Waste from Food and Agro-Food Industries as Pigment Sources: Recovery Techniques, Stability and Food Applications

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Abstract: This review discusses the innovative recovery techniques, the stability and the potential applications of pigments attainable from food waste and agro-food industries. It also discusses the effects of the extraction method on the chemical characteristics of the extracted pigments. The main pigment classes, namely anthocyanins, betalains, carotenoids and chlorophylls, are described with a focus on their beneficial health effects, antioxidant properties and chemical stability. The potential applications as food additives are also discussed, taking into account the legislative aspects of their usage, the stability in food matrices and the improvements of food nutritional and organoleptic quality.

Keywords: anthocyanins; betalains; carotenoids; food by-products; natural colorants

1. Introduction

Appearance is one of the characteristics of food that drives consumers' choices, and color is the first organoleptic attribute that strikes their attention. Consumers, in fact, consistently link food color to other food properties such as freshness, ripeness and food safety [1]. Color is an intrinsic characteristic of all foodstuffs; however, being extremely sensitive to environmental conditions such as temperature, pH and light during storage and processing, it easily degrades, making food less attractive. For this reason, to increase consumers' appreciation, pigments are often added to food to enhance or homogenize color or to replace the color degraded during processing and storage. Food additives and in particular colorants have been used by food industries to conceal unpleasant organoleptic characteristics of food or to level out the color differences from batch to batch.

Consumer choices oriented towards perfect and appealing produce have prompted processing industries to use additives to improve food characteristics and extend food shelf life. The use of colorants to improve the attractiveness of several foodstuffs is quite ancient. Recently the synthetic colorants previously approved by the European Food Safety Authority (EFSA) have been re-evaluated, and some of them banned because of rising concerns about their toxicity and potential carcinogenicity. The toxicity of synthetic colorants has become the limiting factor in their use since a potential carcinogenic effect mediated by the gut microbiota has been demonstrated [2,3]. Additionally, the consumers' awareness of the link between diet and health has prompted manufacturers to seek alternatives to synthetic molecules. Naturally derived and safer food ingredients are increasingly requested by consumers that at the same time require delightful and perfect foodstuffs. In the last few years, the market demands have encouraged the replacement of synthetic colorants with natural ones. Food industries have to satisfy the consumers' expectations for perfect and healthy food at the same time. Natural food colorants perfectly meet this expectation, having good coloring properties and several health effects. Based on this trend, the natural

food color industry is expected to grow consistently at a rate of 6.9% by 2027 [4]. Plant pigments such as anthocyanins, carotenoids, chlorophyll and betalains perfectly meet this double expectation, making food more attractive and promoting health. Natural pigments are present in fruits and vegetables [1,3,5–10]. In plants, they are responsible for colorful appearances and the visual attractiveness of fruits and vegetables, but they also have essential roles in several biological processes. Food waste represents an important source of natural pigments: grape pomace, tomato waste, red beet waste and cactus pear peel fruit are particularly rich in anthocyanins, carotenoids and betalain [11–17].

In this review, we report the innovative recovery techniques, the stability and the potential applications of natural pigments obtained from food waste and agro-food industry by-products. The chemical stability and the health-promoting properties of the main classes of natural colorants are also discussed.

2. Pigments' Health Effects and Antioxidant Properties

The importance of pigments goes beyond their coloring properties. Anthocyanins, betalains and carotenoids have outstanding health effects, including the prevention of and the protection against cancer and cardiovascular diseases, skin protection and antioxidant and antimicrobial activity [9]. These molecules are naturally present in many fruits and vegetables as well as in many food waste and by-products, as reviewed by Carrillo et al. [18].

2.1. Anthocyanins

The health benefits of these water-soluble flavonoid compounds have been studied in several in vitro and in vivo trials [19–21].

These studies highlighted a positive effect on the prevention of cardiovascular and metabolic diseases and cancer. These diseases are often associated with a metabolic oxidative imbalance due to bad dietary patterns based on the intake of saturated fats, high-energy food and refined carbohydrates [21]. By contrast, an anthocyanin-rich diet and more generally a polyphenol-rich diet is able to counteract the damages ensuing from oxidative stress and inflammation.

On several types of cancers, anthocyanins act by targeting inflammation, oxidative stress and apoptotic signaling pathways [22–25].

Anthocyanins present different glycosylations that may impact their bioavailability and hence their anticarcinogenesis activity. Monoglycosylated anthocyanins are prone to degradation under certain external conditions, thus compromising their application. On the contrary, polyglycosylated anthocyanins (PGAs) are less predisposed to degradation, offering a valid alternative in in vitro and in vivo trials [20].

Diabetes mellitus is a chronic metabolic disorder that causes high blood glucose concentration. Anthocyanin-rich food showed hypoglycemic effects and has been proposed for the prevention of the onset of diabetes or as a non-pharmacological approach for the treatment of patients affected by diabetes [26,27] and the prevention of diabetes complications. The mode of action of anthocyanins is still not completely clear; however several studies demonstrated that these pigments target the activity of enzymes such as α-amylase, α-glucosidase (α-GLU), protein tyrosine phosphatase 1B (PTP1B) and dipeptidyl peptidase IV (DPP-IV) [19,27,28]. The antidiabetic properties of anthocyanins are also associated with the modulation of genes involved in the insulin–glucose signaling pathways [27]. Moreover, anthocyanins can prevent the onset of diabetes complications by inhibiting the production of advanced glycation end products (AGEs) [29,30].

Anthocyanin-rich food has a positive role in the prevention of cardiovascular and neurodegenerative diseases. Epidemiological studies revealed that the frequent intake of anthocyanins lowered myocardial infarction and cardiovascular-disease-related mortality [8]. Berry supplementation was associated with reduced total cholesterol levels and low systolic blood pressure.

2.2. Betalains

Betalains are nitrogen-containing pigments with remarkable positive health effects. The toxicological safety of these molecules makes them valid supplements in the prevention of atherosclerosis, hypertension, inflammation, hepatitis, diabetes and cancer [31,32]. Betalains exert anti-inflammatory activity by modulating cyclooxygenase enzymes, COX-1 and COX-2, reducing inflammation mediators [33].

Betalain-rich food has been also proposed as a non-pharmaceutical treatment for the prevention and control of cardiovascular diseases. The intake of beetroot controlled all the risk factors leading to cardiovascular complications: the blood level of homocysteine, glucose, total cholesterol, triglycerides, and LDL. Moreover, this betalain-rich supplement lowered both systolic and diastolic blood pressures [34,35].

