control of plants (Başkan et al.,

Table 3
Ionization methods: principle advantages and disadvantages.[a]

Ionization method	Principle	Advantage	Disadvantages
Electrospray ionization (EI)	EI can be applied to virtually all volatile compounds and the fragmentation provides structural information. Electrospray ionization takes place directly from solution. EI is the tool most widely used in LC–MS and is applied in the analysis of polar compounds and heat-labile compounds or compounds with higher molecular weight (compared to APCI). In EI, the sample solution is passed at atmospheric pressure through a capillary where high voltage is applied (typically 3–4 kV)	Low sample consumption and rapid analysis time. Ions produced by electrospray can be multiply charged, a fact which enables macromolecular analysis. Furthermore, commercial libraries with hundreds of thousands of mass spectra are available and can be easily interrogated for EI mass spectral "fingerprint". Electrospray ionization method has the major advantage of desolvation at relatively low temperatures (typically room temperature to 80 °C) so as not to generate fragments	A major disadvantage is that this technique cannot analyze mixtures very well, and when forced to do so, the results are unreliable. The apparatus is also very difficult to clean and has a tendency to become overly contaminated with residues from previous experiments. Finally, the multiple charges that are attached to the molecular ions can make for confusing spectral data. This confusion is further fueled by use of a mixed sample, which is yet another reason why mixtures should be avoided when using an electrospray ionization mass spectrometer.
Chemical ionization (CI)	Chemical ionization uses ion-molecule reactions to produce ions from the analyte. EI and CI share the same basic setup and source design (in fact, it is quite common for many ion sources to work in dual EI and CI ionization mode). The chemical ionization process begins when a reagent gas such as methane, isobutane, or ammonia (the most common gasses routinely employed) is ionized by electron impact. A high reagent gas pressure (or long reaction time) results in ion-molecule reactions between the reagent gas ions and reagent gas neutrals.	Chemical ionization is a lower-energy alternative to EI for the analysis of volatile molecules. CI provides simple mass spectra with reduced fragmentation compared to EI. One advantage is that CI often gives molecular weight information through molecular-like ions such as [M H].	Molecule must have Lewis or -acid functional group. More external upkeep and cost (gas cylinders). Poor fragmentation produces fragment patterns that are not informative or reproducible enough for library search.
Atmospheric pressure chemical ionization (APCI)	APCI uses gas-phase ion molecule reactions at atmospheric pressure in analogy to GC using CI. APCI is a soft ionization technique used to analyze nonpolar to medium polarity compounds and compounds of low molecular weight.	Good for less-polar compounds, excellent LC/MS interface. Compatible with MS/MS methods Low to slightly high polar compounds can be analyzed Higher LC flow rates (2 ml/min) can be used Higher tolerance to buffers in the mobile phase.	Low reproducibility The analyte analyzed must be volatile APCI does not function well at lower LC flow rates, and may contain more analyte-buffer adducts in mass spectra.
Matrix-assisted laser desorption (MALDI)	MALDI is based on the bombardment of sample molecules with a laser light to bring about sample ionization. The sample is pre-mixed with a highly absorbing matrix compound for the most consistent and reliable results, and a low concentration of sample to matrix works best. The matrix transforms the laser energy into excitation energy for the sample, which leads to sputtering of analyte and matrix ions from the surface of the mixture. In this way energy transfer is efficient and also the analyte molecules are spared excessive direct energy that may otherwise cause decomposition. Most commercially available MALDI mass spectrometers now have a pulsed nitrogen laser of wavelength 337 nm.	Gentle Ionization technique High molecular weight analyte can be ionized Molecule need not be volatile Sub-picomole sensitivity easy to obtain Wide array of matrices	MALDI matrix cluster ions obscure low m/z species (<600) Analyte must have very low vapor pressure Pulsed nature of source limits compatibility with many mass analyzers Coupling MALDI with chromatography can be difficult Analytes that absorb the laser light can be problematic

[a] Van Galen, 2005; Hillenkamp & Peter-Katalinic, 2013; Picó, 2012; de Oliveira Silva, de Castro, Milhome, & do Nascimento, 2014.

