


 Cite this: *RSC Adv.*, 2026, 16, 7097

# Exploring natural colorants from plants to insects: chemistry, functions, and modern uses

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Natural pigments and dyes provide a rich interface between biodiversity and chemistry, offering structurally diverse molecules with distinctive reactivity and bioorganic relevance. These compounds occur in plants, marine organisms, fungi, bacteria, insects, birds, animals, and mineral sources. They encompass major chemical classes such as carotenoids, tetrapyrroles and their degradation products. Owing to their biocompatibility and natural origin, these pigments are increasingly explored as safer alternatives to synthetic dyes and as functional ingredients in food, cosmetic, textile, and pharmaceutical applications. In recent years, these natural pigments have gained significant attention as bioactive molecules with antioxidant, anti-inflammatory, antimicrobial, antiviral, anticancer, neuroprotective, hepatoprotective, and immunomodulatory potential, exhibiting beneficial effects in preventing chronic disorders like diabetes, cardiovascular and degenerative eye diseases. This review provides an integrated examination of biodiversity, chemical classes, biosynthetic logic, structure–activity relationships, and biological properties of these natural pigments and dyes. Key challenges related to chemical stability, bioavailability, and scalable production are discussed, together with emerging biotechnological strategies designed to enhance their stability and sustainable supply.

Received 30th November 2025

Accepted 27th January 2026

DOI: 10.1039/d5ra09252c

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## 1. Introduction

Natural pigments are chemically diverse, biosynthetically unrelated compounds. They share a chromophore as a common feature, which is responsible for the distinctive colors of these compounds. They are found in almost all taxonomic groups, from bacteria to animals.<sup>1–3</sup> The availability of pigments has enabled organisms to develop new and diverse survival tactics, mimicry, advertisement, and aposematism concerning their traits.<sup>4</sup> Apart from the academic interest in pigment chemistry, there is a growing demand for safe, non-toxic, sustainable coloring alternatives for a variety of applications in foodstuff, cosmetics, textiles, pharmaceuticals, and packaging industries, as well as concern about the negative impact of synthetic

colorants on the consumers, on the environment, and on the ecosystem.<sup>5,6</sup> Economic reports have recognized the biopigments market as a multi-billion-dollar industry, where the global market size for dyes and pigments was valued at USD 32.9 and 38.2 billion in 2020 and 2022, respectively. It is predicted to rise at a compound annual growth rate (CAGR) of over 5% between 2023 and 2030.<sup>4,6,7</sup>

Natural pigments can be classified according to several criteria.<sup>8</sup> The prevailing classification of natural dyes is conducted based on their chemical structures, comprising categories such as indigoids, pyridine-based dyes, carotenoids, quinonoids, flavonoids, dihydropyran-based dyes, betalains, and tannins. Other systems categorize these dyes according to their origins into plant or vegetable dyes, animal-derived dyes, insect dyes, and mineral dyes. Additional subcategories include mordant, vat, direct, acid, basic, and disperse dyes.

This review highlights diverse sources of natural pigments, their chemical classes and biological activities, emphasizing their therapeutic potential (Fig. 1). Examples of plant pigments, such as chlorophylls, carotenoids, and anthocyanins, play a crucial role in controlling photosynthesis, growth, and development.<sup>9,10</sup> Pigments serve as visible signals to attract insects, birds, and other animals for pollination and seed dispersal. Pigments also protect plants from damage caused by UV and visible light.<sup>9,11</sup> However, carotenoids and anthocyanins are secondary metabolites and accessory pigments that have a much wider range of structures and functions in plants than chlorophylls, as well as potential nutritional and health

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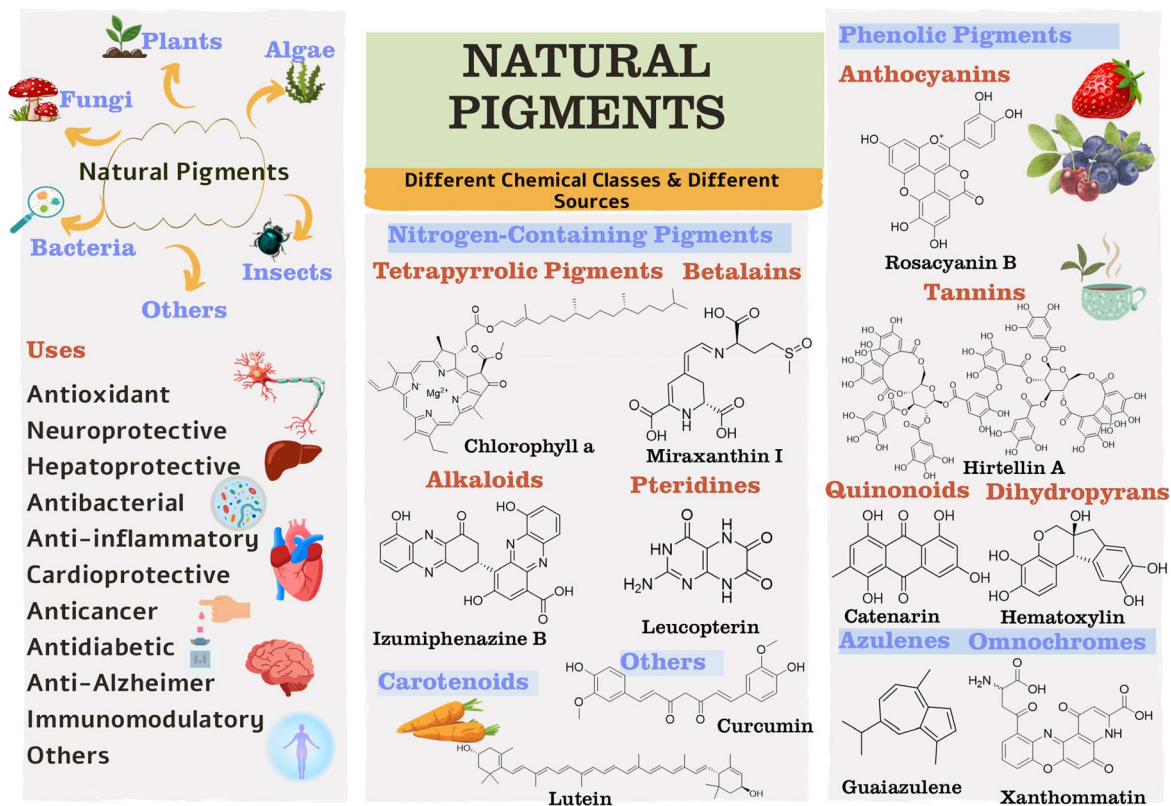



Fig. 1 Structures of different classes of natural pigments and their medicinal uses.

benefits.<sup>9,12</sup> Furthermore, marine organisms exhibit a wide range of color patterns and color variation based on depth and geographic location, serving diverse purposes,<sup>13</sup> where nitrogenous pigments (e.g., porphyrins, pteridines, and bilins) predominate.<sup>14</sup> In addition to playing an important role in how marine organisms interact, pigments may be involved in cellular physiological processes and survival.<sup>15</sup> Moreover, the brilliant colors and their variations displayed by a wide range of insect taxa have long been an interesting research topic because of several prominent attributes associated with them. Among these pigments are pterins, which act as cofactors in omochrome biosynthesis and are present in combination with the latter in the pigment cells of the eyes.<sup>16</sup>

Other sources of natural pigments include birds, which do not only contain carotenoid and melanin pigments as the primary pigments in their feathers across avian orders, but also porphyrins and iron oxides that confer color on bird feathers.<sup>17</sup> Besides, animal pigments are polymeric compounds (e.g., melanins, pterins, porphyrins, and psittacofulvins), which are associated with hair, skin, and hemoglobin colors.<sup>18</sup>

Although natural pigments are synthesized as previously reviewed,<sup>19–21</sup> the present article aims to provide a comprehensive discussion on the chemistry of diverse classes of natural pigments and dyes synthesized by different living organisms belonging to plants, marines, yeasts, bacteria, insects, birds, and animal taxa, and also minerals. It may provide new insights into the beneficial applications in the various industry sectors, including pharmaceuticals. Moreover, a few drawbacks of

natural pigments which hinder their applications, like their instability, limited bioavailability, and insolubility in water, will be discussed in the current article. In the near future, these findings might aid in the resolution of these issues and the development of creative new solutions.

## 2. Materials and methods

**Data collection:** for this review, we selected all accessible chemical structures, biological activities, sources, and pharmacological potential of natural pigments *via* recorded literature from Web of Science, Google Scholar, Scopus, PubMed, Biological Abstracts, EMBASE, Chemical Abstracts, Medline-Plus, PubChem, and Springer databases (1945–2024). The following key words were used for searching in databases: “microorganism and pigment”, “plant and pigment”, “animal and pigment”, “insect and pigment”, “bird and pigment”, “natural dye”, “salts and pigment”, and “natural pigment”. In addition, each pigment name was searched with the keywords “biological activity”, “pharmacological activity”, and “chemical structures”.

## 3. Chemistry of natural pigments

### 3.1. Carotenoids and carotenoproteins

Carotenoids are widespread pigments from plants, marines, animals, bacteria, fungi, yeasts, and insects, with yellow, orange, or red colors and are composed of a 40-carbon skeleton



of isoprene units covalently linked together giving them multiple conjugated double bonds (Table S1 and Fig. 2). The structure may be cyclized (leading to a five- or a six-membered ring) at one or both ends, have various hydrogenation levels, or possess oxygen-containing functional groups. Each double bond of the carotene-polyene chain can exist as *cis*- or *trans*-geometric isomers, with the *trans*-isomer usually being predominant in nature. The defining structural feature of carotenoids is their extended system of conjugated double

bonds, which forms the core of the molecule. This conjugated chain determines their molecular shape, governs their chemical reactivity, and is responsible for their characteristic light-absorption properties. There are two main groups of carotenoids, the carotenes and the xanthophylls. Carotenes are hydrocarbons (composed of carbon and hydrogen atoms only), highly soluble in organic solvents and insoluble in polar solvents, while the xanthophylls contain oxygen atoms in their structures, forming alcohols, aldehydes, ketones, and

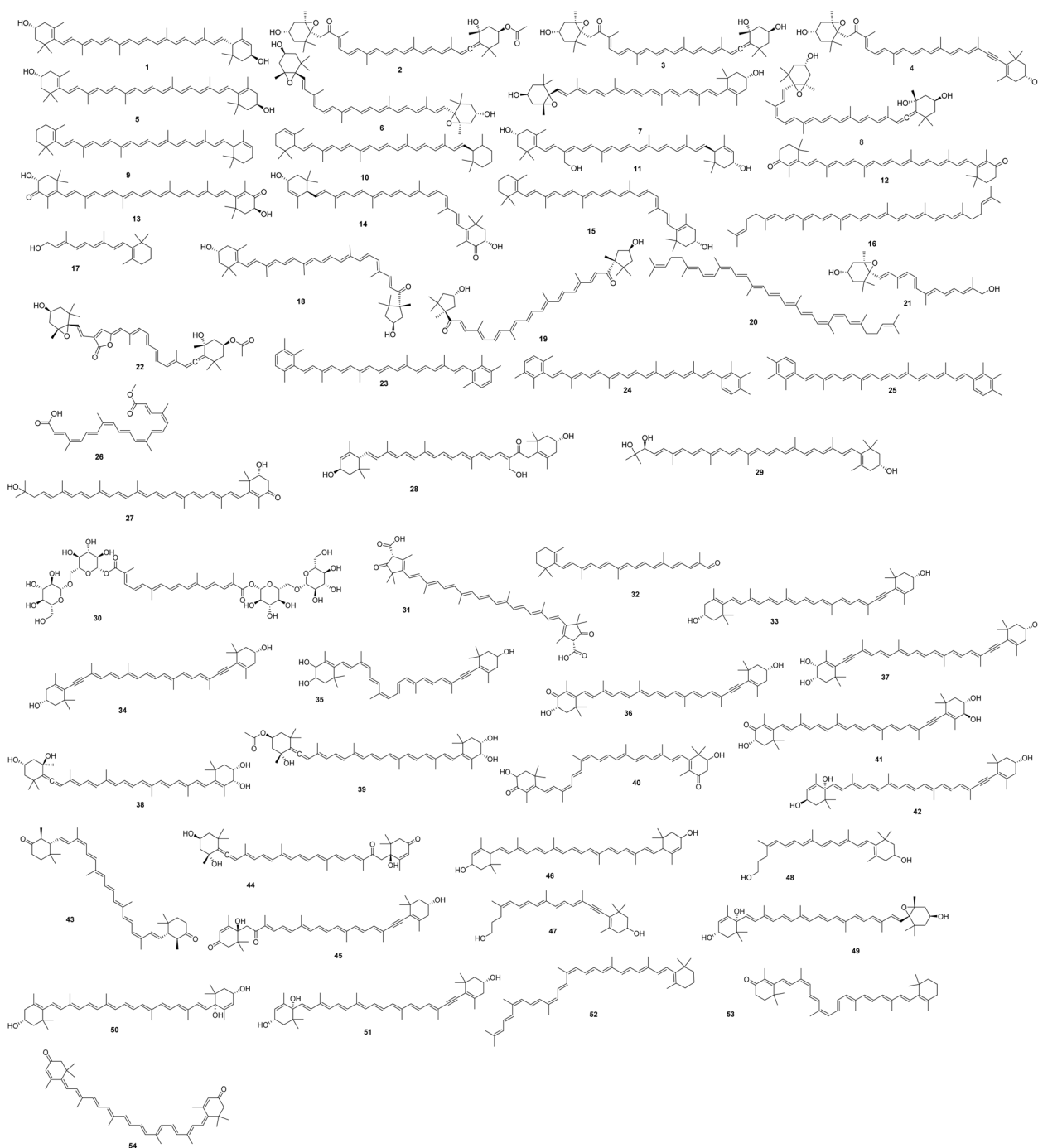


Fig. 2 Selected identified carotenoids that have been isolated from different natural sources. Chirality is indicated where known; otherwise, the configuration is left unspecified.



