

FOOD CHEMISTRY PIGMENT



Introduction

No matter how nutritious, flavorful, or well textured a food, it is unlikely to be eaten unless it has the right color.

Factors which influence the acceptability of color in a certain food:

- Culture
- Geography
- Sociology



No matter the biases or habits of a given area, certain food groups are acceptable only if they fall within a certain of color array

Color acceptability → economic worth, i.e. in many raw food materials



■ Color

- To denote the human eye's perception of colored materials,
- part of the electromagnetic spectrum visible to the human eye and generally regarded as lying between 380 - 730 nm i.e. red, blue, or green.
- Together with flavor and texture, color plays an important role in food acceptability.
- Color is mainly a matter of transmission of light for clear liquid foods, such as oils and beverages.
- Color may provide an indication of chemical changes in a food, such as browning and caramelization.

■ Pigment

- Normal constituents of cells or tissues (which is synthesized and accumulated in, or excreted from, living cells) that impart color. It has other properties, i.e. energy receptor, carriers of O_2 , protectants against radiation



■ Colorant

- A general term referring to any chemical compound (synthetically made) that impart (communicate) color i.e. dye & lake

■ Dye

- Colorants used in textile industry, has no place in food usage.

■ Lake

- A food colorant is synthetically made, absorbed on the surface of an inert carrier (i.e. alumina) and added to processed foods
- referred to as certified colors



- The colors of foods are the result of natural pigments or of added colorants.
- The natural pigments (non-certified colors) are a group of substances present in animal and vegetable products.
- Four groups of natural pigments:
 - **tetrapyrrole compounds**: chlorophylls, hemes, and bilins
 - **isoprenoid derivatives**: carotenoids
 - **benzopyran derivatives**: anthocyanins and flavonoids
 - **artefacts**: melanoidins, caramels



Non-Certified Colors (natural colors)

- Do not need certificate to sell or use.
- Most are from nature (Natural Colors)
- Members Include:
 - Annatto extract
 - Beet juice powder
 - Canthaxanthin
 - Caramel



Non-Certified Colors (natural colors)

- Beta-Apo-8' Carotenal
- Beta carotene
- Cochineal extract/carmine
- Grape color extract
- Grape skin extract
- Fruit Juice



Non-Certified Colors (natural colors)

- Vegetable juice
- Paprika oleoresin
- Riboflavin
- Titanium dioxide
- Turmeric
- Turmeric oleoresin



Artificial Color vs. Natural Color

■ Artificial Colors

- Obtained by chemical reactions
- Relatively stable (in most cases)
- Less costly to use
- Health concerns
 - Allergens
 - Cancer risks?
- Consumer acceptability:
Questionable

■ Natural Colors

- Obtained from nature
- Processed by physical means
- May be less stable than synthetic ones
- May be more costly to use.
- No health concerns
- Benefits to health
- Consumer acceptability:
Good



Pigments Indigenous to Food

- A. Chlorophylls
- B. Myoglobin & Hemoglobin
- C. Antocyanins
- D. Carotenoids
- E. Flavonoids
- F. Proanthocyanidins
- G. Tannins
- H. Betalains
- I. Quinones & Xanthoness
- J. Miscellaneous Natural Pigments

