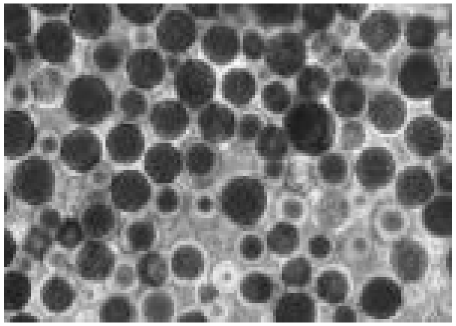
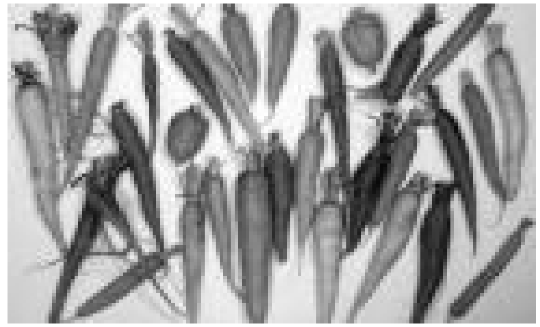
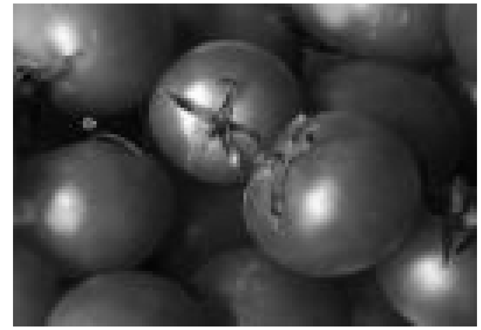
  

FOOD CHEMISTRY

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 (<u>non-certified colors</u>) 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

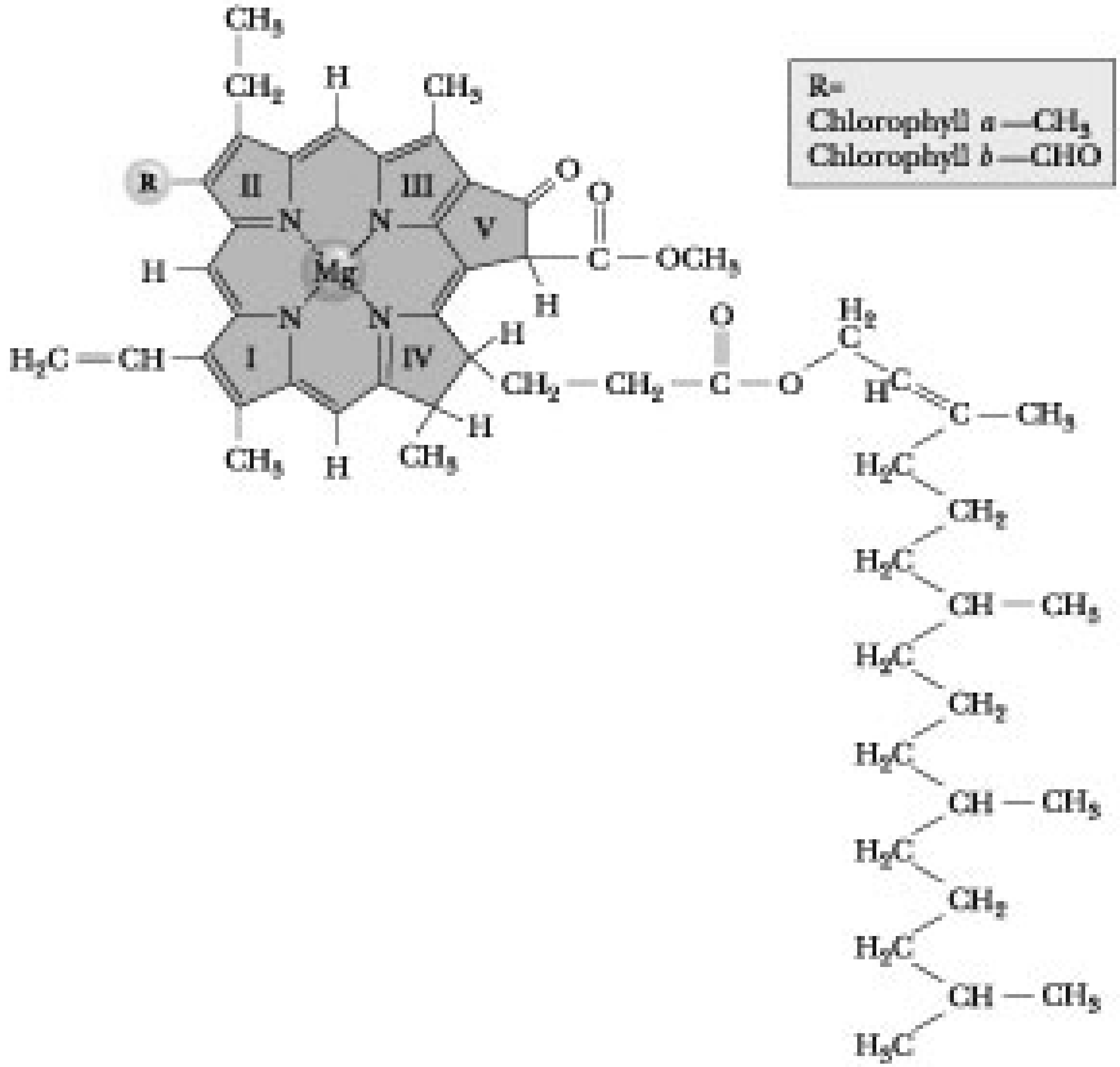
A. Chlorophylls
B. Myoglobin & Hemoglobin
C. Antocyanins
D. Carotenoids
E. Flavonoids
F. Proanthocyanidins
G. Tannins
H. Betalains
I. Quinones & Xanthones
J. Miscellaneous Natural Pigments

