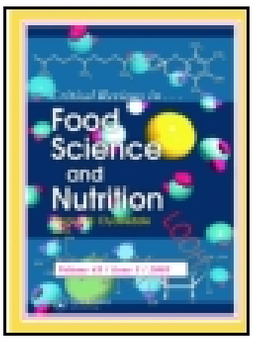

Critical Reviews in Food Science and Nutrition

ISSN: 1040-8398 (Print) 1549-7852 (Online) Journal homepage: https://www.tandfonline.com/loi/bfsn20

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To cite this article: Kejing Xu, Min Zhang, Zhongxiang Fang & Bin Wang (2020): Degradation and regulation of edible flower pigments under thermal processing: a review, Critical Reviews in Food Science and Nutrition, DOI: 10.1080/10408398.2020.1752142

To link to this article: https://doi.org/10.1080/10408398.2020.1752142

Published online: 17 Apr 2020.

CRITICAL REVIEWS IN FOOD SCIENCE AND NUTRITION
https://doi.org/10.1080/10408398.2020.1752142

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REVIEW

Degradation and regulation of edible flower pigments under thermal processing: a review

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ABSTRACT

More and more consumers are aware of the potential health benefits of edible flower pigments. With the increased popularity and broader application of edible flower pigments, their degradation under thermal processing has attracted researchers' attention, because this may affect the pigment functionalities. At high temperature of thermal processing, polyene pigments are easy to oxidize, degrade and isomerize due to high unsaturation, and phenolic pigments may hydrolyze and isomerize of glycosides, which will result in the decreased antioxidant activity and eating quality, and discounted potential health benefits. Therefore, it is very important to understand the degradation mechanisms of edible flower pigments under thermal processing, which is important to develop corresponding control methods to minimize such negative impacts. This review paper discussed the recent development in the degradation mechanisms and regulation methods of edible flower pigments under thermal processing.

KEYWORDS

Edible flower pigments; thermal; degradation; regulation

Introduction

Flowers have been a symbol of beauty with their rich, attractive and variable colors. As a plant, flowers not only have ornamental value, but also have edible value (Melillo 1994). Edible flowers can be made into food such as dishes, porridge, soups and cakes (Tanji and Nassif 1995), as well as flower tea, flower wine and flower beverage (Cichewicz et al. 2002). In addition, it can also be used as spices, pigments and flavoring agents in food industry (Kopec 2004). From the nutrition point of view, flowers have three major structure components. Pollen is a rich source of protein, amino acids and carbohydrates, carotenoids, and flavonoids. However, its taste is usually not very delicious or pleasant. Nectar is usually a sweet liquid containing a balanced mixture of sugars (fructose, glucose and sucrose), amino acids (mainly proline), proteins, inorganic ions, lipids, organic acids, phenolics, alkaloids, and terpenes etc. The third group includes petals and other parts of the flowers, which is also an important source of vitamins (yellow flowers are usually a good source of vitamin A), minerals, and phenolics etc. Edible flower pigments refer to the colored substances extracted from the whole flowers. Edible pigments can be divided into natural pigments and synthetic pigments according to their sources. As natural edible pigments, edible flower pigments are derived from flowers. They have many kinds, and most of them have no toxic side effects. They have outstanding advantages over synthetic pigments: (1) Most natural pigments come from edible animals and plants, which are safe, low toxicity and side effects; (2) Many natural pigments contain nutrients needed by the human body or are vitamins or vitamins themselves; (3) Some natural pigments have pharmacological effects and have preventive and therapeutic effects on some diseases. For example, flavonoid pigments play an active role in the prevention and treatment of cardiovascular diseases; some pigments have antioxidant, analgesic and hypotensive effects. In recent years, consumers have gradually deepened their understanding of the relationship between diet and health, and pay more attention to food safety. Food flower pigments are also more sought after by consumers.

Edible flower pigments come from a wide variety of plant sources, including fruits, vegetables, medicinal plants and ornamental plants (Kopec and Balik 2008). However, there is no official classification of flower pigments. According to chemical structures and characteristics, edible flowers pigments can be mainly classified into polyene pigments (lutein, carotene, crocin) and phenolic pigments (flavonoids, anthocyanins). According to solubility, they can be divided into two categories: fat-soluble and water-soluble pigments. According to the color, edible flower pigments can be divided into red, yellow, blue pigments and so on. In this review, edible flower pigments are classified according to their chemical structures. Among them, the main structural characteristics of polyene pigments are conjugated double bond long chains composed of isoprene residues, which can

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be further divided into two sub-categories: oxygen-containing and oxygen-free pigment. The oxygen-free pigment is called carotene and the oxygen-containing one is called lutein; Phenolic pigments are derivatives of polyphenols, which can be further divided into flavonoids and anthocyanins. Pigments in some representative flowers were shown in Table 1.

Because edible flowers are easy to decay and difficult to preserve for a long time even at low temperature, it is necessary to extract the pigments from edible flowers. In addition to non-heat treatment, food industry has been using heat treatment technology for centuries (Rawson et al. 2011). Blanching, pasteurization, sterilization, and thermal drying such as hot air drying, fluidized bed drying (Wang et al. 2014), spray drying, freeze drying (Huang et al. 2009) and microwave drying are commonly used in the food sector (Roknul et al. 2014). The effects of three typical thermal processing methods on edible flower pigments were shown in Table 2. However, thermal processing has some detrimental effects on secondary metabolites (Zhang et al. 2017). Especially, the unsaturated double bonds in the chemical structure of polyene pigments and unstable glycosides in phenolic pigments are easy to hydrolyze and isomerize, which result in the degradation of the pigments under thermal processing (Zhang et al. 2006). If this issue can be solved or regulated, the application of edible flower pigments will be much broader.

