Pigments and other colorants

Coloured compounds (colorants, pigments)

colour effect based on the selective absorption of certain wavelengths

resulting colour is determined by the spectrum of reflected wavelengths of light

light – elmg. radiation visible to the human eye (400-800 nm)

- natural pigments
- synthetic pigments identical to natural pigments
- synthetic pigments

natural colorants - also derived from natural raw materials by technological processes (caramel)

discoloration - undesirable colour change

NATURAL COLOURS

formation

- primary compounds
  natural food components
  natural components of other materials (microorganisms, algae, higher plants)
  used as additives

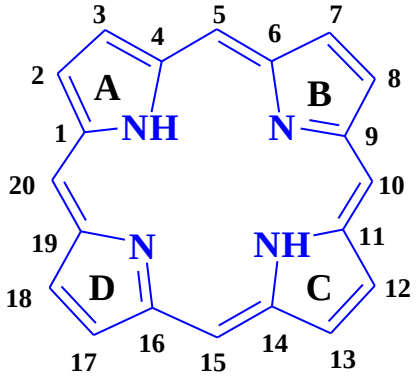
- secondary compounds
  enzymatic reactions (non-enzymatic browning reaction)
  chemical reactions

important groups

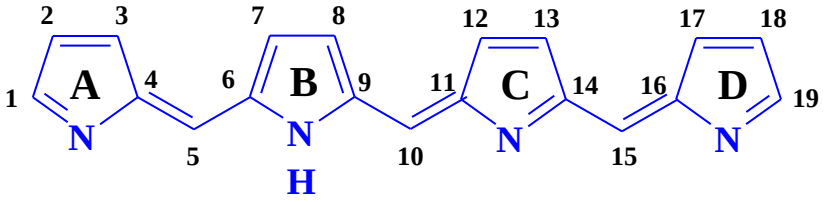
♦ **tetrapyrrole colours**	plants, animals
hem colours	
chlorophyll colours	
♦ **betalain colours**	plants
betacyans	
betaxanthins	
♦ **flavonoid colours**	plants
anthocyanins	
anthoxanthins	
♦ **phenolic and quinoid colours**	plants, animals
phenols	
quinones	
♦ **carotenoid colours**	plants, animals
carotenes	
xanthophylls	

TETRAPYRROLE PIGMENTS (TETRAPYRROLES)

- **porphyrin pigments (porphyrins)** — **cyclic**
  - **hem pigments (haems)**
  - **chlorophyll pigments (chlorophylls)**
- **biline pigments (bilines)** — **linear**
  - **phycobilins**



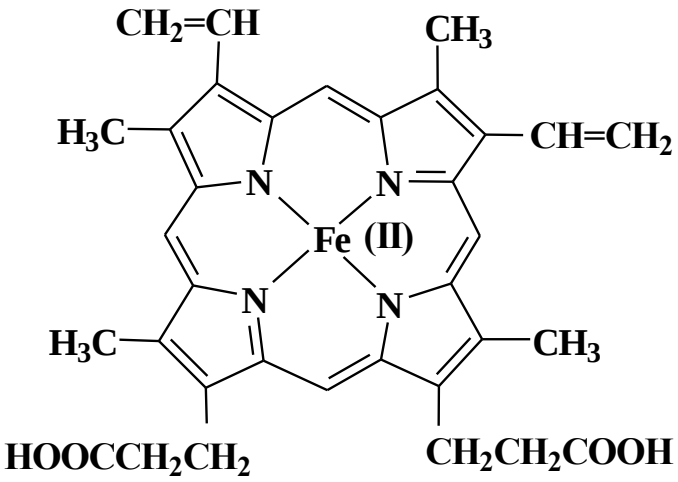
porphyrins

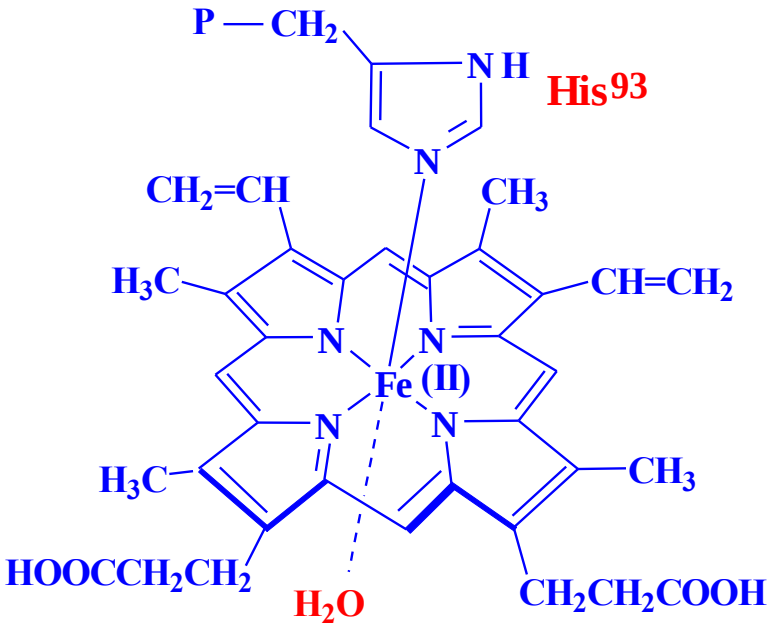


bilines

haem pigments

meat, meat products

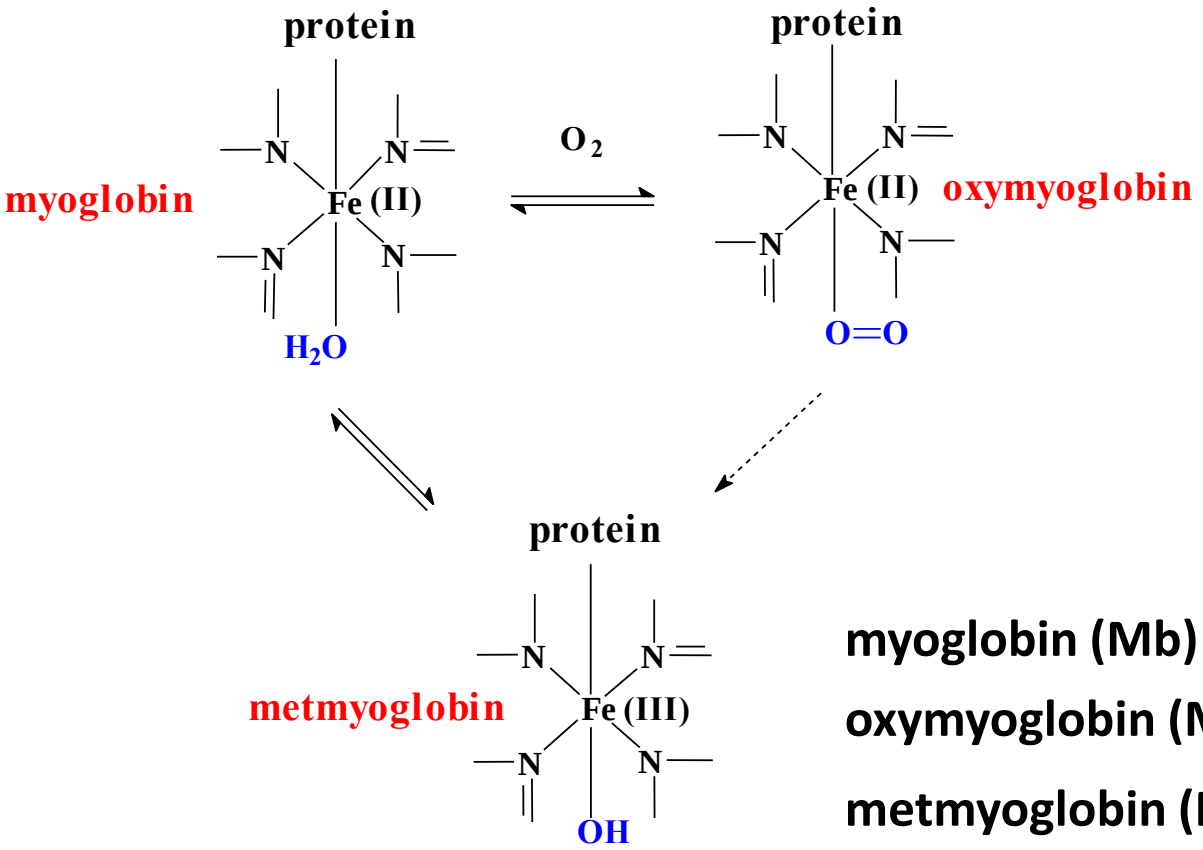




haem (reduced haematin, Fe^{2+})
haematin (Fe^{3+})

haemoglobin
myoglobin (P = globin residue,16,8 kDa)