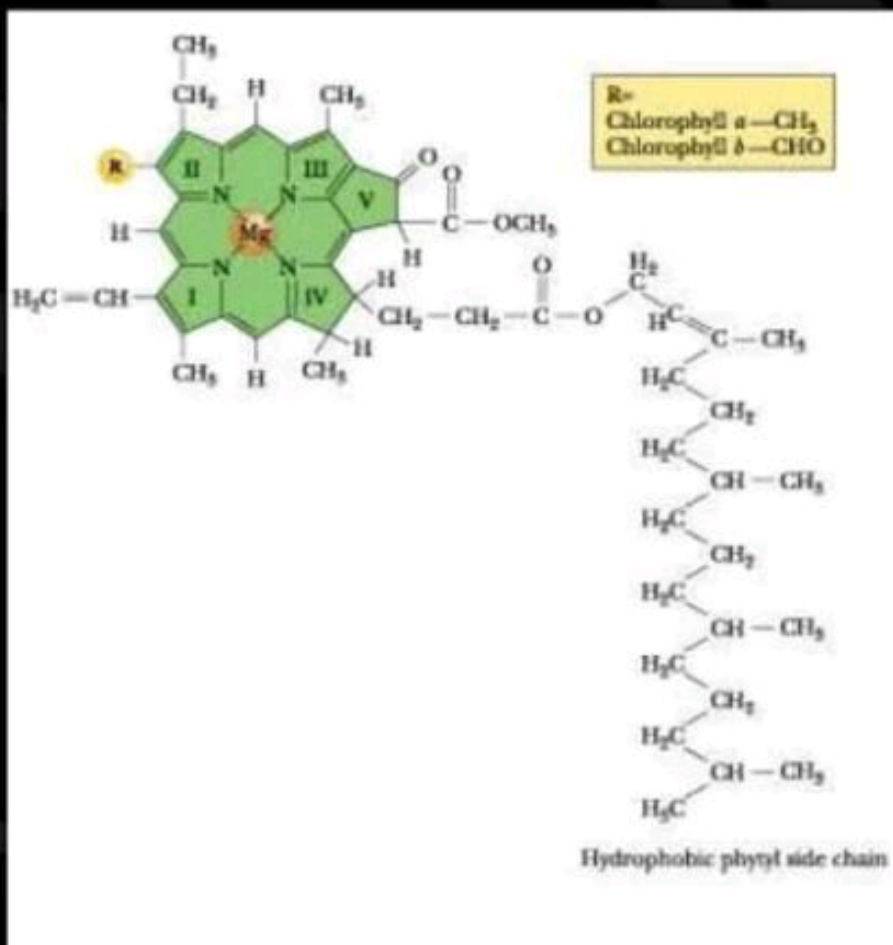


A. Chlorophylls

→ Green pigments involved in the photosynthesis of higher plants, incl. algae.

Location in plants

- In foods, concern focused on chlorophylls a & b → occur in approximate ratio of 3 : 1
- In leaves, chlorophylls are located in plastid bodies, so called chloroplasts (5-10 long μm ; 1-2 thick μm) → within it are smaller particles, called grana (Φ 0.2-2 μm) → they are composed of lamellae (Φ 0.01-0.02 μm) → chlorophylls molecule are surrounded by lamellae.

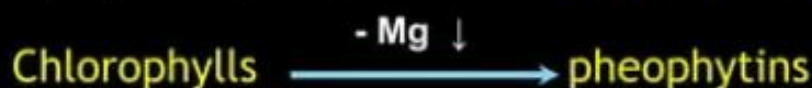


Physical Properties

- Chlorophyll a & pheophytin a → soluble in alcohol, ether, benzene & acetone, slightly soluble in petroleum ether; insoluble in water.
- Chlorophyll b & pheophytin b → soluble in alcohol, ether, benzene & acetone, almost insoluble in petroleum ether; insoluble in water.

Chemical properties

- In food processing, the most common alteration in green chlorophylls → PHEOPHYTINIZATION; the replacement of the central Mg by the hydrogen → form a dull olive-brown pheophytins.



