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A Review on Anthocyanin Pigments with respect to its Nutraceutical Properties

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ABSTRACT

Anthocyanin pigments are readily degraded during processing and storage of foodstuffs that can have a dramatic impact on color quality and may also affect the nutritional properties. Total anthocyanin pigment content and indices for polymeric color and browning are easily measured with simple spectrophotometric methods. Once individual pigments are identified, their changes can be monitored by high-performance liquid chromatography (HPLC). The edible fruits of 12 plants were extracted in methanol and subjected to solvent–solvent partitioning to yield three fractions, hexane, ethyl acetate, and aqueous. A number of factors affecting anthocyanin stability and color are discussed in this review. Anthocyanins are probably the most spectacular of plant pigments since they are responsible for most of the red, purple and blue pigmentation of flowers, hits and vegetables. However, because of their highly reactive nature, anthocyanins readily degrade, or react with other constituents in the media, to form colorless or brown colored compounds. The presence of an oxonium ion adjacent to carbon 2 makes the anthocyanins particularly susceptible to nucleophilic attack by such compounds as sulfur dioxide, ascorbic acid, hydrogen peroxide and even water. Loss of anthocyanin pigmentation also occurs in the presence of oxygen and various enzymes, and as a result of high temperature processing. Certain degree of pigment stabilization may be conferred by acylation with various organic acids, co pigmentation, self-association and/or metal chelation. In addition, pH has a marked effect on anthocyanin stability, and on the color of media containing these pigments. A number of anthocyanin-rich sources have been investigated for their potential as commercial pigment extracts. Although their application is primarily limited to acidic media, continued research on the chemistry of anthocyanins may lead to application and stabilization of these pigments in a wider variety of food products.

KEYWORDS: *Anthocyanins, Natural pigment, Pigmentation, acylation, chelation, stabilization, fortification.*

I. INTRODUCTION

Anthocyanins are water-soluble vacuolar pigments which depend on their pH, which may appear red, purple, blue or black. There are many food plants which are rich in anthocyanins include the blueberry, raspberry, black rice, and black soybean and many others pigments colored red, blue, purple or black.[12]Anthocyanins comprise a group of naturally occurring pigments which are responsible for the blue, red, purple, violet and magenta coloration of most species in the plant kingdom. These polyphenolic substances are glycosides of anthocyanins, polyhydroxy and polymethoxy derivatives of 2-phenylbenzopyrylium or flavylium salts. The large number of glycosyl and acyl groups which may bind to the sixteen different naturally occurring anthocyanidins has contributed to the more than 247[18] different anthocyanin pigments which have been reported in the literature. The structural diversity of these pigments, in addition to their highly reactive and amphoteric nature, has made their identification and quantitation tedious and difficult. Qualitative and quantitative methods used for anthocyanin analysis have been reviewed by several authors [1]. The safety of synthetic pigments has been in question for a number of years, leading to progressive interest in the use of natural coloring compounds in food processing and manufacture. A major problem, however, is their inherent instability, especially in complex systems such as food. The anthocyanins show greatest stability under acidic conditions, but are generally unstable and degrade by one of several possible mechanisms to form first colorless, then insoluble brown colored products. These changes may occur under normal conditions of processing and storage. Therefore, knowledge of the factors governing the stability of anthocyanins, and the possible mechanisms by which they may degrade, is important if these pigments [25] are to be utilized as ingredients in the manufacture of products for which maximum color retention is desired throughout their shelf-life. A number of factors influence anthocyanin pigment stability including pH and temperature, as well as the presence of ascorbic acid, sugars, metal ions and co pigments. Several comprehensive reviews have been published which deal with the stability and color of anthocyanins as influenced by these factors. This paper will review the factors known to influence anthocyanin color and degradation, and the attempts which have been made to stabilize anthocyanin pigments in light of their possible use as colorants in a variety of food systems.