2.3. Carotenoids

Carotenoids play important biological, chemical and physiological roles in cell processes. They also exhibit health effects by preventing or treating different disorders and diseases related to skin and eye aging, cardiovascular diseases, cancer and neurodegenerative diseases [36,37]. Some of these health effects are associated with their antioxidant and anti-inflammatory properties [36,37].

The antioxidant properties of carotenoids are associated with their antioxidant properties. This is particularly important for the health properties of carotenoids linked to age-related macular degeneration. The free radical quenching ability increases with the increase in the number of conjugated double bonds in carotenoid molecules [38]. The antioxidant mechanism of carotenoids has been recently reviewed [39]. In cell culture models, the antioxidant activity of carotenoids involves the protection of membrane lipids and the modulation of cellular responses to inflammation mediated by nuclear receptors [39].

Under certain circumstances, carotenoids may behave as pro-oxidants and trigger ROS-mediated apoptosis [39,40]. In cancer cells characterized by a high level of intracellular ROS, carotenoids acting as pro-oxidants trigger ROS-mediated apoptosis of cancer cells. The shift between antioxidant and pro-oxidant activity depends on different factors; at high concentrations, carotenoids trigger ROS production, and this happens particularly in cancer cells with unbalanced and high ROS concentrations, low levels of antioxidants and endogenous antioxidant enzymes, and high levels of redox-active metal ions (e.g., $Fe(III)$ and $Cu(II)$) [40,41].

Most of the health-promoting properties of the molecules indicated as natural colorants are associated with a modulation of the gut microbiota. Some recent reviews highlighted the effect of food additives on the gut microbiota [42–44]. This topic is gaining increasing attention because a strong relationship between the changes in the gut microbiota and some chronic diseases has been highlighted [42,45]. Dietary factors can exert selective pressure on microorganisms, changing the microbial community populations. For example, the intake of persimmon and blueberry by-products in the form of functional powders containing anthocyanins and carotenoids promoted the growth of beneficial bacteria such as lactobacillus and bifidobacterium [11]. Similarly, red beet consumption affected gut microbiota composition, exerting a prebiotic-like effect [46], whereas carotenoids can counteract dysbiosis caused by high-fat diets [47]. The intake of tomato powder rich in carotenoids increased gut microbiota diversity and decreased the clostridium bacteria population [48]. Additionally, being at the interface between the gut's internal environment and the gut epithelium, the microbiota plays a crucial role in the bioavailability of natural compounds, including natural colorants. Anthocyanins for example are transformed into phenolic acids by bacterial β-glucosidases opening their pyrylium ring structure [49].

2.4. Chlorophylls

Besides providing food with a green color, chlorophylls and their derivatives have several bioactive and health-promoting properties. Chlorophylls a and b possess strong antioxidant properties which are mainly related to their porphyrin structure and are

affected by the presence and the nature of the central metal [50]. The central metal seems to affect the cell uptake of chlorophyll derivatives, determining their pharmacokinetics and properties [51,52].

3. Innovative Extraction Methods

Natural pigments have received increasing interest as food additives and sources of biomolecules with interesting health properties due to the consumer awareness of natural and healthy products for humans and the environment. Besides the pigments themselves, the method for their extraction is increasingly affecting the recent research that is moving towards more sustainable methods.

At laboratory and industry levels, hydro distillation, Soxhlet extraction and maceration are conventionally employed, but recently other alternatives have been proposed for the extraction of natural pigments. The choice of the proper extraction method has a pivotal role in the definition of the biological and antioxidant properties of the pigments extracted as well as their stability [10,53]

Traditionally, the extraction of pigments is performed by maceration with solvents. The type of solvent used determines which molecules are preferentially extracted: polar molecules such as anthocyanins, chlorophylls or betalains are extracted with polar solvents, mainly water, ethanol, methanol and acetone, whereas carotenoids, being non-polar molecules, are preferentially extracted with chloroform, hexane isopropanol or diethyl ether. For both polar and non-polar molecules, a wide array of solvent combinations and experimental conditions in terms of temperature and extraction time have been proposed to increase extraction yield and to provide enhanced biological and antioxidant activities [9,10,54,55].

The drawback of these methods for industrial application is that they are time-consuming and expensive, present batch-to-batch variations and often use toxic organic solvents. Moreover, the stability of natural pigments is affected by temperature and long extraction times. To overcome these problems, novel extraction technologies have been developed and optimized for different types of raw materials and for each class of natural pigments.

Food waste provide a wide range of natural pigments that can be effectively extracted with supercritical fluid extraction, pressurized liquid extraction, microwave-assisted extraction, ultrasound-assisted extraction, pulsed-electric field extraction and enzyme-assisted extraction, as recently reviewed by Carrillo et al. [18].

Natural colorants can be added to food as plant extracts or purified molecules. The purification process has been the topic of several studies and patents, and different steps have been developed for the purification of coloring molecules. Purification affects the color and the stability of natural colorants. On anthocyanins extracted from grape skin by-products, the purification with a Sep-Pak C18 cartridge produced extracts with less vivid colors and less stability, maybe as a consequence of the removal of natural co-pigmenting molecules such as flavonols [56]. Carotenoids were purified from *Pistacia lentiscus* leaves, residues of essential oil production, and applied to the methanolic crude extract, chromatographic procedures based on centrifugal partition chromatography (CPC) separation and medium pressure liquid chromatography to obtain a purified extract of quercetin and loliolid [57]. A cost-effective and simplified one-step purification scheme was developed for the purification of four major xanthophyll carotenoids from lettuce by utilizing preparative thin layer chromatography on a Hyflo-Super-Cel: MgO (Heavy): calcium sulfate hemihydrate (9:9:2 *w/w*)-based adsorbent, obtaining high recovery of each xanthophyll, with 95–96% purity [58].

