Paper No: 1

Paper Title: Food Chemistry

Module No: 29: Food Pigments: Properties and stability during processing

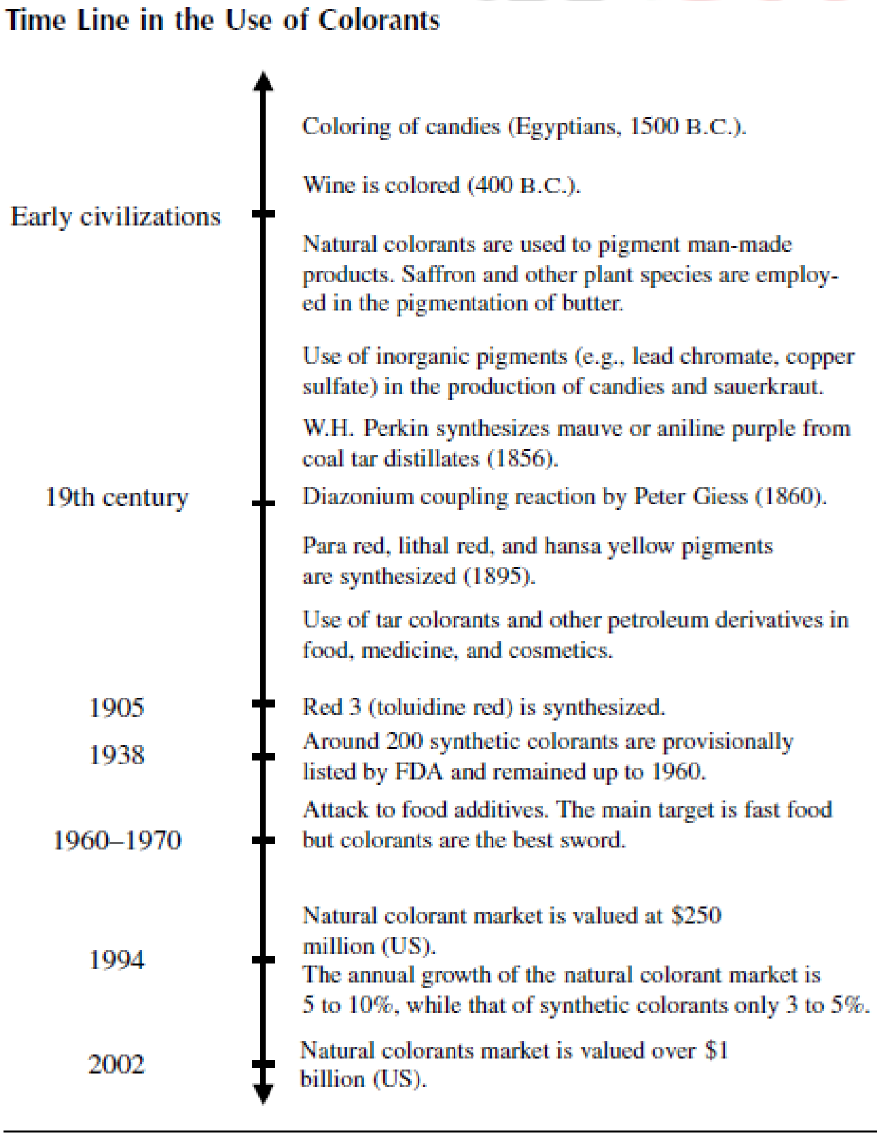
DEFINITION

As previously established, color is a complex phenomenon, and to provide an absolute definition of pigment is not an easy task. Some definitions are provided below:

- *Pigments* are compounds that absorb light in the wavelength range of the visible region. This absorption is due to a molecule-specific structure (chromophore) that captures the energy from a radiant source. Some energy is not absorbed and is reflected and/or refracted; this energy is captured by the eye and generates neural impulses, which are transmitted to the brain, where they could be interpreted as a color.

- Colorants are defined as substances that modify the perceived color of objects, or impart color to otherwise colorless objects. With this definition, pigments and dyes are grouped within the term colorants. It is reasoned that if only solubility is considered, the same substance could be a dye or a pigment depending on how it is used.

Table. 29.1 – Time line in the use of colorants



PIGMENTS IN BIOLOGY

Pigments are widely distributed in living organisms, and a large number of structures have been reported; the anthocyanin group alone has more than 250 different structures. Also, it is common to find pigments with great structural complexity; in fact, it is not a simple task to establish a universal classification that covers all the pigments known to date, especially a classification that permits indexing of newly discovered pigments.

MOLECULAR AFFINITIES OF PIGMENTS

Most biological pigments are grouped into no more than six kinds of structures: tetrapyrroles, isoprenoids, quinones, benzopyrans, *N*-heterocyclic compounds, and metalloproteins. Scientific reports have described about 34 tetrapyrroles (28 cyclic and 6 linear), over 600 carotenoids, more than 4100 flavonoids and within this group over 250 anthocyanins (although constituted of only 17 anthocyanidins).