Previous reviews have already discussed the effects of thermal and non-thermal processing on some natural food pigments. Tiwari, O'Donnell, and Cullen (2009) reviewed the effects of nonthermal processing technologies on the anthocyanin content of fruit juices and Rawson et al. (2011) reported the effect of thermal and non-thermal processing technologies on the bioactive content of exotic fruits and the derivative products. Murador, Cunha, and Rosso (2014) elaborated the effects of cooking techniques on vegetable pigments such as carotenoid and anthocyanin levels. Nayak, Liu, and Tang (2015) presented extensive data on the effects of processing on phenolic antioxidants of fruits, vegetables, and grains. In addition, Ioannou et al. (2012) also summarized the thermal effects on flavonols and anthocyanin and studied the degradation kinetics in some fruits and vegetables. These reviews concluded that processing treatments can affect plant pigments either positively or negatively. However, there is no information about the effect of thermal processing on edible flower pigments, especially for its degradation and regulation. Therefore, the objective of this review was to illustrate the effect of thermal processing on the edible flower pigments from different plant food sources. Specifically, the mechanism of the pigment degradation and regulation methods were discussed.

Degradation and regulation of polyene pigments under thermal processing

Polyene pigments is a group of carotenoids, which are multifunctional natural red, yellow and orange pigments that provide vitamin A activity and peroxidation protection for cells and organisms (Bendich 1994). These pigments are widely used as natural colorants and sources of vitamin A in food industry. Epidemiological studies have also shown that carotenoids may play a protective role in degenerative diseases affected by oxidative stress. Because carotenoids are highly unsaturated molecules and contain many conjugated double bonds, they are easily oxidized. Therefore, they act as the main oxidizable substrates in the process of protecting compounds from harmful oxidation by trapping free radicals or quenching single peak oxygen (Kennedy and Liebler 1991). When the pigments are oxidized, they will lose their characteristic color and vitamin A function, which in most cases is undesirable in food processing.

The degradation kinetics of carotenoid have not been extensively studied. Degradation reactions are influenced by factors such as reaction medium, temperature, type of pigment, and environmental conditions (Pesek and Warthesen 1988). First-order kinetic models were reported for the photodegradation of carotene adsorbed onto a matrix, carotene dispersed on microcrystalline cellulose, and in other low moisture systems (Minguez-Mosquera and Jaren-Galan 1995). However, zero-order reaction kinetics were reported for the oxidation of carotene dissolved in toluene and exposed to molecular oxygen (Haralampu and Karel 1983.

Degradation and regulation of lutein under thermal processing

Lutein is a dihydroxy carotenoid containing ionone ring, which is widely existed in vegetables, flowers and fruits. For example, chrysanthemum flower mainly contains lutein. The basic structure of lutein was shown in Figure 1a. Lutein, as the main pigment of retina, can not only protect eyesight (West, Oren, and Moroi 2006), but also effectively prevent and assist in the treatment of ocular diseases such as senile macular degeneration and cataract (Humphries and Khachik 2003). Because lutein has antioxidant properties (Hoyoku, Michiaki, and Harukuni 2009), it can resist the damage of

Table 1. Pigments in some representative flowers.

Common name	Latin name	Color	Main pigment contained
Rose	*Rosa spp.*	Various (cultivar-dependent)	Flavone, Anthocyanin
Chrysanthemum	*Chrysanthemum spp.*	Various (cultivar-dependent)	Lutein, Flavone
Marigold	*Tagetes patula*	Orange	Lutein, Flavone
Dianthus	*Dianthus*	Various (cultivar-dependent)	Anthocyanin
Begonia	Begonia * tuberhybrida	Various (cultivar-dependent)	Anthocyanin, Carotene
Tulip	Tulipa spp.	Various (cultivar-dependent)	Lutein, Anthocyanin
Lilac	*Syringa vulgaris*	Violet or white	Anthocyanin
Dandelion	*Taraxacum mongolicum Hand-Mazz*	White	Lutein, Flavone
Peony	*Paeonia suffruticosa Andr*	Various (cultivar-dependent)	Flavone, Anthocyanin

Table 2. Effects of three typical thermal processing methods on edible flower pigments.

Technologies	Definition	Advantages	Disadvantages
Blanching	A thermal method frequently means heating the objects with saturated steam or hot water.	Inactivation of specific enzymes in raw materials, reduction of microbial nutrient cells, killing some bacterial microorganisms, especially those remaining on the surface of products, and obtaining the stability of pigments in storage.	The loss of vitamins was greater, mainly due to oxidation and water loss, followed by thermal degradation.
Pasteurization	A method of heating food at a lower temperature (usually 60–82 °C) within a specified time to kill microbial nutrients.	Induces increased concentrations of pigments in dairy product, had higher total pigments content during storage than untreated sample.	Various types of reactions such as thermal degradation, depolymerization, and polymerization are the main reason for the degradation of pigments during pasteurization.
Microwave	A thermal process with microwave radiation of frequency range between 300 MHz and 300 GHz, and 915 and 2450 MHz can be used commercially.	More pigments are extracted from cells after treatment with microwaves, lower microwave power is more suitable for extraction of individual pigment content from materials.	Heating uniformity.