Meat	Myoglobin mg.kg^{-1}	Haemoglobin mg.kg^{-1}	Proportion of haemoglobin (%)
Beef	3140-7020	340-520	6-10
Pork	790-2320	360-1200	25-50



myoglobin (Mb) dark red

oxymyoglobin (MbO2) scarlet

metmyoglobin (MMb) red to brown

- **formation of MMb autoxidation**

$P\text{-}Fe^{2+}(Mb) + O_2 \rightarrow P\text{-}Fe^{3+}(MMb) + \bullet O_2^-$ (superoxide anion radical)

$2 \bullet O_2^- + 2\ H^+ \rightarrow H_2O_2 + O_2$

$P\text{-}Fe^{3+} + H_2O_2 = P\text{-}Fe^{3+}\text{=}O \leftrightarrow P\text{-}Fe^{4+}\text{-}O^-$ (oxen, hypervalent Fe)

initiation of lipid peroxidation

reaction of MMb during temperature processing of meat

metmyoglobin

↓

globin denaturation (70-80 °C)

↓

globin hydrolysis

↓

hematin or haem

↓ (loss Fe^{3+} nebo Fe^{2+})

linear tetrapyrroles

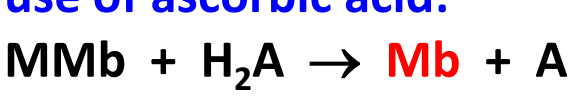
stabilization of meat and meat products colour

heating:

MbNO = nitroxymyoglobin

Mb(NO)2 = nitroxyhaemochrom (nitrosylhaemochrom, nitroxymyochromogen)

use of ascorbic acid:

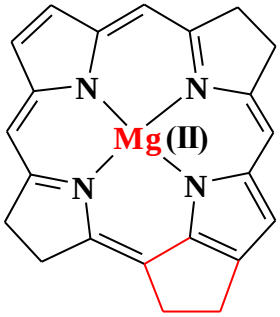


fuscous up to green colours
(sulfomyoglobin, verdochrom, cholemyoglobin)