Quinones are widely distributed, probably by virtue of the importance of their functions. In addition, several of the most important pigments in ancient times were quinones, which were used in dyeing textile products (anthraquinones from the roots of *Rubia tinctorum*) and in the preparation of cosmetics (naphthaquinones from *Lawsonia alba*). In addition, anthraquinones from the insects *Kermococcus ilicis* (dyestuff kermes) and *Dactylopius coccus* (carminic acid) have been used as food color additives. Further, the *N*-heterocyclic compound indigoid was also used in the textile industry. Indigoid is obtained from *Indigofera tinctoria* and *Isatis tinctoria.* This is one of the oldest known colorants. Moreover, tyrian purple is a derivative of indigotine, which was isolated from several Mediterranean mollusks.

In the food industry, betalains are the most important pigments of the *N*-heterocyclic group. In addition, this subgroup of pigments has been related to melanins, which are the main pigments in hair and skin of mammals. Purines and pterins are pigments of this group; they are important in fish and insects, whereas flavins (another member) are widely distributed (e.g., riboflavin is involved in redox biological processes). Interestingly, some marine invertebrates are pigmented by riboflavin; the same is true for several bacteria. Other *N*-heterocyclic pigments, such as phenazines (bacterial pigments) and phenoxazines (present in bacterial and invertebrate organisms).

The group metalloproteins comprises a large number of proteins that are widely distributed among living organisms because their biological function is essential for life (Table 29.2). These metalloproteins are not considered food additives, but chlorophyll has commercial importance. However, the quality of some foods is related to coloration of metalloproteins (e.g., the red color of meat products). Another important aspect of metalloproteins is that some of them could be produced through biotechnology in sufficient quantity to be considered potential colorants in the future.

Table 29.2. Metallo proteins – Functionality & Colour

Metalloproteins — Functionality and Color

Protein(s)	Metal (cofactor)	Main Function	Color
Hemoglobin, myoglobin	Fe	Transport of O_2 and CO_2	Red
Chlorophyll binding proteins	Mg	Photosynthesis	Green
Ceruloplasmin	Cu	Liver functionality	Blue
Haemovanadin	V	O_2 transport in ascidians	Apple-green

Source: Adapted from Hendry (1996).[4]

However, and as pointed out above, the tremendous variability of organisms over the world means that a large group of miscellaneous pigments do not fit into this classification. In particular, it is common to find reports on the discovery of new pigments in bacteria, fungi, and invertebrates, whose structural characteristics are a clear reflection of their functionality and specificity in the host organism.

NATURAL DISTRIBUTION OF PIGMENTS

Chlorophylls and carotenoids are the most abundant pigments in nature. They are involved in fundamental processes, and life on Earth depends on them. Plants, photosynthetic bacteria, and protozoa (plankton) are the main sources of the organic materials that are required for the development of other living organisms such as vertebrate and invertebrate animals. Chlorophyll is not found in animals but carotenoids accumulate in some organs (e.g., eyes) and tissues (e.g., skin of fish, bird plumage). In general, animal carotenoids are obtained from the common diet. Other pigments are also found in animals (Table 29.3); some have important functions (e.g., heme proteins, riboflavin), whereas the function of others is not yet completely clear (e.g., melanins, flavonoids).

Other organisms have interesting pigments that have been used or have potential use. Lichens produce depsides, the ancient and most extensively used dyes which were used as textile dyeing agents. In addition, they have application as sunlight filters, as chemical indicators (litmus paper, pH indicators), and as cytological stains. Some of the pigments obtained by treatment of lichen substances are orcein and parietin: More than 1000 pigments have been identified in fungi. Consequently, the diversity of fungi pigments is the second in importance, after plant flavonoids. Fungi are not photosynthetic and do not contain chlorophyll.

TABLE 29.3
Pigment Distribution in Animals

Organisms	Group of Pigments	Distribution
Vertebrates	Haem proteins	Wide distribution
	Melanins	Wide distribution
	Carotenoids	Mammals, birds, reptiles, amphibians, and fish
	Riboflavin	Reptiles, amphibians, and fish
Invertebrates	Carotenoids	Echinoderms, insects, malocostraca, crustacea, arachnida, cnidaria, porifera, and protozoa
	Quinones	Echinoderms, insects, and arachnida
	Melanins	Echinoderms, insects, malacostraca, and crustacea
	Heme	Mollusks, malacostraca, crustacea, arachnida, and annelids
	Flavonoids	Insects and crustacea

Carotenoid distribution in fungi is restricted to some orders (e.g., Pharagmobasidiomycetidae, Discomycetes). In addition, flavonoids are scarce in fungi whereas riboflavin imparts the yellow color in the genera *Russula* and *Lyophyllum*. Betalains, melanins, and a small number of carotenoids and certain anthraquinones are common to fungi and plants.