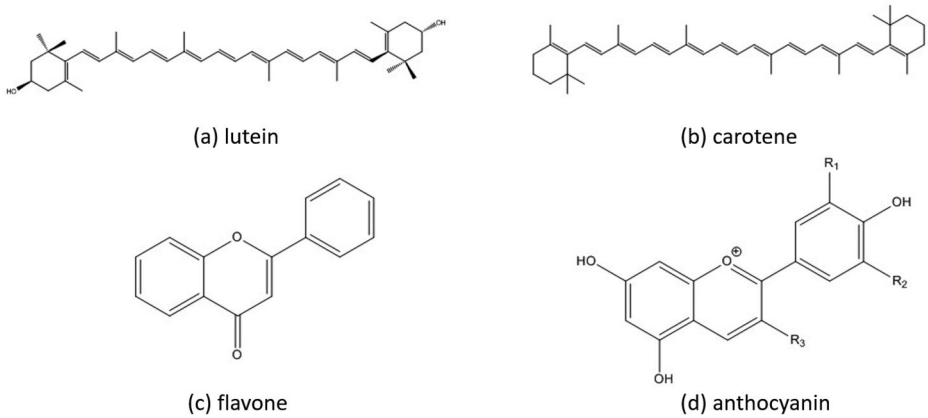

Figure 1. The basic structure of edible flower pigments.

cells and organs caused by free radicals in human body, thus preventing cardiovascular sclerosis, coronary heart disease and cancer caused by aging (Schunemann et al. 2002). In plant tissues, lutein exists in the form of lutein fatty acid esters. After entering human body, lutein esters can be converted into lutein, which can be further absorbed and utilized (Liu et al. 2011).

In terms of chemical structure, lutein contains eleven unsaturated double bonds, and its high unsaturation leads to oxidative degradation and isomerization during thermal processing (Hiranvarachat, Suvarnakuta, and Devahastin 2008). The oxidative degradation of lutein under heat treatment will result in the decrease of antioxidant capacity and color change from yellow to colorless. In addition, high temperature heating can degrade lutein into epoxides, derivatives containing aldehydes or ketones produced by hydroxyl oxidation, etc. (Li, Fang, and Liu 2007). Natural lutein exists in flowers in trans form (Vecchia 2002), but heating will lead to the cis-form and the number of cis-isomers increasing with the increase of temperature and treatment time. In addition to high temperature, light can also facilitate the isomerization of carotenoids, but the degree is lower than that of the temperature. It is generally believed that the degradation of lutein during heat treatment follow to the first order reaction kinetics (Koca, Karadeniz, and Burdurlu 2007; Ahmed, Shivhare, and Sandhu 2002; Bechoff et al. 2010; Wu et al. 2012). Studies have shown that all-trans beta-carotene has better antioxidant activity than cis-carotene, so isomerization at high temperature would lead to the reduction of lutein antioxidant activity (Liu and Chen 1998).

Due to the above negative influence of lutein degradation, the regulation of lutein degradation under thermal processing is very important. Li, Liu, and Liu (2008) studied the effects of light, heat, acid, alkali, metal ions, oxidant and reductant on the stability of lutein ester and lutein. The results showed that the preservation rate of lutein ester and lutein were decreased and the degradation rate was increased with the increase of temperature and heating time. Under same light and heat conditions, the stability of lutein ester is better than that of lutein. Lutein in the form of combining with fatty acids has stronger stability. Strong acidic conditions can destroy lutein ester and lutein, but they are stable under neutral and alkaline conditions. Metal ions Fe^{3+}, Fe^{2+}, Cu^{2+} have strong destructive effect on them; the oxidant H_2O_2 has a slight destructive effect on it, when the concentration of H_2O_2 is 1.2%, the retention rate of lutein is as high as 95%. And the degradation degree of lutein ester is higher when it is coexisted with vitamin C. Therefore, besides avoiding the destruction of lutein by strong acids, Fe^{3+}, Fe^{2+}, Cu^{2+}, H_2O_2 and other substances, the heating time should be shortened as far as possible.

In addition, if the hydroxyl group of epsilon-ionone ring of lutein is esterified with fatty acid, the lutein active group is protected and oxidation can be avoided. Esterification of

xanthophyll hydroxyl with fatty acids effectively reduces the conversion and oxidation degradation of xanthophyll from all-trans structure to cis-structure under thermal processing (Li et al. 2009). Therefore, the application of lutein can be combined with fatty acids, such as lutein as an oil-soluble colorant, and the degradation of lutein active groups by fatty acids can reduce the degradation of lutein under thermal processing. Further studied the thermal degradation kinetics of lutein and carotene in different kinds of oils. The results showed that the degradation rate of lutein was slower than that of carotene, i.e., lutein had higher heat resistance than carotene. The degradation rate in vegetable oil is lower than that in palm oil, which is related to the initial composition of the oil, including the content of peroxide and vitamin E. Vegetable oil contains 93% unsaturated fatty acids. But palm oil only contains 49% unsaturated fatty acids, and the rest are saturated fatty acids. So during the processing, oil with high unsaturated fatty acid content can be selected to protect lutein. In addition, in the same oil medium, the activation energy of degradation of cis-isomers is lower than that of all-trans lutein, and the reaction rate constant of the former is generally larger than that of the latter. Therefore, the degradation reaction of cis-isomers is easier to be stimulated than that of all-trans lutein, and faster.