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.



Hydrophobic phytyl side chain

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

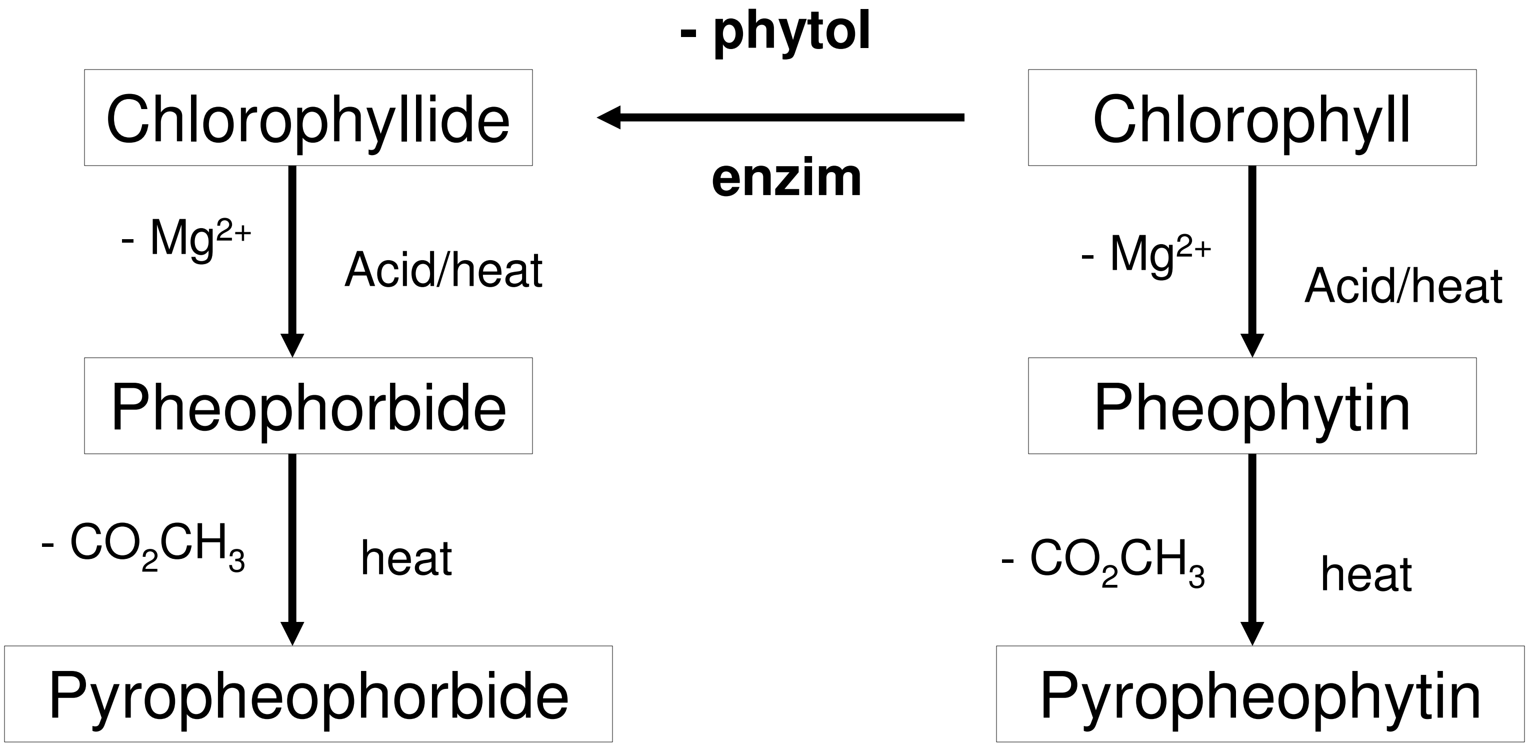
- In food processing, the most common alteration in green chlorophylls → PHEOPHYTINIZATION; the replacement of the central Mg by the hydrogen → form a dull olive-brown pheophytins.