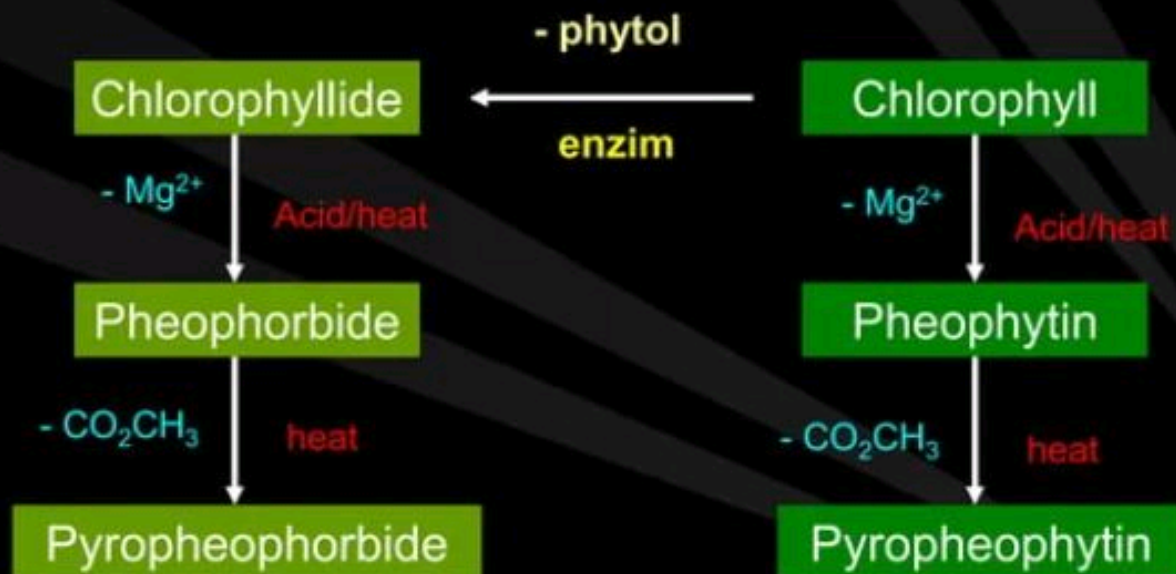


Alterations of Chlorophyll

- Chlorophyll can be degraded by the activity of enzyme chlorophyllase, which catalyze cleavage of phytol from chlorophylls & pheophytins forming chlorophyllides & pheophorbides.
- The enzyme is active in solutions containing water, alcohols or acetone.
- Formation chlorophyllides in fresh leaves does not occur, until the enzyme has been heat activated postharvest.



- The optimum temperature for chlorophyllase activity is ranges between 60 – 82.2°C.
- The activity of enzyme decreases when plant tissue is heated above 80°C, and it loses its activity if heated to 100°C.
- Storing green vegetables in refrigerator can decrease the activity of enzyme.



Heat & Acid

- The Mg atom in chlorophyll is easily displaced by 2 H ions, resulting in the formation of pheophytins.
- Formation of pheophytins occur more rapidly from chlorophyll *a* than chlorophyll *b* (which is more heat stable).
- Chlorophyll degradation in heated vegetable tissue is affected by tissue pH.
- In pH 9, chlorophyll is very stable toward heat, whereas in pH 3 it is unstable.



- A decrease of 1 pH unit can occur during heating of the plant tissue through the release of acids.
- The addition of chloride salts (Na, Mg or Ca) decrease pheophytinization.
- The salts have **electrostatic shielding effect** → the addition of cations neutralizes the negative surface charge of the fatty acids and protein in the chloroplast membrane, thereby reduces the attraction of H ions to the membrane surface.

Allomerization & Photodegradation



- Chlorophyll will be oxidized when dissolved in alcohol/ other solvents and exposed to air → **allomerization**.
- Once green plant is harvested, the chlorophylls are susceptible to **photodegradation**, which results in opening of the tetrapyrrole ring and fragmentation into the lower molecular weight compounds.
- Singlet oxygen and hydroxyl radicals are known to be produced during exposure of chlorophylls to light in the presence of oxygen.



- Once the free radicals formed, they will react further with tetrapyrrole to form peroxides and more free radicals → leading to destruction of the porphyrins and total loss of color.



Effects in Food Handling, Processing & Storage

- Almost any types of food processing and/or storage → cause deterioration of chlorophyll pigments.
- Dehydrated foods packed in clear containers → autooxidation ← the blanching degree before dehydration
- Lipxygenases → produced free radicals → degraded the chlorophylls
- Fermentation of cucumber → produced pheophytins, chlorophyllides & pheophorbides
- Heating of green veggies in acid condition → pheophytins production





- Loss of green color in thermally processed vegetables → caused by the formation of pheophytin & pyropheophytin.
- Blanching and commercial heat sterilization can reduce chlorophyll content about 80-100%.