2007). The main advantages of CE compared with HPLC are its higher resolving power and its selectivity. It is useful for the detection of some very polar compounds that cannot be analyzed by RP-HPLC. Moreover, the possibilities of the CE approach for following the degradation of antioxidants has also been demonstrated (Crego et al., 2004).

Supercritical fluid extraction/Capillary electrophoresis–Ultraviolet detection (SFE/CE–UV) method is a reliable, efficient analytical tool which uses a simple background electrolyte and the normal polarity mode for the determination of rosmarinic and caffeic acids present in virgin olive oil enriched with natural antioxidants (Nevado, Robledo, & Callado, 2012).

Galeano-Díaz, Acedo-Valenzuela, and Silva-Rodríguez (2012) developed a new CE method using the fluorescence detection of tocopherols in vegetable oils; the fluorescence detection improved the sensitivity and the selectivity.

Capillary electrophoresis is excellent for the simultaneous separation of 16 phenolic compounds (e.g., rutin, myricetin, kaemppferol, quercetin, natitutin, morin, (−)-epicatechin, ( )-catechin, cinnamic acid, *trans*-resveratrol, ferulic acid, vanillic acid, gallic acid, caffeic acid and 3,4-dihydroxybenzoic acid) present in red, white and rosé wines (Ballus et al., 2012). This method is fast and consumes little reagent.

Lee et al. (2011a) developed a fast CE method (7 min) for determining sinapic, *p*-coumaric, ferulic and caffeic acids from broccoli, broccolini, Brusselsprouts, cabbage and cauliflower.

3.4.3. Nuclear magnetic resonance (NMR)

Nuclear magnetic resonance (NMR) is a rapid, non-invasive and non-destructive technique. NMR offers the opportunity to recognize a given compound without an internal standard (Soininen, Jukarainen, Julkunen-Tiitto, Karjalainen, & Vepsäläinen, 2012) and without any preparative manipulation which could alter, among others, the real distribution of water in the sample (Ruan & Chen, 2001). It is a powerful tool for simultaneously profiling diverse compounds in the food matrix (Rochfort, Ezernieks, Bastian, & Dowdey, 2010). In ^{1}HNMR, hydrogen atoms are selectively targeted, submitted to a strong magnetic field and excited by a radio frequency (RF). After the RF pulses, the excited nuclei emit and the absorbed energy is monitored. The signals obtained are related to the chemical and physical environments surrounding the spins and, therefore, different information can be extracted from them (Otero & Préstamo, 2009).

NMR spectroscopy has been widely recognized as the most important tool for the structural elucidation of flavonoids (Fossen & Andersen, 2006) and it is also increasingly used as an analytical tool for the evaluation of

Table 4
Advantages, disadvantages and application of mass analyzers.