$$\text{Chlorophylls} \xrightarrow{\textbf{- Mg} \downarrow} \text{pheophytins}$$

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.



- phytol
enzim
Chlorophyllide
Chlorophyll
- Mg^{2+}
Acid/heat
- Mg^{2+}
Acid/heat
Pheophorbide
Pheophytin
- CO_2CH_3
heat
- CO_2CH_3
heat
Pyropheophorbide
Pyropheophytin

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
- Lipoxygenases → 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 → oxymyoglobin (O_2Mb) forms bright red pigment

• Oxidation reaction

Myoglobin oxidation → metmyoglobin (MMb) forms brown color

• Ferrous covalent complexes of myoglobin (purple) with :

- Molecular O_2 → oxymyoglobin
- Nitric oxide → nitrosomyoglobin
- Carbonmonoxide → 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 → Na^+ + NO_2^- (nitrite ion) → 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) ---> HNO_2 (nitrous acid) + HNO_3 (nitric acid)

Meat Curing:

HNO_2 + Mb (myoglobin in meat) → 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

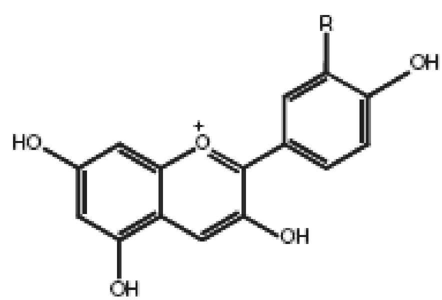
  Certain metallic ions (esp. Cu) → extremely active in promoting autooxidation of O_2Mb to MMb, while Fe, Zn, Al are less active

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.



Pelargonidin, R = H
Cyanidin, R = OH

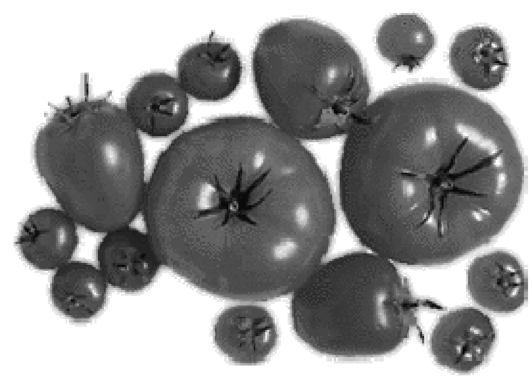


Fig. Anthocyanin aglicone

Stability in Food

• Anthocyanins show a marked change in color with changed in pH → the higher the pH → the faster the rate of destruction

Chemical Reactions

• The addition of sulfite, sulfite oxide → rapid bleaching of the anthocyanins → yellowish colors.

i.e. in the making of jams, preserves such as dried fruits & vegetables

• The reaction with ascorbic acid → the degradation of both compounds ← the intermediate, peroxide produces by ascorbic acid degradation

i.e. Cranberry juice cocktail stored at room temperature:

0 days – 9 mg/100 g anthocyanins & 18 mg/100 g ascorbic acid

6 months – ascorbic acid degradation & 80% degradation of anthocyanin

- Group of anthocyanins:
  - Chalcone
  - Flavonones
  - Flavones
  - Flavonoids
  - Flavonols
  - Cathechins
  - Anthocyanidins