3.1. Supercritical Fluid Extraction (SFE)

SFE is a green extraction method successfully employed for the extraction of different bioactive molecules coming from plants or food processing residues. This technique is suitable for compounds that have low volatility and are sensitive to thermal degrada-

tion; moreover, the absence of oxygen and light during the extraction process protects the extracted molecules from oxidation, thus preserving their biological properties and extending their storage time. Tuning the process conditions allows SFE to be applied for the extraction of pigments with different chemical characteristics. Supercritical CO_2 extraction is mainly used for the extraction of non-polar compounds, such as carotenoids, from several vegetable matrices and food industry by-products [12]. Lycopene and β-carotene were extracted with supercritical carbon dioxide extraction from industrial tomato waste. The yield of both molecules was significantly affected by temperature and pressure [59]. Temperature, pressure, time, CO_2 density (solvent power) and CO_2 flow rate significantly affect the extraction efficiency. Temperature, in particular, determines the stability of the carotenoids during the extraction process since too high temperatures cause carotenoids' thermal degradation and isomerization [54]. The optimized conditions depend on each biomass or raw material: in general, pressures between 100 and 400 bar, temperatures ranging from 40 to 80 °C and CO_2 flow rates of 3 mL/min provide high carotenoid extraction yields [54].

The use of polar co-solvents in association with CO_2 has been proposed to enhance extraction selectivity and increase the polar pigment extraction yield [60–62]. Ethanol in fact is able to both lower the interactions of the extracted compound with the sample matrix and induce matrix modifications resulting in an easier release of metabolites [54]. Ethanol and water were used as co-solvents for the extraction of anthocyanins from *Crocus sativus* petals of saffron industry residues [63].

Similarly, chlorophyll was obtained by spinach by-products with supercritical CO_2 extraction using ethanol as a co-solvent that significantly enhanced the recovery of chlorophyll [14].

Recently, on carotenoid analysis, a fast, effective and green separation technology based on the coupling of supercritical fluid chromatography to mass spectrometry has been developed [64,65]. This technique has the advantage of a good separation due to the supercritical carbon dioxide physical–chemical properties and the possibility of changing the fluid density by modifying temperature and pressure. Moreover, it requires low amounts of toxic solvents normally used for carotenoid separation.

Even more recently, a direct online supercritical fluid extraction coupled to supercritical fluid chromatography and mass spectrometry has been developed for the characterization of carotenoids and apocarotenoids in different chili pepper cultivars [66,67]. The automated on-line system enables the detection of very low amounts of analytes, reducing sample loss and avoiding sample degradation.

3.2. Pressurized Liquid Extraction (PLE)

PLE is a green extraction technique suggested for the sustainable extraction of bioactive compounds, including pigments [68,69]. PLE employs solvent extraction at high temperatures and pressures, below their respective critical points, that keep the solvents in their liquid state during the whole extraction process. The advantages of this extraction technique rely on solvent saving, good extraction yield, solvent physicochemical modification, an enhancement of the mass transfer rates, a decrease in the solvent surface tension and viscosity and an enhancement of molecule solubility.

A comparative evaluation of PLE, stirred-tank extraction (STE) and stirred-tank extraction with ultrasonication pre-treatment (STE/UP) for the recovery of anthocyanin pigments from saffron processing waste revealed that PLE produced extracts with lower polyphenolic concentration and weaker antioxidant properties than the other extraction methods [70]. The authors concluded that the short extraction time when using PLE might have negatively affected the anthocyanin extraction yield.

Anthocyanins from grape marc were effectively recovered with PLE [17]. The association of ultrasound with PLE enhanced the recovery of anthocyanins from *Aronia melanocarpa* pomace. Sonication, in fact, by enhancing the mass transfer of anthocyanins

from the pomace to the solvent, had a positive effect on anthocyanin recovery, and this effect was greater at low temperatures [71].

PLE significantly improved the extraction of betalains from *Opuntia Stricta* var. *Dillenii* prickly pears, enhancing the extraction of neobetanin. Moreover, the PLE extracts provided enhanced in vitro antioxidant and anti-inflammatory properties [72].

Depending on the compound to be extracted, a wide range of solvents are suitable for PLE extraction. Recently, generally recognized as safe (GRAS) solvents, such as ethanol, ethyl acetate, ethyl lactate or D-limonene have been preferred over more toxic (*n*-hexane, methanol, dichloromethane) solvents for the extraction of polar and non-polar compounds [73,74]. The extraction selectivity can be tuned by modifying the extraction parameters, in particular the temperature. Water, for example, the greenest and the most polar solvent known so far, has been employed alone or in combination with ethanol for the extraction of medium- or low-polarity compounds, such as carotenoids, increasing the extraction temperature [68]. The temperature rise, in fact, lowers the polarity of the solvent, allowing the extraction of low-polarity compounds [55]. The drawback of the use of high temperatures is the thermo-lability of compounds such as carotenoids.

3.3. Pulsed Electric Field Extraction (PEF)

Pulsed electric field (PEF) technology is a non-thermal extraction method that enables the extraction of food colorants at low temperatures and is particularly suitable for thermo-labile pigments. PEF is based on the application of an external electric field that increases cell membrane poration, thus making the solvent extraction of bioactive compounds easier. PFE is normally applied as a pre-treatment before solvent extraction and has been optimized in terms of electric field strength, frequency, time and pulse numbers for several food matrices and food processing by-products [16,75]. By making the contact of the solvents with the biomolecules easier, this technique has the advantage of solvent saving and, as already underlined, a reduction in temperature during the extraction process. By contrast, it seems to enhance the formation of free radicals and promote the enzymatic degradation of pigments. Moreover, as recently highlighted by Bocker and Silva [76], the effectiveness of PEF depends on the conductivity of the food matrices to which it is applied. On an industrial scale, the application of this technique is still limited, mainly because of the high equipment costs [76].

3.4. Enzyme-Assisted Extraction

Enzyme-assisted extraction is an eco-friendly extraction technology used to maximize biomolecules' extraction efficiency. It has been applied for the extraction of coloring molecules from several food matrices such as strawberries and cherries and recently from tomato waste, grape pomaces and red beets [13,77]. Enzyme-assisted extraction relies on a pre-treatment of the biomass to be extracted with cell wall-degrading enzymes allowing the release of the molecules bound to the macromolecules that make up the cell wall. The efficiency of the extraction is affected by the factors that regulate the enzymatic activity, such as temperature, pH and ionic strength of the environment, but even the time of extraction and particle size of the substrate are critical for the extraction process.

Enzymes employed to aid extraction are sourced from bacteria, fungi, yeast, archaea, animal organs or plant extracts. Microbial enzymes present some advantages over the other sources, being more stable and easily adapted to modifications, and their production is cost-effective [78].