Chlorophylls and carotenoids are present in photosynthetic bacteria. In nonphotosynthetic bacteria β- and γ -carotene have been identified; however, quinones, melanins, and flavonoids are very scarce in this group. Phenazines are found exclusively in bacteria (e.g., iodinin from *Chromobacterium* sp., the dark blue pyocyanine from *Pseudomonas aeuruginosa*). Several phenazines have been described and some have antibiotic properties. As can be deduced, fungi and bacteria are characterized by a considerable diversity of pigments. Thus, single-celled organisms (fungi, bacteria, and algae) are considered the most likely commercial sources of new pigments, with biotechnology and, in particular, cell culture techniques the tools for their exploitation (e.g., *Dunaliella* sp. has been used for the commercial production of β-carotene).

Table 29.4. Systems of classification of colourants

Basis of System	Kind of Grouped Pigments	Characteristics	Examples
Origin	Natural	Organic compounds obtained from live organisms	Carotenoids, anthocyanins, curcumin
	Synthetic	Organic compounds obtained by chemical synthesis	FD&C[a] colorants
	Inorganic	Found in nature or obtained by synthesis	TiO_2
A global chemical characteristic	Chromophores with conjugated systems	Multiple double bonds, separated by only one single bond	Carotenoids, anthocyanins, betalains, caramel, FD&C colorants, lakes
	Metal-coordinated compounds	A metal present in their chemical structure	Heme colors (myoglobin, hemoglobin, chlorophyll)
A specific structural characteristic of the natural pigment	Tetrapyrrole derivatives	Compounds with four pyrrol-structures	Chlorophylls, heme colors
	Carotenoids	Isoprenoid derivatives, most of the compounds are polymers of eight isoprene monomers	Lycopene, carotene, lutein, capsanthin
	Iridoids	Isoprenoid derivatives	Geniposide, randioside
	N-Heterocyclic compounds but not tetrapyrrols	Nitrogen is present in their chemical structure	Purines, pterines, flavins, phenazines, phenoxazines, betalains
	Benzopyran derivatives	Oxygenated heterocyclic compounds	Anthocyanins and other flavonoids
	Quinones	Quinone functional groups are found in the chemical structure	Benzoquinones, naphthoquinones, and anthraquinones
	Melanins	Polymeric structures obtained from nitrogen-containing monomers.	Eumelanins, phaeomelanins
Legislation	Certifiable	Anthropogenic synthetics	FD&C colorants and lakes
	Exempt from certification	From natural origin (vegetable, mineral or animal) or synthetic counterparts	Grape juice, TiO_2, carmine, and synthetic β-carotene

[a] FD&C = certifiable colorants permitted to be used for foods, drugs, and cosmetics.
Source: Delgado-Vargas, F. et al. 2000. *Critical Reviews in Food Science and Nutrition* 40: 173. With permission.

CLASSIFICATION OF FOOD COLORS

Pigments have been classified in accordance with different systems (Table 29.4). These systems are clearly defined, but all are closely related; the same type of colorants could be classified in different groups (e.g., carotenoids could be ordered in every group). Today, classifications of colorants by their origin and legislation are the most important systems. This is in agreement with consumer preferences, which clearly favor natural pigments over synthetic pigments obtained from laboratories. In addition, the introduction of natural colorants as additives is not an easy task by the actual FDA, EU, and WHO legislations.

CHOICE AND APPLICATION OF COLORS

Color is a major factor of quality in the natural products to be commercialized. Nowadays, natural products are commonly processed or stored before their consumption, and quality characteristics and particularly color are affected; consequently, color additives have been used since remote times.

However, diverse factors must be considered when selecting the better color additive for the specific application, such as

(1) color hue required;
(2) physical form (e.g., liquid, solid, emulsion);
(3) properties of the foodstuff that will be colored (e.g., oily or water-based product, content of tannins, pH); and
(4) processing conditions (e.g., whether the process requires heating or cooling, storage conditions).

In addition, one factor of paramount importance is the relevant legislation. Pigment regulations differ between countries and sometimes between regions in the same country. Moreover, application of color is dependent on the color used. Thus, it is common to find product application forms (or formulations) that are specific for one manufactured product: spray dried powders are preferred for mass coloration, whereas oil-soluble colorants must be emulsified to be applied in citrus oils. As can be observed, colorant properties must be taken into account to achieve the correct product coloration; solubility, physical form (liquid, solid powders, pastes, emulsions, etc.), pH, microbiological quality (products of high water activity are more susceptible to microbiological attack), and other ingredients must be considered.

Additionally, the importance of other factors must be taken into account: anthocyanins and betalains are water soluble, whereas carotenoids and xanthophylls are oil soluble; temperature produces severe changes in the profile of carotenoid colors; pigments are manufactured at pH values that are near their maximum stability (e.g., norbixine is alkaline, anthocyanins are acid). As an example of how these factors affect color properties, anthocyanins are water soluble and they contain significant levels of sugars; consequently, microbiological attack is a relevant factor that must be considered in the manufacture of products pigmented with them.

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