Extracted the pigment from Chrysanthemum petals and discovered that chrysanthemum petals contained up to 16 luteins. Chen (1992) studied the effects of microwave and conventional heating on the stability of carotenoids of chrysanthemum species. The results showed that microwave processing at 180 W can retain more beta-carotene but less lutein than traditional processing. However, with the increase of heating time, the contents of cis-lutein and cis-beta-carotene were higher, and the isomerization of lutein occurred. The increased levels of cis-beta-carotene also mean that decreased vitamin A activity. Therefore, choosing appropriate microwave power heating instead of traditional thermal processing can protect the lutein in chrysanthemum. Yang, Liu, and Zhou (2006) suggested that the drying temperature of Calendula must be controlled below 60 °C to reduce the degradation of lutein. Pal and Bhattacharjee (2017) extracted lutein from marigold seeds by supercritical CO_2 and studied the product characteristics. To extend the shelf life, Pal and Bhattacharjee (2017) encapsulated lutein with maltodextrin-gum Arabic as wall material and its half-life was 6.9 times longer than that of the extracted lutein, indicating microencapsulation has protective effect on the stability of lutein.

Degradation and regulation of carotene under thermal processing

Carotene is composed of four isoprene double bonds connected from the head to the tail (De-Sa and Rodriguez-Amaya 2003), and each end of the molecule has a beta-violone ring (Figure 1b). Its chemical structure is similar to lutein, but has two less hydroxyl groups than that of lutein (Budowski and Bondi 1960). Carotene is widely found in various plants, including medlar and marigold. Carotene is the safest product to supplement vitamin A at present (Yajnik, Dolan, and Ng 2010). It can protect eyes and skin, as well as the immune system (Trumbo and Ellwood 2006).

The main reaction of carotene during thermal degradation is similar to that of lutein, i.e. oxidation degradation and isomerization caused by unsaturated carbon-carbon double bond (Qiu, Chen, and Li 2009). Natural carotene exists in all-trans form, which is also the most stable thermodynamics form. Under thermal processing, isomerization will occur and turn carotene into cis-structure, such as 9-cis, 13-cis and 15-cis, which will lead to the decline of antioxidant properties of carotene. Studied the thermal degradation and oxidation degradation of carotenoids in oil model system. It was found that the degradation kinetics of carotenoids followed the first-order kinetics model and the degradation rate of carotenoids was higher than lutein. Qiu, Chen, and Li (2008) reported that the isomerization of carotene is mainly carried out by free radical cations under external forces. Oxidative degradation is similar to lutein, which also resulted in color change (from red to colorless) and reduction of activation energy. Suggested that high temperature can weaken the cell physical barrier surrounding carotene, thus promoting the release of carotene. By heat treatment, cell membranes are easily destroyed, resulting in the acceleration of cell wall softening at high temperatures. Achir et al. (2011) investigated the heat treatment of two carotene-rich oils (palm oil essence and coconut oil) at 120–180 °C and observed that the isomerization of carotene was dominant and reversible, and the cis-isomers and trans-carotene were obtained at the same rate constant. At the same time, oxidation and pyrolysis reactions were taken place. Kinetic analysis showed that the isomerization rate constant does not conform to Arrhenius law, which is contrary to the oxidation decomposition reaction. However, the isomerization equilibrium constant increases with the increase of temperature, which is conducive to the formation of isomerized products, especially 9-cis-carotene.

Measured the thermal degradation and isomerization rates of trans-carotene in air and triacylglycerol. It was found that the content of trans-carotene was decreased with the increase of heating time. And the ratio of 13-cis-carotene was increased, which also proved that heat treatment lead to the thermal isomerization of trans-carotene to cis-carotene. In addition, it was found that the level of 13-cis-carotene in triacylglycerol was higher than that in air, i.e. the degradation rate of carotene in triacylglycerol was faster than that in air. This is because the oxidation of triacylglycerol may have promoted the isomerization of carotene, leading to degradation. Studied the effects of heat treatment and complex heat/high pressure treatment on carotene isomerization. It was found that the number of cis-isomers increased with time and increased more significantly at higher temperatures. In addition, at 100 °C, high pressure did not affect carotene isomerization in the oil phase. While at 700 MPa, the reaction in the oil phase was almost insensitive to temperature. It can be seen that compared with the pure high temperature conditions, the combined treatment with high pressure can prevent the degradation of carotene

in the oil phase. Suggested that high pressure delayed the dissolution of pectin, then the raw materials under pressure have higher hardness and microstructures, which may have protected carotene against degradation. The isomerization of carotene was significant during heat sterilization, but almost no isomers were formed during high pressure sterilization. Although the cost of high-pressure processing is higher than that of thermal processing, the advantages of high-pressure processing over thermal processing are worthwhile in terms of carotene preservation. The experimental results of Lemmens et al. (2013) also show that the isomerization of carotene at high pressure homogenization can be neglected, but the formation of isomers can be observed at high temperature only.