Anthocyanins are prominent members of the secondary plant metabolite class of flavonoid compounds that belong to the super family of antioxidants named phenolics or polyphenolics. A great interest of botanists, chemists, and biochemists has been always aroused by these vegetal chameleons, as they were called by the eminent botanist Tswett, discoverer of the adsorption column chromatography. Flavonoids are perhaps the most important single group of phenolics in foods; they comprise a group of phytochemicals predominant in teas, honey, wines, fruits, vegetables, nuts, olive oil, cocoa, and cereals. Anthocyanins are the largest group of phenolic pigments and the most important group of water-soluble pigments in plants, responsible for the red, purple, and blue colors of many fruits, vegetables, cereal grains, and flowers, being odorless and nearly flavorless and contributing to taste as a moderately astringent sensation. Generally, the structures of the anthocyanins isolated from fruits and vegetative tissues are simpler than those found in flowers. Anthocyanins are almost universally found in higher plants (occurring in about 30 families), but in general anthocyanins seem to be absent in the liverworts, algae, and other lower plants, although some of them have been identified in mosses and ferns. Anthocyanin biosynthesis was one of the first branches of the general propanoid metabolism, for which biosynthetic enzymes and corresponding transcription factors were identified, given the ease of visualization and control of mutants and genetic imbalances. Anthocyanins are effective donors of hydrogen. Owing to anthocyanin's positive charge (Figure 1), the number and arrangement of aromatic hydroxyl groups, the extent of structural conjugation, and the presence of electron-donating and electron withdrawing substituent in the ring structure, these compounds can easily donate protons to highly reactive free radicals, thereby preventing further radical formation. This protects cells from oxidative damage, which leads to aging and various diseases, such as cancer, neurological, and cardiovascular diseases, inflammation, diabetes, and bacterial infections. Laboratory-based evidence was provided of the potential health benefits of anthocyanins. Consumption of diets rich in natural bioactive components (i.e., fruits and vegetables) as an alternative to pharmaceutical medication has been a subject of considerable interest to researchers. However, much work remains to achieve definitive conclusions and the need for additional basic and applied research in this area is evident.

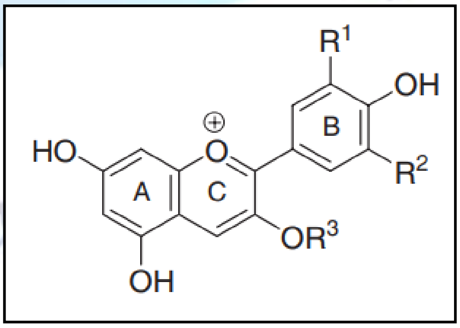


FIG.1. Structure of the major anthocyanins-3-O-glucoside present in fruits.

TABLE 1

MAJOR ANTHOCYANINS-3-O-GLUCOSIDE PRESENT IN FRUITS

				λ_{max} (nm)*		
Anthocyanidin	Abbrev.	R1	R2	R3=H	R3= gluc	Some of the produced colors
Delphinidin	Dp	OH	OH	546	541	Purple, mauve, & blue
Petunidin	Pt	OH	OCH3	543	540	Purple
Malvidin	Mv	OCH3	OCH3	542	538	purple
Cyanidin	Cy	OH	H	535	530	Magenta & Crimson
Peonidin	Pn	OCH3	H	532	528	Magenta & Crimson
Pelargonidin	Pg	H	H	520	516	Orange salmon

II. ANTHOCYANINS

Chemically, anthocyanins are glycosilate poly hydroxy or polymethoxy derivatives of 2-phenylbenzopyrilium, usually with molecular weights ranging from 400 to 1200 (medium-size biomolecules), and containing two benzyl rings (A and B), i.e., anthocyanins are heteroxides of an aglycone unit (anthocyanidin), which is a derivative of flavylium ion. The major anthocyanins are shown in Figure 1 and Table 1, and the most commonly accepted nomenclature numbering of their carbon atoms is shown inside the structure in Figure 2. The red, violet, or blue colors of numerous fruits, flowers, and vegetables are due to the presence of anthocyanins.

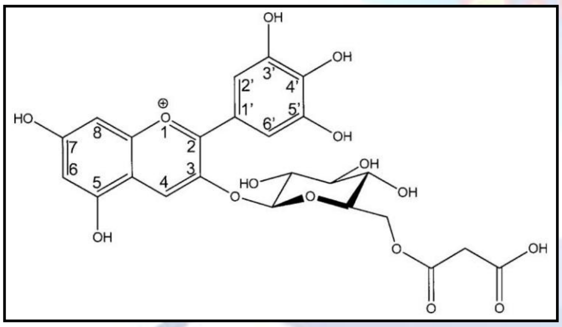


FIG.2) Structure of delphinidin-3-malonylglucoside.