- Anthocyanidins which can be found in food (red → violet spectrum):
  - Pelargonidin
  - Cynaidin
  - Delphinidin
  - Peonidin
  - Petunidin
  - Malvidin

Fruit juice

- Source:
  - Mature, edible fruits
    - Elderberry
    - Black currant
    - Blackberry
    - Others
- Coloring agent: anthocyanins
- Applications:
  - Beverages
  - Tomato paste
  - Fruit preparation

- Solubility: water
- Stability:
  - Light: good
  - Heat: fair
  - pH: color changes heavily as pH changes
    - Acidic: red
    - Neutral: purple
    - Alkaline: Blue

- the lower pH the darker the color

- Ascorbic acid accelerates anthocyanin degradation.

Vegetable Juice

- Source:
  - Fresh or dehydrated vegetables
    - Red cabbage
    - Red radish
    - Black carrot
    - Purple yam
- Coloring components
  - Anthocyanins
- Solubility: water
- Stability:
  - Light: good
  - Heat: fair
  - pH: color changes heavily as pH changes (the lower the pH is, the more condense the color is)
    - Acidic: red
    - Neutral: purple
    - Alkaline: Blue

Cabbage Color

- One of the most stable anthocyanin colors
- Purplish red in acidic solution
- Low odor version available
- Both liquid and powder forms available
- Application:

  beverage, tomato paste,

  snack foods, dairy, confectionery

Red Radish Color

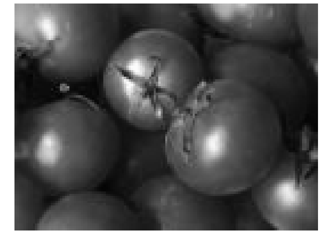
- One of the most stable anthocyanin colors
- red in acidic solution
- Low odor version available
- Both liquid and powder forms available

- Keeps red at higher pH up to 6

0038-ralb in a model rice beverage, pH 6.0

- Wide applications
  - Beverage
  - Tomato paste
  - Snack foods
  - Dairy
  - Confectionery

D. Carotenoids

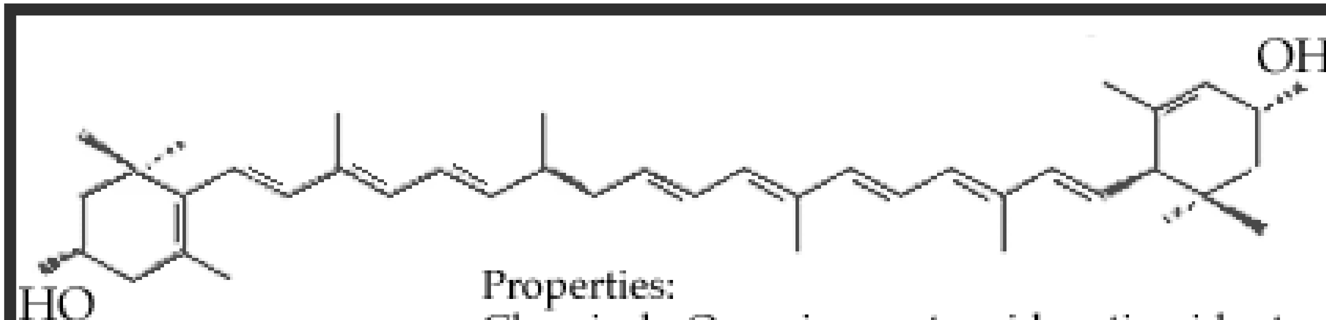


→ A group of mainly lipid soluble compounds responsible of the yellow & red colors of plants & animal products (430 – 480 nm).

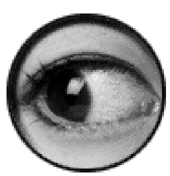
- Most of produced carotenoids in nature is in form of fucoxanthin in various algae, in green leaves : lutein, violaxanthin, neoxanthin; β-carotene; lycopene in tomatoes; capxanthin in red peppers

LUTEIN

kiwi, egg yolk, corn, zucchini, red grapes, pumpkin



Properties:
Chemical - Organic, carotenoid, anti-oxidant
Physical - yellow colored slightly hydroscopic crystalline solid
Formula - $C_{40}H_{52}O_2$
Molecular weight - 568.88

Good for 

- Carotenoids include a class of HC, called carotenes, and their oxygenated derivatives, called xanthophylls.
- They consist of 8 isoprenoids units joined in such a manner that the arrangement of isoprenoid units is reversed in the center of the molecule.