The choice of the enzyme is tailored to the composition of the cell wall of the biomass to be extracted, and sometimes a mix of enzymes is preferred over a single enzyme. A wide range of cell wall-degrading enzymes is generally used during enzyme-assisted extraction: a mix of polygalacturonase, pectin lyase, cellulase and xylanase was employed to extract carotenoid-containing chromoplasts from tomatoes [79]. Similarly, industrial tomato waste pre-treated with a combination of cellulolytic and pectinolytic enzymes followed by ethyl acetate extraction had the highest phenolic compound concentration
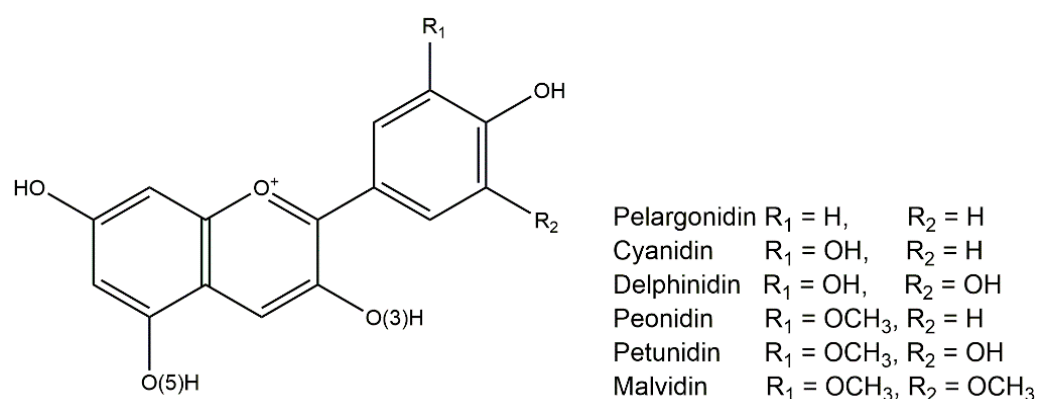
and improved antioxidant properties, as well as the highest lycopene recovery [13]. A mix containing polygalacturonase, hemicellulase, cellulase, protease and amylase was successfully employed to extract chlorophyll from spinach [80].

The advantage of this method relies on the use of mild conditions, mainly in terms of temperature and pH, that preserve the natural colors extracted and their biological properties, being very useful for the extraction of thermo-sensitive molecules.

4. Chemical Characterization and Stability of Natural Colorants

4.1. Anthocyanins

Anthocyanins are a subgroup of pigments belonging to flavonoids. They are found in almost all members of the plant kingdom, with more than 600 compounds identified [81]. The structure of the corresponding aglycones (anthocyanidins) is reported in Figure 1, and the glycosidation can take place at positions 3 and 5 forming the 3-glycosides or the 3,5-diglycosides.

Pelargonidin R_1 = H, R_2 = H
Cyanidin R_1 = OH, R_2 = H
Delphinidin R_1 = OH, R_2 = OH
Peonidin R_1 = OCH$_3$, R_2 = H
Petunidin R_1 = OCH$_3$, R_2 = OH
Malvidin R_1 = OCH$_3$, R_2 = OCH$_3$

Figure 1. Structures of the six more common anthocyanidins. Positions 3 and 5, where glycosylation takes place, are indicated.

Their color depends on the number and nature of the substituents of the rings, going from the orange-red of pelargonidin to the blue-violet of delphinidin. However, the color of anthocyanins strongly depends on the pH of the medium. In fact, they are stable only in very acidic environments, where they exist as flavylium cations (Figure 2). They undergo nucleophilic attack of water and subsequent proton loss followed by ring opening to give the light-yellow E- and Z-chalcones. With an increase in pH, the flavylium cation undergoes deprotonation to form the blue-violet quinoidal base [82].

Anthocyanins are a particular class of flavonoids that are stable only in a narrow pH range, and they are susceptible to oxidation analogously to flavonoids. However, there are differences among the six more common anthocyanins. In fact, those having only a free phenol group in the B ring (and eventually one or two methoxy groups) are more stable in alkaline solutions in comparison with those having a catechol moiety (and eventually another phenol or methoxy group) [83]. Their lower stability depends on the fact that they oxidize more easily because they can form semiquinones, stabilized by resonance, and quinones after the loss of one and two electrons, respectively (Figure 3).

The color of anthocyanins can be stabilized by co-pigmentation or self-association; both these mechanisms entail stacking interaction between aromatic rings with other aromatic components, e.g., flavonoids, or with the same anthocyanins [84]. The stabilization of the color could be important when employing anthocyanins as colorants for foods. Other stabilization phenomena towards the degradation of anthocyanins due to ascorbic acid can be achieved by the addition of (heat-denatured) whey protein isolate [85]. The interaction with the protein through the formation of hydrogen bonds hinders the interaction with other components which otherwise leads to degradation.
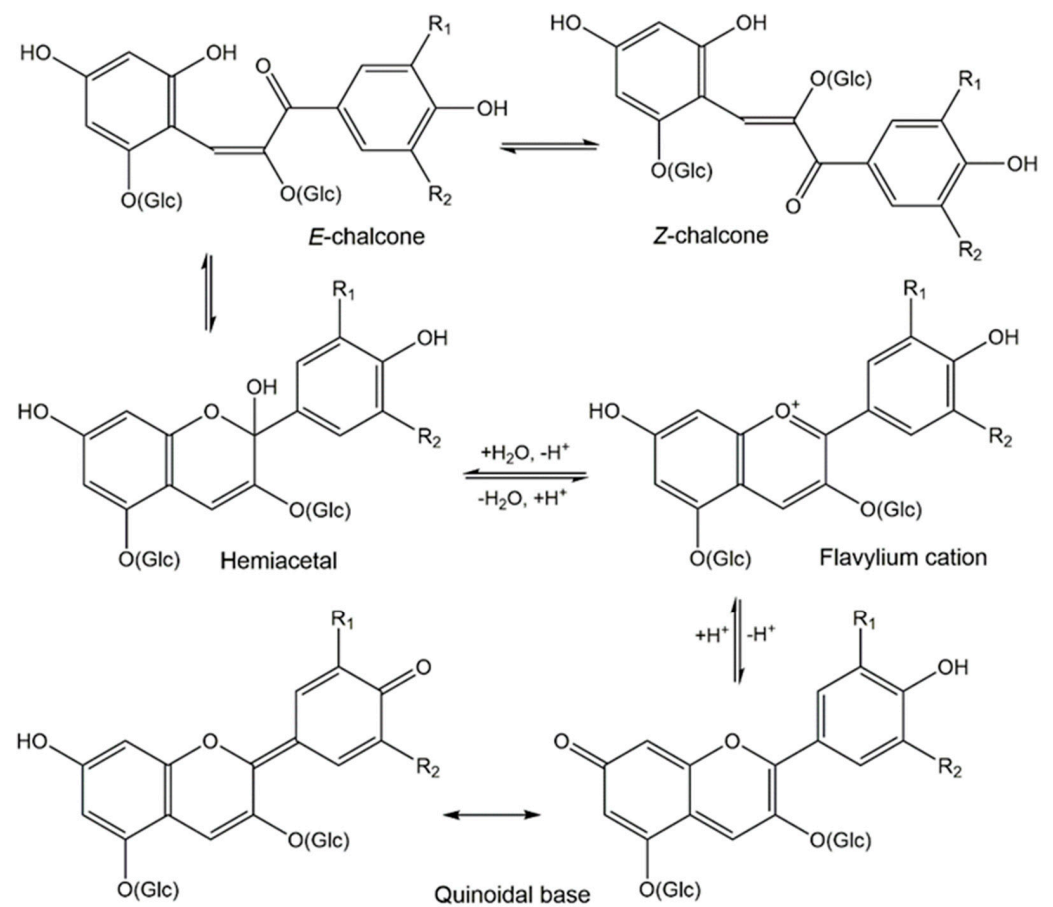
Figure 2. pH-dependent reactions of anthocyanins.