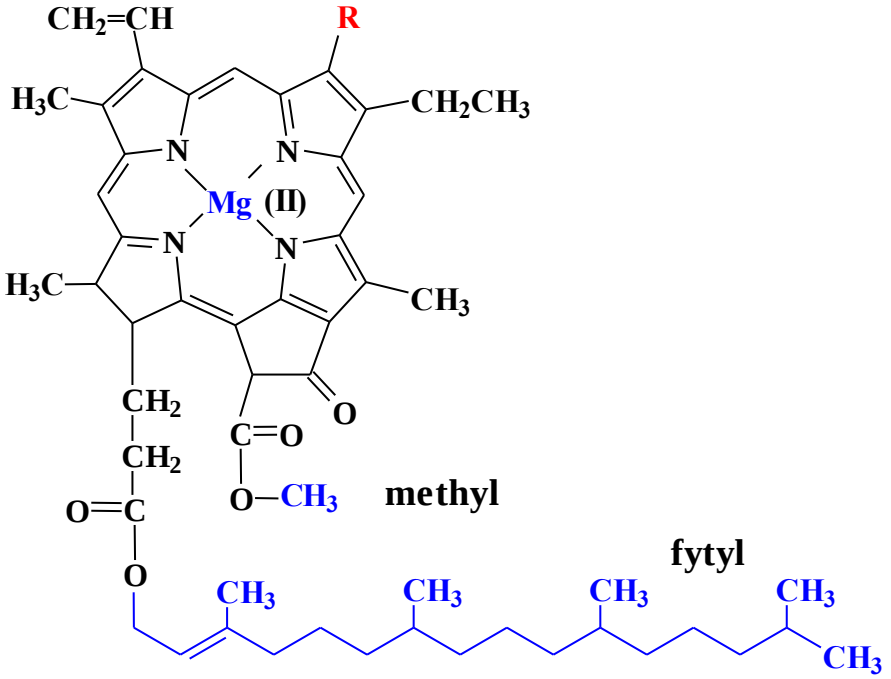
CHLOROPHYLL PIGMENTS

green parts of fruits and vegetables

porphyrins

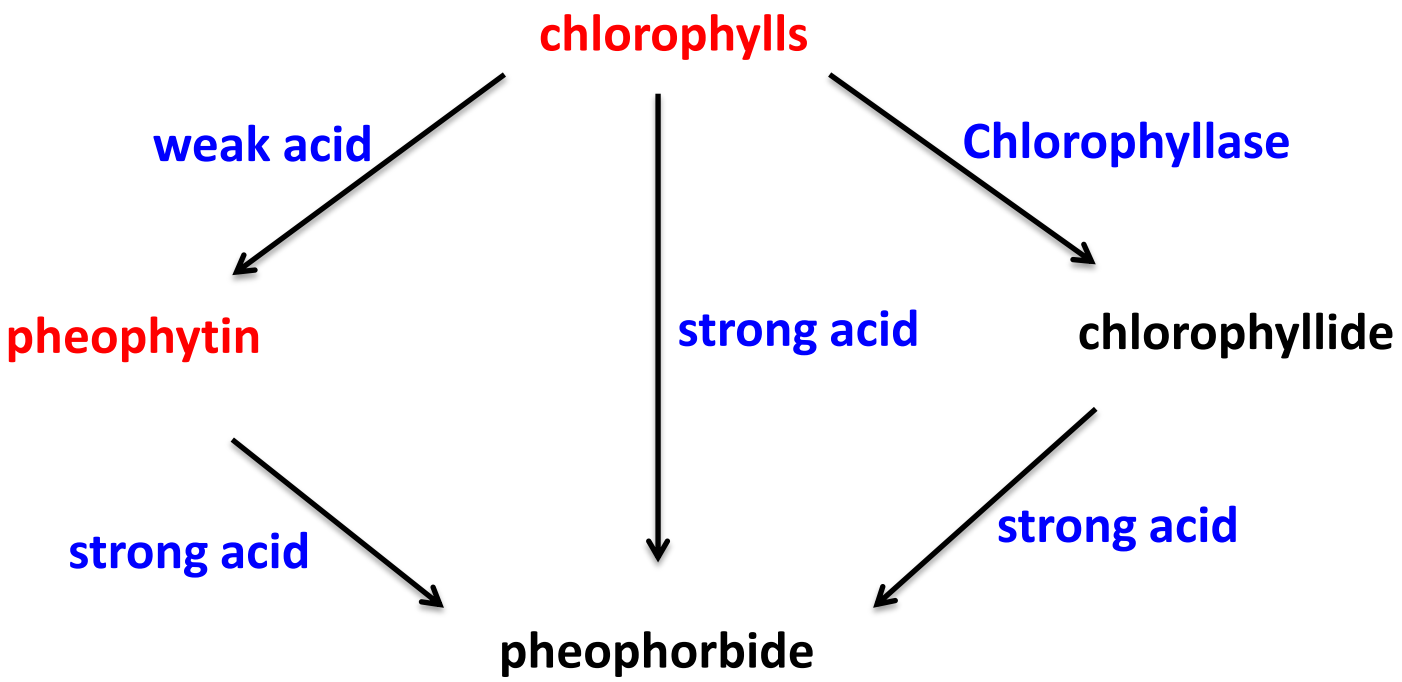


chlorophylls

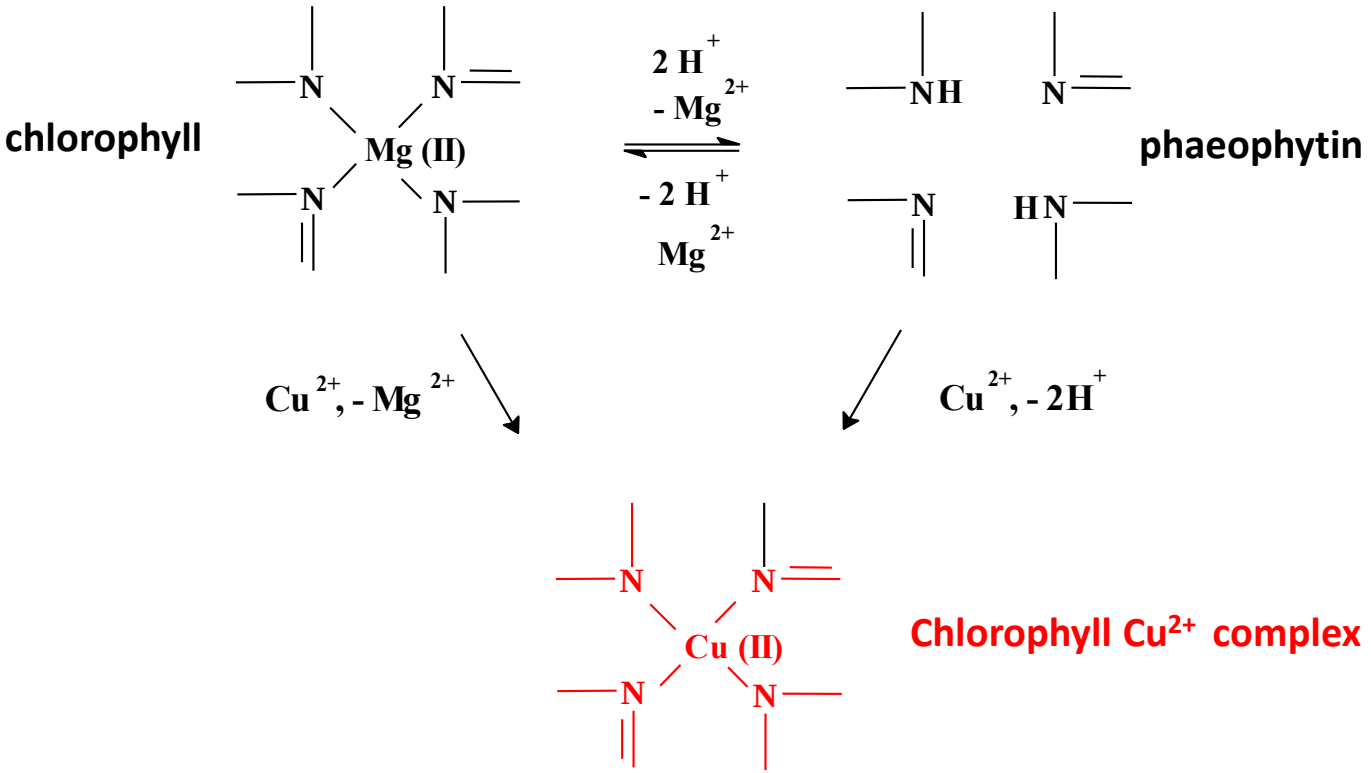


complex Mg (II) chlorophylls	R = CH_3 chlorophyll a	yellow-green	3
	R = CH=O chlorophyll b	blue-green	1
without Mg (II)	pheophytin		
without phytol	chlorophyllide		
without Mg (II) and phytol	pheophorbide		

reactions of chlorophylls during processing (acids, enzymes)



colour stabilisation



- chlorophylls, Cu complex of chlorophylls - Fat-soluble green dye mixture
- chlorophyllin (Na and K salts of various compounds) - teal, soluble in water
- Cu complex of chlorophyllin – green stable colorants

BETALAIN PIGMENTS

beetroot *Beta vulgaris*

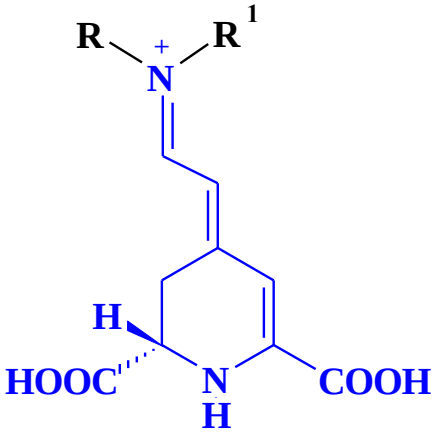
prickly pear

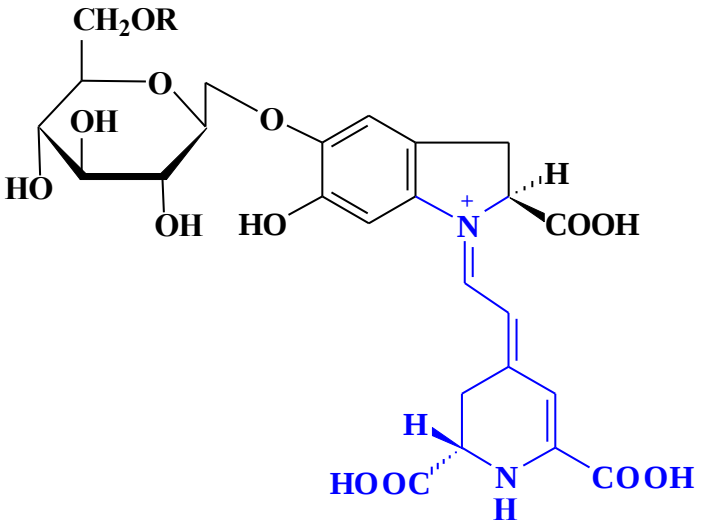
amaranth

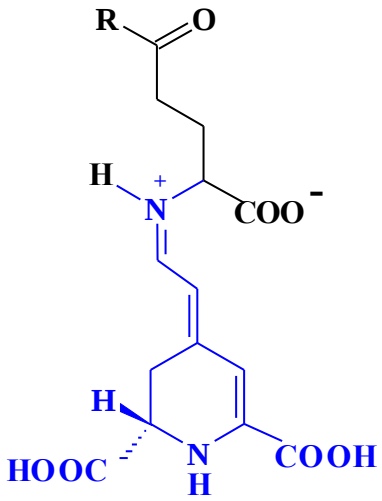
Amanita muscaria

- **betacyanins** — red, orange
- **betaxanthins** — yellow, orange

basic structure







betanin (R = H)

vulgaxanthin I (R = NH_2)
vulgaxanthin II (R = H)

dominating betacyamin in beetroot (1-2 g/kg)
use powder with 6-7% dyes beet (after fermentation, drying)

dyeing of dairy and meat products, soft drinks, sweets

FLAVONOID PIGMENTS

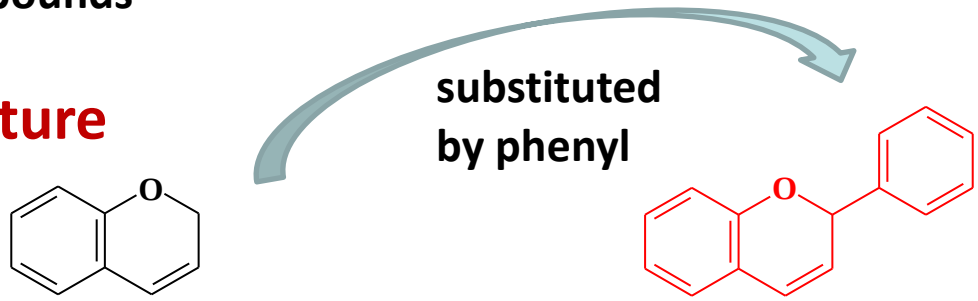
fruits, vegetables, flowers

- **anthocyanins** red, violet, blue
- **anthoxanthins** yellow, orange

(anthos = flower, kyaneos = blue, xanthos = yellow)