carboxylic acids. Although animals cannot synthesize them, some animal foods contain carotenoids, and animals can thus absorb, modify, and deposit dietary carotenoids in tissues.<sup>22</sup>

Carotenoids are also found in the feathers of birds from at least ten orders (and 19 families).<sup>23</sup> Carotenoids produce most of the bright red, orange, and yellow hues of feathers.<sup>23–26</sup> Feather color usually correlates with the types of carotenoids deposited, particularly the number of conjugated double bonds that they bear. Feather carotenoids include dietary carotenoids: lutein (**1**), zeaxanthin (**5**), sometimes deposited unaltered in feathers to produce orange-yellow to orange colors (Table S1 and Fig. 2). Red 4-oxo-carotenoids, produced through the enzymatic addition of one or two oxo (=O) functions at carbon 4 of the carotenoid end-rings, extend the central chain of double bonds of dietary carotenoids and shift the color toward red. Examples are, *i.a.* canthaxanthin (**12**) and astaxanthin (**13**) (Table S1 and Fig. 2). Yellow carotene-3-ones are produced through the migration of a double bond on the carotenoid end-rings from position 5,6 to 4,5, shortening the chain of double bonds by one or two double bonds, yielding bright-yellow pigments. Examples: canary xanthophylls (Table S1 and Fig. 2).<sup>24,27</sup> Light-yellow picrofulvins produced through hydrogenation of the double bond 7,8 to produce 7,8-dihydro-carotenoids, in several woodpeckers.<sup>28</sup> An unusual, bright-red, retrodehydro-carotenoid, rhodoxanthin (**54**), presumed to be acquired directly from the diet, is responsible for blue, violet, and red feather colors in several fruit pigeons, and dark-red colors of cotingas.<sup>29,30</sup>

Carotenoproteins are non-covalent associations of carotenoids with proteins, which are common among the invertebrates, providing, yet again, a multitude of colors (blue, green, purple, red *etc.*). There are two major types of carotenoproteins: Type A, in which the carotenoid (chromogen) is associated stoichiometrically with a simple protein or glycoprotein, and Type B, usually less stable, in which the carotenoid is associated with a lipo (glyco) protein. Type A usually occurs at the external surface, such as the carapace of *Crustacea* and the skin of *Echinodermata*, while Type B is commonly found in eggs, ovaries, and blood. The observed color of a bound protein pigment depends on the binding status of the chromogen and the nature of the protein. The most frequently occurring carotenoid in the combinations is astaxanthin (**13**) (Table S2 and Fig. 2).<sup>14</sup>

A list of carotenoids and carotenoprotein pigments, biological effects, and natural sources is presented in Tables S1 and S2, and their structures (compounds **1–54**) are illustrated in Fig. 2.

### 3.2. Nitrogen-containing compounds

**3.2.1. Tetrapyrrolic pigments and their degradation products.** Following the carotenoids, the next most abundant class of pigments are the tetrapyrroles. Tetrapyrrolic pigments are among the most important natural products on Earth. Some of these pigments are involved in essential processes in living organisms, which brought them the name “pigments of life”. Among these, the green leaf pigment chlorophyll (Chl)<sup>31</sup> and the

red blood pigment heme play important roles in several biological processes.<sup>32</sup>

**3.2.2. Chlorins, bacteriochlorins, chlorophylls, bacteriochlorophyllides, and phyllobilins.** Chlorins (**55**) and bacteriochlorins fall in the generic class of hydroporphyrins; these are porphyrin derivatives in which one or more double bonds are saturated by the addition of hydrogen or other substituents. The resulting decrease in the  $\pi$ -system of the molecules affects their frontier orbitals and causes significant changes in their optical and redox properties. In addition to the obvious major changes in the  $\pi$ -system caused by redox changes or by the loss of one or more double bonds in chlorins and bacteriochlorins, conformational variations appear to be among the major structural modes available to modulate a wide range of physicochemical properties of porphyrins, particularly hydroporphyrins<sup>33,34</sup> (Table S3 and Fig. 3).

Chlorophylls and bacteriochlorophyllides are based on a porphyrinic structure, comprising four pyrrole rings ( $C_4H_4NH$ ), which jointly coordinate a magnesium ion in the central position, with a long hydrophobic alkyl chain attached to the macrocycle.<sup>35,36</sup> They are examples of porphyrin ring structures with one reduced double bond, called chlorin (**55**) (Table S3 and Fig. 3). At the center of the chlorin macrocycle is a magnesium ion coordinated to the tetrapyrrole ring. These molecules consist of a hydrophilic porphyrin head group and a lipophilic hydrocarbon tail (the phytol moiety) (Table S3 and Fig. 3). Owing to the presence of this long phytol chain, they are largely insoluble in polar solvents.<sup>35,36</sup> They are oil-soluble, amphiphilic pigments with a green color that are widely distributed in plants, algae, and cyanobacteria. In higher plants, chlorophylls occur mainly in two structural forms: chlorophyll a and chlorophyll b.<sup>31</sup> Chlorophyll a (**57**) ( $C_{55}H_{72}MgN_4O_5$ ) has a methyl ( $-CH_3$ ) group at the carbon-7 position, while chlorophyll b (**58**) ( $C_{55}H_{70}MgN_4O_6$ ) has an aldehyde ( $-CHO$ ) group at the same position (Table S3 and Fig. 3).<sup>35</sup> The distinct structural features of chlorophyll molecules lead to differences in their color: chlorophyll a (**57**) exhibits a blue-green hue, whereas chlorophyll b (**58**) appears yellow-green. In plants, chlorophyll a (**57**) and chlorophyll b (**58**) typically coexist at an approximate ratio of 3 : 1.<sup>35</sup> Chlorophylls are among the most prominent bioactive compounds and have been shown to exert numerous beneficial health effects, including anti-inflammatory, antioxidant, and anticancer activities.<sup>37</sup> However, despite their health benefits, natural pigments have a variety of downsides, including instability and low utilization.<sup>38</sup>

Seven types of bacteriochlorophyllides were found from different bacteria.<sup>36</sup> For example, bacteriochlorophyllides a (**61**), b (**62**), and g (**64**), which have bacteriochlorin ring structures, were found in purple phototrophic bacteria (Table S3 and Fig. 3).<sup>36</sup> In addition, bacteriochlorophyllide d (**63**), which has a chlorin ring structure, was found in green bacteria (Table S3 and Fig. 3).<sup>36</sup> The unique structural features allow bacteriochlorophyllide d (**63**) to form supramolecular structures and to self-assemble within chlorosomes. The diverse applications of bacteriochlorophyllides include photosensitizers, immunosensors, lamellar spacing, dye-



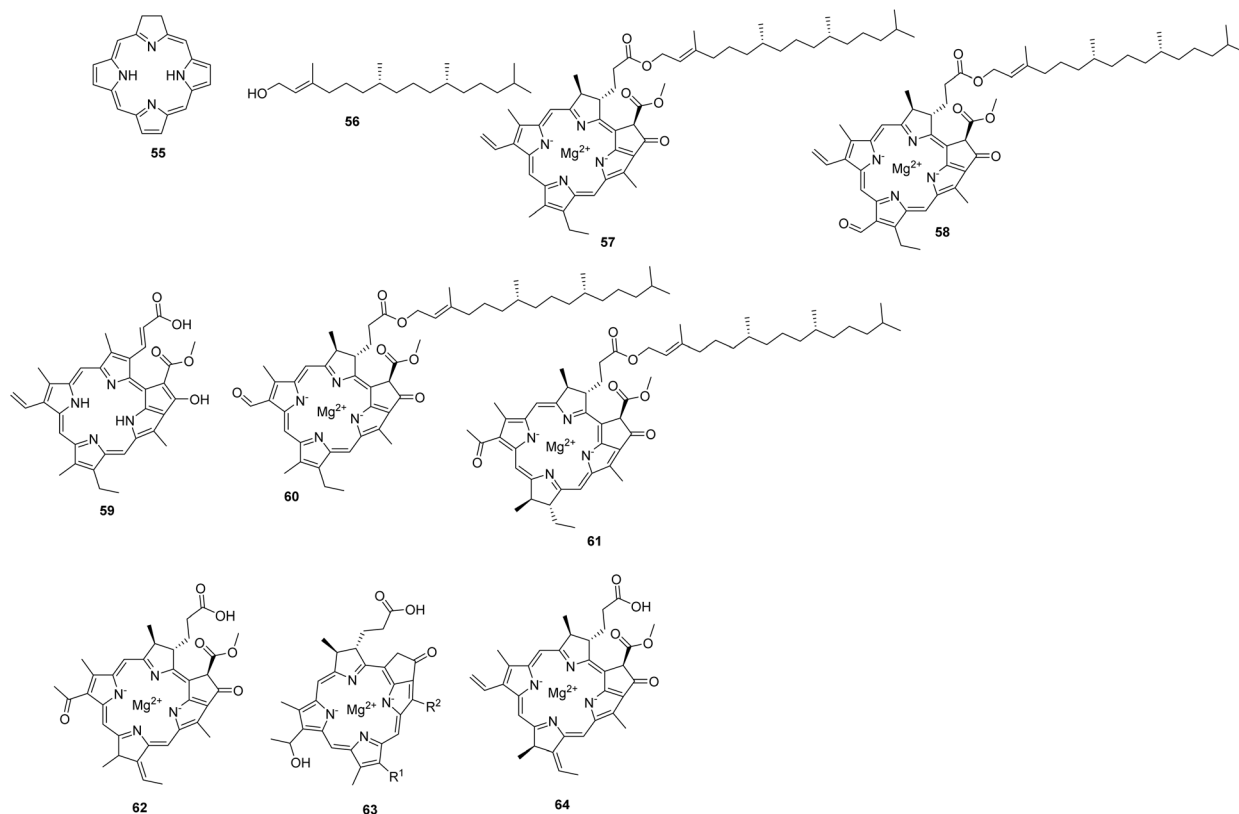


Fig. 3 Identified structures of selected chlorophylls and bacteriochlorophyllides. Chirality is indicated where known; otherwise, the configuration is left unspecified.

sensitized solar cells, synthetic substituted heme, and light energy systems.<sup>36</sup>

Phyllobilins (PBs) are the degradation products of the green plant pigment Chl and are generated in senescent leaves during autumn, and in ripening fruit and vegetables.<sup>32</sup> PBs were first suspected to be “only” products of a detoxification process, involving an enzymatic opening of the macrocycle, catalyzed by pheophorbide a oxygenase.<sup>39</sup> In a strictly controlled process, non-colored Chl catabolites, the phylloleucobilins (PleBs), are generated and accumulate in the vacuoles of the plant cell.<sup>32</sup> In 2008 and 2011, oxidation products of a PleB, so-called phyllochromobilins, were identified: a yellow phylloxanthobilin (PxB) and a pink phylloroseobilin (PrB). The mechanism of the formation of PxB and PrB in plants is not yet elucidated; recent studies, however, suggest an enzymatic “oxidative activity” that effectively transforms PleBs to PxBs.<sup>32</sup>

A list of chlorophylls and bacteriochlorophyllide pigments, biological effects, and natural sources is presented in Table S3, and their structures (compounds 55–64) are illustrated in Fig. 3.

**3.2.3. Hemoglobins, hematins, and bilins.** Hemoglobin (Hb) is widely known as the iron-containing protein in blood that is essential for O<sub>2</sub> transport in mammals. Less widely recognized is the fact that erythrocyte Hb belongs to a large family of Hb proteins, with members distributed across all three major domains of life – bacteria, archaea, and eukaryotes. Hematin (65) is a dark-bluish or brownish pigment containing

iron in the ferric state, obtained by the oxidation of heme (as heme A (66) and heme B (67)) (Fig. 4).

Bilins are primarily known as the metabolic products of heme catabolism in mammals, but can also be found in lower vertebrates, plants, algae, and bacteria. During heme degradation, heme oxygenase catalyzes the oxygenolytic opening of the macrocycle at one of the four methene bridges furnishing the dark-green linear tetrapyrrole biliverdin (BV) (68). In the mammalian liver, BV is reduced to the orange-colored bilirubin (BR) (69) (Fig. 4) by biliverdin reductase A.

**3.2.4. Chlorocruorin.** Chlorocruorin (70) (in Greek, *khloros* means green and in Latin, *cruur* means blood) (Fig. 5) exists in the blood plasma of polychaete worms. Likewise, in insects such as *Manduca sexta*, the color of hemolymph is green due to the presence of chlorocruorin (70). Though it closely resembles hemin, its affinity for oxygen is comparatively low.

**3.2.5. Phycobilins.** Phycobilins are noncyclic tetrapyrroles in which the pyrrole units are linked by  $\alpha$ -,  $\beta$ -, and  $\gamma$ -methine bridges. These compounds have molecular masses of approximately 600 g mol<sup>-1</sup> and, unlike hemes and chlorophylls, do not contain metal atoms. Four major structural types of phycobilins are found in cyanobacteria: phycocyanobilin (PCB) (71), phycoerythrobilin (PEB) (72), phycourobilin (PUB) (73), and phycoviolobilin (PVB) (74) (Fig. 6).