Cyanidin   R = H
Delphinidin R = OH
Petunidin   R = OCH$_3$
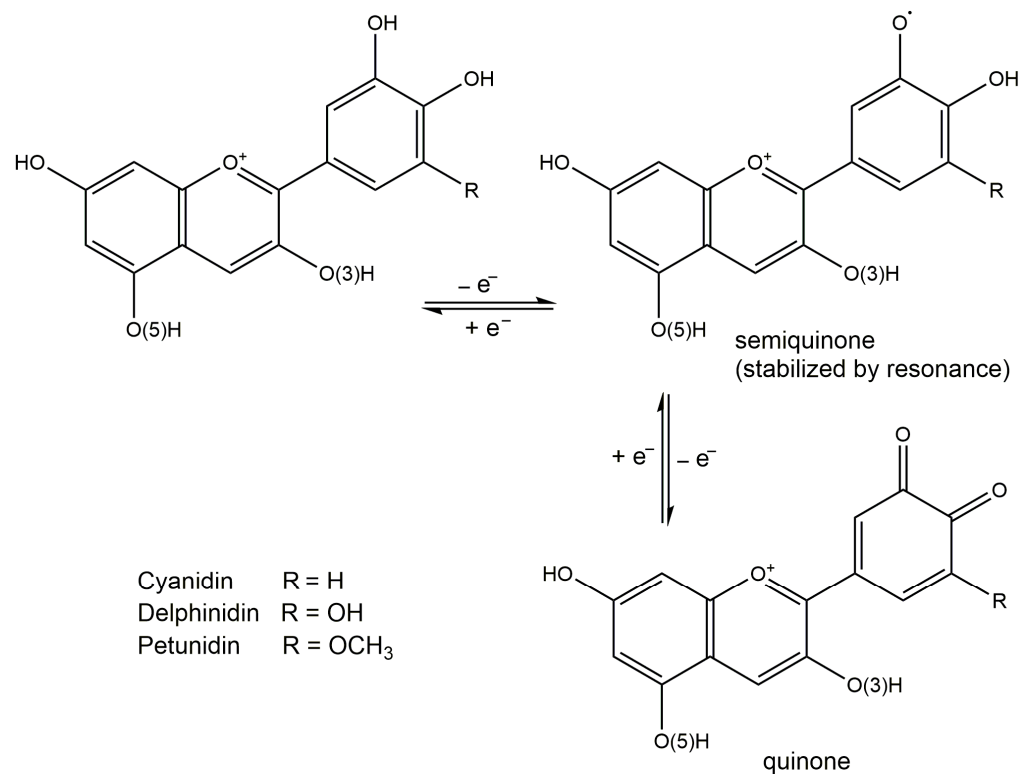
Figure 3. Two-electron oxidation of anthocyanins which contain the catechol moiety in their structures.

Co-pigmentation can also change the color of the anthocyanins towards blue shades. Metal complexation is another mechanism that leads to color change. Some interesting examples are given by flowers with blue colors [86]. As an example, we can mention Hydrangea macrophylla, which can show various colors ranging from pink to blue but contains only one anthocyanin, delphinidin 3-glucoside.

Recent studies demonstrated that this anthocyanin can coordinate Al^{3+} ions, and the interaction of this complex with a co-pigment contained in the sepals, acylquinic acid, leads to the formation of a supramolecular structure that originates the blue color. This structure is stable only around pH 4.0, while acidic soils destabilize it, leading to pink- or red-colored flowers [86]. As previously mentioned, the color stability of anthocyanins strongly depends on the pH of the matrices to which they are added. In fact, anthocyanins are susceptible to nucleophilic addition and oxidation with consequent color loss and browning.

4.2. Betalains: Betacyanins and Betaxanthins

Betalains comprise betacyanins (red-colored) and betaxanthins (yellow-colored). Both these classes of compounds are derived from the condensation reaction of betalamic acid (Figure 4) with amines or amino acids originating betaxanthins or with cyclo-Dopa with the formation of betanidin, whose glycosides or acylglycosides are the betacyanins [87].
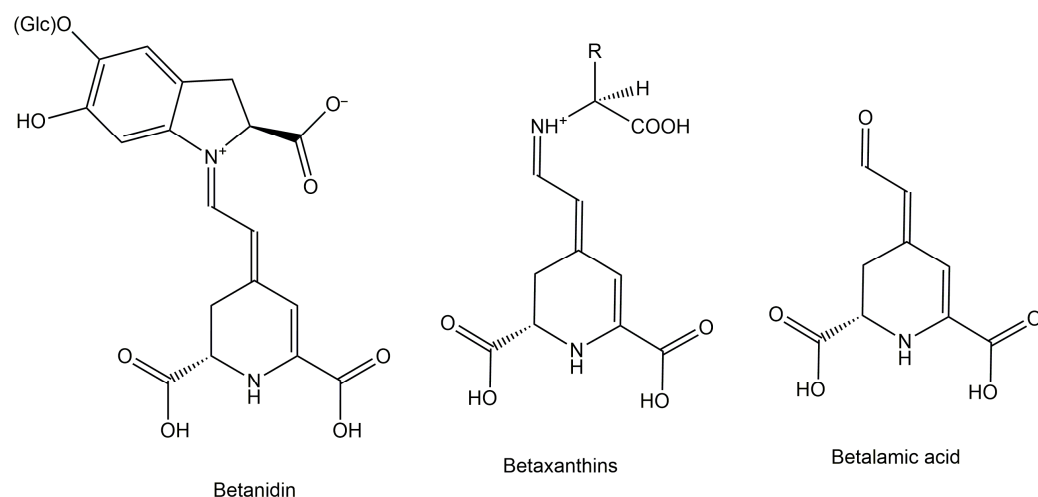
Figure 4. Structures of betanin, betaxanthins and betalamic acid.