- Forms of carotenoids :

    (1) free state in plant tissues (crystals or amorphous solids)

    (2) solution in lipid media, i.e. capxanthin- lauric acid ester in paprika

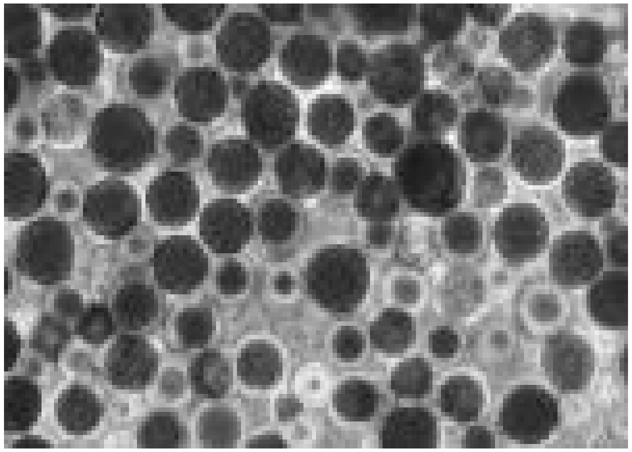


Fig. Red pigment of astaxanthin

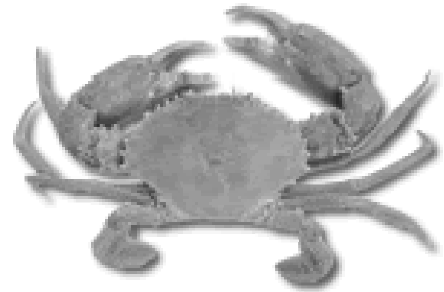


Fig. Mud crab

Fig. Lobster

- The association of carotenoids with proteins stabilised the pigment & also change the color, i.e. red carotenoid astaxanthin when complexed with protein → blue colorant in lobster shells; ovoverdin, the green pigment in lobster eggs; carotenoid-protein complexes found in fruits, vegetables.

- Carotenoids may occur in combination with reducing sugars via a glycosidic bond, i.e. CROCIN - containing 2 molecules of the sugar gentiobiose united with crocetin, found as the main pigment in SAFFRON

Chemical Reactions

Provitamin A

- Beta carotene is precursor of vitamin A, which yields 2 molecules of vitamin A by cleavage at the center of the molecule.
- Alpha carotene is precursor of one molecule of vitamin A; which is half identical to beta carotene.

Oxidation reaction

- Stability of carotenoids depend on whether the pigment is in vivo or in vitro in environmental condition, i.e. lycopene in tomatoes is quite stable, but the extracted purified pigment is unstable.
- Enzyme degraded carotenoids rapidly, i.e. lypoxygenase.
- In processed food → heat, light, presence of pro- and antioxidant influence carotenoids degradation.

Beta carotene/natural mixed carotenes

- Synthetic or extracted from natural source, plants or algae.
- Solubility: oil soluble
- Stability:
  - Heat stability: good
  - Light stability: poor

Stability comparison. Both were boiled, hot filled and exposed to outdoor direct sunlight for 5 days, pH 2.3

Lutein

- A member of carotenoids
- Solubility:
  - Oil soluble
- Applications
  - As a nutritional supplement

    can be added to all foods

    (plain in taste and flavor)
  - As a natural colorant:

    can be added to all food

    (a bright yellow color in water solution)
- Reasons to use lutein
  - Extended studies have proved the importance of lutein to eye health
  - Antioxidant--a free radical scavenger

Lycopene

- Sources:
  - Synthetic
  - Extracted from nature, plants or microorganisms
- A member of carotenoids
- Solubility: oil soluble

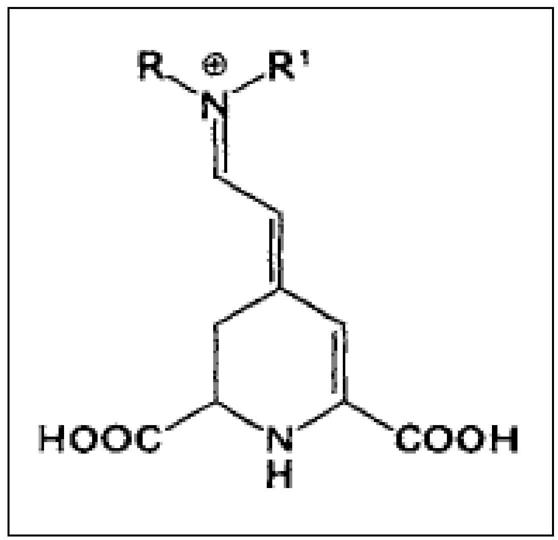
- ACRC has made stabilized and water-dispersible lycopene — for beverage and other food applications