Phycocyanobilin (71) (C<sub>33</sub>H<sub>38</sub>N<sub>4</sub>O<sub>6</sub>) is an isomer of meso-biliverdin and serves as the chromophore of the biliproteins phycocyanin and allophycocyanin, to which it is covalently



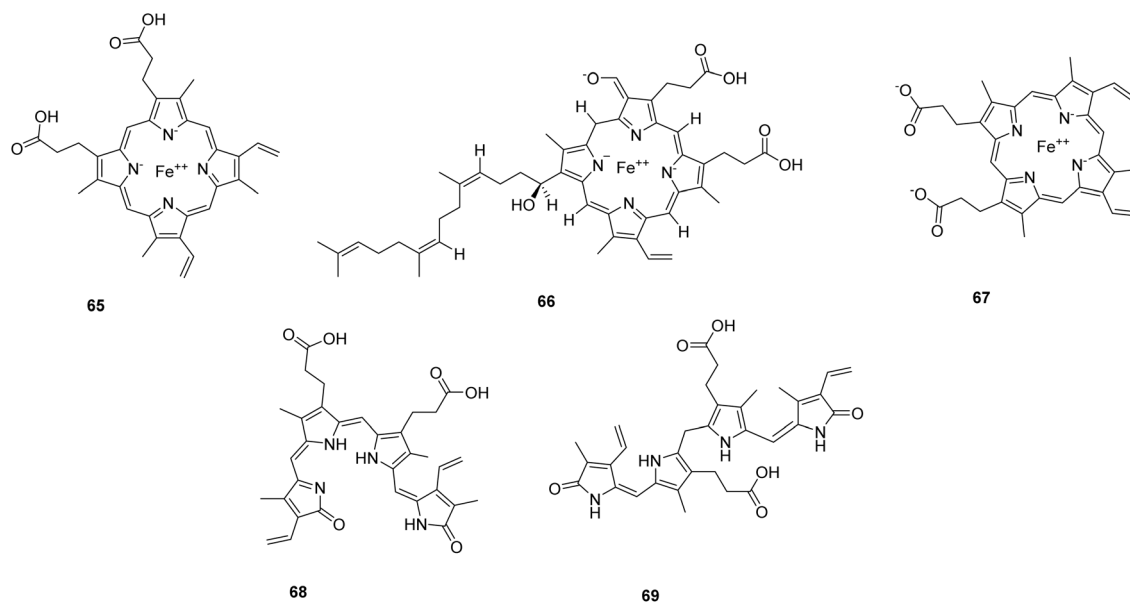


Fig. 4 Identified structures of selected hemoglobins, hematin, and bilins.

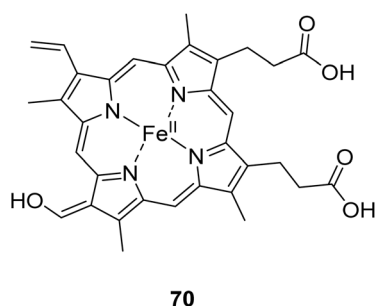


Fig. 5 Structure of chlorocruorin.

attached *via* a thioether bond. It contains a blue tetrapyrrole chromophore. Phycoerythrobilin (72) ( $C_{33}H_{38}N_4O_6$ ) is a red phycobilin and acts as the terminal energy acceptor in phycoerythrin; it may also occur in phycocyanin in some rhodophytes or oceanic cyanobacteria and is likewise covalently bound to phycobiliproteins through a thioether linkage. The ratio of phycoerythrobilin to phycoerythrin varies among species.

Phycourobilin (73) ( $C_{33}H_{42}N_4O_6$ ) is an orange-colored chromophore associated with phycoerythrin and functions as an efficient energy donor. It was first identified in red algae and represents an important adaptation to marine environments because it absorbs maximally at 495 nm, a wavelength that penetrates deeper into seawater. Phycoviobilin (74) ( $C_{33}H_{38}N_4O_6$ ) is a structural isomer of phycocyanobilin and absorbs light at shorter wavelengths, enabling organisms to survive in deeper layers of the water column.

Cyanobacteria can synthesize a wide variety of tetrapyrrole pigments, including hemes, chlorophylls, and phycobilins. In most organisms, the biosynthesis of these compounds (Fig. 6) originates from  $\delta$ -aminolevulinic acid ( $\delta$ -ALA) as a common precursor.<sup>40</sup>

**3.2.6. Alkaloids and alkaloid-related pigments.** Alkaloidal pigments are well-known natural compounds with bioactive properties. The main backbones of many alkaloid-based natural pigments are derivatives of prodigiosins, phenazines, isoquinolines, kuanoniamines, and indoles (Fig. 7). A list of alkaloid pigments, their biological effects, and their natural sources

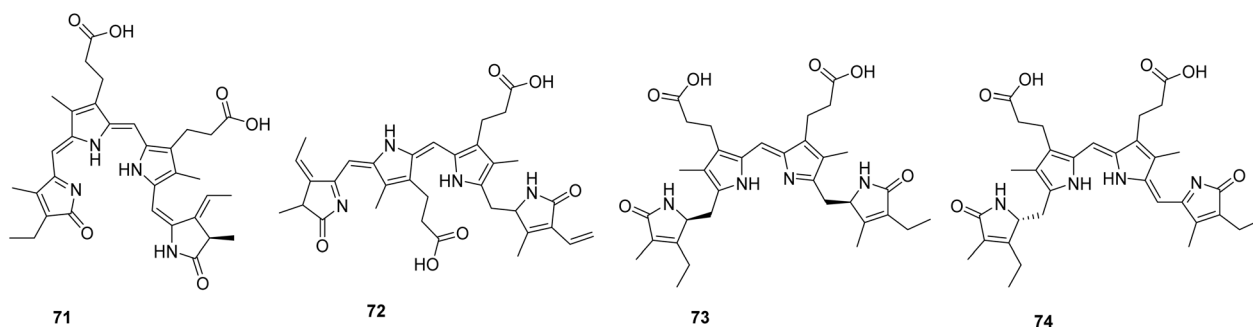


Fig. 6 Structures of different classes of phycobilins. Chirality is indicated where known; otherwise, the configuration is left unspecified.



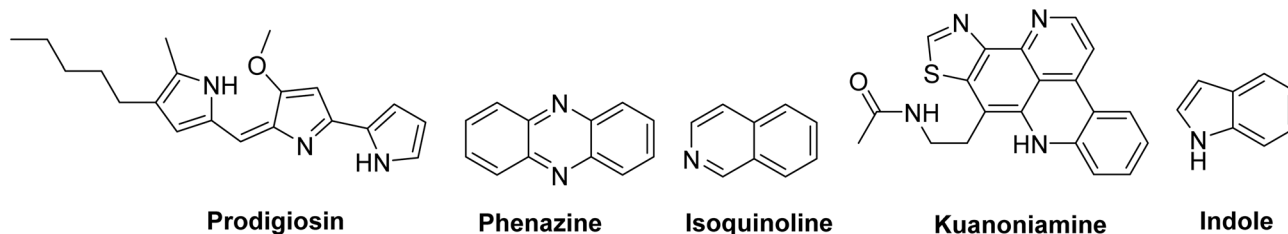


Fig. 7 Structures of alkaloids and alkaloid-related pigments of different classes.

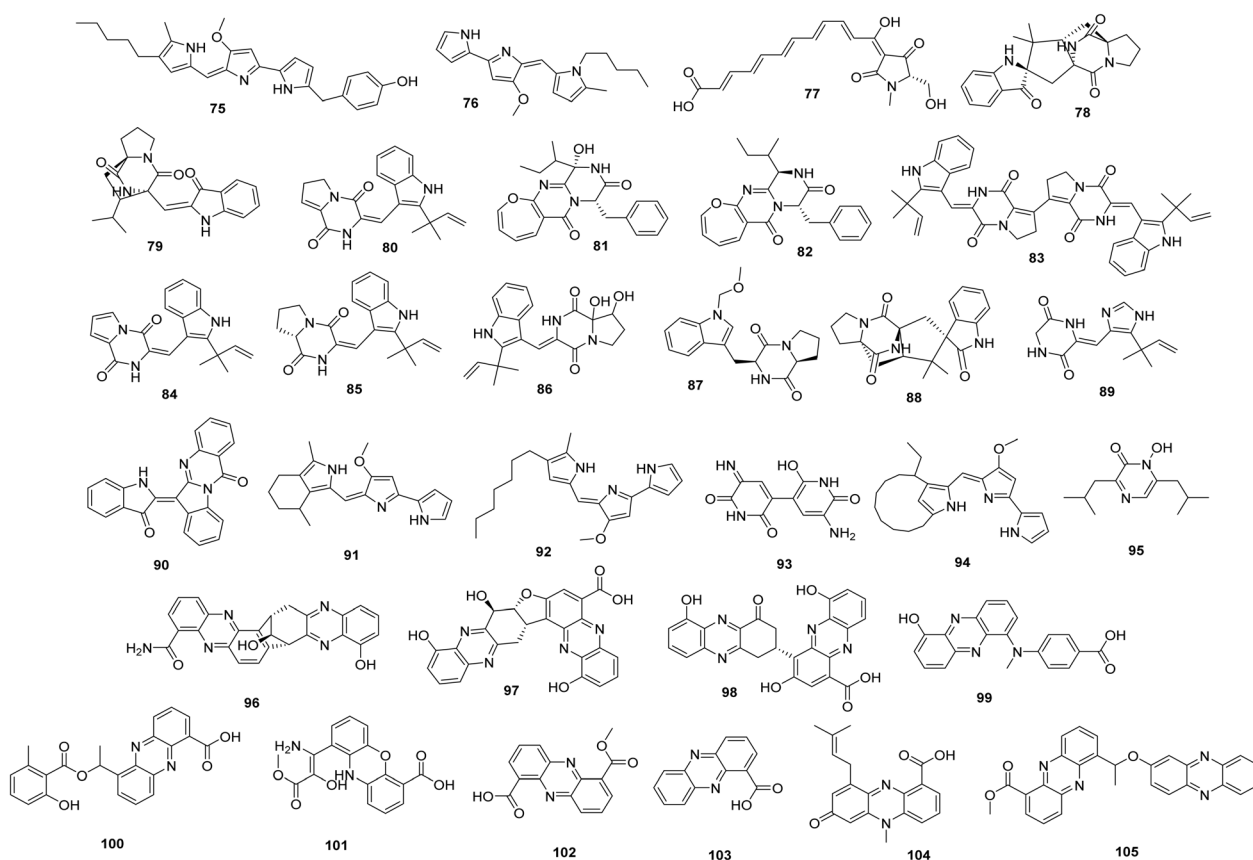


Fig. 8 Structurally identified alkaloids and alkaloid-related pigments (75–105). The complete set of compound structures is presented in Fig. S1–S3. Chirality is indicated where known; otherwise, the configuration is left unspecified.

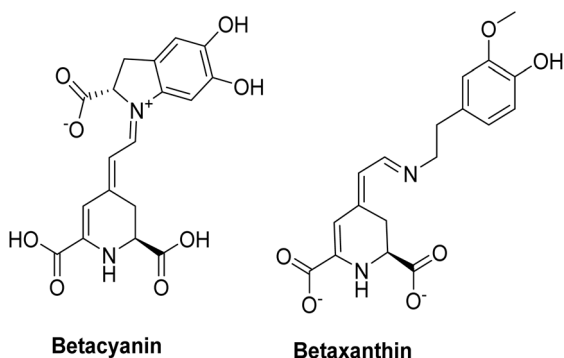


Fig. 9 Structures of different classes of betalains.

is shown in Table S4, and their structures (compounds 75–180) are presented in Fig. 8.

**3.2.7. Betalains.** Betalains are natural water-soluble pigments containing nitrogen in their basic structure, so they are also recognized as chromoalkaloids.<sup>41</sup> These pigments are divided into two main structural groups: betacyanins and betaxanthins (Fig. 9). Chemically, betalains are derived from betalamic acid (**181**) [4-(2-oxoethylidene)-1,2,3,4-tetrahydropyridine-2,6-dicarboxylic acid], which is biosynthesized from the amino acid *L*-tyrosine. According to their chemical structures by a most particular biosynthetic condensation and their glycosylation or acyl glycosylation patterns, they can provide different hues such as red-violet (by betacyanins) and yellow-orange (by betaxanthines). Betalains are mostly