Mass analyzer	Mass range and resolution	Advantages[a]	Disadvantes[a]	Application in the field of antioxidant identification
Quadrupole	Range m/z 3000 Resolution 2000	Ease of switching between positive/negative ion Relatively low cost Small size Medium resolution	Mass range limited to about 3000 m/z Poor adaptability to MALDI	Phenolic compounds from *Ramorinoa girolae* Speg (Fabaceae) seeds (Luna et al., 2013) Flavonoids from spinach (Dehkharghanian, Adenier, & Vijayalakshmi, 2010) Flavonoids from *Citri Reticulatae* pericarpium (Liu et al., 2013a; Liu et al., 2013b)
Ion trap	Range m/z 2000 Resolution 1500	Simple design, low cost Well-suited for tandem mass spectrometry (MS^n, $n \leq 4$) Easy for positive/negative ions	Limited mass range of current commercial version, however, progress is being made in their development	Phenolic profile of pomegranate (*Punica granatum*) juice (Sentandreu, Cerdán-Calero, & Sendra, 2013) Red cabbage anthocyanins (Wiczkowski et al., 2013)
Time-of-flight (TOF)	Range m/z ∞ Resolution 350	Highest mass range Very fast scan speed Simple design, low cost Ease of adaptation to MALDI	Low resolution Difficulty of adaptation to electrospray	Proanthocyanidinds in almond blanch water (Pérez-Jiménez & Torres, 2012) and cranberry (Feliciano, Krueger, Shanmuganayagam, Vestling, & Reed, 2012).
Fourier transform ion cyclotron resonance (FT-ICR)	Range m/z 10 000 Resolution 30 000	High resolution Well-suited for tandem mass spectrometry (MS^n, n≤)	High vacuum (10^{-7} Torr) required Superconducting magnet required, expensive Instrumentation massive	Antioxidant compounds in white cabbage (Hounsome, Hounsome, Tomos, & Edwards-Jones, 2009)
Orbitrap	Range 2000 Resolution >10,000	Small, simple devices Resolving power of 70 000 Fellget advantage as in FT-ICR Comparable performance to FT-ICR without the need for cryogen	Requires low pressure because a mean-free path of ~100 km is required High cost Inefficient trapping of the product ions	Beer polyphenols (Quifer-Rada et al., 2015) Antioxidants from Chinese medicine (Su, Zou, Preiss, Zhang, & Zou, 2010)

[a] Siuzdak, 1996; Watson & Sparkman, 2007; Ahearn, 2012; Cole, 2012; Dawson, 2013.

quality traits in foods (Le Gall, Puaud, & Colquhoun, 2001). Together with its undisputed potential in structural elucidation, NMR has other advantages such as quick sample preparation and short analysis time, and its total sample recovery permits distinguishing stereoisomers and makes it possible to identify the two epimeric forms of flavone glycosides (Maltese, Erkelens, van der Kooy, Choi, & Verpoorte, 2009) or for tannin isomers (Chai et al., 2012).

The NMR technique has been used for the structural elucidation of anthocyanins, as in the case of *Acanthopanax senticosus* (Siberian Ginseng) (Lee, Lim, & Choung, 2013), tamarillo (*Solanum betaceum* Cav.) and Andes berry (*Rubus glaucus* Benth.) fruits (Osorio et al., 2012) and wine (Cui et al., 2013). Anthocyanins with rhamnoside derivatives are found in some fruits like blackberries (Longo & Vasapollo, 2005), and in pomegranate flowers (Zhang et al., 2011).

Khoo, Clausen, Pedersen, and Larsen (2012) reported a prediction of total phenolic content, total anthocyanin content and total antioxidant capacity of sour cherries by applying multivariate data analysis to ^{1}H-NMR data.

The NMR has been proven to be a suitable instrumental platform for the coverage of both abundant primary metabolites (e.g., sugars, amino acids) as well as secondary plant metabolites (e.g., flavonoids) (Leiss, Choi, Verpoorte, & Klinkhamer, 2011). An advantage of NMR is that its signals are proportional to the metabolite molar concentrations, which allows the direct comparison of concentrations of all metabolites without the preparation of calibration curves (Kim, Choi, & Verpoorte, 2010). On the other hand, a major drawback of NMR is its relatively low sensitivity compared with MS-base methods. Therefore, hyphenated techniques that couple chromatography to mass spectrometry or to NMR are considered as powerful combinations, in particular with respect to compound identification (Bino et al., 2004; Frank, Engel, Weimer, & Slupsky, 2013). The term "metabolome" has been used to describe the observable chemical profile or fingerprint ot the metabolites in whole tissues. The NMR combined with PCA has been used to obtain metabolomic profile of plant, traditional phytomedicines and pine-mushroom (Cho, Kim, & Choi, 2007). Lee et al. (2011a), Lee et al. (2011b) investigated the metabolic behavior of green tea (*Camellia sinensis*) during tea fermentation using ^{1}H NMR spectroscopy coupled with multivariate statistical analysis for achieving comprehensive information on changes in metabiles induced by the fermentation. The metabolic differentiation between green tea and fermented tea was observed in the case of fourteen metabolites (epicatechin, epigallocatechin, epicatechin-3-gallate, epigallocatechin-3-gallate, theanine, etc.).