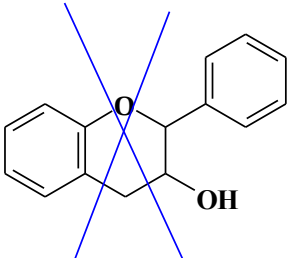
cca 5000 compounds

basic structure

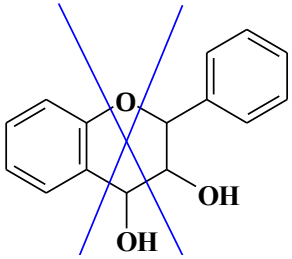


2*H*-chromene flavan

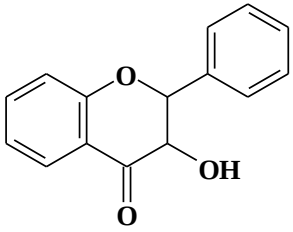
- oxidation of 3C chain (ring B)
- OH groups in rings A, B, C
- aglycones, glycosides



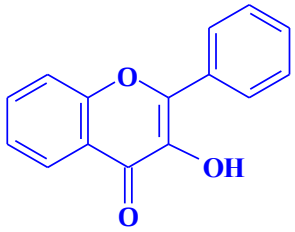
Favan-3-ols
catechins



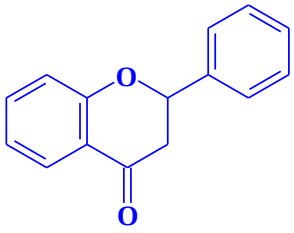
Favan-3,4-diols
leucoanthocyanidins



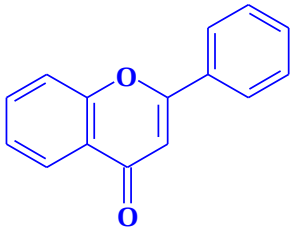
flavanonols



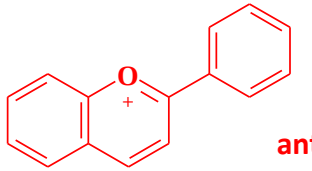
flavavonols



flavanones



flavones



anthocyanidines

colourless

colourless-
light pale yellow

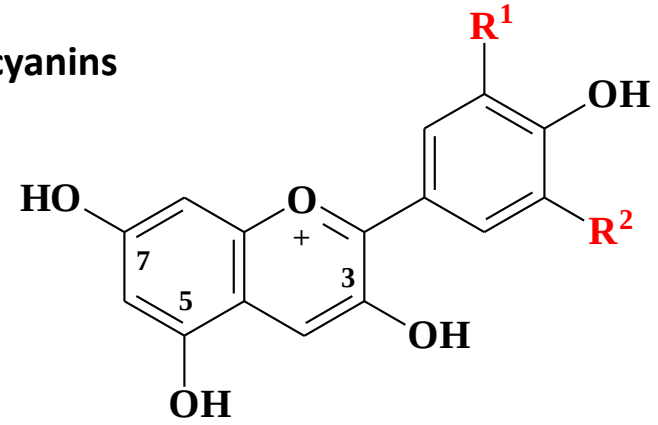
light yellow
red-blue

yellow

Anthocyanins

aglycones=anthocyanidins glycosides=anthocyanins

basic structure



pelargonidin	Pg	$R^1 = H$	$R^2 = H$	violet-red
cyanidin	Cy	$R^1 = H$	$R^2 = OH$	violet
delfinidin	Dp	$R^1 = OH$	$R^2 = OH$	blue-violet
peonidin	Pn	$R^1 = H$	$R^2 = OCH_3$	violet
petunidin	Pt	$R^1 = OH$	$R^2 = OCH_3$	dark red
malvidin	Mv	$R^1 = OCH_3$	$R^2 = OCH_3$	blue-violet

saccharides: Glc, Gal, Xyl, Ara, Rha,

always at C-3, often at C-3 and C-5, seldom at C-7

acids: p-cumaric, caffeic, ferulic

anthocyanins fruits and vegetables

fruit	anthocyanins	sacharide, acid
Blueberry	Dp	3-rutinoside, 5-glucoside, 3-glucoside (myrtillin)
Grapes	Cy, Pn, Dp, Pt, Mv	3-p-kumaroyl, 3-kaffeoyl-3-glucosids
Strawberries	Pg, Cy	3-glucoside
Raspberries	Cy, Pg	3-sophoroside, 3-rutinoside, 3-glucoside
Blackberry	Cy, Mv	3-glucoside, 3-rutinoside, free/acyls
Black currant	Cy, Dp	3-glucoside, 3,5-diglucoside, 3-rutinoside
Cherries	Cy, Pn	3-glucoside, 3-rutinoside
vegetable	anthocyanins	sacharide, acid
Onion	Cy	3-glucoside, 3-galactoside (idaein)
Eggplant	Dp	3-glukoside, 3-rutinoside, 3,5-diglucoside
Cabbage	Cy	malonyl (*p*-coumaroyl, di-*p*-coumaroyl, feruloyl)-3-sophoroside-5-glucoside

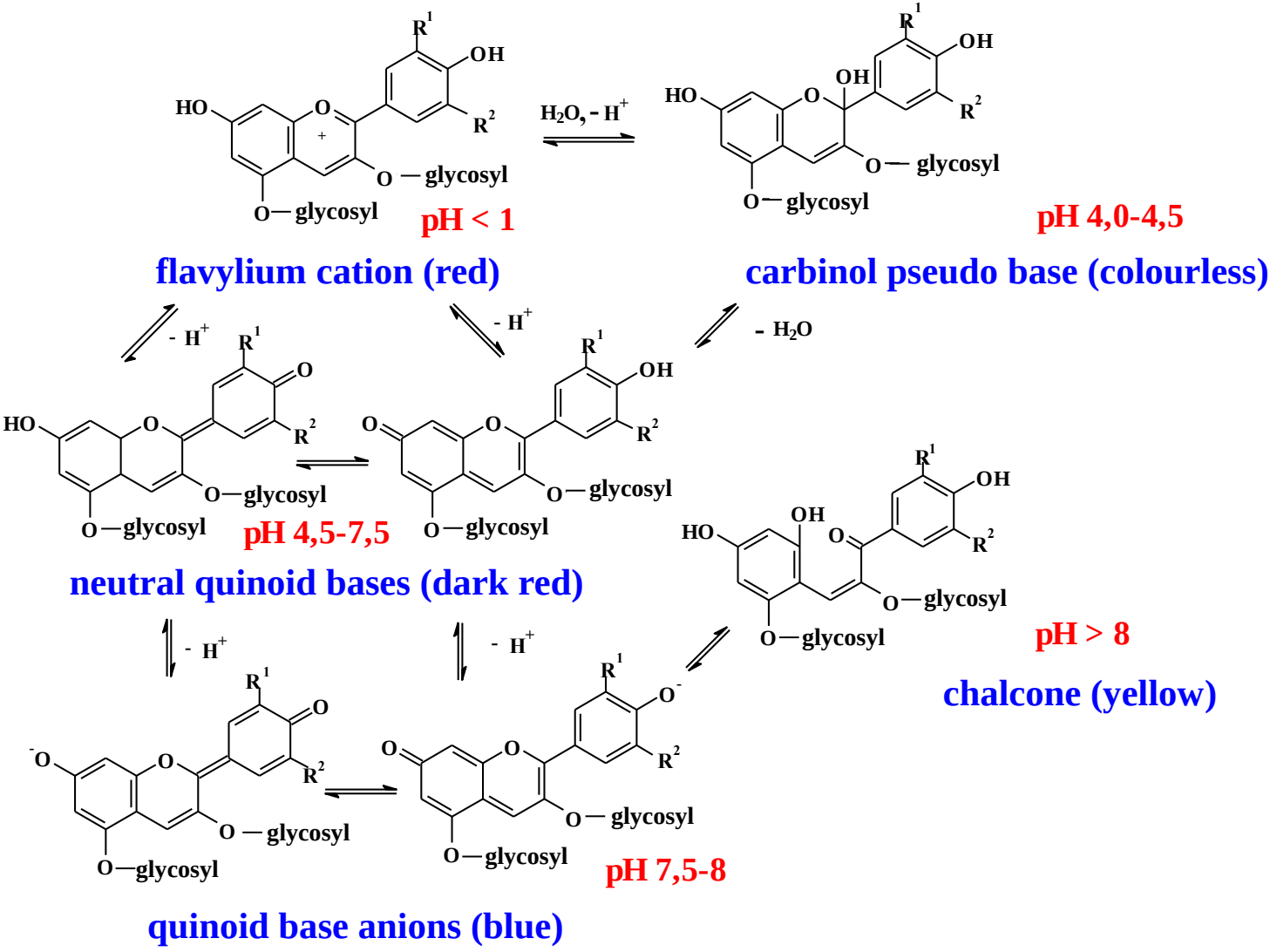
sophorose = β-D-Glc*p*-(1→2)-D-Glc*p*

rutinose = α-L-Rha*p*-(1→6)-D-Glc*p*

colour changes due to different factors

- pH
- co-pigmentation, eventual transformation into other pigments
- SO_2
- H_2O_2

pH


pH < 1
flavylium cation (red)
pH 4,0-4,5
carbinol pseudo base (colourless)
pH 4,5-7,5
neutral quinoid bases (dark red)
pH > 8
chalcone (yellow)
pH 7,5-8
quinoid base anions (blue)