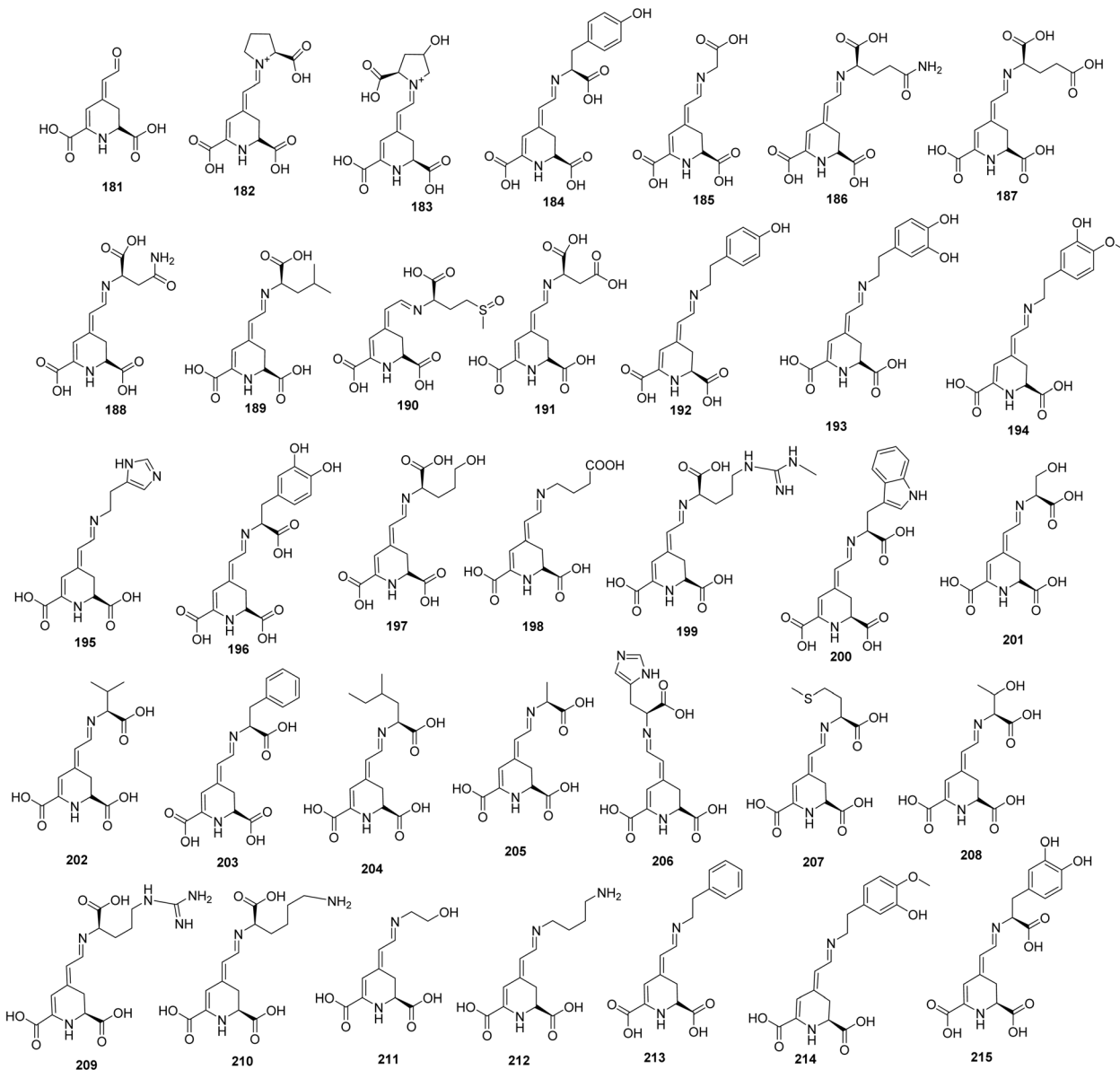


Fig. 10 Structurally identified betalain pigments (181–215). The complete set of compound structures is presented in Fig. S4–S6. Chirality is indicated where known; otherwise, the configuration is left unspecified.

accumulated/stored in plants into flower/inflorescence, petiole, bract, fruit, seeds, stem, leaf, or root.<sup>42,43</sup> A list of betalain pigments, biological effects, and natural sources is presented in Table S5, and their structures (compounds 181–313) are illustrated in Fig. 10.

**3.2.8. Pteridines.** Pteridine is an aromatic organic compound composed of fused pyrimidine and pyrazine rings, containing a wide variety of substituents on this parent structure (Table S6 and Fig. 11, compounds 314 and 315).<sup>44</sup> In nature, pterins were discovered as animal pigments, isolated for the first time from butterflies, such as those included in the genus *Colias*, as they are part of the pigments that give color to the wings of the butterflies.<sup>45</sup> Pteridines are, however, also found in the skin of other insects and vertebrate animals such as some colored fishes (salmon), reptiles (snakes), and amphibians.

Thus, in nature, one of the common roles of pteridines is to be part of animal pigments, being present for instance in the colored eyes of *Drosophila melanogaster*, in which, apart from other tryptophan-derived visual pigments named “ommochromes” (see Section 3.7) there is a group of dimeric pteridines

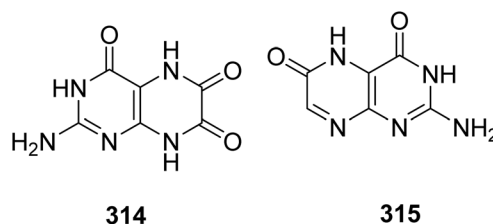


Fig. 11 Selected identified pteridine compounds isolated from insects.



known as “drosopterins”. However, not all pterins found in nature are pigments; in fact, other naturally synthesized pterins play essential metabolic roles as enzymatic cofactors and are involved in the synthesis of nucleic acids, amino acids, neurotransmitters, nitrogen monoxides as well as purine and aromatic amino acids.<sup>45</sup>

### 3.3. Phenolic pigments

**3.3.1. Anthocyanins.** Although 35 naturally monomeric anthocyanidins (an aglycone, containing polyhydroxy or polymethoxy derivatives of 2-phenylbenzopyryllium) have so far been identified, 92% of the reported anthocyanins are based on six anthocyanidins (cyanidin, delphinidin, pelargonidin, malvidin, peonidin, and petunidin), referred to as the common anthocyanidins (Table S7 and Fig. 12, compounds 316–331). The deoxyanthocyanins (Table S7 and Fig. 12, compounds 332–340) have a limited distribution in angiosperms and are the anthocyanins of ferns and bryophytes. Sphagnorubins, which have two additional aromatic rings connected to the A-ring (Table S7 and Fig. 12, compounds 341–343, from peat moss, *Sphagnum* spp.), and rosacyanins (Table S7 and Fig. 12, compounds 344–348, from petals of roses, *Rosa hybrida*) are among the few anthocyanidins that occur in plants. Until recently, it was assumed that the red flavonoid pigments of

liverworts, typified as riccionidin A (Table S7 and Fig. 12, compound 349), were anthocyanins. However, Berland *et al.* (2019) demonstrated that the red pigments of liverworts are biosynthesized from a previously unreported branch of the flavonoid pathway. As this pathway proceeds *via* aurones, they named the pigments auronidins<sup>46</sup> (Table S7 and Fig. 12, compounds 349–350).

During the past decade, the group of pyranoanthocyanidins (Table S7 and Fig. 12, compounds 351–352) has attracted considerable attention, mainly because of their role in color evolution during wine maturation. Only a few studies have reported the identification of pyranoanthocyanins in fruit juices and fresh plant materials. Most anthocyanidins occur in nature as monomeric compounds. However, another class of flavonoids, consisting of one or more anthocyanidin moieties covalently linked to flavanol aglycones (proanthocyanidins; Table S7 and Fig. 12, compounds 353–354), has also been identified. These structures are also formed during storage and processing in plant-derived foods, including wines (Table S7 and Fig. 12, compounds 355–359).<sup>47</sup>

The anthocyanins also consist of an aglycone, sugar(s), and in many cases acyl group(s). The sugar moieties of anthocyanins are commonly connected to the anthocyanidins through *O*-linkages, and rarely *via* a *C*-linkage. The anthocyanin sugars are

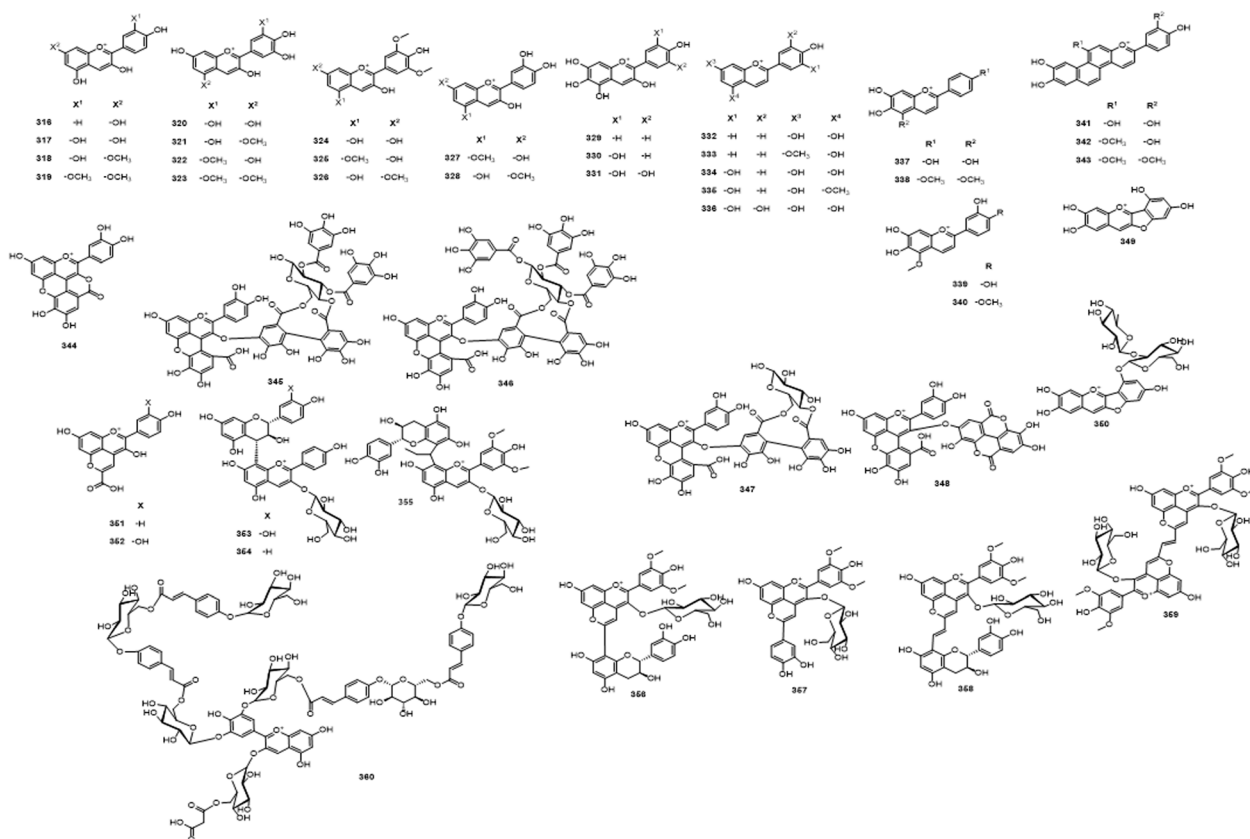


Fig. 12 Different classes of anthocyanins (anthocyanidins 316–331, 3-deoxyanthocyanins 332–340, sphagnorubins 341–343, rosacyanins 344–348, auronidins 349–350, pyranoanthocyanidins 351–352, proanthocyanidins 353–354, wine pigment 355–359, and acylated anthocyanidins 360), which are the predominant pigments in flowering plants, ferns, mosses, and liverworts. Chirality is indicated where known; otherwise, the configuration is left unspecified.



represented by one or more units of glucose (most common), galactose, rhamnose, apiose, arabinose, xylose, or glucuronic acid. The glycosyl moieties are connected to the aglycone *via* the 3- and sometimes also to the 5-, 7-, 3'-, 4'-, or 5'-hydroxy groups. The sugars increase the anthocyanin stability and water-solubility. In their native form, over 66% of identified anthocyanins are acylated with one or more acyl substituents, which significantly influence the pigments' color expression and biological roles in plants. About 320 distinct anthocyanins possess *O*-acyl groups containing aromatic residues, including a variety of hydroxycinnamoyl moieties such as *p*-coumaroyl, caffeoyl, feruloyl, sinapoyl, and 3,5-dihydroxycinnamoyl, as well as hydroxybenzoyl groups like *p*-hydroxybenzoyl and galloyl. Among the aliphatic acyl groups, malonyl is the most prevalent, found in about 25% of anthocyanins. Other aliphatic acyl substituents include acetyl, oxalyl, succinyl, malyl, tartaroyl, and 3-hydroxy-3-methylglutaryl groups. These acyl groups predominantly esterify the 6-position of the sugar moieties (accounting for 86% of cases), although acylation at the 2-, 3-, and 4-*O*-positions has also been documented (Table S7 and Fig. 12, compound 360).<sup>47</sup>

Co-pigmentation plays a critical role in modulating the final color manifestation of anthocyanins in plants. Numerous anthocyanins have been identified or hypothesized to form noncovalent complexes with various co-pigments, including organic acids such as benzoic and cinnamic acids, other classes of flavonoids, anthocyanins themselves, alkaloids, primary metabolites like polysaccharides, peptides, and nucleotides, as well as metal ions. These interactions not only alter the chromatic properties of anthocyanins but also enhance their stability. The co-pigmentation effect is typically characterized by a bathochromic shift (bluing effect), wherein the maximum visible absorption ( $\lambda_{\text{max}}$ ) is displaced toward longer wavelengths relative to the free anthocyanin. This phenomenon is often accompanied by a hyperchromic effect, resulting in increased color intensity.<sup>47</sup>

A list of anthocyanins pigments, and natural sources is presented in Tables S7 and 8 and their structures (compounds 316–360) are illustrated in Fig. 12.

**3.3.2. Tannins.** Tannins are polyphenolic secondary metabolites of higher plants, and are either galloyl esters and their derivatives, in which galloyl moieties or their derivatives are attached to a variety of polyol-, catechin-, or triterpenoid cores (gallotannins, ellagitannins, and complex tannins), or they are oligomeric and polymeric proanthocyanidins that can possess different interflavanyl coupling and substitution patterns (condensed tannins).<sup>48</sup> Gallotannins comprise tannins in which galloyl groups or their *m*-depsidic derivatives are esterified to various polyol backbones, catechin units, or triterpenoid scaffolds. Ellagitannins are characterized by the presence of at least two galloyl moieties covalently linked through carbon–carbon (C–C) bonds and notably lack glycosidically bound catechin units. Complex tannins consist of catechin units glycosidically attached to either gallotannin or ellagitannin structures. Condensed tannins, also known as proanthocyanidins, are oligomeric or polymeric flavonoids formed through C–C linkages between the C-4 position of one catechin monomer and the C-8 or C-6 position of an adjacent catechin unit (Fig. 13).<sup>48</sup> During the past 20 years, many representatives of this class of compounds have been isolated and characterized.<sup>49–56</sup> Currently known tannins with unambiguously determined structures already number far more than 1000 natural products (Table S9 and Fig. 14).<sup>57</sup>

Although tannins have traditionally been included alongside other classes of plant specialized metabolites, it is important to clarify that they are not intrinsic plant pigments. Condensed tannins (proanthocyanidins) are generally colorless in their native, reduced forms; visible brownish or reddish colors arise primarily after oxidation, when they are converted into quinone-type products (*e.g.*, phlobaphenes), which contribute to tissue browning. This oxidative transformation explains their association with color changes in plant materials, but condensed tannins themselves are not considered as pigments in the strict phytochemical sense. We have included this clarification to avoid conceptual confusion.

