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Anthocyanin Enigma

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Abstract:
The color is the first quality characteristic of a food product which highly affect the consumer acceptance. Therefore, synthetic colorants have been used to improve the appeal of the food products because of having high stability with respect to oxygen, light, pH and temperature. In recent years, the legal restrictions applied to the use of synthetic colorants, due to the reason of causing serious health problems. So, food manufacturers have replaced the synthetic food colorants by their natural alternatives. Anthocyanins are water-soluble coloring pigments in fruits and vegetables responsible for the characteristic color ranging from blue to red. Anthocyanins have been used to color confectionary, jam and jellies, ice cream, fruit preparations, yoghurt, desserts and bakery fillings. In addition, anthocyanin extract may improve the nutritional quality of food and beverages. Thus, there has been a great interest in anthocyanins not only their colorant abilities and aesthetic value, but also their beneficial effect from a nutritional standpoint and their potential role in reducing the risk of coronary heart disease, cancer and stroke. Anthocyanins' usage in folk medicine have an important role in treatment of diarrhea, vision disorders and microbial infections. However, the main drawbacks in applications of anthocyanins in food matrix due to low stability to pH and temperature, incompatibility with food matrix, color loss during food and beverage processing and storage. Researches indicate that the main mechanism providing color stability is the molecular interaction between anthocyanins and co-pigments. The most effective way of this interaction is provided with the acylation of aliphatic and/or aromatic over the anthocyanidin nucleus via a sugar molecule, intra-molecular co-pigmentation. On the other hand, it is possible to improve the stability by the inter-molecular non-covalent interaction between anthocyanin and co-pigment molecules. The present study aimed to review beneficial effects, usage area, structure and stability of anthocyanins.

Key words: anthocyanin, bioactive compounds, structure of anthocyanins, stability of anthocyanins

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1. Introduction

Color plays an important role in the first judgement and acceptability of food products. Thus, color is received as the first characteristics which is perceived as the quality indicator strongly affecting consumer acceptance. Therefore, in order to eliminate the color differences in fruit and vegetables because of the seasonal conditions and the negative effects of conventional processing and storage different types of synthetic colorants have been commercially used to improve the visual appearance [1, 2]. The safety of synthetic colorants have been questioned in recent years correspondingly increasing public awareness of health issues. Thus, the food industry has become interested in substitution of synthetic food colorants by their natural alternatives as a result of legislative action and consumer awareness [2-4]. Anthocyanins are the most abundant found pigments in nature and have been categorized as the group of water-soluble coloring pigments in fruits and vegetables impart a characteristic color ranging from blue to red [5-7].

1.1. Structure of Anthocyanins

They are a sub-group of flavanoids which possess a basic C6-C3-C6-skeleton (C6– ring A and C3– ring C and other aromatic ring C6– ring B). It was reported that more than 600 anthocyanin pigments have been identified in the nature [6, 8-10]. Of those pigments, cyanidin, pelargonidin, delphinidin, peonidin, malvidin and petunidin occur most often in food materials [11].

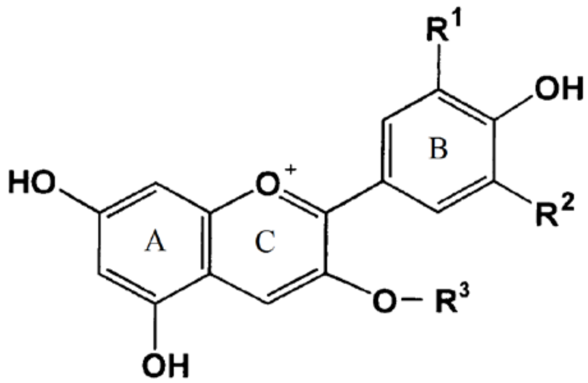

Fig. 1. Molecular structure of anthocyanidin

Anthocyanins are glycosylated derivatives of 2-phenylbenzopyrylium cation (anthocyanidins) (Fig. 1) [12]. Structural variation arises from substitution with OH and OCH_3 groups, presents in the B ring accompanying with different sugar substituents at the 3 and 5 positions, and the capability of acylation of sugar substituents with different phenolic compounds [10].

The color of anthocyanidins shows an alteration according to their being acylated or non-acylated and the number of OH and OCH_3 groups in the B ring. The color will shift the color from red to bluish-red to purple with an increased number of OH and OCH_3 groups. [8,10,12]. The color of the solution and the presence of co-pigments, concentration of the solution and pH of the medium may affect the color of anthocyanin pigment [13]. Although a co-pigment is basically not colored pigments can enhances the color of the solution. A co-pigment may be one of alkaloids, flavonoids, nucleotides, organic acids, polysaccharides, metals, and anthocyanins themselves [14]. The color of anthocyanins is dependent on their substitutions, and whether they are acylated or non-acylated. Under acidic conditions, the color of non- and mono-acylated anthocyanins is determined to a great extent by substitution in the B-ring of the aglycon. Increased OH substitutions on the B-ring resulted in a shift of the visible absorption maximum (λ_{max}) to longer wavelengths, producing a bathochromic shift to yield a more blue tint. In general, it is believed that acylated anthocyanins may be more suitable for various applications due to their higher stability [15].