The stability of the color of betalains extends over the pH range 3–7, making these pigments a valid alternative to anthocyanins when the foodstuff is not very acidic [88]. Moreover, since these pigments are intensely colored, their coloring properties could be competitive with synthetic colorants [7].

The red and violet colors of betacyanins result from different substitution patterns (glycosylation and acylation) of one or both hydroxyl groups located at position 5 or 6 of betanidin [89].

When used as colorants, a wide range of shades of colors going from the red-violet of betacyanins to the yellow-orange of betalains [89] can be obtained.

Betalains can react with molecular oxygen causing their degradation; therefore, during storage, antioxidants should be added or oxygen should be removed.

The principal thermal degradation reactions of betalains are isomerization, decarboxylation and cleavage [89]. The products of the latter reaction, when starting from betanin (Figure 4), are cyclo-Dopa glycosides and betalamic acid. As an example, betanin thermal degradation proceeds via deglycosylation, isomerization or decarboxylation [90].

4.3. Carotenoids

Carotenoids are a class of hydrocarbons consisting of eight isoprenoid units. The end groups are identified by Greek letters (β, γ, ε, κ, φ, χ, ψ) in the IUPAC nomenclature

system [91] and are cyclic structures except in the case of lycopene, which is the parent compound in the biosynthesis of all carotenoids. Carotenoids are biomolecules employed in photosynthesis, photo-protection, plant coloration and cell signaling. This class of molecules includes carotenes, which are hydrocarbons and contain only hydrogen and carbon in their structures, and xanthophylls, which also contain oxygen. Carotenoids are found in chloroplasts of photosynthetic tissues and in chromoplasts of fruits and flowers.

In leaves of higher plants, the carotenoid composition is very similar, with lutein, β-carotene, violaxanthin and neoxanthin being the more abundant components [91]. β-Carotene (Figure 5), as its name suggests, belongs to the category of carotenes, while lutein, violaxanthin and neoxanthin are xanthophylls.
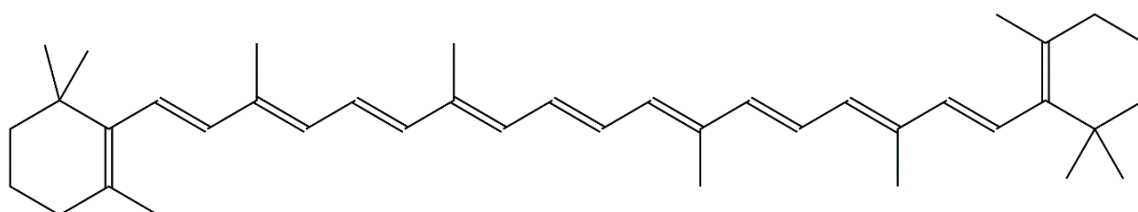
Figure 5. Structure of β-carotene.

4.4. Chlorophylls

The most widespread structure among terrestrial plants is chlorophyll a (Figure 6). Chlorophyll b, found also in plants, has a formyl instead of a methyl group at C7. Chlorophylls c1 and c2 are found in algae, while d and f are contained in cyanobacteria. These differ in the structure of the substituent groups at C2, C3, C7 and C8 and in the C17-C18 bond, which is double only for chlorophylls c1 and c2. Only these latter two do not have the phytyl group (Figure 6) and therefore are more soluble in water.
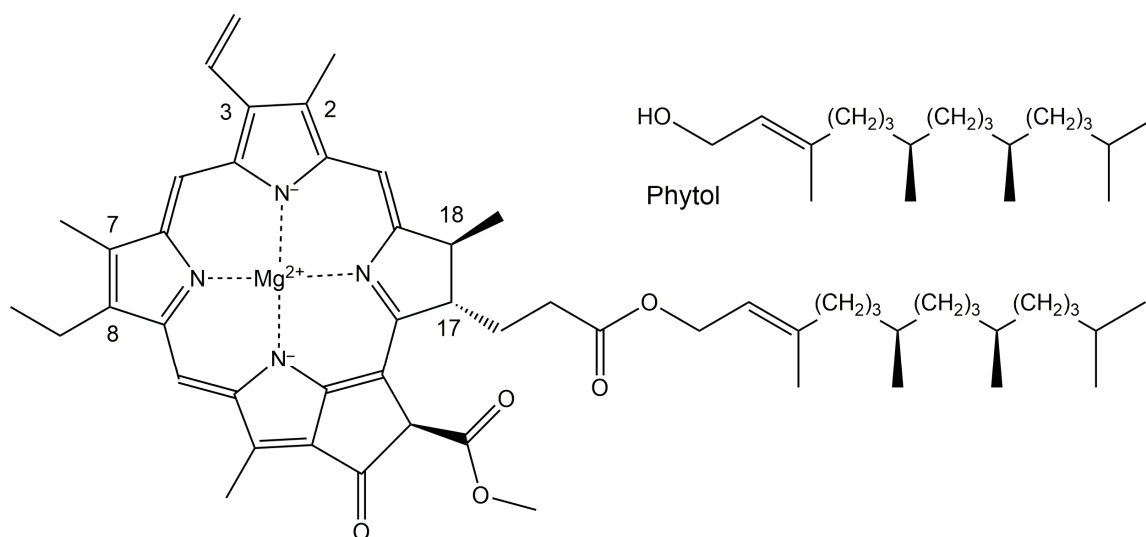
Figure 6. Structure of chlorophyll a, with numbering at the chlorin ring.