Tannins are used in the dyestuff industry as caustics for cationic dyes (tannin dyes), and in the production of inks (iron gallate ink). In the food industry tannins are used to clarify

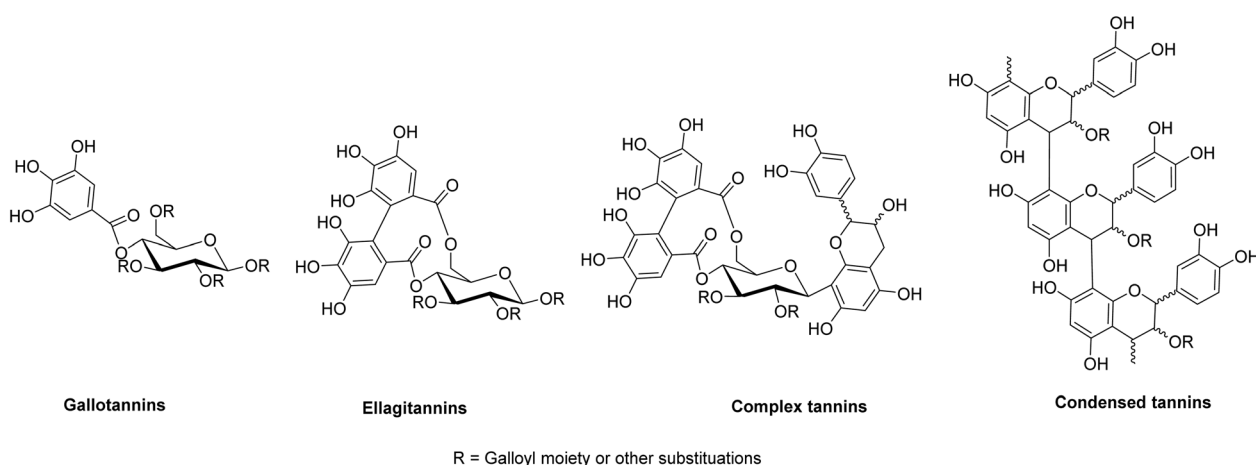


Fig. 13 Classes of the tannins.



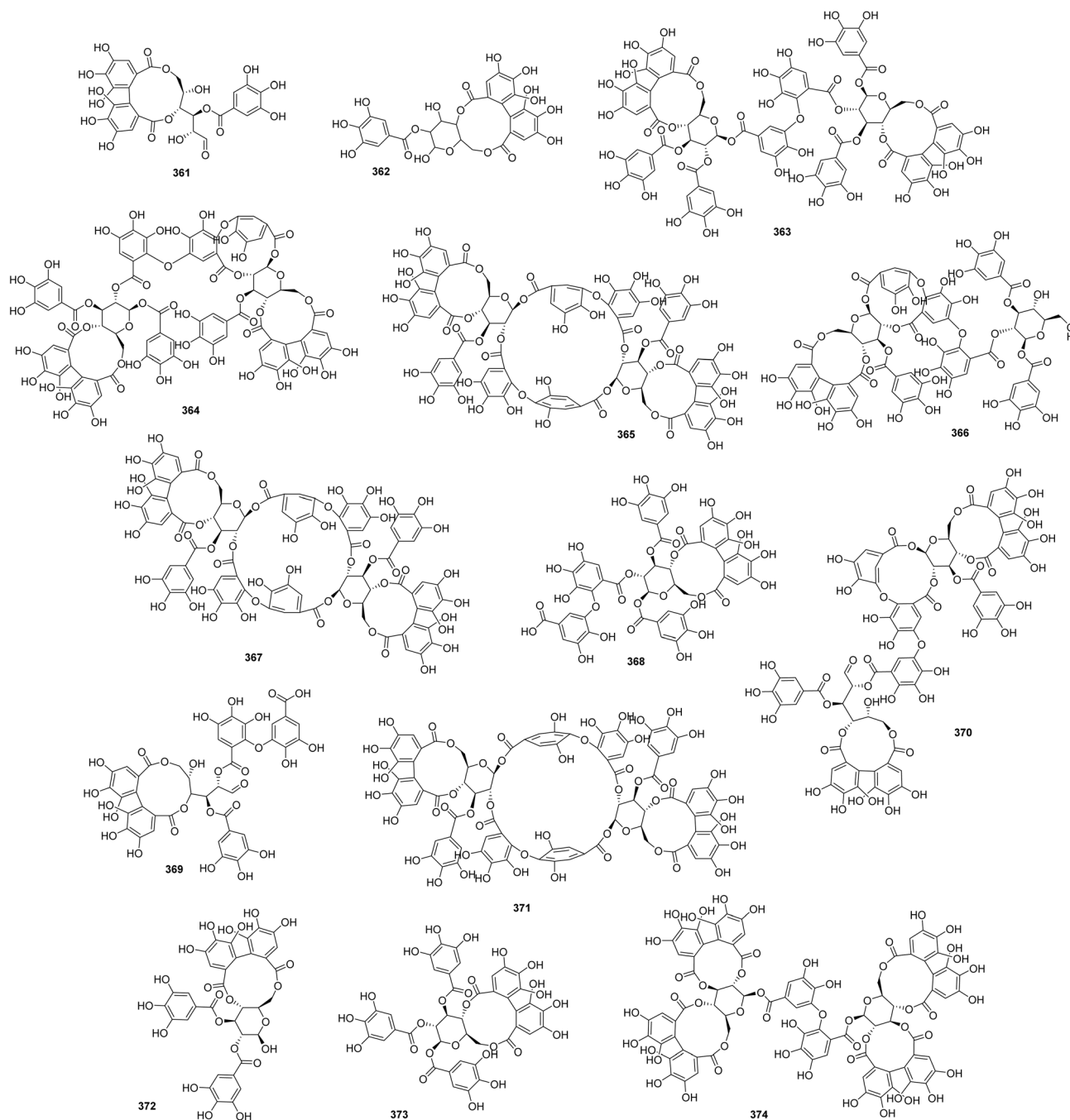


Fig. 14 Selected identified tannins isolated from plants (351–374). The complete set of compound structures is presented in Fig. S7. Chirality is indicated where known; otherwise, the configuration is left unspecified.

wine, beer, and fruit juices.<sup>58</sup> Other industrial uses of tannins include textile dyes, as antioxidants in the fruit juice, beer, and wine industries, and as coagulants in rubber production.<sup>59</sup>

A list of tannins pigments, biological activity, and natural sources is presented in Table S9, and their structures (compounds 361–392) are shown in Fig. 14.

**3.3.3. Quinonoids and pyranonaphthoquinones.** Quinonoids exhibit yellow to red coloration. Depending on the size of the fused aromatic system, they are commonly divided into benzoquinones, naphthoquinones, and anthraquinones.

Anthraquinone is an aromatic organic compound with the formula  $C_{14}H_8O_2$  in the form of a 9,10-anthraquinone, wherein the keto groups are located on the central ring. Anthraquinone compounds are found in plants, fungi, insects, bacteria, and lichens (Table S10 and Fig. 15).<sup>44,60–65</sup> Benzoquinone naturally occurs in many plants (Table S10 and Fig. 15).

Aphins are a class of compounds known as the pyranonaphthoquinones, which are isolated from various strains of insects, bacteria and fungi, the majority being microbial in origin. The core structure of these compounds is



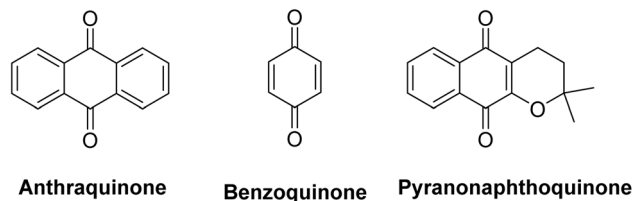


Fig. 15 Chemical basic structures of anthraquinones, benzoquinones, and pyranonaphthoquinones.

the naphtha[2,3-*c*]pyran-5,10-dione ring system, with some members of the family containing an additional  $\gamma$ -lactone ring fused to the dihydropyran moiety as the basic subunit (Table S10 and Fig. 15).<sup>60</sup>

A list of quinonoids, pyranonaphthoquinones pigments, biological activities, and natural sources is presented in Tables S10; their structures (compounds 393–462) are shown in Fig. 16.

**3.3.4. Dihydropyran-based dyes.** These pigments (Fig. 17) are made up of hematoxylin (463) from logwood (*Haematoxylon campechianum*) and brazilin (464) from brazilwood (*Caesalpinia sappan*).

### 3.4. Azulenes

Linderazulene (465) and guaiazulene (466) have been isolated from the gorgonians *Paramuricea chamaeleon* Koch and *Euplexaura erecta* Kü, respectively. Other examples of this class include echinofuran (467), occurring in the gorgonian *Echinogorgia praelonga* Ridley. Also, dihydro-derivatives of linderazulene have been described, namely 2,3-dihydrolinderazulene (468) from the gorgonian *Acalycigorgia* sp. (Fig. 18).

### 3.5. Hemocyanin

Hemocyanin is the respiratory protein that transports oxygen in invertebrates like insects. It is generally observed in the blood of arthropods such as crabs and lobsters, apart from some molluscs. A hemocyanin molecule contains two copper atoms, which can bind oxygen. Due to the binding of the O<sub>2</sub> the copper atom changes the colorless deoxygenated form 'Cu I' into the blue oxygenated form 'Cu II'. In some animals, hemocyanin forms giant polymers of large molecular weights. Unlike hemoglobin, hemocyanin does not bind to the blood cells. Moreover, hemocyanin is not very efficient in binding gases. It is found in very few species of insects and spiders. Instead, insects have evolved with a tracheal system to directly mediate the transfer of oxygen to the tissues through trachea.<sup>66</sup>

### 3.6. Phycobiliproteins

Phycobiliproteins constitute a class of colored, water-soluble proteins that function as light-harvesting complexes in cyanobacteria, red algae, cryptomonads, and cyanelles. These proteins consist of apoproteins covalently linked to linear tetrapyrrole chromophores known as phycobilins (Section 3.2.5) *via* cysteine residues. Phycobiliproteins are classified into four primary types: phycoerythrin, phycocyanin, phycoerythrocyanin, and allophycocyanin, differentiated by their

characteristic absorption maxima and structural features. Each phycobiliprotein is composed of two homologous polypeptides, designated  $\alpha$  and  $\beta$ , which originated from ancestral gene duplication events. Both  $\alpha$ - and  $\beta$ -subunits bind at least one phycobilin chromophore. These subunits assemble predominantly into trimeric ( $\alpha\beta$ )<sub>3</sub> or hexameric ( $\alpha\beta$ )<sub>6</sub> complexes, often associated with linker proteins. The overall structural organization of phycobiliproteins is determined by the specific phycobilin composition. Maturation of the apoprotein involves post-translational modifications, including the enzymatic attachment of phycobilins by specific lyases, followed by methylation of an asparagine residue on the  $\beta$ -subunit catalyzed by an *S*-adenosylmethionine-dependent methyltransferase, culminating in the formation of the mature phycobiliprotein complex.<sup>40</sup> Phycocyanin is the predominant phycobiliprotein in cyanobacteria and consists of  $\alpha$ - and  $\beta$ -subunits arranged in a hexameric ( $\alpha\beta$ )<sub>6</sub> structure at pH 5.0–6.0, which transitions to a trimeric ( $\alpha\beta$ )<sub>3</sub> form at neutral pH (7.0). Its sole chromophore is phycocyanobilin. Phycoerythrin, primarily found as R-phycoerythrin in red algae and C-phycoerythrin in cyanobacteria, exhibits a hexameric ( $\alpha\beta$ )<sub>6</sub> assembly with four phycoerythrobilin chromophores attached to each  $\alpha$ -subunit and two bound to each  $\beta$ -subunit. Some cyanobacteria contain phycoerythrocyanin as an alternative to phycoerythrin; this pigment exists in trimeric ( $\alpha\beta$ )<sub>3</sub> or hexameric ( $\alpha\beta$ )<sub>6</sub> forms and incorporates phycoviolobilin as its chromophore. In contrast, allophycocyanin typically forms a trimeric ( $\alpha\beta$ )<sub>3</sub> complex and functions as an energy transfer intermediate within the photosynthetic apparatus, absorbing energy from other phycobiliproteins and channeling it to photosystem I (PSI).<sup>40</sup>

### 3.7. Ommochrome and ommochromes

Ommochrome refers to several biological pigments that occur in the eyes of crustaceans and insects. Ommochromes are also found in the chromatophores of cephalopods and in spiders. They are metabolites of tryptophan, formed *via* kynurenine and 3-hydroxykynurenine. They are responsible for a wide variety of colors, ranging from yellow over red and brown to black. Lighter colors tend to be generated by ommatins, while mixtures of ommatin and ommins are responsible for darker colors. In spiders, ommochromes are usually deposited as pigment granules within the cells of the hypodermis, immediately beneath the cuticle.<sup>44</sup>