Chen et al. (2014) investigated the effect of encapsulation on the stability of carotene. The results showed that the thermal stability of carotene in apolipoprotein nanocapsules was significantly higher compared with that in free carotene. Fu et al. (2019) also observed that encapsulation of carotene in biopolymers of wheat gluten nanoparticles (wgn) or wheat gluten nanoparticles xanthan gum (wgn-xg) complex can effectively protect carotene from l degradation during storage. Found that lipid-soluble crystalline carotene was the prerequisite for carotene isomerization. Moreover, the control of heat treatment temperature was very important. Pasteurization and 121 °C sterilization only led to slight isomerization of carotene, but 130 °C sterilization and blanching resulted in a significant increase in cis-isomer content. Unlike the protective effect of fat on lutein, the addition of grape seed oil in raw slurry would increase isomerization; model formulations containing crystalline carotene showed very good stability during heating, while heat treatment of carotene dissolved in toluene led to temperature-dependent isomerization. As a non-thermal processing technology, high hydrostatic pressure processing (HPP) can increase the carotenoid precursors and carotenes contents in vegetable food. Compared with thermal processing, the carotene content in HPP treated material was significantly higher during storage period (Ramos-Parra et al. 2019). Etzbach et al. (2019) studied the effects of traditional hot pasteurization and ultrasonic treatment on peroxidase activity and carotene content. It was found that peroxidase could be completely inactivated by traditional hot pasteurization and carotene loss was about 11.5%. Ultrasound could only inactivate part of peroxidase with residual activity of 10%, but no carotene content was affected. Therefore, ultrasound treatment could be used to preserve carotene in the material.

Degradation and regulation of phenolic pigments under thermal processing

Flavonoids are universal plant pigments, which are responsible for the color of flowers, fruits and leaves (Ramos-Parra et al. 2019). Phenolic pigments are mostly based on 6C-3C-6C. They are linked by two benzene rings (A, B) through three carbon chains, and often have methyl, methoxy and isoprenyl substituents, and the basic structure is 2-phenyl-pyrene (Etzbach et al. 2019). Phenolic pigments have antioxidant and anti-free radical effects. They also have protective and anti-tumor effects on cardiovascular system (Harborne and Williams 2000).

The results show that light, temperature, acidity and alkalinity, oxidant, reductant, salt metal ions and food additives all have certain effects on the stability of the pigment solution. Phenolic pigments can be divided into anthocyanins and flavonoids. Generally speaking, the thermal stability of flavonoids is better than that of anthocyanins, and the thermal stability of different anthocyanins is also different.

Degradation and regulation of flavone under thermal processing

Flavones originally refer to a class of compounds with 2-phenylchromone as the basic mother nucleus. Now they generally refer to a class of chemical constituents with two phenyl rings linked by three carbon chains in the middle (Figure 1c). The main natural flavone can be classified according to the degree of oxidation of the three carbon chains between A and B rings, the position of B ring connection, and whether the three carbon chains are cyclized or not. Flavones are widely distributed in vegetables and fruits. Rose, peony and dandelion are the main flowers containing flavones (Toumi et al. 2009). Kashchenko and Olennikov (2017) found that *M. chamomilla* flower contains flavones, and their microcolumn HPLC-UV quantitative analysis of cosmosin can effectively measure the measurement parameters of flavones in hydrolysis process. Determined six main flavonoids in edible flowers of *Euphorbia officinalis* by pressurized liquid phase extraction (PLE) and high performance liquid chromatography (HPLC). Flavones are effective antioxidants, which can inhibit the production of reactive oxygen species and human free radicals (Jamen et al. 2004). There are two main antioxidant mechanisms: First, scavenging oxygen free radicals or reactive oxygen species; second, inhibiting the activity of oxidases that produce reactive oxygen species (Tomás-Barberán, Ferreres, and Gil 2000). The basic active site of flavone scavenging free radicals is the hydroxyl oxygen structure of B ring in diphenyl structure. Some flavones also act as antimicrobial agents, while others have antifungal activities, anti-osteoporosis, anti-tumor and anti-inflammatory effects (Azzini et al. 2007). Studies have shown that the intake of rich flavone in diet could reduce the risk of colon cancer (Terao 2009), prostate cancer (Michihara et al. 2012), and breast cancer (Akhtar et al. 2014).

Because flavone contain unsaturated double bonds, they are easily degraded at high temperature. The oxidation stability is related to their specific chemical structures, such as the number, relative position of phenolic hydroxyl groups, whether they are linked to sugar chains, methylation, lipophilicity and charge distribution (Sharmila et al. 2014). Therefore, the modification of its structure, such as alkylation or glycosylation, will lead to the change of antioxidant activity (Pan et al. 2014). The storage environment such as light, oxygen, acidity, alkalinity, temperature and darkness will lead to the decrease of antioxidant activity.

Reported that the petals of Malachia oleracea contained dihydroflavonoid pigments, which were unstable at

temperature above 60 °C. He et al. (2016) showed that thermal treatment (heating at 80 °C for 30 min) markedly increased individual flavonoid content (naringin, hesperetin-rutinoside, naringenin-trisaccharide, luteolinrutinoside, quercetin-trisaccharide, hesperidin, phloridzin, epigallocatechin gallate, andproanthocyanidin), but elevated temperature (heating at 90 °C for 30 s) resulted in a lower concentration of epicatechin and phloridzin. The degradation could be related to polyphenol oxidase and peroxidase (Wu et al. 2012).