III. POTENTIAL USES OF ANTHOCYANIN PIGMENTS

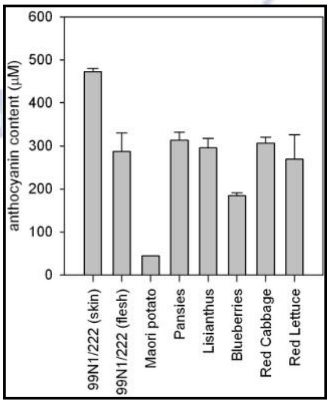
Anthocyanins extracted from plants have been used as food additives. Food additive, E163, is one of the commercial additives derived from fruit anthocyanin such as grape skin. It is a purple food additive for use in producing purple-colored jam, confectionaries, and beverages. Recently, synthetic food dyes attracted public concern regarding safety and the adverse effect on human health, particularly neurological functions and behavioral effects. A clinical trial involving a total of 153 three-year-old and 144 eight to nine-year-old children suggested that artificial colorants that contained a mixture of sunset yellow (E110), carmoisine (E122), tartrazine (E102), ponceau4R (E124), quinoline yellow (E104), and Allura red AC (E129) when combined in the diet with sodium benzoate (E211), resulted in a significant increase of hyperactivity in normal children and aggravated the condition as well at least up to middle childhood. This finding has drawn great interest in exploring natural food colorants such as anthocyanin as a promising alternative to synthetic food dyes.

The use of anthocyanin-based colorants in yogurt drink and some mixed fruit juice is becoming more popular. Some companies did use synthetic dyes in their products. However, these synthetic dyes may be toxic if overconsumed. Recently, acylated anthocyanins are food colorants used in the food industry due to their high stability over nonacylated anthocyanins. A high level of nonacylated anthocyanins is produced from certain fruits, such as elderberry and barberry, at relatively low cost. These commodities have potential as colorants for use in the food industry.

IV. ANTHOCYANIN PIGMENTS WE GET FROM FRUITS & VEGETABLES:

Fruits or Vegetables	Total Anthocyanin content (mg.kg-1)
Apple (peel)	100-2160
Bilberry	4600
Blackberry	820-1800
Blueberry	825-5300
Cherry	3500-4500
Chokeberry	5060-10000
Cranberry	460-2000
Elderberry	2000-15600
Grape(red)	300-7500
Grape(blue)	80-3880
Orange, blood	2000
Plum	19-250
Raspberry (red)	100-600
Raspberry (black)	763-4277
Strawberry	127-360
Currant(black)	1300-4000
Cabbage(red)	250
Currant(red)	119-186
Eggplant	7500
Radish(red)	110-600
Onion (red)	up to 250
Rhubarb	up to 2000

[86]



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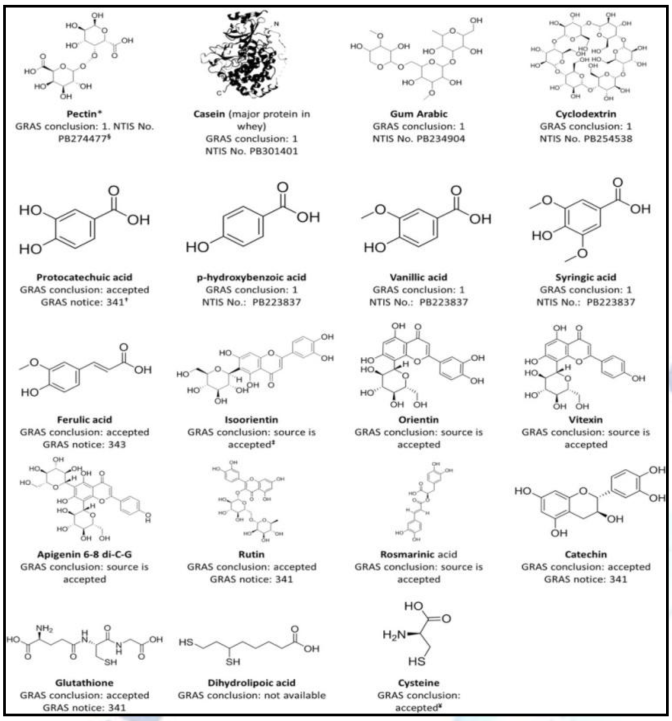