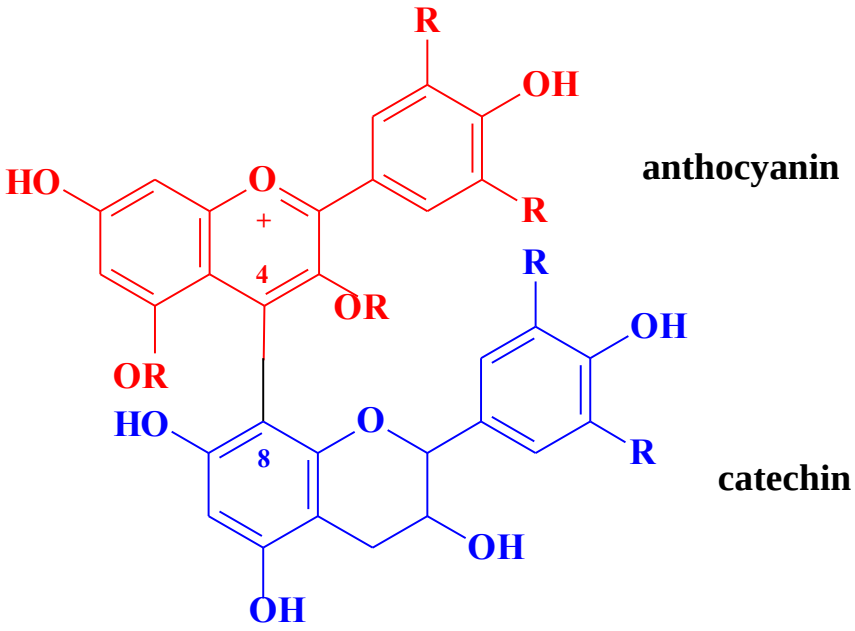
copigmentation

interaction with procyanidinins

(catechins = copigments) → coloured complexes

transformation into other pigments

coloured complexes → dimers (oligomers)



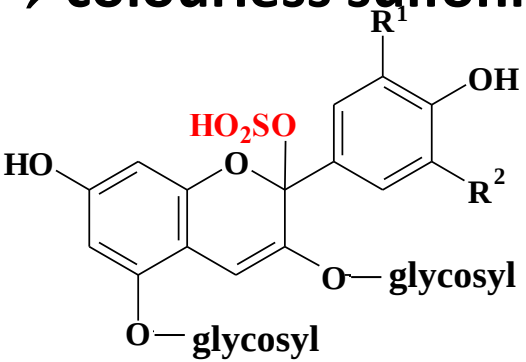
anthocyanin

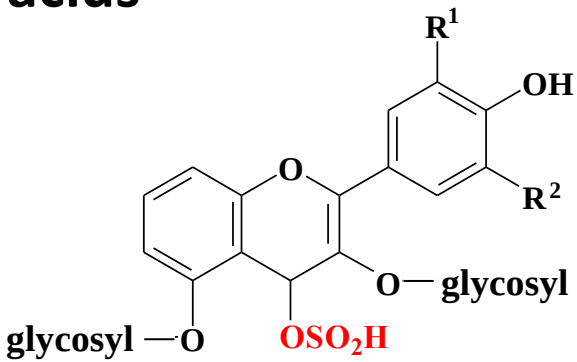
catechin

non-soluble condensation products, polymeric compounds

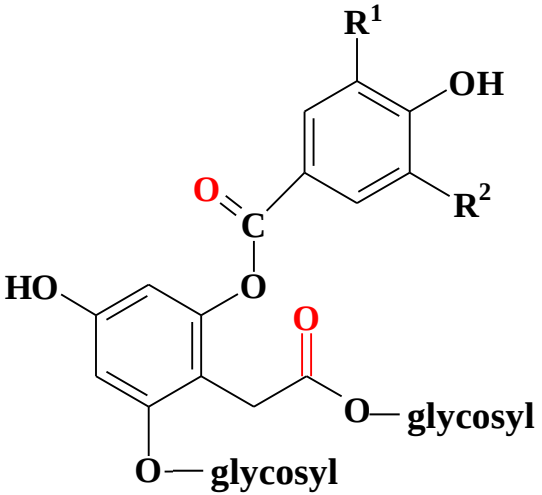
flobafens

SO_2→ colourless sulfonic acids





H_2O_2→ colourless products



Anthoxanthins

flavanones

- pigments of low importance
- bitter compounds of grapefruits

  naringin = naringenin + neohesperidose

  neohesperidin = hesperetin + neohesperidose

flavanonols

- pigments of low importance

flavones

- important anthoxanthins

flavonols

- important anthoxanthins
- antioxidant activity,

rutin = kvercetin + rutinose, bioflavonoids

Isoflavones

- pigments of low importance (e.g. in soybeans)
- estrogenic activity

chalcones and aurones

- important pigments of flowers
  (karthamin)

dihydrochalcones

- pigments of low importance

neohesperidindihydrochalcone (synthetic sweet compound)

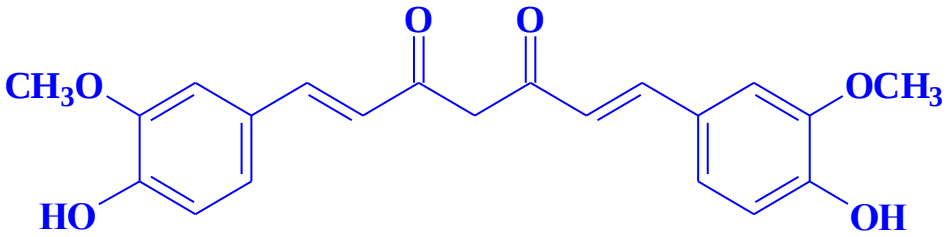
QUINOID PIGMENTS

lichens, mushrooms, higher plants

- phenols
- quinones

phenols

curcuminoides (diarylheptanoides)



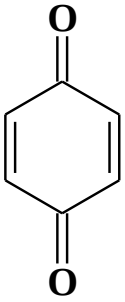
curcumin (curcuma, curry)- yellow to orange

Extraction from rootstock

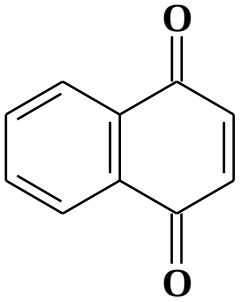
Turmeric (*Curcuma longa*)

quinones

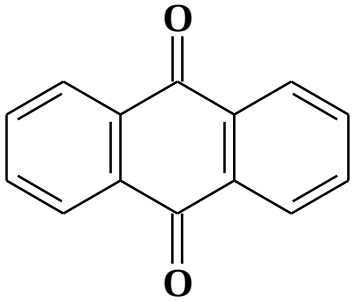
- benzoquinones
- naphtoquinones
- anthraquinones



benzo-1,4-quinone



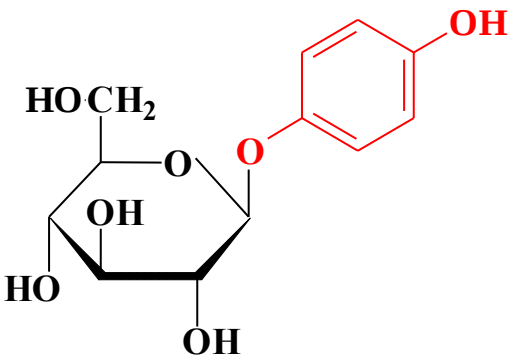
naphtho-1,4-quinone



anthra-9,10-quinone

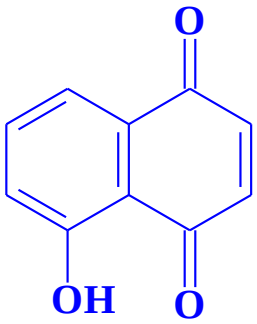
Benzoquinones

arbutin (cranberry leaves, antiseptic activity)