Ommochromes usually occur as granules in conjugation with proteins, which also contain calcium. Examples of ommochrome coloration in insects are the pink-colored immature adults of *Schistocerca* (Orthoptera: Acrididae), the red color in Odonata, and the red and brown color in nymphalid butterflies. The blue color in blue Odonata is due to the presence of dark-brown ommochrome. Ommochromes can be divided into ommatins and ommins. Ommatins have low molecular masses, they are alkali-labile and are responsible for lighter colors, whereas ommins have high molecular masses and are stable in alkali. Dark colors are the result of mixture of ommatin and ommins.<sup>44</sup>



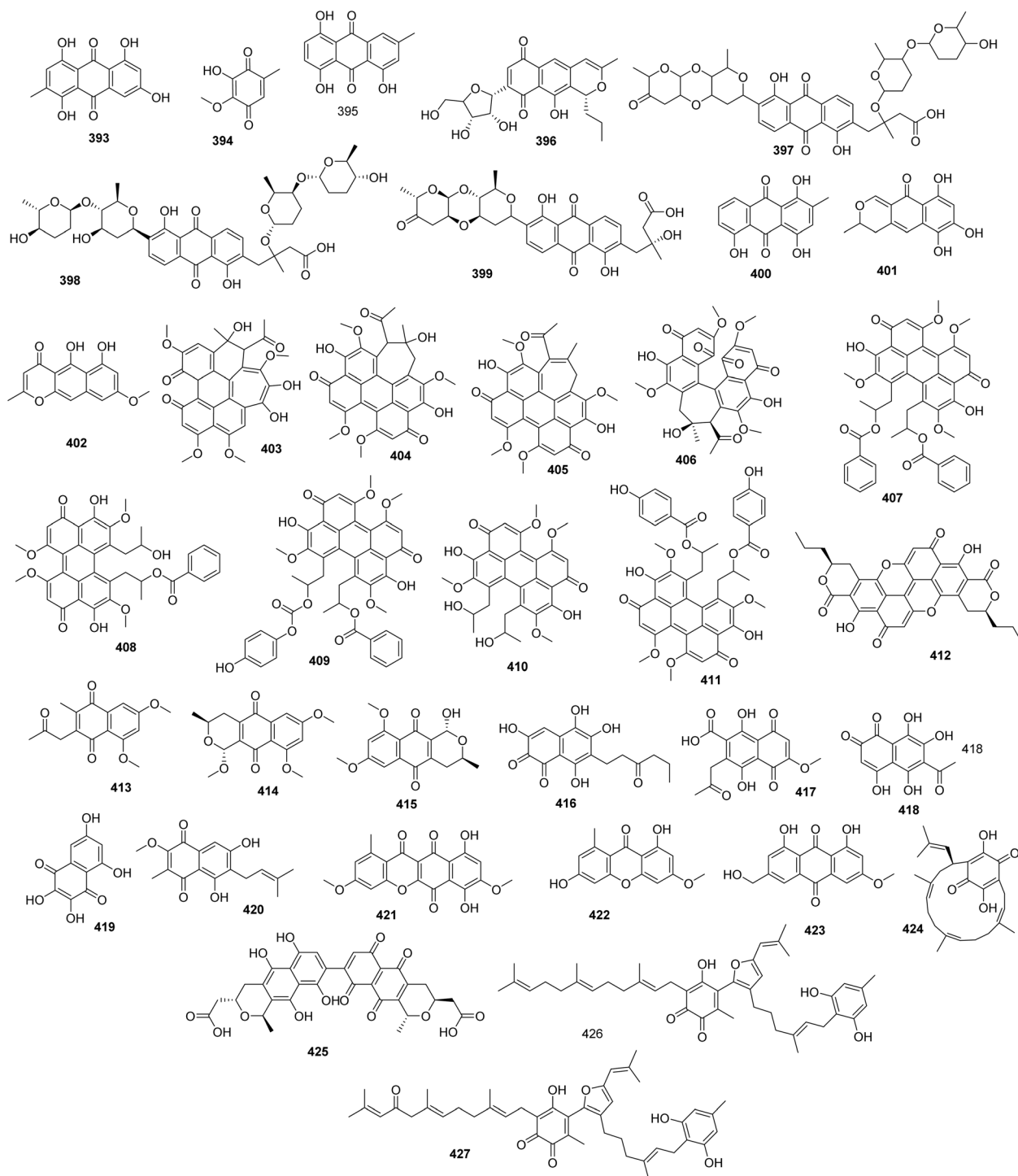


Fig. 16 Selected identified quinonoid and pyranonaphthoquinone compounds. The complete set of compound structures is presented in Fig. S8. Chirality is indicated where known; otherwise, the configuration is left unspecified.

Omnochromes can broadly be subdivided into two groups: the yellow, orange, bright red, and brownish-violet, alkali-labile ommatins (e.g., xanthommatin (**469**), Fig. 19) of low molecular weight found in crustaceans, and the dark-purple sulfur-containing ommatins of high molecular weight, which usually occur as a mixture of compounds and are commonly found among crustaceans and cephalopods and situated in the

chromatophores. The darkening or lightening of the common shrimp *Crangon vulgaris* is due to the movements of ommatins granules in processes involving skin chromatophores. They are also responsible for the spectacular rapid color changes in the skin of cephalopods; they are brought about by radial muscles attached to each pigment cell. Omnochromes occur in cells as melanosomes; they are insoluble in water and neutral solvents.



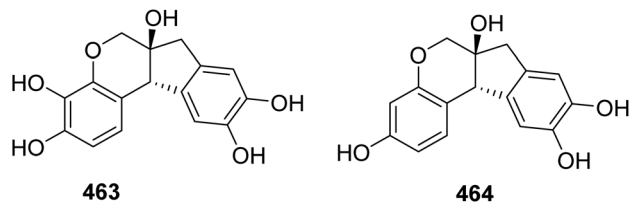


Fig. 17 Identified dihydropyran-based dye components.

Biogenetically, they arise from tryptophan, occur associated with proteins, and are often found in animals that also synthesize melanins.

### 3.8. Papiliochromes

Papiliochromes are slightly analogous to the ommochromes in providing white, yellow, and red coloring to the wings of some butterflies. These pigments are derived from tyrosine and tryptophan through well-known pathways of melanin and ommochrome biosynthesis; they occur only in swallowtail butterflies, Papilionidae. Papiliochrome II, a wing pigment of the swallowtail butterfly *Papilio xuthus* (Lepidoptera: Papilionidae), is formed from one molecule of L-kynurenine, derived from tryptophan, and one molecule of  $\beta$ -alanyl-dopamine. Papiliochrome II, a white pigment, is a peptide in which two aromatic rings are linked by a bridge between the aromatic amino group of L-kynurenine and the catecholamine side chain of norepinephrine derived from the respective quinone. Its biosynthesis involves the non-enzymatic condensation of *N*- $\beta$ -alanyl-dopamine quinonemethide with L-kynurenine to produce a mixture of two diastereomers of papiliochrome II.<sup>44</sup>

### 3.9. Melanins

The melanins are a broad group of pigments with greatly different structures that are responsible for dark, tan, and even yellowish or reddish pigmentations, and are derived from the aerobic oxidation of phenols. Melanins constitute the most common and widely distributed class of pigments in bird feathers, and almost the only one in mammals. Melanins also occur widely in plants, animals, fungi, and bacteria.<sup>67,68</sup> Melanin is a heterogeneous polymer synthesized through the oxidation of the amino acid tyrosine by a process that is, in part, autocatalytic, involving free radicals, but initially requiring the enzymatic activity of the copper-containing oxidase tyrosinase.

Tyrosinase catalyzes the conversion of the amino acid L-tyrosine to 3,4-dihydroxyphenylalanine (L-dopa), then to dopaquinone, followed by some further steps.<sup>68</sup> Most melanins are insoluble and cannot be extracted, but some are slightly soluble in alkali. The colors produced by melanins depend on the type of melanin involved, and secondarily on the number of granules laid down. Due to the fact that melanin is an aggregate of smaller-component molecules, there are several different types of melanins with different proportions and bonding patterns of the component molecules. Nitrogen-free melanins or allomelanins are found in higher plants, fungi, and bacteria, and nitrogen-containing melanins occur widely in the animal kingdom. The latter class is subdivided into several types, mainly eumelanins, pheomelanins, neuromelanins, and erythromelanins; eumelanin granules are typically rod-shaped (0.5–1.2  $\mu\text{m}$ ). The pheomelanins produce light-brown, reddish-brown, or yellow granules. Pheomelanin granules are spheroid or ovoid and smaller than those of eumelanin, the smallest granules giving rise to rusty brown to pale-yellow colors.<sup>69</sup> Pheomelanins differ in solubility, as well as spectrally and chemically, from eumelanins.<sup>70</sup> Unlike eumelanins, pheomelanins are soluble in alkali and can be extracted with a cold 0.25% NaOH solution.<sup>70</sup> An iron pigment closely related – or possibly identical – to trichosiderin is the iron pigment of human red hair; it has also been isolated from red, brown, and buff feathers of chickens, turkeys, junglefowl and obwhites.<sup>69</sup> Erythromelanins produce chestnut red and have been hypothesized to occur in birds mainly on genetic grounds but have never adequately been characterized chemically.

Eumelanins are commonly found in a variety of biological systems ranging from integuments and body fluids of various invertebrates to mammalian skin and eyes. Dark-brown melanin (melanoprotein) is stored in high concentrations in the ink sac of the cuttlefish *Sepia officinalis* and *Octopus bimaculatus* and widely distributed in the classes Echinoidea (sand dollars, heart and sea urchins), Holothuroidea (sea cucumbers), and Ophiuroidea (basket, brittle, and snake stars) in the phylum Echinodermata. They may be polymers arising from repeated couplings of simple bi- or polyfunctional monomeric intermediates or may be of high molecular weight because these intermediates have been coupled to large molecules, *e.g.*, to proteins. Pheomelanins, found in reddish hair and feathers, on the other hand, are very unusual polymers containing benzothiazole and tetrahydroisoquinoline ring systems. Common features of these pigments include high molecular

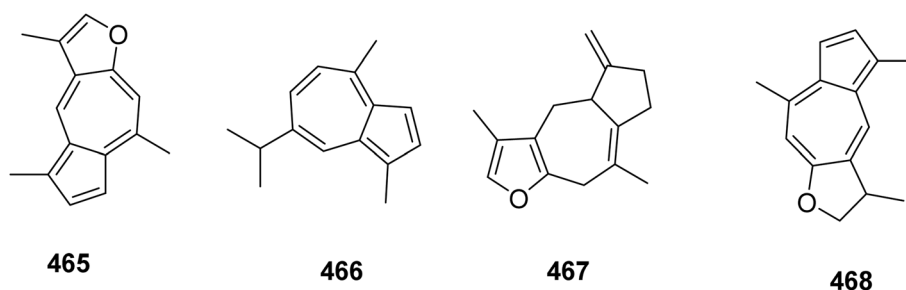


Fig. 18 Selected identified azulene compounds.



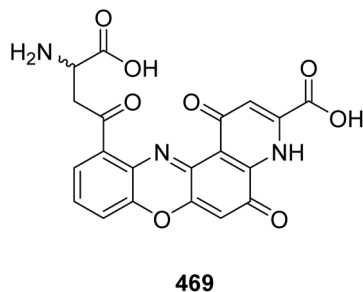


Fig. 19 Structure of xanthommatin.

weight, insolubility, and lack of well-defined physical properties and characteristics. These pigments act as UV-absorbing compounds.<sup>14</sup>

### 3.10. Others

**3.10.1. Turmeric.** Turmeric is basically the root of the turmeric plant (*Curcuma longa*). It produces yellow color on clothing, curcumin (**470**) (Fig. 20). It is useful for dyeing cotton, wool, silk and others. It has medicinal value; it does not produce any health hazards.

**3.10.2. Minerals.** Mineral dyes are derived from naturally occurring minerals. These natural dyes include several colors derived from inorganic metal salts and metal oxides. The classification of mineral dyes can be done based on the color obtained. The most important mineral dyes are as follows.<sup>8,71</sup>

Red pigments include cinnabar, red ochre, and red lead (sindur), each with unique properties and applications. Cinnabar, also known as vermillion, is a dense, reddish mineral with a metallic adamantine luster, derived from mercury sulfide (HgS), and is widely used for red hues. Red ochre, a naturally occurring earth pigment, also referred to as limonite, contains both anhydrous and hydrated iron oxide ( $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ); it remains stable under exposure to light, acids, and alkali. It was traditionally used by monks to dye their robes and was commonly employed in paintings and murals, often mixed with gum as a binding agent. Red lead, or sindur ( $\text{Pb}_3\text{O}_4$  or  $2[\text{PbO}] \cdot [\text{PbO}_2]$ ), is extensively used in Indian art for its vivid red and orange tones. Composed primarily of lead tetroxide (85–98%) and litharge (2–15%), it is also utilized for achieving various shades of red.

Yellow pigments include yellow ochre, raw sienna, orpiment, and litharge, each with distinct compositions and uses. Yellow ochre gets its color from various hydrated forms of iron oxide,

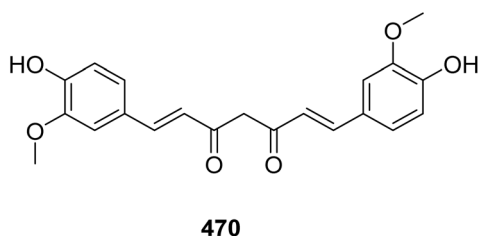


Fig. 20 Structure of curcumin.

particularly the mineral limonite ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), and is used in painting fabrics such as sails, natural fibers, and synthetic polyacrylonitrile. Raw sienna, an earth pigment from the sienna class, contains iron oxide and manganese oxide; it was among the first pigments used in human cave drawings alongside ochre and is valued for its high transparency, making it ideal for glazing in paintings. Orpiment, a deep orange-yellow arsenic sulfide mineral ( $\text{As}_2\text{S}_3$ ), is used as a pigment in the paper industry. Litharge, also known as massicot, is a natural secondary mineral form of lead oxide (galena), produced by roasting white lead. During decarboxylation and dehydration at approximately 300 °C, white lead, chemically lead carbonate ( $2[\text{PbCO}_3] \cdot [\text{Pb}(\text{OH})_2]$ ), is converted into pale-yellow lead monoxide (PbO) powder.