Preservation of Green Color

The use of high quality materials → process as quickly as possible → store the product at low temperatures





How to retain the green color:

- Acid neutralization to retain chlorophyll
- HTST
- Enzymatic conversion of chlorophyll to chlorophyllides
- Commercial application of metallo complex
- Regreening of thermal processed vegetables



B. Myoglobin & Hemoglobin

→ Myoglobin is a complex muscle proteins

→ Hemoglobin is the blood pigment

- **Hb** → contains 4 polypeptide chains & 4 heme groups, which are planar collection of atoms with the iron atom at the center.
- Heme group function : to combine reversibly with a molecule of O_2 → carried by the blood from the lungs to the tissues.
- **Myoglobin** → a quarter its size compared to Hb; consists of a single polypeptide chain (± 150 AA units) attached to a single Hb group; it is contained within the cell tissues & it acts as a temporary storehouse for the O_2 brought by the Hb in blood.

Hb → considered the linking together of 4 myoglobins (the discussion of these pigments can be limited to myoglobin)

Physical properties

- Myoglobin is part of sarcoplasmic proteins of muscle; soluble in water & dilute salt solution.



Chemical Properties

- Oxygenation reaction

Myoglobin + molecular $O_2 \rightarrow$ oxymyoglobin (O_2Mb) forms **bright red pigment**

- Oxidation reaction

Myoglobin oxidation $\rightarrow$ metmyoglobin (MMb) forms **brown color**

- Ferrous covalent complexes of myoglobin (purple) with :

- Molecular $O_2 \rightarrow$ oxymyoglobin
- Nitric oxide $\rightarrow$ nitrosomyoglobin
- Carbonmonoxide $\rightarrow$ carboxymyoglobin

Effect of Handling, Processing & Storage

- Cured Meat Pigment



In commercial practice, sodium nitrite ($NaNO_2$) is the source of nitrous acid:

$NaNO_2$ (salt cure) in water $\rightarrow Na^+ + NO_2^-$ (nitrite ion) $\rightarrow HNO_2$ (in the curing brine)

Or using combustion gas (NO_2) to smoke or gas-oven fresh meat:

$2 NO_2$ (gas cure) + H_2O (in meat) $\rightarrow HNO_2$ (nitrous acid) + HNO_3 (nitric acid)

Meat Curing:

$HNO_2 + Mb$ (myoglobin in meat) $\rightarrow NOMb$ (pink cured meat pigment)



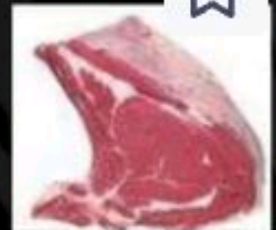
The formation of cured meat pigments viewed as 2 processes.

- (1) **Biochemical reaction**, which reduce nitrite → nitric oxide; iron in heme → the ferrous state
- (2) **Thermal denaturation of globin** ← heating at 66 C or higher & may involve the coprecipitation of the heme pigment with other protein in meat



- **Packaging**

Because meat pigment easily reacts with oxygen to produce either an acceptable oxygenated products or unacceptable oxidized products



- **Carbon monoxide (CO) flushing**

It was done before sealing of fresh beef → very effective for preserving & stabilizing color for 15 days

Certain metallic ions (esp. Cu) → extremely active in promoting autooxidation of O₂Mb to MMb, while Fe, Zn, Al are less active





C. Anthocyanins

→ A group of reddish water-soluble pigments in plants which exist in the cell sap/juice, i.e. flowers, fruits, vegetables,

- An anthocyanin pigment is composed of an aglycone (an anthocyanidin) **esterified** to 1 or more sugars. Only 5 type of sugars found in it, which are, in order of relative abundance : glucose, rhamnose, galactose, xylose, arabinose
- Anthocyanins may also be "**acylated**" which adds a third component to the molecule, i.e. p-coumaric, ferulic, caffeic, malonic, vanillic, or acetic acids may be **esterified** to the sugar molecule.

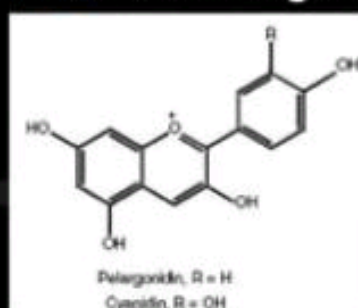


Fig. Anthocyanin aglycone