Studied the difference of phenol content and antioxidant ability of honey in Longan Flower treated at different temperatures. The experimental results showed that there was no significant difference in all antioxidant components between the heat treated at 50 °C or 70 °C and the control. But the samples heated to 100 °C contained the lowest level of phenol and antioxidant ability. So the temperature of thermal processing of pigment was very important for its degradation. Studied suitable drying methods for extracting bioactive compounds from Catharanthus roseus. They found that vacuum drying at 50 °C was more suitable for drying leaves and flowers containing high levels of phenols and flavones than hot-air drying at 80 °C.

Treated three different honey samples (longan flower, litchi flower and wild flower nectar) with conventional heat treatment (90 °C/5 min) and ultrasonic treatment (40% and 80% amplitude/20 kHz/30 min). The results showed that both heat treatment and ultrasonic treatment can eliminate the indicative microorganisms, and ultrasonic treatment can produce higher quality antioxidant compounds and properties than traditional heat treatment technology. In addition, ultrasound treatment with 40% amplitude significantly improved the total phenol, total flavones and antioxidant capacity. Therefore, ultrasonic treatment is an alternative to heat treatment to preserve honey samples. Raquel et al. (2016) studied the composition and antioxidant activity of phenolic compounds of thrips, especially the effect of drying temperature on the phenolic compounds and antioxidant activity of thrips. The experimental results show that the thistle can obtain the minimum moisture content at 60 °C for about 3 h, at 50 °C for 4 h, and at 40 °C for 5.5 h. The content of flavones is similar under the three different drying conditions, but its antioxidant activity is the lowest at 60 °C. Zheng, Xia, and Lu (2015) studied the effects of different drying methods on the content of active ingredients in loquat flower tea. Flavones contained relatively high content in Florescence and petal tissues. Flowers were dried to produce loquat flower tea by three drying methods: freeze drying, microwave drying and hot air drying. The results showed that the content of flavones in flower tea prepared by freeze-drying was the highest. The content of flavones in flower tea obtained by microwave drying and hot-air drying decreased with the increase of temperature, and the damage of hot-air drying to flavones was the most obvious. In contrast, freeze-drying can effectively protect the active components of flavones. Observed that stir-frying can also degrade flavones in spinach, mushrooms (Lagnika, Zhang, and Mothibe 2013), cluster beans, chicken legs and beet roots, but Rodrigues (2009) suggested that oven drying would not affect the flavonoid content in onion bulbs. Mohd Zainol et al. (2009) also reported that freeze-drying resulted in higher contents of quercetin, myricetin, kaempferol, catechin, apigenin, luteolin and naringin in *Centella asiatica*, followed by vacuum oven and air oven drying. These results suggested that freeze-drying or oven drying is better than natural air-drying in preservation of flavonoids.

Degradation and regulation of anthocyanins under thermal processing

Anthocyanins is a class of flavane-3-alcohols and water-soluble pigments widely exist in plants. The basic structure of anthocyanins was shown in Figure 1d. At present, there are more than 250 kinds known anthocyanins in nature. Their structure depends on five aspects (Ranilla, Genovese, and Lajolo 2009): (1) Types of flavane-3-alcohol units; (2) Connection between units; (3) Degree of aggregation (number of constituent units); (4) Spatial configuration; (5) Whether hydroxyl groups are substituted (e.g. esterification, methylation etc.). According to the degree of polymerization, anthocyanins can be divided into monomers, oligomers and polymers. The haploid is the basic structural unit, and the oligomer is made of 2–10 haploids, while the polymer is made of more than 10 haploids. They all contain unsaturated double bonds, which leads to their easy degradation at high temperature, and their oxidation stability is related to the specific chemical structure. Anthocyanins exist in rose, peony, crabapple, wolfberry, carnation and other flowers. Common anthocyanins include pelargonium pigments, cornflower pigments, delphinium pigments, peony pigments, morning glory pigments and mallow flower pigments. The specific chemical structure was shown in Figure 2. It has been proved that anthocyanin is an effective antioxidant to scavenge free radical and inhibit lipid peroxidation (Gradinaru et al. 2003). Its mechanism of action is that many phenolic hydroxyl groups in anthocyanin structure release H^+ in vivo, which competently bind with free radicals, thus protecting lipids from oxidation, blocking free radical chain reaction, and producing free semiquinone after reaction. Other studies have shown that anthocyanin extracts can effectively prevent cardiovascular diseases. It also has the function of resisting myocardial ischemia-reperfusion injury (Fracassetti et al. 2013) and atherosclerosis (Nishizuka et al. 2011), protect vascular endothelial cells (Shao et al. 2009), reduce blood pressure (Sano et al. 2007), reduce blood lipid (Aldini et al. 2003), reduce blood sugar (Belcaro et al. 2013), and have anti-cancer potential (Tamura et al. 2013). Anthocyanins can not only be used as nutritional fortifiers in food, but also as food preservatives instead of synthetic preservatives such as benzoic acid (Moldovan and David 2014). They can also be used as food colorants in ordinary beverages and foods, which meets the requirements of natural, safe and healthy food additives.