1.2. Natural Food Colorants with Health-Improvement Properties:Anthocyanins

Nowadays, there has been a great interest in anthocyanins not only their colorant abilities and aesthetic value but also their being rich in terms of bioactive compounds, beneficial effect from a nutritional standpoint and their potential role to promote disease preventative properties i.e. reducing the risk of coronary heart disease, cancer and stroke [2, 16]. Beneficial effects associated with anthocyanin extracts include capable of scavenging free radicals in vitro, antioxidant capacity, enhancement of sight, treatment of various blood circulation disorders, controlling diabetes, anti-inflammatory properties, reducing the risk of neuro-degenerative diseases. (3, 4, 12). Also in some preliminary studies it has been noted that anthocyanins usage in folk medicine have been shown to play an important role in treatment of diarrhea, vision disorders and microbial infections. Anthocyanins can be found in i.e. black carrot, cherries, strawberries, elderberries, blueberries, raspberries, black currant and their juices [17, 18]. As a result of these qualities anthocyanins are of utmost importance alternatives to synthetic dyes.

Anthocyanins are used as food colorants primarily in the beverage industry. Because anthocyanins' stability are highly sensitive to pH changes and show the major effect at pH 3-3.5 which is the pH range of most fruit drinks. Natural anthocyanin colorants have been generally used in beverages, jellies, yogurt, jam, ice-cream, canned fruits, toppings and confections and many other food products [19]. The use of natural anthocyanin-based colorants in yoghurt and some mixed fruit juice is becoming more popular. Recently, acylated anthocyanins are generally used as food colorants in the food industry because of having high stability compare to non-acylated anthocyanins [17].

1.3. The Stability of Anthocyanins

Although promosing a health- promoting effects of anthocyanins, anthocyanin pigments are highly reactive and color stability of anthocyanins are highly susceptible to degradation through factors such as oxygen, light, especially pH and temperature [12, 18].

Anthocyanins are more stable at low pH values (acidic media) compare to high pH values (alkaline media) [18]. Anthocyanins' color change depending on pH of the medium dramatically and exist as four main equilibrium species according to the pH of the media: the quinoidal base, the flavylium cation, the carbinol or pseudobase, and the chalcone [14, 18, 20]. In strongly acidic aqueous media (at pH$\leqslant$2) the red-colored flavylium cation is predominant species, with an increase in pH values, not only color intensity but also the concentration of flavylium cation starts to decrease and a colorless carbinol is mainly observed between pH 2-4. Hydration of flavylium cation, generating the carbinol or pseudobase which reaches equilibrium slowly with the colorless chalcone form. A further pH increase shift to 6 causes the ring opening and leads to formation of quinoidal bases with purple and finally anionic structures with a bluish hue [12, 18, 20-22]. The relative amounts of flavylium cation, the carbinol or pseudobase, the chalcone and the quinoidal bases forms at the equilibrium condition vary according to pH [12].

The color stability of anthocyanins is influenced not only pH but also magnitude and duration of heating. During processing and storage stability of anthocyanin decreases as temperature rises. Especially in the presence of the oxygen, thermal degradation cause to the formation of browning products [12]. Increasing in temperature and duration of heating results in anthocyanin degradation and changes in co-pigmentation complex [6, 12].

Researchers investigated that acylated anthocyanins with aliphatic or aromatic acids show greater thermal and pH stability compared to non-acylated anthocyanins. It is believed that the aromatic residues of the acyl groups stack with the pyrylium ring of the flavylium cation, which reduces the probability of the hydration reaction in the C-2 and C-4 positions [21]. Researches conducted recently, indicate that the main mechanism providing color stability in plants is the molecular interaction between anthocyanins and co-pigments. The most effective way of co-pigmentation is the acylation of aromatic and/or aliphatic acids onto the anthocyanidin nucleus via a sugar molecule (intra-molecular co-pigmentation). Another co-pigmentation form, on the other hand, is the inter-molecular non-covalent interaction between anthocyanin and co-pigment molecules (hydrophobic complex formation) [18,23-25].

Intramolecular co-pigmentation is defined as that the co-pigment is part of the anthocyanin molecule, means the chromophore of anthocyanins and the co-pigment are covalently linked to the same sugar residue

[12]. Jettanapornsumran (2009) reported that the number of acyl groups, structure and the positon of attachment to glycosyl parts, the number and structure of saccharides have an impact on intramolecular co-pigmentation. In addition, it is emphasized that intramolecular co-pigmentation is stronger than intermolecular co-pigmentation due to strength of covalent bonds [9]. Brenes et al. (2005) evaluated the stability of red grape anthocyanins (*Vitis vinifera*) in a model juice system during normal (25 °C) and accelerated storage (35 °C) in the presence of ascorbic acid. Rosemary polyphenolic cofactors (0, 0.2, and 0.4% v/v) were added as stabilizing agents of anthocyanin. Cofactor addition resulted in concentration-dependent hyperchromic (up to 178%) and bathochromic (up to 23 nm) shifts, indicating a more intense red coloration [26].

Cavaltanti (2011) summarized the intermolecular co-pigmentation as the interactions between a colored anthocyanin and a colorless co-pigment. In an intermolecular co-pigmentation it is suggested that the main mechanistic driving forces are Van der Waals forces, hydrophobic effects and ionic interactions [12]. Pacheco-Palencia and Stephen (2010) investigated the effect of different classes of naturally occurring and externally added polyphenolic cofactors on the phytochemical and color stability of anthocyanins in açai fruit (*Euterpe oleracea*). It is reported that externally added cofactors from rooibos tea, resulted in up to 45.5% higher anthocyanin colour and up to 40.7% increased anthocyanin stability compared to uncopigmented anthocyanin isolates [5].

2. Conclusion

Nowadays, the demand for healthy, nutritious and environmentally friendly food has increased in society. In this way, there is an increasing trend for minimally processed foods and foods which contain bioactive compounds such as anthocyanins and natural derived preservation ingredients. Thus, recent studies focus on the use of anthocyanins in food matrix, alternative stabilization mechanisms of anthocyanins, the combination of various stabilizing agents to improve anthocyanin color hue. Thus, these studies highly effective to enhance the application of natural dyes in food products.

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