Green pigments include malachite, a material that occurs naturally along with azurite, an intense-green mineral, copper carbonate mixed with copper hydroxide, producing a vivid, deep-green pigment used for green nuances; terre-verte, also known as “green earth”, which is a combination of hydro-silicates of iron, magnesium, aluminum, and potassium (gluconite and celadenite) and has most often been utilized as a green pigment since ancient times, with the hue of the earth differing depending on the source; and vedgiris, a color frequently employed in paintings during the Mughal era and afterwards in miniature paintings, which is made by rubbing copper foils with vinegar, producing the typical copper acetate  $[\text{Cu}(\text{CH}_3\text{COO})_2]$ , resulting in a vivid, deep-green pigment that can char paper or textiles if not used cautiously.

Blue pigments include ultramarine blue, a rich blue dye obtained from the semi-precious mineral lapis lazuli, which has been employed in textiles and miniature art in India; lapis lazuli, also known as lapis, a blue rock consisting of a mixture of azurite, calcite, pyroxenite, and other silicate minerals besides pyrite, used for blue nuances; and azurite  $[\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2]$ , a soft, blue to dark-blue copper mineral produced by weathering copper ore deposits and often found together with the green mineral malachite, used for blue nuances in Chinese and Indian paintings.

White pigments include chalk, a variety of calcium carbonate ( $\text{CaCO}_3$ ) frequently utilized in paintings and widely used as a pigment since ancient times, typically found with quantities of limestone, and conch shell white, which is favored by artists in India for its unique qualities; white lead, a complex salt containing lead carbonate ( $\text{PbCO}_3$ ) and hydroxide, which occurs naturally as the mineral cerussite and was previously a component of lead paint, now typically made artificially; aragonite, a usually colorless or white mineral used for white nuances; zinc white ( $\text{ZnO}$ ), an important color used in painting, along with other white pigments such as talc, barium white, and titanium white, with titanium white (titanium dioxide,  $\text{TiO}_2$ ) also serving as a delustrant used in textiles.

Black pigments include manganese, a metallic element used for black nuances; charcoal black, produced from wood after burning in a closed container; ivory black, made by roasting ivory shavings in a closed earthen pot, then ground, washed, and dried, though currently unpopular due to environmental and animal-rights concerns; bone black, created by charring



animal bones in covered earthen pots, serving as a replacement for ivory black, but not as vivid; graphite, a mineral found across India and historically used in writing implements, with the pigment being a dull grey, primarily used for drawing rather than painting; black chalk, which refers to black clay used in pottery and paintings; and terre-noire, the same as black clay, containing clay along with calcium, iron, and manganese carbonates.

## 4. Biological applications of pigments

Carotenoids are broadly used in the food industry as colorants, additives, feeds (aquaculture) and in the cosmetic industry for treating sunburns or skin-related disorders.<sup>72</sup> Moreover, recent studies have indicated that carotenoids display a broad spectrum of biological activities including antioxidants, anti-inflammation, anti-cancer, anti-aging, immunomodulatory, cardioprotective, neuroprotective, and hepatoprotective functions.<sup>22,73–75</sup> These beneficial effects are thought to be due to their role as antioxidants, which is a result of the ability of the conjugated double bond structure to delocalize unpaired electrons. This structural feature underlies the exceptional ability of carotenoids to quench singlet oxygen and to terminate tissue-generated free radicals.<sup>76</sup> The function of carotenoids is determined by their molecular properties, such as size, structure, presence of functional groups, and potential interaction with other carotenoids. Most important is the conjugation of double bonds linked to their antioxidant properties.<sup>76,77</sup> Because carotenoids are a part of a hydrophobic group of antioxidants, the major mechanism of this action is located within the lipid membranes. They are also associated with proteins or lipoprotein structures. This means that the local environment of carotenoids affects their properties and *vice versa*. The structural differences of carotenoids entail different types of interaction with the membrane lipids, thus affecting membrane fluidity and thermostability in different ways.<sup>76</sup> Although not a property of all carotenoids, provitamin A activity has long been their most recognized role in human health. Structurally, retinol (17) is essentially the molecular half of  $\beta$ -carotene (10).  $\beta$ -Carotene (10) is recognized as a highly effective provitamin A, assigned a reference activity of 100%. For a carotenoid to function as a vitamin A precursor, it must possess an unsubstituted  $\beta$ -ionone ring coupled with an intact  $C_{11}$  polyene chain. Carotenoids such as  $\gamma$ -carotene,  $\alpha$ -carotene (9), and  $\beta$ -cryptoxanthin (15), each containing a single unsubstituted  $\beta$ -ring, exhibit approximately half the provitamin A activity of  $\beta$ -carotene. In contrast, acyclic carotenoids lacking  $\beta$ -rings, as well as xanthophylls bearing hydroxy, epoxy, or carbonyl substitutions on both  $\beta$ -rings, do not display provitamin A activity. Currently, lutein (1), zeaxanthin (5),  $\beta$ -carotene (10), and astaxanthin (13) are the well-recognized carotenoids in the nutraceutical market. Carotenoids exist in a free or in an esterified form (linked to fatty acids), and both forms are well absorbed in the intestine and transported (in a free form) by lipoprotein (high-density lipoprotein-cholesterol, HDL-c or low-density lipoprotein-cholesterol, LDL-c) in the blood. Hence, commercialized

carotenoids (supplements) are available in free or esterified forms.<sup>22</sup>

Green vegetables are widely recognized for their health-promoting properties, including antioxidant activity, anti-mutagenic effects, and the ability to support detoxification processes.<sup>78</sup> Chlorophylls and their derivatives have shown important health-promoting functions, exhibiting anti-mutagenic, anti-cancer, and anti-inflammatory activities.<sup>79–81</sup> Dietary supplementation with chlorophyll during early developmental stages has been reported to reduce weight gain, enhance glucose tolerance, and attenuate inflammatory responses, thereby contributing to obesity prevention.<sup>82</sup> Furthermore, the impact of chlorophyll on Type 1 diabetic rats has been studied, confirming that chlorophyll a (57) can mitigate diabetes-related risks.<sup>83</sup> Phytol (56) has also been reported to alleviate joint inflammation and pain through the inhibition of key inflammatory mediators.<sup>84</sup> Additionally, chlorophyll pigments in dark green vegetables have demonstrated protective effects against certain cancers, including colon and liver carcinomas.<sup>81</sup> The mechanism of chlorophyll involves binding to hydrophobic molecules such as hydrocarbons and aflatoxins, which are implicated in carcinogenesis, rather than promoting their elimination.<sup>85</sup> In addition, chlorophylls have demonstrated notable antimicrobial activity.<sup>86</sup> Elbatany *et al.* (2019)<sup>87</sup> evaluated the antimicrobial effects of pigment extracts from *Punica granatum* L. leaves, containing a total chlorophyll content of  $4.9 \pm 0.25 \text{ mg g}^{-1}$ . Their findings showed that a 150  $\mu\text{L}$  dose of the pigment extract inhibited the growth of various bacterial, yeast, and fungal strains within 60 min. The incorporation of natural bioactive compounds into traditional foods to develop functional foods can support consumers in preventing diet-related diseases and adopting healthier dietary patterns. Functional foods, enriched with secondary plant metabolites, provide enhanced concentrations of bioactive compounds that contribute to health promotion and overall well-being.<sup>88</sup> The fortification of food products with these bioactives can significantly improve their health benefits.<sup>89</sup> For example, Zen *et al.*<sup>90</sup> incorporated microencapsulated spirulina, which is an abundant source of chlorophyll, into pasta to enhance its antioxidant capacity, while Batista *et al.* (2017)<sup>91</sup> utilized microalgal biomass rich in chlorophylls to fortify cookies, increasing their bioactive content. Furthermore, Bacteriochlorophyllides exhibit strong absorption bands in the near-infrared region, along with notable photosensitizing and photochemical properties. These features underpin their applications as photosensitizers, immunosensors, and modulators of bacteriochlorophyll aggregation. Additionally, they are utilized in dye-sensitized solar cells, heme biosynthesis, light energy conversion, and anti-aging interventions.<sup>33,36,92</sup>

The late-stage chlorophyll catabolites PxB and PrB share a remarkable structural similarity with BV (68) and BR (69). PxB resembles the final heme degradation product BR, featuring a double bond at C-15, whereas PrB, the oxidation product of PxB, represents the analogue of BV due to an extended conjugated  $\pi$ -system. PBs were found to possess very interesting chemical properties, and possible bioactivities have already been suggested.<sup>93–95</sup> First indications were provided by Moser



*et al.* 2008; and Wang *et al.* 2021, demonstrating that a PleB in the peels of apples and pears possesses strong antioxidative activities.<sup>94,96</sup> In the meantime, antioxidative properties as well as anti-inflammatory activities could also be revealed for PxBs.<sup>32</sup> Furthermore, PxBs were shown to be taken up by cells and to possess promising anti-cancer activities.<sup>94,97</sup>

Originally, bilins were assumed to be waste products of a catabolic pathway, however, extensive literature has reported beneficial activities of BV (68) and BR (69), like, for example, their potential as strong endogenous antioxidants. Moreover, studies have demonstrated protective capabilities against a variety of pathological conditions including cardiac injuries, gastrointestinal inflammations, or neurodegenerative diseases.<sup>32</sup>

Additionally, other publications discuss the various biological actions of betalains, anthocyanins, and phenolic pigments in detail as antidiabetic, hepatoprotective, anti-inflammatory, antioxidant, antimicrobial, antiviral, anti-Alzheimer, and anti-cancer, immuno-enhancement and reduction of the risk of developing chronic degenerative diseases such as cardiovascular diseases (CVD), cataracts, and macular degeneration.<sup>42,43,98–109</sup> Consequently, these pigments are useful as pharmaceutical agents and dietary supplements.

Hemocyanin (Hc), which was purified from the hemolymph of Indian white shrimp *Fenneropenaeus indicus*, exhibited hemolytic activity against chicken erythrocytes, and antibiofilm activity against both Gram (+) and Gram (–) bacteria. Moreover, the hemolysis can be inhibited to different degrees by osmoprotectants of diverse molecular masses, signifying that it follows a colloid-osmotic mechanism.<sup>110</sup> The protein hemocyanin isolated from the hemolymph of the flower crab (*Portunus pelagicus*) also showed antibacterial potential against five Gram-positive and ten Gram-negative bacteria, and antibiofilm activity against five biofilm-forming Gram-negative bacteria, *viz.*, *Vibrio alginolyticus*, *Vibrio harveyi*, *Vibrio parahaemolyticus*, *Pseudomonas aeruginosa*, and *Proteus vulgaris* at a concentration of 100  $\mu\text{g mL}^{-1}$ .<sup>111</sup>

Phycobiliproteins have potential applications in the pharmaceutical industry as antioxidants, anti-inflammatory, neuroprotective, and hepatoprotective medicines, and as natural colorants and fluorescent compounds,<sup>112</sup> while ommochrome pigments have demonstrated encouraging antibacterial and antioxidant properties.<sup>113–116</sup> The ommochromes, which were isolated from insects of five different families, including Stratiomyidae, Sphingidae, Blaberidae, Acrididae, and Tenebrionidae, showed high antiradical activity measured from the degree of chemiluminescence quenching in a model system containing luminol, hemoglobin, and hydrogen peroxide. The ommochromes strongly inhibited peroxidation of the photoreceptor cell outer segments induced by visible light in the presence of lipofuscin granules from the human retinal pigment epithelium, and they suppressed iron/ascorbate-mediated lipid peroxidation. These results are important for understanding the biological functions of ommochromes in invertebrates and identifying invertebrate species that could be used as efficient sources of ommochromes for pharmacological preparations to prevent and treat pathologies

associated with the development of oxidative stress.<sup>117</sup> The ommochromes isolated from the complex eye of the adult *Hermetia illucens* fly showed antimicrobial activity against *B. subtilis* ATCC 6633, *Candida albicans* ATCC 2091, and *Aspergillus niger* INA 00760. The *H. illucens* imago was concluded to be a promising renewable source of natural pigments with good antioxidant characteristics and antibacterial properties.<sup>118</sup> In addition, melanins had a significant role in pharmacological activities, such as antimicrobial, antioxidant, hypoglycemic, anti-radiation, photothermal conversion effect, anti-cancer, heavy-metal ion absorbent, anti-inflammatory, anti-hemolytic, and antiviral activities.<sup>119–124</sup>

## 5. Challenges in the stabilization of pigment molecules

The application of carotenoids as functional ingredients in foods and beverages is often limited by their poor water solubility, chemical instability, and low bioavailability. These challenges can be mitigated by developing water-dispersible formulations such as colloidal suspensions, emulsions, or dispersions, which enhance carotenoid stability and solubility in aqueous systems.<sup>125</sup> Latterly, research in this area focused on encapsulation and nanoencapsulation strategies.<sup>126</sup> Both modified forms of the pigment achieved a higher color homogeneity. Developing water-compatible formulations for hydrophobic colorants is a key step toward broader industrial applications, with clear benefits for consumers.

