

Chemical additives in food

**Pigments** 

Flavor

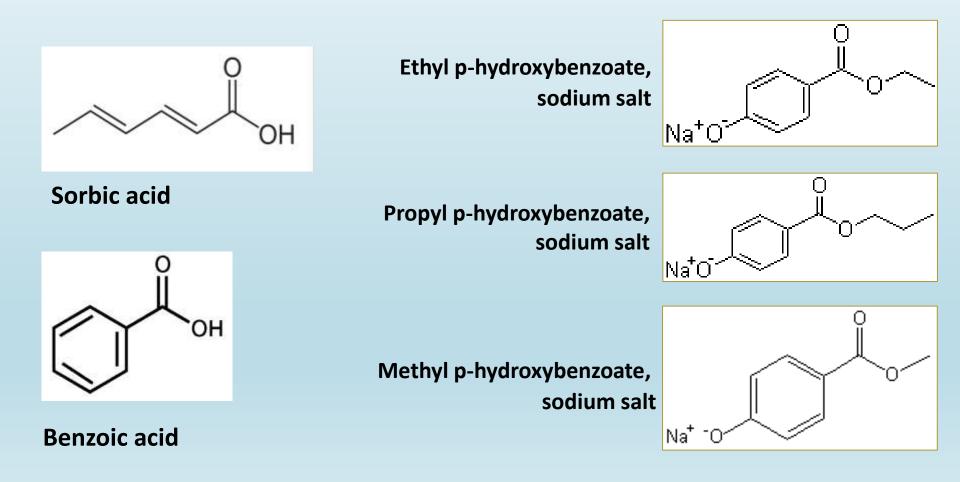
## **18. Antioxidants**

"substances that extend the shelf life of food, protecting from alterations caused by oxidation"

## **19. Preservatives**

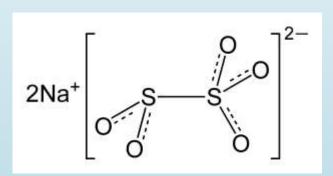
"substances that extend the shelf life of food protecting from alterations caused by microorganisms"

PART A: Sorbates, benzoates, and p-hydroxybenzoates (acids and their salts with K, Na, Ca, etc)



#### PART B: Sulfur dioxide and sulfite salts

Sulfur dioxide Sodium sulfite Sodium hydrogensulfite Sodium metabisulfite Potassium metabisulfite Calcium sulfite Calcium hydrogensulfite  $SO_2$   $Na_2SO_3$   $NaHSO_3$   $Na_2S_2O_5$   $K_2S_2O_5$   $CaSO_3$  $KHSO_3$ 

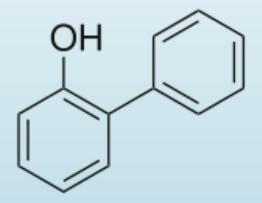


Sodium metabisulfite

- Levels of SO<sub>2</sub> are expressed as mg/kg or mg/l (ppm)
- Content <10 mg/kg or mg/l is considered non existing</li>

#### **PART C: Other Antioxidants - Preservatives**

Biphenyl o-Phenylphenol Nisin Natamycin Boric acid/sodium salt Nitrates Nitrites Lysozyme Propionic acid / salts