Anthocyanins are very unstable and easily affected by temperature, pH value, oxygen and metal ions. In particular, severe thermal processing condition will cause degradation and discoloration. Common food thermal processing includes steaming, boiling, frying and microwave, often lead

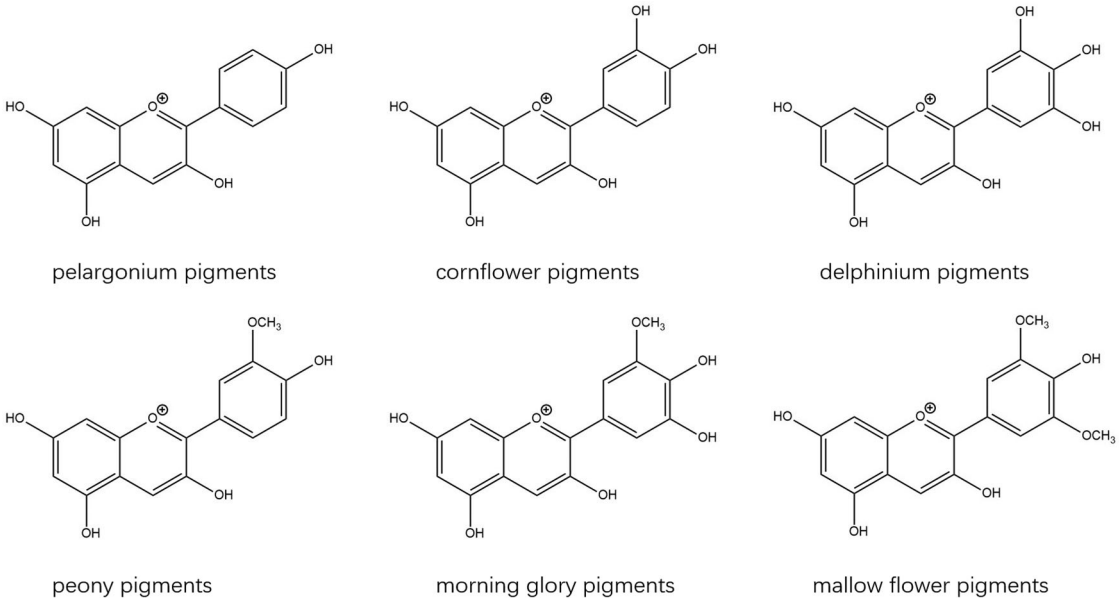

Figure 2. Chemical structure of six common anthocyanins.

to different degrees of anthocyanin degradation. The loss of anthocyanin during food thermal processing is closely related to the processing methods. It is proposed that the anthocyanin thermal degradation process starts from hydrolyzation of C3 glycoside to form pseudo-alkali form of anthocyanin, and then isomerizes to form chalcone and its isomer alpha-diketone (Cedo, Castell-Auvi, and Pallares 2013). Another degradation mechanism is that anthocyanin becomes pseudo-alkali glucoside, and then opens to form chalcone glycoside. Chalcone glycoside continues to be removed to form chalcone and its isomer alpha-dione. Finally, phenolic acid and aldehydes, cyanidin-3-glucoside and geranium-3-glucoside are completely degraded (Connor et al. 2014). The specific thermal degradation pathway is shown in Figure 3.

The thermal degradation of anthocyanins is affected by pH, and the weak acidity condition is more suitable for the protection of anthocyanins (Cavalcanti et al. 2011). Furtado et al. (1993) studied the thermal degradation of chrysanthemum pigments, geranium pigments, mallow pigments and delphinium pigments in acidic solution. It was found that under polar acid conditions (pH $<$ 4), the thermal degradation process of anthocyanins may be as follows: firstly, hydrolysis occurs at the C3 position, and then degradation proceeds to obtain benzoic acid and alpha-hydroxyacetone, and then hydrolysis of alpha-hydroxyacetone to benzoic acid (Song, Liu, and Dong 2011). As a natural pigment, anthocyanin can be regulated by adding metal ion blocking agent, antioxidant, natural pigment stabilizer (such as cysteine) and adjusting pH lower to regulate its stability at high temperature (Aramwit, Bang, and Srichana 2010).

Metal ions, such as Al^{3+}, Zn^{2+}, Cu^{2+}, Fe^{3+}, can destroy the stability of anthocyanins and affect the degradation of anthocyanins. Among them, Fe^{3+} can cause the solution of anthocyanin to turn black, and Fe^{3+}, Pb^{2+}, Sn^{4+}, Bi + can cause the solution of anthocyanin to precipitate (Lachman et al. 2013). Du, Li, and Cheng (2006) showed that Zn^{2+}, Cu^{2+}, Fe^{3+} ions accelerated the degradation of anthocyanins in food.

Adjusting of pH, addition of stabilizers or metal ions are common means of regulation of anthocyanin degradation. Specific regulation conditions are related to specific flower varieties. For example, anthocyanins in roses are more stable under acidic conditions (pH $<$ 3) and stable in citric acid, sucrose and sodium chloride, and sodium alginate has better protection effect than CMC (Chanukya and Rastogi 2016). Also, ferulic acid and tannic acid can be used as auxiliary colorants, malonic acid and caffeic acid can enhance its color, and Mn^{2+} can increase its stability; anthocyanin in carnation is more stable under acidic conditions; citric acid can fix its color; Ca^{2+}, Cu^{2+} can enhance its color; but sodium benzoate, sodium chloride and sucrose can degrade carnation anthocyanin, which needs to be avoided (Janna, Khairul, and Maziah 2007).