Naftoquinones

juglone (leaves of walnut, 4-β-D-glucosid 1,4,5-trihydroxynaphtalene)
(relative gossypol in cotton seeds, related coenzymes Q, vitamins K)

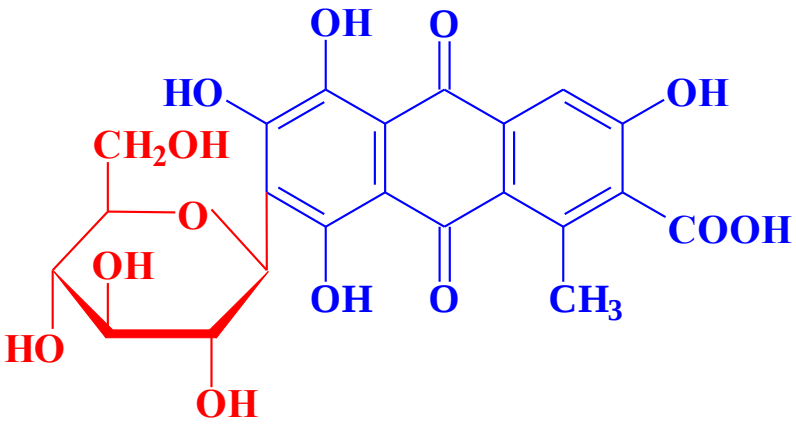


Anthraquinones

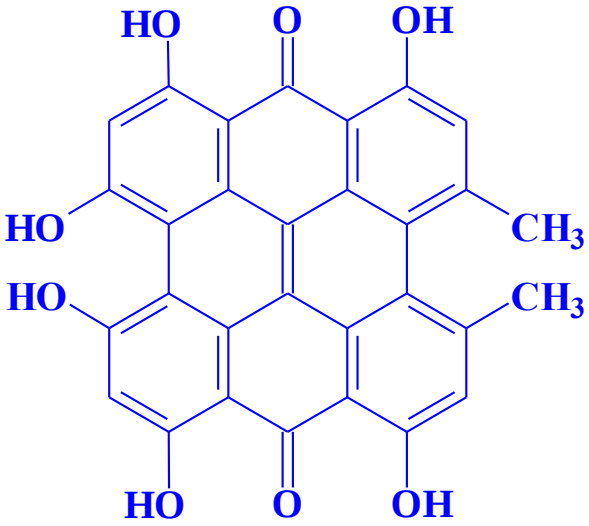
related emodins, bianthrons

carminic acid (cochineal, dried bodies of female beatles Coccus cacti)

E120 – meat and diary products, candy



hypericine (St. John's wort)



carotenoid pigments

yellow, orange, red up to violet

pigments of plants and microorganisms (in mammals)

- **carotenoids (tetraterpenes, 40 C atoms, trans-isomers)**

  hydrocarbons — **carotenes**

  O-derivatives — **xanthophylls**

  neocarotenoids (*cis*-isomers)

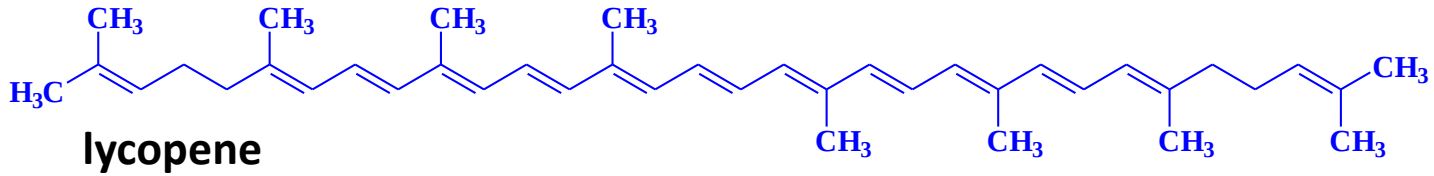
- **degradated carotenoids**

  (30, 20, 15, 13, 10 C atoms)

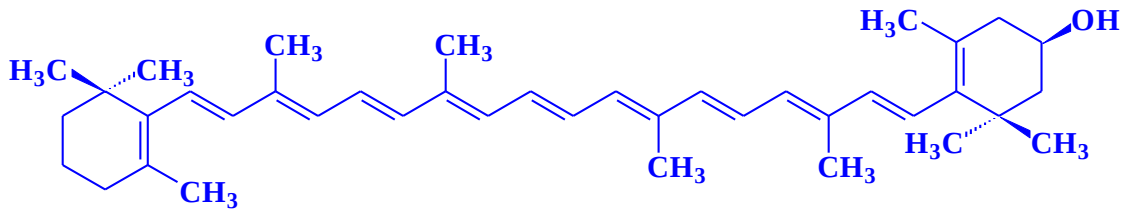
Carotenes

acyclic and alicyclic hydrocarbons

lycopene: tomato, rose-hip,
β-carotene: carrot, apricot, mango



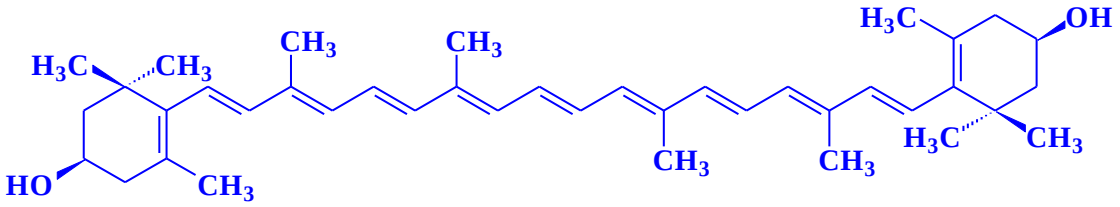
lycopene



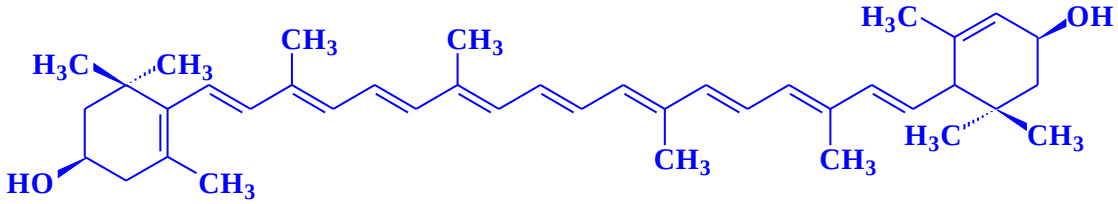
β-carotene

Xanthophylls

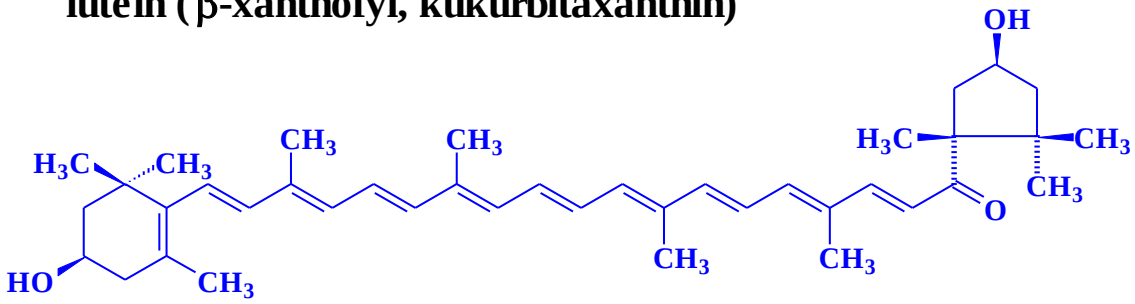
alcohols, ketones, epoxides
free, bound (glycosides,
fatty acids esters,
carotenoproteins)