Thermal degradation of chlorophyll generates pheophytins and pyropheophytins, which are the derivatives where the Mg^{2+} ion and both Mg^{2+} and the carbomethoxy group, respectively, have been lost [92]. It was also found that chlorophyll a degrades more rapidly than the b form. Recently, it was found that soybean protein isolate improved the thermal stability of chlorophyll [93]. The improvement in stability was explained due to interactions of the chlorophyll molecules with a hydrophobic cavity of the protein, with electrostatic interaction of the Mg^{2+} ion with a side chain Asp residue.

5. Natural Colorants as Food Additives

5.1. Legislative Aspects

After the Industrial Revolution, food processing at a large scale entailed a more general use of natural and synthetic colorants. During the 20th century, some colorants were banned in Europe and US since it became evident that they were toxic or induced cancer. Nowadays, only approved colorants can be used in the EU and in the US. Colorants in the EU are classified among food additives with numbers in the range E100–E199. The list of authorized colorants in the EU can be found in EU Regulation No 1129/2011 [94] and in the consolidated text amending Annex II to EC Regulation No 1333/2008 [95]. New food additives should be approved in the EU by the European Food Science Authority (EFSA).

In the US, color additives require approval by US Food and Drug Administration (FDA) and are grouped into two categories: certified [96] and exempt from certification [97] color additives. The first category includes synthetic organic dyes and pigments, while the latter includes color additives from plants, animals or minerals. Certified color additives can be used in all foods, while those exempt from certification may have limitations for their usage.

Based on Regulation EC 1333/2008 [98] and after the Southampton study [99], the safety of all food additives authorized for use in the EU prior to 20 January 2009 has to be re-evaluated. The deadline for completion of the re-evaluation of all food additives was originally 2020; however, given the large volume of work, the program is still in progress, and updates can be found on the website of the European Commission [100]. The authorization process for a new food additive in the EU is very rigorous, and the application, submitted to EFSA, should contain information about (i) chemistry and specifications, (ii) existing authorizations and evaluations, (iii) proposed uses and exposure assessment and (iv) toxicological studies. The process is described in detail in [101].

5.2. Effects on Food Nutritional and Organoleptic Quality

As previously described in this paper, natural colorants have health-promoting properties mainly mediated by their anti-inflammatory and antioxidant activities and by their interaction with gut microbiota.

Besides their health-promoting properties, natural colorants applied as food additives improve the organoleptic qualities and the nutritional properties of food. However, their employment as coloring additives is challenging because their stability is affected by food components, temperature, light, oxygen, pH, packaging materials and storage conditions.

Natural colorants have been used on a wide range of food and beverages to improve their color properties, but since their application should be tailored to each food matrix, there are many reports in the literature highlighting the proper doses, the interaction with the other food components and the stability of natural colorants [3,83,102–108].

To overcome stability problems and to protect natural pigments during food processing, storage encapsulation and incorporation in smart packaging are emerging as innovative technologies [1,104,109].

The largest example of natural colorant application is in food beverages [110]. Food additives based on anthocyanin extracts (red grape skin extract) can be used in alcoholic and nonalcoholic beverages according to the Codex Alimentarius of the Food and Agricultural Organization (FAO) of the United Nations [111]. As discussed in the previous paragraph, these colorants can undergo degradation and color loss depending on the interactions with the other beverage components. Recently Gérard et al. [112] studied, on a beverage model, the interaction of ascorbic acid, frequently added as an additive in beverages, with anthocyanins extracted from black carrot, grape juice and purple sweet potato, describing a possible mechanism of action and studying the effect of stabilizers such as chlorogenic acid, sinapic acid, tannic acid and fumaric acid on anthocyanin stability in the presence of ascorbic acid. Carotenoids, betalain and chlorophylls are also frequently added to beverages to improve their color properties, particularly during storage [113–115]. Different extracts containing carotenoids, betalaine or curcuma obtained from gardenia, safflower

and curcuma, all providing a yellow color, were tested for stability in model beverages, highlighting the greater resistance of the safflower extract to temperature and light [116].

Natural colorants extracted from plants are used to improve the coloring and the nutritional properties of several products, including bakery, diary, confectionery and meat products [115]. Recently, natural colorants extracted from flowers were studied as a possible alternative to E163 (anthocyanin extract) for yogurt coloration, demonstrating that flowers extracts, rich in anthocyanins, maintained yogurt nutritional properties, in terms of free sugars and fatty acid composition, and had a similar coloring effect to E163 [107]. Similarly, a mix of colorants extracted from plants (10% hibiscus, 4% turmeric, 6% spinach and 4% blue pea) maintained the yogurts' physicochemical (pH, total phenols), microbiological and organoleptic properties (color, sedimentation) at stable levels for over 14 days at 4 °C compared to the colorless control [117]. Natural colorants are also used to fortify pasta. The enrichment of pasta with carrot extract enhanced the concentration of carotenoids and increased the pasta antioxidant activity at the same time [108]. Similarly, the enrichment with saffron extract left the pasta textural properties unaltered while enhancing the antioxidant properties [102].

In edible oils, the enrichment with natural colorants preserved the nutritional properties during storage and cooking [15,103,118]. The addition of β-carotene inhibits the formation of flaxseed oil oxidation products [119]. The addition of chlorophyll to a smart biodegradable film based on wheat gluten used to package sesame oil improved all oils' oxidative indices during storage [120].

5.3. Stability in Food Matrices

The stability of the classes of colorants described above is determined by their intrinsic chemical features and by those of the matrices to which these are added.

The stability of anthocyanins in food matrices is influenced by many parameters such as pH, co-pigmentation, water activity (a_w), light, temperature and oxygen availability.

The effect of the temperature on their stability depends on the interaction with other components eventually present in food matrices. Co-pigmentation seems to be a key factor in determining the stability of anthocyanins.

In a recent review [121], it was shown that more thermally stable anthocyanins are contained in crude extracts in comparison with purified ones, and this was explained due to inter- and intramolecular co-pigmentation reactions with other phenolic compounds. In food matrices, the interaction with other components such as proteins and polysaccharides may stabilize anthocyanins. The thermal stability of pomegranate juices was examined by heating at temperatures up to 90 °C and from 15 to 300 min [105]. Even if the color losses were marked, the antioxidant capacity and the total phenolic amount were not significantly lowered upon heating. In fact, the anthocyanin loss was compensated by the abundance of colorless phenolics already present in the juice and by those formed upon heating.