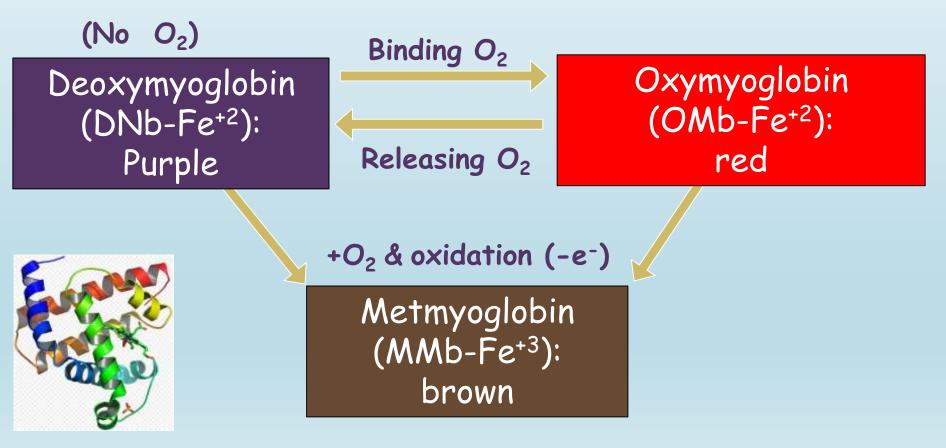


o-Phenylphenol

#### Nitrates, Nitrites

Used in non-thermally processed meat products, cured, dried, canned, foie gras, hard, semi-hard & semisoft cheeses, fish, pickles, etc.

# Muscle tissue - color

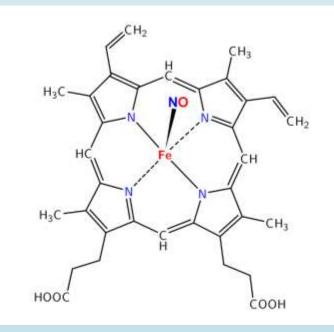


Nitrates, Nitrites

#### Nitrates & nitrites action:

maintenance & stabilization of a desired red-pink color in meat products, by reaction with myoglobin (Mb)

Mb +  $NO_2$   $\rightarrow$  red stable pigment nitrosomyoglobin  $\xrightarrow{heat}$  a more stable pink pigment, Nitroso chromogen, with its protein moiety denatured, which is responsible for the characteristic pink color of cured products

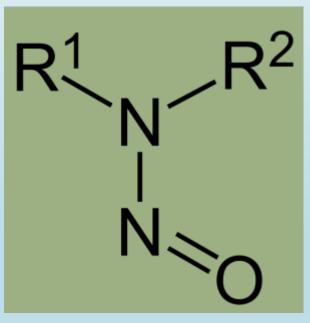


nitrosomyoglobin (heme)

Nitrates, Nitrites

safety-toxicity:

react with proteins to form carcinogenic substances (**nitrosamines**)

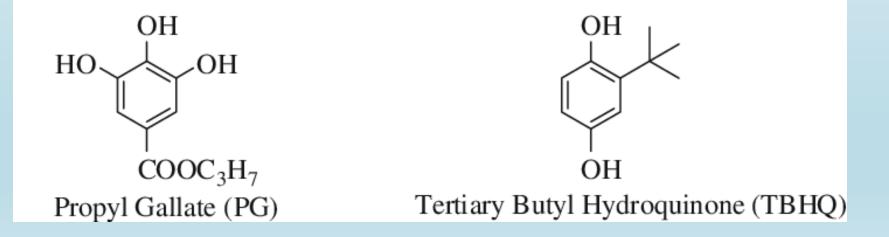


Nitrosamine

**PART D: Other Antioxidants - Preservatives** 



Butylated Hydroxy Anisole (BHA) Butylated Hydroxy Toluene (BHT)



**PART D: Other Antioxidants - Preservatives** 

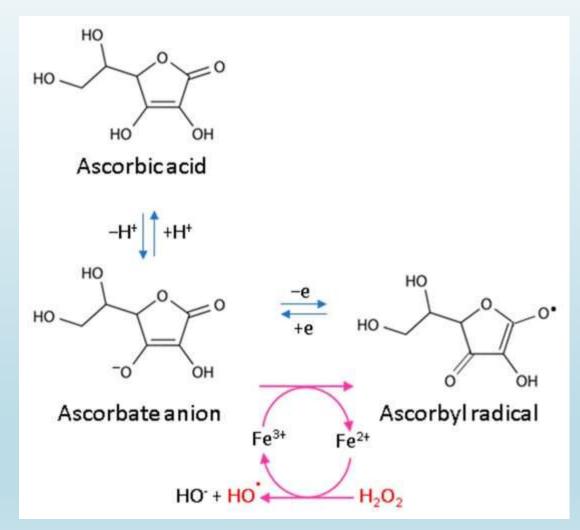
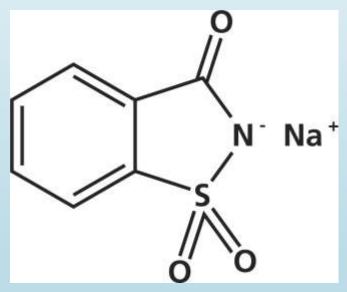