zeaxanthin

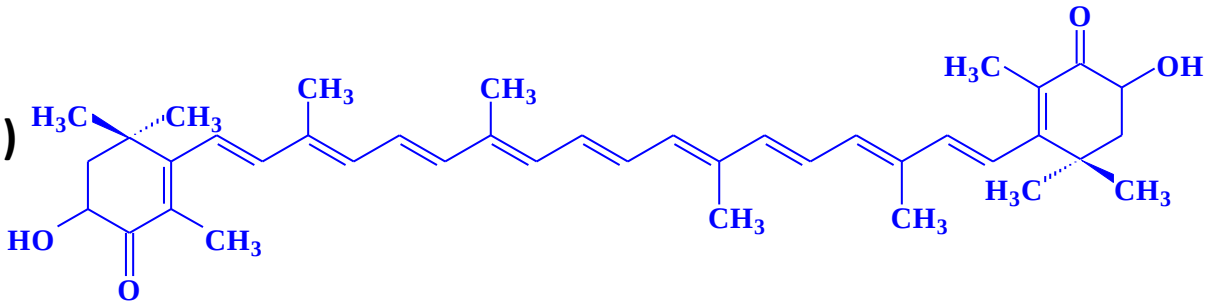


lutein (β-xanthofyl, kukurbitaxanthin)



kapsanthin

zeaxanthin, lutein:
generally wide-spread
kapsanthin:
red bell pepper
astaxanthin:
fish, shellfish (α-crustacyanin)



astaxanthin

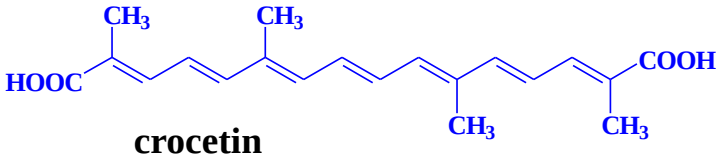
Contenten (mg/kg)

Carotenoids	Apricot	Orange	Carrots	Spinach	Tomato
Carotnes					
Lycopene	0.1				16-750
Neurosporene					3.0
ξ-Carotene	0.4	0.5			8.4
Phytofluene	0.3	1.3			5.1
Phytoene	0.6	0.4			6.0
β-Carotene	64	0.1-0.4	46-103	33-89	2.8-5.8
α-Carotene		0.1-0.2	22-49	trace	
γ-Carotene	0.2		6.3-27		0.4-1.6
Xanthophylls					
5,6-epoxylycopene					5.3
β-Cryptoxanthin		0.1-7.1			
Zeaxanthin		0.5			
Lutein		0.3	1.1-5.6	42-81	0.4-1.3
Antheraxanthin		0.6			
Violaxanthin		0.7		74	
Neoxanthin				24	
Mutatoxanthin		0.6		5.0	
Luteoxanthin		1.7			
Auroxanthin		1.2			

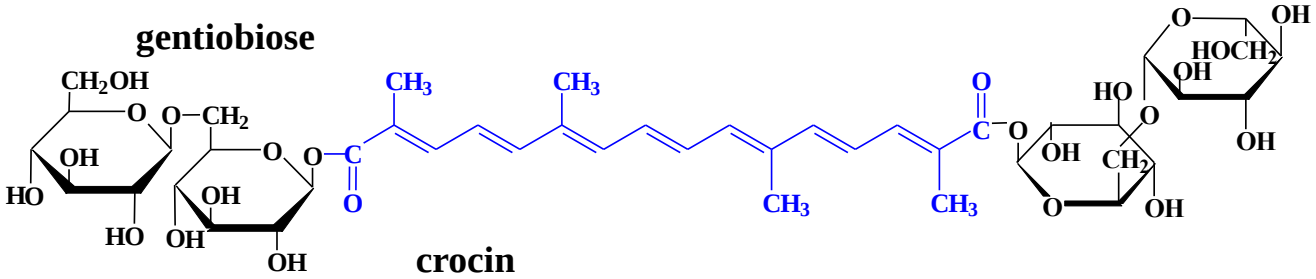
degradated carotenoids

crocin (18 C)

saffron (Crocus sativus), spice



crocetin



crocin

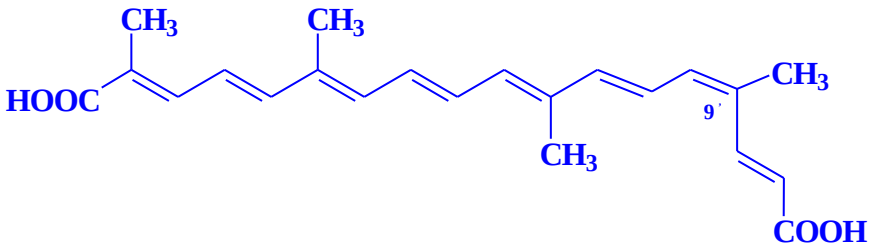
- 1 kilogram of dried saffron is roughly 150 000 and 200 000 flowers →high price
- odor is sharp and pungent, tastes warm, earthy, musky

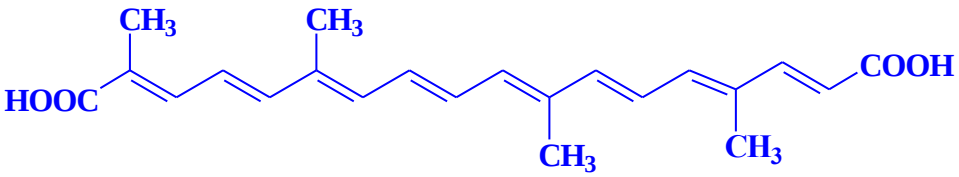
annato (20 C)

bixin (Bixa orellana)

- **extract 0,2-0,5% = mixture cis/trans-isomers,**
- **cheese and margarine colouring**

Annatto is commonly used in Latin American and Caribbean cuisines as both a coloring and flavoring agent.





reactions

- hydrolysis of esters, glycosides
- dehydration of alcohols to hydrocarbons
- cis/trans isomeration

  (neocarotenoids, low colour intensity)
- autoxidation

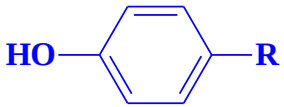
  (low colour intensity, even decolourisation)
- antioxidants

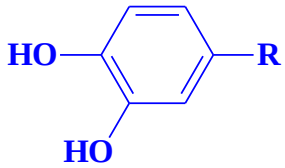
consequences

- flour bleaching
- colour changes of orange juices
- food flavour
- beneficial food components

ENZYMATIC BROWNING REACTIONS

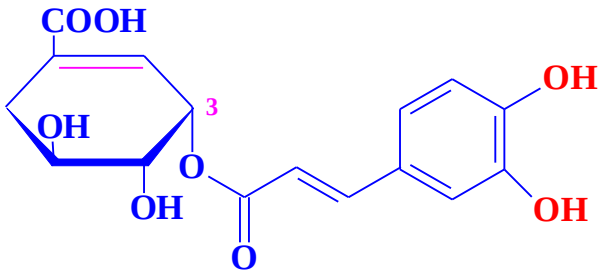
substrates



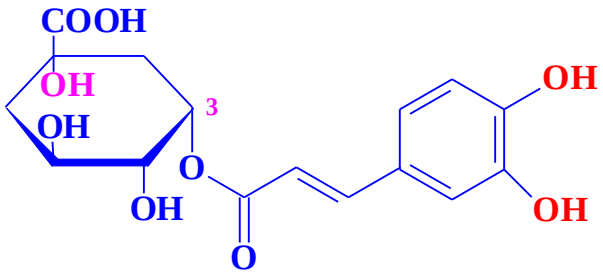


phenols, diphenols (polyphenols), esters (depsides), glycosides

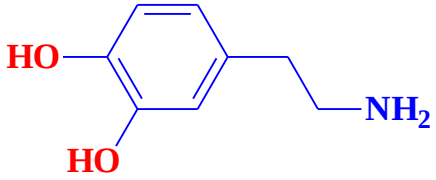
Food	Substrate
Potatoes	Tyr, chlorogenic acid, catechins
Apple flesh	chlorogenic acid
Apple skin	flavonoids (catechins)
Pears	chlorogenic acid (caffeic + quinic)
Olives	3,4-dihydroxyphenylethanol and its derivatives
Bananasy	3,4-dihydroxyphenylethylamie
Dates	dactyliferic (caffeic + shikimic) acid
Beans	DOPA
Mushrooms	Tyr, terfenylchinons
Tea	flavonoids (catechins)
Coffee	chlorogenic and caffeic acid
Cocoa	flavonoids (catechins)