E. Betalains

- Betalains are vacuolar plant pigments.
- Betalains represent immonium derivatives of betalamic acid.
- Betalains are subdivided into the red-violet betacyanins (λ_{max} ~540 nm) and the yellow-orange betaxanthins (λ_{max} ~480 nm).
- Plants containing betalaines have colors similar to plants containing anthocyanins.
- Anthocyanins and betalains mutually exclude each other — they have never been found together in the same plant.

Chemical properties

- Betalains are slightly soluble in ethanol and methanol, but most soluble in water.
- The betaxanthins are most stable at pH 5.5 to 7.
- Betacyanins are considered to exhibit optimum stability at pH 5 to 6, while betalamic acid remains intact at pH 9.
- The general structure of betalains:



- The color of betalains is not affected by pH, contrary to the behavior of anthocyanins.
- About 50 betalains have been identified. The majority have an acylated sugar moiety.
- The acids involved are sulfuric, malonic, caffeic, sinapic, citric and *p*-coumaric acids.

Red beet juice

- Betanin is the main pigment of red beet. It is a betanidin 5-0-β-glucoside.
- Peeling is required to get optimum betalains, since the greatest polyphenoloxidase activity, which is deleterious to both betacyanins and betaxanthins, is located in the requires blan
- Small beets a accumulate h
- Poor stability to heating process

Stability of betalains

- In most cases, purified or non-purified pigment solutions and juices were investigated with respect to their color stability in the presence of heat, light, varying aw, metal ions, and oxygen.
- In general, betalains are considered to be most stable at near neutral conditions in foods that are devoid of sulfites, protected from oxygen and light, and stored for short times at cooling temperatures

The application of betalains

- dairy products
- Fruit fillings for bakery products
- relishes
- various instant products
- confectionary
- meat substitutes
- sausages

Non-certified Colors (Natural Colors)

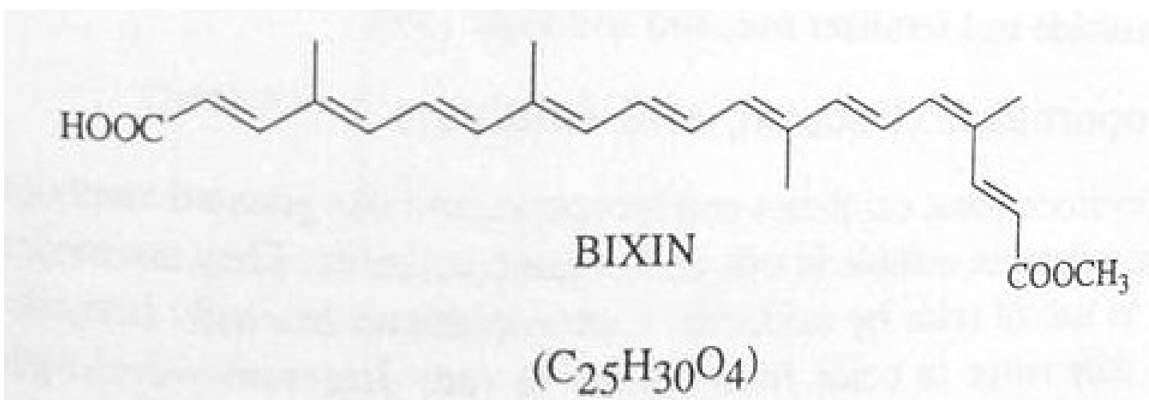
Food processing applications

Annato

- Annatto extract.
  – Extracted from annatto seeds, *Bixa orellna* L., a tropical bush.