Different heating methods include steaming, cooking, frying, and microwave heating are usually accompanied by different degrees of anthocyanin loss. Mahsa, Russly, and Chin (2016) studied the effect of heating on the stability of anthocyanins. It was found that the absorbance of anthocyanins decreased by 20% when heated at 85 °C, and decreased by 53% when heated at 95 °C. It can be seen that the choice of heating temperature is closely related to the degree of degradation of anthocyanins. Zhou, Zhang, and Ye (2011) studied the thermal stability of anthocyanins and found that anthocyanins in eggplant were stable below 60 °C. When the temperature was higher than 80 °C, anthocyanins began to degrade. At room temperature, when the pH was $<$ 4 or $>$11, the content of anthocyanins decreased significantly. Burgos et al. (2013) found that the total anthocyanin content decreased by 23% after boiling for 20–25 min, and the content of anthocyanin decreased to half after heated for 10 min at 121 °C. Also confirmed that anthocyanin content decreased significantly under microwave processing (240 W, 360 W, 480 W) (Cheng et al. 2014). Found that anthocyanins

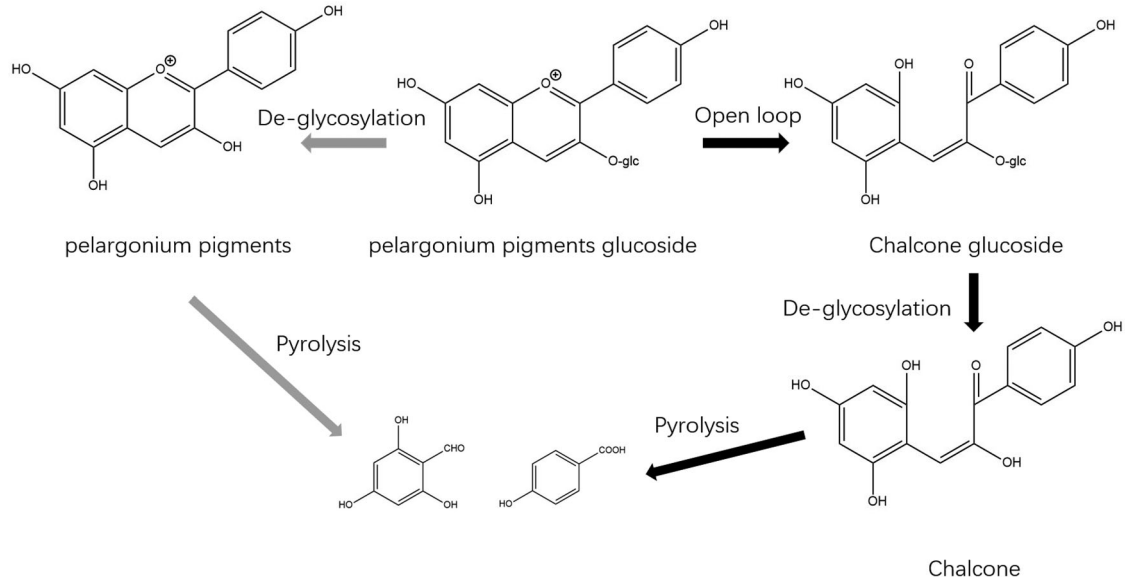

Figure 3. Two specific thermal degradation pathways of anthocyanins.

degraded significantly above 80 °C by hydrothermal heating, and the decrease of anthocyanins affected the antioxidant activity of food. Studied the effects of steam heating and microwave heating on anthocyanins and their free radical scavenging activities. Compared with steam heating, microwave heating had positive effects on the relative contents of two anthocyanin components, namely, sinapyrin-3-sophoridin and dissinapyridin-3-sophoridin-5-glucoside, but had no significant effects on the relative contents of another two different anthocyanins, namely, sinapyridin-3-sophoridin and sinapyridin-3-sophoridin. Microwave heating and steam heating affected the free radical scavenging activity of anthocyanins, and steam heating is stronger than that of microwave heating. This may due to the mutual transformation of anthocyanins during heat processing. The difference between the increase and decrease of anthocyanin components may be the partial degradation of anthocyanins. Therefore, different thermal processing methods, such as steam, microwave, frying and boiling, have great influence on the content and antioxidant activity of anthocyanins in food. However, little research has been done on the chemistry of degradation products and mechanism of anthocyanins in food. Some limited reports suggested that the degradation products of anthocyanins could be some aldehyde derivatives containing benzene ring, such as monohydroxybenzaldehyde, p-hydroxybenzaldehyde or trihydroxybenzaldehyde, which could stimulate cells and cause liver damage.

Conclusion

In recent years, food safety is not only the concern of consumers, but also manufactures. The increased awareness of consumer health have resulted in an increased demand for nutritious and healthy foods. In addition to fruits and vegetables, edible flowers with attractive pigments are becoming more and more popular. However, their perishable nature is a hurdle to consume them in fresh form. Therefore, it is necessary to preserve the pigments in edible flowers and maintain their nutritional value, through various processing methods including thermal processing. In most cases, thermal processing can lead to the degradation of edible flower pigments, which has a great negative impact on the nutritional value of the processed products. In this paper, the degradation of edible flower pigments in the process of thermal processing was discussed, and the degradation mechanism and related control measures were presented. This review might have provided useful information for consumers, researchers and product developers to preserve the pigments in edible flowers during thermal processing.

Funding

The authors gratefully acknowledge the financial supports from National Key R&D Program of China (Contract No. 2017YFD0400901), the 111 Project(BP0719028), Jinan City Science & Technology Innovation Project of Ten Agricultural Characteristic Industries, National First-Class Discipline Program of Food Science and Technology (No. JUFSTR20180205), Jiangsu Province (China) "Collaborative Innovation Center for Food Safety and Quality Control" Industry Development Program.

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