The thermal and storage stability of an anthocyanin aqueous solution was monitored by examining the color and the antioxidant capacity after thermal treatment up to 65 °C [122]. It was shown that the anthocyanin degradation in an aqueous solution was much faster than that in real foods, and this was explained by the lack of other food components which could stabilize the color of anthocyanins. Only anthocyanins solutions stored at 4 °C showed excellent color and chemical stability, while there were considerable losses at higher temperatures.

The pH stability of anthocyanins extracted from purple corn pericarp was examined during storage up to 12 weeks [123]. Purple corn pericarp is rich in anthocyanins condensed with flavonols, and these compounds are only stable at pH 2, while at higher pH, these degrade during storage with kinetics similar to those of uncondensed anthocyanins. The authors suggested that "pigments extracted with water from purple corn pericarp can be used successfully in acidic foods and beverages with an acceptable shelf-life" even if it could be expected that co-pigmentation in foods and beverages could contribute to color stabilization.

Mulberry anthocyanin extract was stabilized with phenolic co-pigments (gallic acid, ferulic acid, (-)-epigallocatechin gallate and rutin) and subjected to thermal treatment at 80 °C for 120 min [124]. The best results in terms of total anthocyanins and color stabilization were achieved with rutin (0.8 mg/mL) and whey protein isolate.

Analogously to anthocyanins, the stability of betalains in food matrices is influenced by many parameters such as pH, a_w value, temperature and oxygen availability, leading to isomerization, hydrolysis, decarboxylation and dehydrogenation reactions.

The color of betalains extracted from red beetroots was stabilized by the addition of soy protein isolate fibrils [125]. The interaction with betalains changes the secondary structure of the proteins, increasing the β-sheet content and leading to their thermal stabilization.

The thermal stability of betalains extracted from beetroots was enhanced by the addition of black carrot anthocyanins [126], a colorant allowed in the EU, known as E163. However, the mechanism underlying stabilization is unknown.

Carotenoids are lipid-soluble pigments and, being rich in conjugated double bonds, are susceptible to the same reactions that unsaturated fatty acids undergo. These compounds quench free radicals and singlet oxygen [127] which otherwise would react with unsaturated fatty acids, generating peroxides. Therefore, the largest degradation is achieved when oxygen and light are available, and the matrices, to which carotenoids are added, are heated. Thermal treatment of α- and β-carotene contained in raw carrot juices at boiling and pasteurization temperatures does not lead to significant changes, while sterilization causes rearrangement with the formation of the cis isomers, in particular 13-cis [128].

Thermal and photochemical degradation of carotenoids leads to isomerization (formation of cis isomers) and formation of volatile and non-volatile degradation chain-breaking degradation products [129]. The formation of cis isomers does not significantly change the color of carotenoids, while degradation products are less colored. The intermediate in the photochemical trans–cis isomerization is the carotenoid triplet excited state; the activation energy to reach this excited state in the photochemical process is 4 or 5 times lower than that in thermal isomerization. However, the stability of carotenoids and the formation of their degradation products are dependent on the medium properties, such as solvent polarity, pH and viscosity.

Chlorophyll may undergo enzymatic and/or chemical degradation leading to color change. Mg^{2+} loss, with replacement by two protons, in acidic conditions leads to the formation of pheophytin a, with olive-brown color, while the de-esterification reaction of the phytol chain, due to chlorophyllase or alkaline conditions, leads to pheophorbide a when starting from pheophytin a, or chlorophyllide a when starting from chlorophyll a [130]. The phytol loss, although generating more polar compounds, does not lead to a color change. Further degradation leads to chlorin ring opening with the formation of fluorescent and finally non-fluorescent colorless compounds.

Chlorophylls a and b have a long lipophilic tail (the phytyl group) which makes them insoluble in aqueous environments. Therefore, their use as colorants is limited to foods rich in oils and fats.

Among chlorophyll derivatives, copper complexes of chlorophylls (E141i) and chlorophyllins (E141ii) are allowed in the EU (in the US, only sodium copper chlorophyllin is allowed as a colorant for citrus-based dry beverage mixes [131]). These colorants contain copper(II) instead of Mg^{2+} coordinated by the chlorin ring, and the EFSA recently expressed a scientific opinion of re-evaluation of these colorants [132], concluding that that reliable data ADME, genotoxicity, toxicity, carcinogenicity and reproductive and developmental toxicity were lacking, and therefore the safety of their use as food additives cannot be assessed and the current acceptable daily intake should be withdrawn. Chlorophyllins can be used in foods rich in water since they are chlorophyll derivatives where the phytyl group has been removed, making them water-soluble.

6. Conclusions

The visual aspect of food and beverages influences their selection and appreciation by consumers. A vivid and brilliant color of a food or beverage is an index of freshness and wholesomeness. On the contrary, food and beverages with dull and non-inviting colors induce consumers to think of some sort of spoilage. This is an instinctive response of humans because freshly prepared foods or beverages have a more inviting color in comparison with stale ones. Now it is clear that food or beverages can maintain their nutritional features even if the color is slightly changed to a less bright color, but it is not easy to convince the consumers to select such aliments. To satisfy the consumers' demands for inviting colors, the food industries turn to making use of colorant additives. The safety concerns about the toxicity of some synthetic colorants pushed public opinion to move towards natural colorants. To comply with these needs, research focused on new extraction methods for natural colorants and on the stabilization of their color. It is clear that the stabilization of the color of natural colorants is the key factor that is limiting their widespread usage. Anthocyanins are stable only in a narrow pH range, but their color could be stabilized by co-pigmentation; in this regard, crude extracts could be more profitably used in comparison with purified ones because other extracted components may contribute to color stabilization. Betalains are stable in a wider pH range in comparison with anthocyanins, and some stabilization procedures have also been identified for this class of colorants. Literature data indicate that the addition of crude extracts of these two classes of natural colorants to foods and beverages is more effective in comparison with the addition of purified ones. Secondary products present in the extracts not only contribute, by co-pigmentation, to the color stability of foods and beverages, but also enhance their antioxidant capacity.

Another factor that limits the diffusion of natural colorants is the economic affordability of the extraction processes. These extraction processes could become cheaper if plant waste is used as a source of natural colorants, in agreement with better exploitation of natural resources and with the principles of the circular economy.

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