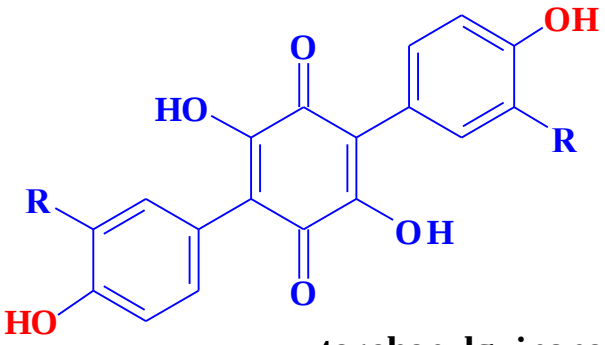
chlorogenic acid



dactyliferic acid



3,4-dihydroxyphenylethylamie

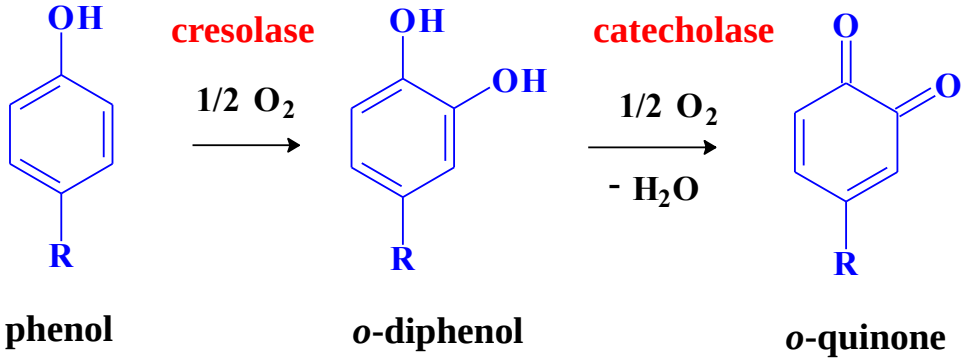


terphenylquinones

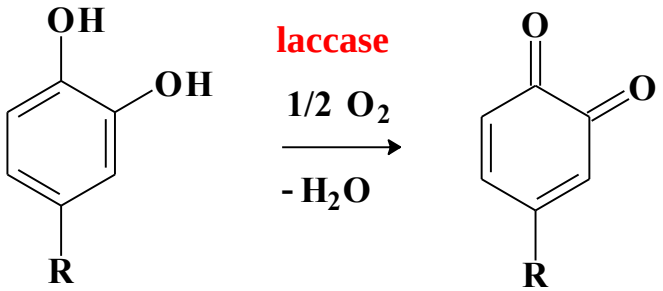
enzymes

Polyphenoloxidases

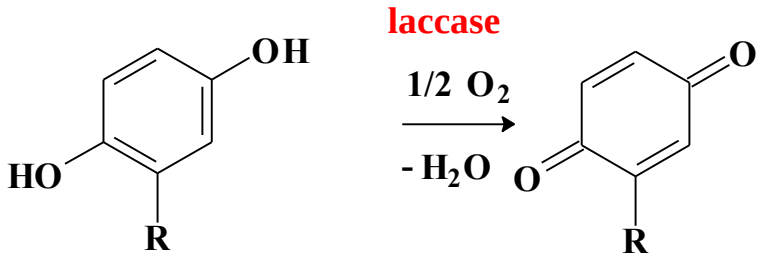
- **catecholoxidase**



♦ laccase



o-diphenol *o*-quinone



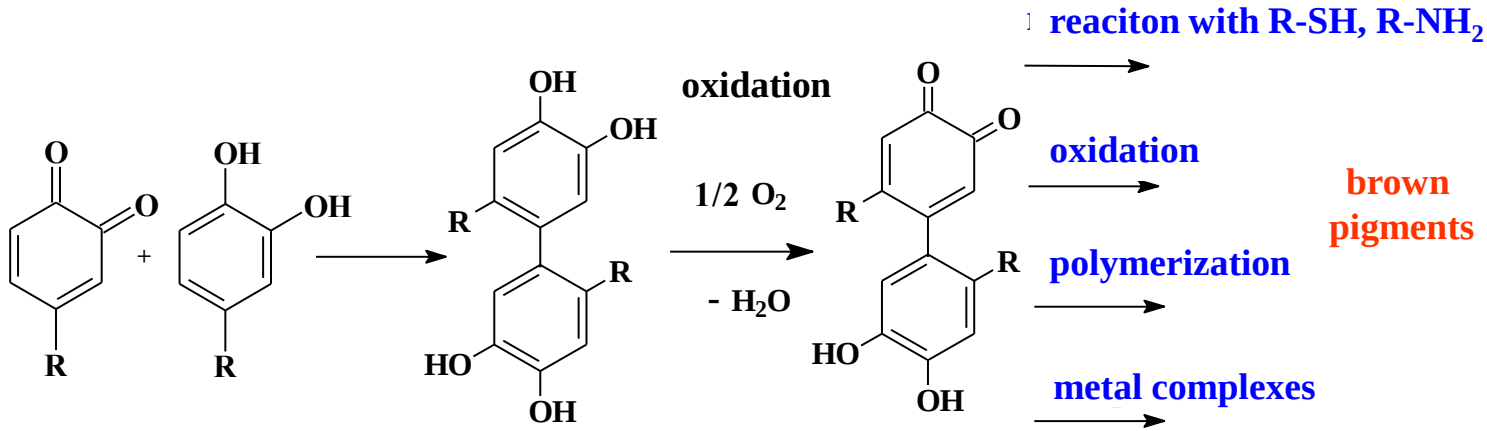
p-diphenol *p*-quinone

catechin oxidation — yellow quinone

chlorogenic acid oxidation — yellow-orange quinone

DOPA oxidation — orange quinone

Non-enzymatic oxidation



inhibition of browning (book 3, tab. 9.16)

- inhibition of enzymes (oxygen elimination , decrease of pH)
- chelatation of metals (Cu^{2+})
- use of reducing compounds (ascorbic acid, SO_2)

desirable reactions

- tee fermentation
- cocoa fermentation
- olive fermentation

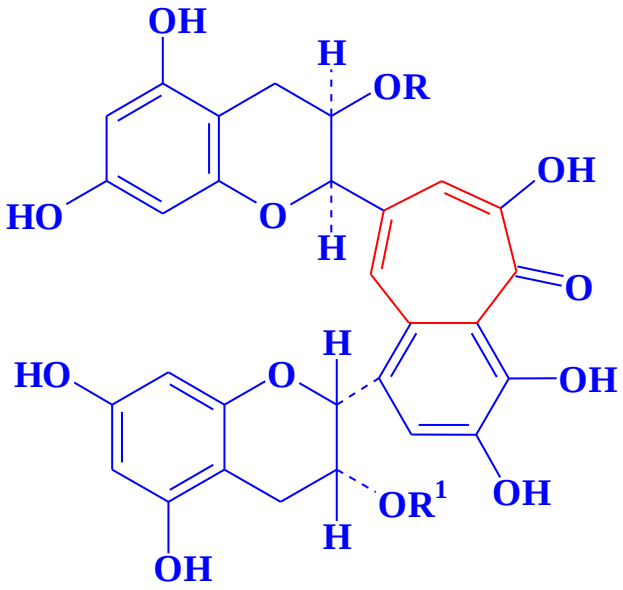
black tea

precursors in green tea

- epigallocatechingallates
- epicatechins
- epicatechingallates
- epigallocatechins

main types of black tea pigments

- theaflavins (oxidised flavonoid dimers),
  orange-red (seven-carbon tropolone cycles)



- **thearubigines** (polymers, 700-400 000 Da),
  red-yellow up to orange-brown