Natural chlorophylls consisting of both chlorophyll a (57) and chlorophyll b (58), are approved as food additives.<sup>127</sup> The use of natural colorants as food additives can improve both the sensory qualities and nutritional value of food products.<sup>128</sup> For instance, Jayasinghe *et al.*<sup>129</sup> utilized chlorophyll extracts derived from seaweed to formulate a jelly dessert, reporting that the color remained stable for over 30 days under ambient conditions. Despite this, the application of chlorophyll as a food colorant is often challenged by its sensitivity to various factors including interactions with food matrix components, temperature, light, oxygen, pH, packaging materials, and storage conditions.<sup>128</sup> One promising strategy to enhance chlorophyll stability is nanoformulation, such as encapsulation. Liu *et al.*<sup>130</sup> developed a chlorophyll nanoemulsion from pomelo leaves, demonstrating improved stability suitable for health-related applications. Additionally, substitution of the central magnesium ion in chlorophyll with copper yields a semi-synthetic pigment known as chlorophyllin, which is water-soluble and exhibits greater color stability. Chlorophyllin is commercially employed in the food industry as a durable green colorant.<sup>131</sup> The attractive properties of bacteriochlorophyllides were highly useful in various applications.<sup>33</sup> It has been known that the feature of bacteriochlorophyllides is the reduced stability.<sup>33</sup> The problems of stability and high cost of production may lead to its delay in the functional study. In recent years, researchers have focused on synthetic bacteriochlorophyllide derivatives that provided new opportunities for the enhancement of stability. However, there is still a growing demand and challenges with



naturally occurring bacteriochlorophyllides, due to their instability and difficult production.

Chemical modification has always been an effective way to enhance the bioactivities of natural products. For PBs, the esterification of the propionic acid group at C-12 is of particular interest for chemical modification among the four main modification positions. Interestingly, upon modifying inactive PleBs by esterification, an antiproliferative activity was observed, which increased with the chain length of the alkyl esters. This indicates that the polarity might make a difference in terms of cytotoxic potential for these modified PleBs.<sup>95</sup>

Also, Betalains are notably unstable pigments but exhibit optimal stability within a pH range of 4 to 6; their chromophore, betalamic acid, undergoes complete dissociation at pH values  $\geq 5.32$ . Their stability decreases with increasing moisture content and exposure to chelating agents and oxygen. Conversely, betalain stability is improved by higher pigment concentrations in plant matrices or food products and by the addition of antioxidants such as ascorbic acid. Among all factors, temperature, particularly thermal processing, is the most critical determinant of betalain degradation.<sup>132</sup> For example, betanin subjected to mild alkaline conditions during heating or thermal treatment decomposes into colorless cyclo-dopa 5-*O*-glucoside and betalamic acid.<sup>125</sup> Delia *et al.*<sup>133</sup> reported successful microencapsulation of betalains extracted from *Escontria chiotilla* and *Stenocereus queretaroensis* fruits using spray drying with *Opuntia ficus indica* (L.) mucilage as the wall material. Due to their susceptibility to degradation by heat and light, betalains are currently best suited as colorants in frozen foods, refrigerated dairy products, and short shelf-life items such as yogurts, ice creams, and processed meats.<sup>132</sup>

Despite extensive efforts to identify natural colorant sources and enhance their yields, relatively few natural pigments have successfully reached commercial application in the food industry.<sup>125</sup> Commercially available anthocyanins, including cyanidin-3-*O*-glucoside, pelargonidin-3-*O*-glucoside, and peonidin-3-*O*-glucoside, have been applied in food products, with growing evaluations of their efficacy.<sup>134</sup> It is well established that anthocyanin color expression and stability are significantly affected by extrinsic factors such as pH, temperature, humidity, salinity, and storage conditions, as well as by intrinsic interactions with enzymes, proteins, metal ions, other polyphenols, ascorbic acid, and sugars.<sup>125</sup> These factors cause anthocyanin coloration to vary from red to purple and blue within the pH range of 1–2. Consequently, the widespread use of anthocyanins as food colorants and functional ingredients has been constrained by their limited stability and susceptibility to interactions within complex food matrices.<sup>135</sup> In recent years, multiple stabilization strategies have been developed and increasingly applied to overcome these limitations and expand the applicability of anthocyanin pigments as food additives. Cortez *et al.*<sup>136</sup> provided a comprehensive review of key stabilization methods, including co-pigmentation with polymers, phenolic compounds, and metals; oxygen exclusion during processing and storage; and encapsulation techniques such as microencapsulation and nanoencapsulation. Among these, spray drying encapsulation offers significant protection to anthocyanins,

enabling controlled and targeted release in food matrices and enhancing stability during storage. However, research on alternative encapsulation methods remains limited. While maltodextrin has been commonly employed as a coating material for anthocyanin microencapsulation, exploration of novel coating agents is recommended.<sup>137</sup> García-Tejeda<sup>138</sup> investigated spray drying microencapsulation of anthocyanins extracted from purple maize using modified normal and waxy maize starches as wall materials. The study demonstrated that starch derivatization improved both solubility and encapsulation efficiency, with esterified normal maize starch providing superior anthocyanin retention during storage. Zhao *et al.*<sup>139</sup> reviewed the chemical implications of glycosyl acylation on anthocyanins, highlighting that acylation enhances the chemical stability of anthocyanins both *in vitro* and *in vivo*. The degree of stability conferred depends on the acylation site, as well as the type and number of acyl groups present.

Dietary supplementation of plant pigments, especially of phenolic compounds and anthocyanins, can be used to prepare tempranillo wines. These provide both color and phenolic attributes to the wine.<sup>140</sup> Anthocyanin pigments are made thermally stable by processing blueberries using metal complexation and cellulose nanofiber/sodium alginate layer-by-layer coating for retaining anthocyanin pigments.<sup>141</sup> Similarly, anthocyanin pigments are made thermally stable by processing whole blueberries, fruits, vegetables, meats, seafood, dairy, and egg products.<sup>142</sup> For color stability, non-saccharomyces yeasts are added during red-must fermentation. Non-saccharomyces yeasts also generate pyranoanthocyanins and polymeric pigments after the addition of (+)-catechin and procyanidin B2 to fresh red grape must. The use of non-saccharomyces yeasts improves the formation of stable pigments in red wines.<sup>143</sup> For wine color, flavonols (flavonoid) and hydroxycinnamic acids are used for co-pigmentation.<sup>144</sup>

Phycobiliproteins have found diverse applications across the pharmaceutical, food, and cosmetic industries, with phycocyanin being the most commercially targeted pigment. Since its approval by the US Food and Drug Administration (FDA), the use of phycocyanin has markedly increased. In Europe, its popularity as a natural, non-toxic, and biodegradable dye has also garnered significant attention.<sup>145,146</sup> The cost of phycobiliproteins varies substantially depending on purity, ranging from approx. \$ 130 to \$ 15 000 (USD) per gram.<sup>147</sup> For food applications, lower purity grades are acceptable, allowing for reduced costs; however, higher purity is required for scientific and pharmaceutical uses, where prices can be up to one hundred-fold higher for food applications, lower purity grades are acceptable, allowing for reduced costs; however, higher purity is required for scientific and pharmaceutical uses, where prices can be up to one hundredfold higher.<sup>145</sup> Borowitzka<sup>148</sup> estimated the global phycobiliprotein market to exceed \$ 60 million (USD) in 2013, while a report by Future Market Insights projected the market value at \$ 112.3 million (USD) in 2018, with expectations to double by 2028.<sup>149</sup> In the same report, Western Europe accounts for the largest share of consumption (33%), with approx. 80% of phycocyanin production utilized within the food sector. The primary challenge limiting broader



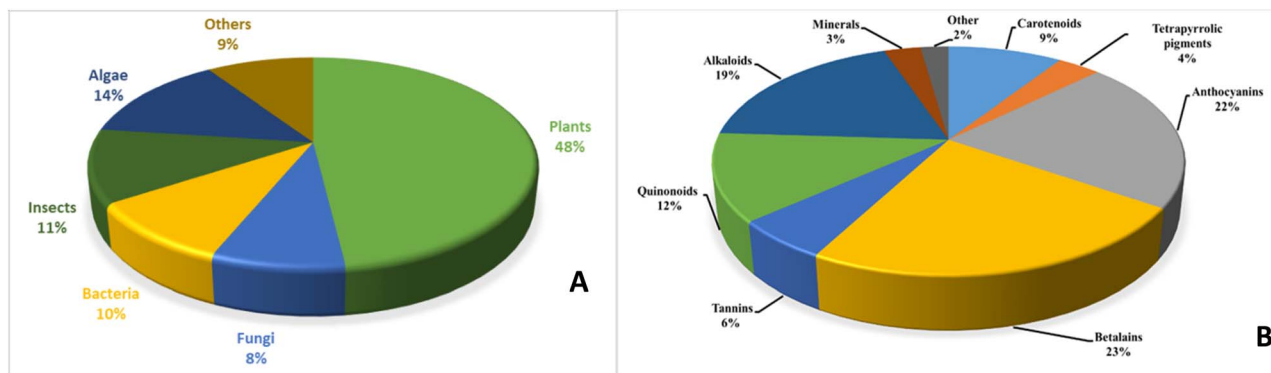


Fig. 21 (A) Classification of natural pigments according to their natural sources; (B): classification of natural pigments according to their chemical structures.

commercialization of cyanobacterial high-value products remains cost reduction. Strategies to address this include optimizing pigment concentration in biomass and exploring novel applications in nutraceutical, cosmetic, and pharmaceutical markets.<sup>149</sup>

Melanin, a natural pigment, shows great potential for biological activity. Poor solubility is one of the major factors that limit its application. Therefore, the improvement of melanin solubility and the synthesis of new melanin complexes are now a popular direction of research. In addition, melanin demonstrates potential applications in the fields of drug delivery, optoelectronics, and materials science. Thus, the full picture of melanin research involves a broader range of fields and aspects.<sup>149</sup> There is also a need to further understand the relationship between the structure of melanin and the specific functions it exhibits, such as light absorption, electrical conductivity, catalytic activity, *etc.* By resolving the complex structures of melanin molecules, their activity and application potential will be better understood.<sup>149</sup>

## 6. Conclusion and future perspective

In this review, we have explored various natural pigments, encompassing different classes from a wide range of sources. Through our comprehensive analysis, we included a total of 566 compounds, categorized into nine distinct chemical classes. This quantitative approach provides valuable insights into the prevalence and diversity of natural pigments across different chemical classifications. As illustrated in Fig. 1, our findings revealed that betalains (23%), anthocyanins (22%), and alkaloids (19%) showed the highest percentages, providing valuable insights into the most prominent natural pigments. We have also classified those 566 compounds according to the source and found that 48% of these compounds come from plant sources, 14% are derived from algae, 11% from insects, 10% from bacteria, 8% from fungi, and 9% from miscellaneous sources (Fig. 21A and B).

Carotenoids, chlorophyll derivatives, betalains, and anthocyanins are natural pigments that possess many favorable medicinal and nutritional properties linked to health

promotion and reducing risks of many diseases. However, they are chemically unstable and prone to oxidation under various storage conditions (light, high temperature, oxygen, acid, and metal ions). To overcome this challenge, various encapsulation techniques, such as microencapsulation, nanoencapsulation, and encapsulation, have been employed. Encapsulation does not only enhance stability and protects them from degradation but also increases their solubility in aqueous systems and their bioavailability. To achieve effective encapsulation, regardless of the encapsulation technology employed, appropriate wall material is essential for their protection and safe delivery. Microencapsulation is the most common method as it employs simple encapsulation techniques and produces good-quality products. However, microcapsules tend to decrease in stability over time. Nanoencapsulation technology, by contrast, allows for obtaining more stable products with excellent absorption and bioavailability. Multiple carriers, such as nanoemulsion nanoliposomes, can be used for encapsulation. On the contrary, alternative technologies or “green technologies” such as supercritical encapsulation, are good alternatives for the micro- and nanoencapsulation of thermolabile compounds and suitable for application in the food industry without having a detrimental effect on the sensory attributes. As carotenoids, chlorophylls derivatives, betalains, and anthocyanins are important for the pharmaceutical and food industry, it will be crucial in the future to examine encapsulation technologies focusing on their biological application as well as their interactions with other components in food systems. Moreover, an evaluation of their *in vivo* behavior is essential, rather than focusing solely on their encapsulation efficiency, particle size, or other physicochemical properties, to identify the most suitable and sustainable encapsulation approach.

Phycobiliproteins, phycobilins, and melanin have demonstrated significant industrial potential owing to their diverse bioactivities; however, their full applicability remains limited by challenges in purification and characterization. Numerous production, extraction, and purification protocols for these compounds have been explored, encompassing a wide range of conditions and parameters. Nevertheless, the optimal biotechnological processes are largely dictated by the desired purity



levels and the available methodologies. A comprehensive understanding of these factors, coupled with the known bioactive properties of phycobiliproteins, phycobilins, and melanin, is expected to drive further research and novel applications of these compounds in the near future.

Recent studies over the past five years have highlighted the significant potential of natural pigments as food additives, offering promising benefits for consumers. To facilitate their broader adoption within the food industry, it is essential to reduce processing costs. Future research should focus on deepening the understanding of the biochemical properties of these pigments, not only to develop effective strategies for improving their stability but also to optimize their utilization as functional food ingredients.

## Author contributions

The work was conceptualized and designed by U. R. A., A. H. E., A. Z., and G. A.; N. B. gathered the data and prepared the manuscript. U. R. A., J. W., and G. B. revised and supervised the manuscript. The article was updated by all co-authors, who also gave their approval to the final submission.

## Conflicts of interest

The authors declare no conflict of interest.

## Data availability

No data is used to create the information discussed throughout the manuscript.

Supplementary information (SI) is available. See DOI: <https://doi.org/10.1039/d5ra09252c>.

## Acknowledgements

During the preparation of this work, ChatGPT (OpenAI) was used in order to improve the readability and language of the manuscript. After using this tool/service, the authors reviewed and edited the content as needed and took full responsibility for the content of the published article.

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