3.4.4. Near infrared spectroscopy

Near infrared reflectance spectroscopy (NIRS) has been widely used as a fast, non-destructive, accurate, non-invasive, cost-efficient, high-throughput and non-polluting method for qualitative and quantitative analysis in food and pharmaceutical fields for the last 30 years (Cen & He, 2007; Roggo et al., 2007). Now, the near infrared (NIR) spectroscopic technique is being employed as an alternative to wet chemistry procedures for quantitative analysis in quality evaluation of agricultural and food products (Cen & He, 2007). The principle of the NIRS technique is based on obtaining the content or the construction of different components of samples through the analysis of the spectrum information within the wavelength range of 800–2500 nm. NIRS is recommended for the determination of antioxidants such as: total carotenoids in carrot fruit and wheat seeds (Atienza, Avila, Ramirez, & Martin, 2005) and especially for individual carotenoids such as lycopene and lutein in tomato products (Pedro & Ferreira, 2005), zeaxanthin and lutein in maize seeds (Brenna & Berardo, 2004) and lutein and β-carotene in Chinese kale (Chen et al., 2009).

Infrared spectroscopy has been used to evaluate phenolic changes occurring during the development of olive fruit using ATR (Attenuated total reflectance)–FT-IR (López-Sánchez, Ayora-Cañada, & Molina-Díaz, 2009) and to determine malvidin-3-glucoside, tannins and pigmented polymers in wine (Cozzolino, Cynkar, Dambergs, Mercurio, & Smith, 2008) and grape skins (Ferrer-Gallego, Hernández-Hierro, Rivas-Gonzalo, & Escribano-Bailón, 2011).

Another approach for the NIR is the development of new techniques for antioxidant activity and total polyphenol content combined with chemometric calibration algorithms. Moncada, González Martín, Escuredo, Fischer, and Míguez (2013) developed a NIR method

combined with chemometrics for evaluating the vitamin E and antioxidant properties of quinoa. They obtained an excellent prediction capacity for vitamin E, phenols and DPPD, with ratio performance deviation higher than 2.5. The NIR techniques used consisted in a NIR spectrometer with optic fiber probe; this method seems to be a rapof and non-destructive one.

Wu et al. (2012) used NIR spectroscopy to achieve good information relating the antioxidant activity of bamboo leaf extract. For this aim they used four different linear and nonlinear regressions tools (partial least squares, multiple linear regressions, back-propagation artificial neural network and least squares support vector machine). From the four statistical methods used, the multiple linear regressions provided the best correlation with the antioxidant activity (measured using DPPH, FRAP and ABTS assays).

Ascorbic acid can be determined using the NIRS. In the case of ascorbic acid there are at least five intense peaks located at 496 nm (electronic transitions, green), 536 nm (electronic transitions, green), 608 nm (electronic transitions, orange), 672 nm (electronic transitions, red) and 696 nm (electronic transitions, red) in the visible region and five shown at 1396 nm (combination band C–H), 1516 nm (first overtone of the N–H stretching vibrations in protein), 1692 nm (first overtone of the C–H stretching vibrations), 1884 nm (combination bands of stretching–bending) and 1924 nm (second overtones of C═O stretching modes of O–H stretching vibrations which can be used for its detection and quantification (Pissard et al., 2013). Taking into account that information, Blanco-Díaz, Del Río-Celestino, Martínez-Valdivieso, and Font (2014) obtained a good correlation for the ascorbic acid ($r^2 = 0.86$) determination in summer sqquas using the NIRS.

4. Conclusions

Recent research carried out in the field of natural antioxidants is increasing knowledge about naturally healthy compounds that are available in food. This will permit the increase of their use instead of resorting to artificial drugs. Their use in food products will increase quality and added value. New methodologies of extraction, purification, identification and quantification of antioxidants using ecofriendly techniques need to be developed to improve the extraction yields.

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