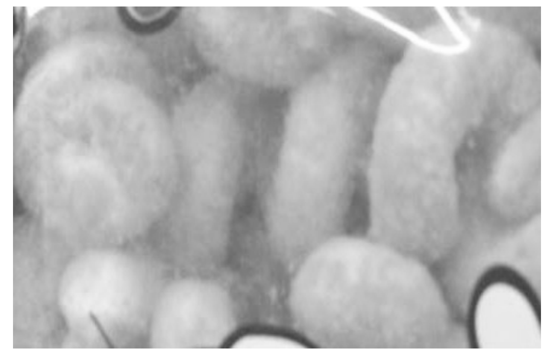
Annatto

– Two forms commercially available:
  - Bixin.



Annatto

- Bixin
  - Color in final foods: orange.
  - Solubility: oil soluble.
  - Stability:
    - Light stability: Fair.
    - Heat Stability: good under 130 ^{o}C.
  - Application: fatty or oily foods, including snack, cake & other bakery products, butter, popcorn oil.



- Norbixin
  - Solubility
    - water soluble in neutral or alkaline solution
    - Precipitates in acidic solutions (pH<5).
  - Stability
    - Light stability: fair
    - Heat Stability: good under 130 ^{o}C
    - Acid stability: poor
  - Application: cheese, bakery, snacks, confectionery, etc.

Annatto

Acid-stable annatto emulsion for beverages

Caramel

- Source:
  - Reaction products of carbohydrates during heating
  - Usually ammonium and sulfate are added
    - Negatively charged
    - Positively charged

- Stability
  - Light: very stable
  - Heat: very stable
  - Acid: use acid stable type

- Application:
  - Beverages
  - Bakery
  - Confectionery
  - Snacks, etc

Cochineal Extract

- Source
  - Extracted from cochineal (*dactylopius coccus costa)*

Cochineal Extract

- Stability
  - Light: excellent
  - Heat: excellent
  - pH: poor
    - Orange in acidic pH
    - Purple in neutral pH
    - Blue in alkaline pH

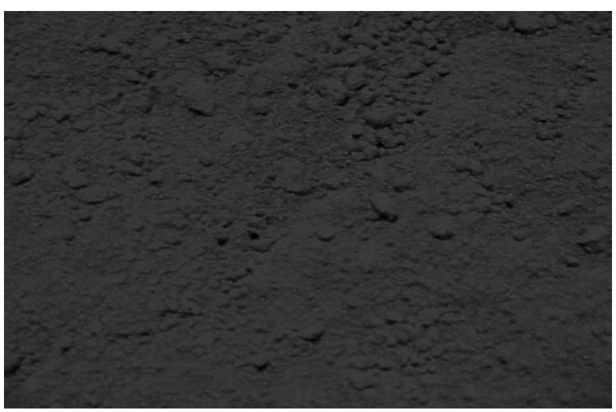
- Acid stable cochineal extract:
  - Can be boiled in 10% citric acid or even 0.01N HCl for at least 3 hrs.
  - Dose not precipitate in acidic beverage → precipate cause discoloration.

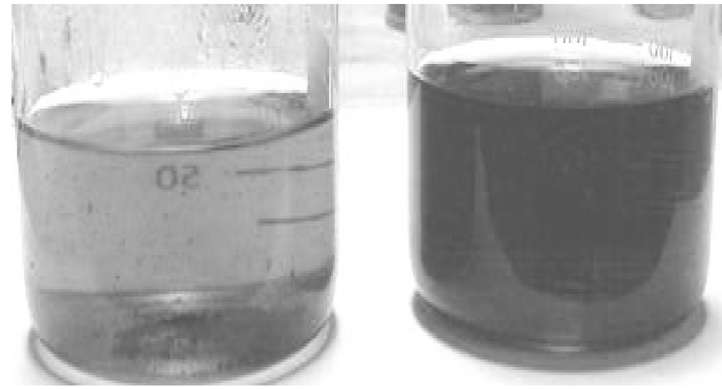
Cochineal Extract

Left: Control (An acid proof cochineal extract from a competitor) in 0.3% citric acid solution.
The original red color faded away after exposure.
Center: ACRC 1162-ralb in 1.0% citric acid solution. The original red color did not fade.
Right: ACRC 1162-ralb in 0.01N HCL. The original red color did not fade.

Carmine

- Source:
  - Aluminum/calcium lake of carminic acid, the coloring component in cochineal extract
  - In powder form, insoluble in water, soluble in alkaline water.