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V. Nutraceutical and Pharmaceutical Effects of Anthocyanins

Anthocyanin is one of the bioactive components as nutraceutical and traditional medicine. It has been traditionally used as a phytopharmaceutical, appetite stimulant, choleretic agent, and for treatment of many other diseases. These colored pigments are potent nutraceutical or pharmaceutical ingredients. As a nutraceutical, the bioavailability of anthocyanin is the key factor for maintaining good health and for prevention of diseases. The low bioavailability of anthocyanins causes low absorption of these compounds into the blood circulating system and a high excretion rate of anthocyanins in urine and feces, thus reducing the efficacy of anthocyanins in scavenging free radical. Anthocyanin with ahigh bioavailability efficiently reduces cellular lipid peroxidation, hence reducing the risk of many diseases. Until now, limited reports on the bioavailability of major anthocyanins are available for comparison. In this review, bioavailability of selected anthocyanidin and anthocyanin will be discussed. Among the major anthocyanins, the bioavailability of cyanidin-3-glucoside and malvidin-3-glucoside isthe most reported. The relative bioavailability of red wine anthocyanins has been reported previously, where the glycosides of peonidin had the highest relative bioavailability, followed by the glycosides of cyanidin, malvidin, delphinidin, and petunidin [65]. Although most red wine anthocyanins have low bioavailability, increased consumption of these anthocyanins may help to increase the efficacy. However, the side effects of overconsumption of anthocyanin remain unknown. A study has determined the absorption of malvidin- 3-glucoside after ingestion of red wine and red grape juice [62], where malvidin-3-glucoside was found in plasma and urine within 3 and 6 h of consumption of these beverages. The result also demonstrates that the bioavailability of malvidin-3-glucoside was about two times higher after consumption of red grape juice compared to red wines. Another study also found that the urine anthocyanin level in the urine of six healthy volunteers who drank 300 ml of red wine (218mg anthocyanins) reached a peak within 6 h of wine consumption [66]. Another study reports on drinking of11 g of elderberry concentrate containing 17.2% w/w of anthocyanins (mainly containing cyanidin -3 -glucoside and cyanidin-3-sambubioside) on an empty stomach [67]. Based on the results obtained, low bioavailability of anthocyanins was suggested by the researchers.

VI. Anthocyanins and Anthocyanidin in Plants

Anthocyanins are found abundant in plants, including red-purplish or red to blue-colored fruits, leaves, flowers, roots, and grains. Types of anthocyanin and anthocyanidin have been determined in fruits and vegetables. Cyanidin-3-glucoside is the most abundant anthocyanin determined in fruits and vegetables. In plants, cyanidin-3-glucoside is formed as the consequence of low pH [54]. All berries that contain glycosides of cyanidin probably do so due to the acidic nature of the berries. Malvidin, peonidin, and petunidin are not commonly found in berries. These anthocyanidins are in methylated forms, therefore, the pigments are not commonly found in red berries. A possible reason is that methylated anthocyanidin haslesser reddening effect[80] than the non-methylated structure. Moreover, these anthocyanidins are typically detected in blue-colored fruit. Petunidin is the anthocyanidin formed in most fruits. Other than the fruits and tomato as fruit vegetable, as well as flowers, petunidin is not commonly determined in purple-colored leaves, roots, and grains. Although most of these purple-colored vegetables contain petunidin and its glycosides, these pigments arenot well-known for the potential health benefits. Similar to petunidin, malvidin is also one of the lesspopular anthocyanidins. Nevertheless, malvidin is apotent antioxidant with high bioavailability [62].

VII. Conclusions

Anthocyanins are colored pigments in plants that possess several health benefits. These colored pigments appear red in acidic condition and show a blue hue in alkaline solution. Acylated and copigmentated anthocyanidins have higher heat stability, thus maintain the structure even in different pH conditions. Anthocyanins are the value-added colorants that can be used for preventing several diseases, including CVDs, cancers, and diabetes, some metabolic diseases, and microbial infection. These compounds also improve visual ability and have neuroprotective effect. Several mechanisms of action are reported for the anthocyanidins and anthocyanins in prevention of these diseases. In a nutshell, free-radical scavenging, changes in blood biomarkers, COX and MAPKs pathways, as well as inflammatory cytokines signaling are the typical mechanisms of action of these colored pigments in prevention of diseases.

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