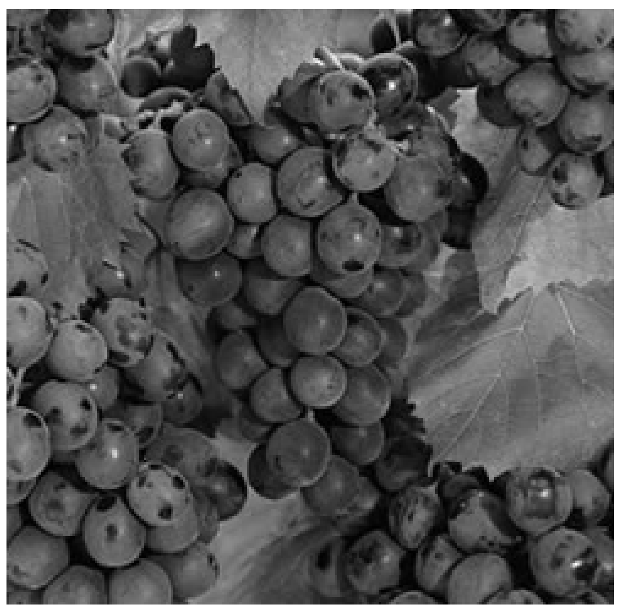




- Carmine is not acid stable:
  - Discoloration
  - Preciptitation
- Application: pasta, surimi, bakery-pie fillings, seafood, bakery, pudding

Grape Color Extract

- Sources:
  - Extract of precipitated lees of Concord grape juice during storage
- Solubility:
  - Water



- Stability:
  - Light: good
    - Heat: fair
    - pH: poor
      - Acidic: red to purple
      - Neutral: purple
      - Alkaline: blue

Grape Color Extract

- Applications:
  - Non-beverage foods
    - Pie filling
    - Fruit preparation
    - others

Grape Skin Extract (Enochianina)

- Source
  - Extract of deseeded marc, remaining after grapes have been pressed for juice or wine.
- Solubility:
  - water
- Stability:
  - Light: good
    - Heat: fair
    - pH: poor
      - Acidic: red to purple
      - Neutral: purple
      - Alkaline: blue
- Application:
  - Beverages (alcoholic, carbonated)

Paprika Oleoresin

- Source:
  - Extracted from red pepper

- Solubility:
  - Oil soluble

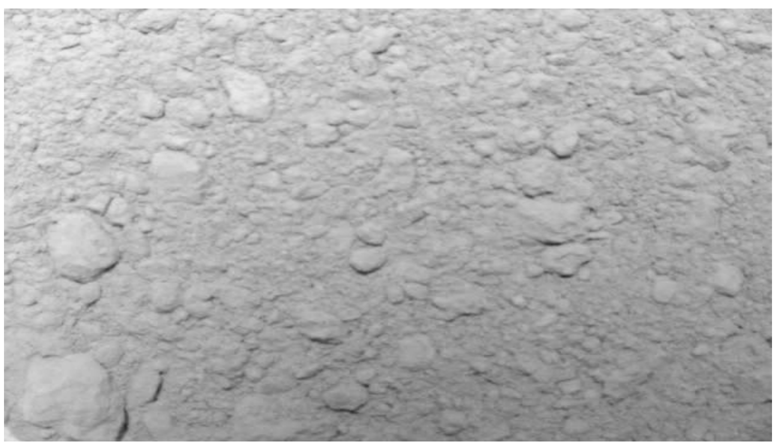
–ACRC made it water dispersible

Paprika Oleoresin

- Stability
  - Light: Fair.
  - Heat: good
- Applications:
  - Seasoning
  - Snack
  - Salad dressing
  - Popcorn
  - Beverage
  - Confectionery
  - Others

Turmeric Oleoresin (Curcumin)

- Source:
  - Extracted from *curcuma longa* L., a member of ginger family.



- Coloring component:
  - Curcumin and curcuminoids
- Solubility
  - Fat and alcohol soluble
  - Cold water insoluble
  - Commercially dissolve curcumin in polysorbate-80 or –60 to make it water dispersible

Turmeric Oleoresin (Curcumin)

- Stability:
  - Heat: good
  - Light: poor
  - pH: color hue change with pH
    - Greenish in acidic pH
    - Orange yellow in neutral pH
    - More stable in acidic pH than in neutral or alkaline pH

- Color hue: Bright yellow in acidic solution

Turmeric Oleoresin (Curcumin)

- Applications:
  - Pickle
  - Bakery
  - Confectionery
  - Others
  - Snack
  - Pudding
  - Gelatin
  - Gummy bear
  - Yogurt
  - Popcorn
  - Finger foods