Figure. Scheme of ascorbic acid reaction under oxidative conditions.

https://doi.org/10.3390/antiox11101993

Sweeteners are defined as food additives which are used:

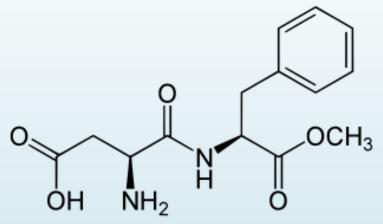
- 1. To impart a sweet taste to food
- 2. As table sweeteners



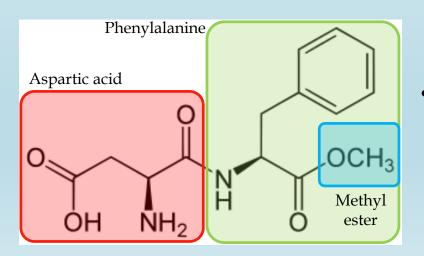
Saccharin (aka saccharine)

- Non-caloric sweetener substance
- x 300 sweeter than sugar
- The first sweetener that was used in food, mainly for diabetics
- Acceptable daily intake (ADI) < 1 mg/kg

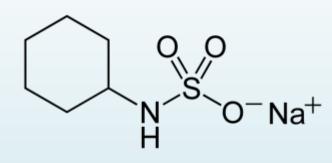
Preferred IUPAC name 1H-1 $\lambda$ 6,2-Benzothiazole-1,1,3(2H)-trione Other names: ortho-benzoic sulfimide, ortho sulphobenzamide



**Aspartame** Preferred IUPAC name Methyl L-α-aspartyl-L-phenylalaninate Other names: N-(L-α-Aspartyl)-Lphenylalanine, 1-methyl ester



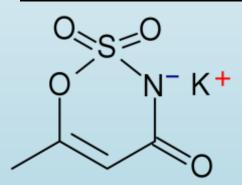
- 4 kcal/g, but the caloric contribution is zero given the small required quantity for achieving the same sweeting result as sugar
- was manufactured by Monsanto and commercialized in 1981
- 2000 tn of aspartame are consumed in Europe annually
- **x 180-200** more sweet than sugar
- Not appropriate for foods that are going to undergo baking, because at high temperature it breaks down and loses the sweet taste
- Its use must be avoided from people
  suffering from the metabolic disease
  phenylketonuria (PKU), an inborn error of
  metabolism that results in decreased
  metabolism of the amino acid phenylalanine



#### Sodium cyclamate

Preferred IUPAC name Sodium cyclohexylsulfamate

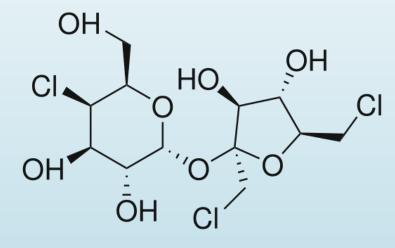
- It is often used with other artificial sweeteners, especially saccharin
- Cyclamate is the sodium or calcium salt of cyclamic acid (cyclohexanesulfamic acid), which itself is prepared by reacting freebase cyclohexylamine with either sulfamic acid or sulfur trioxide
- x 30-50 more sweet than sugar



# Acesulfame potassium (acesulfame K)

Preferred IUPAC name Potassium 6-methyl-2,2-dioxo-2H-1,2λ6,3-oxathiazin-4-olate

- Has no caloric value
- Like saccharin, it has a slightly bitter aftertaste, therefore if often blended with other sweeteners (usually sucralose or aspartame)
- It stimulates the secretion of insulin and may cause hypoglycemic incidents
- x 200 more sweet than sugar



#### Sucralose

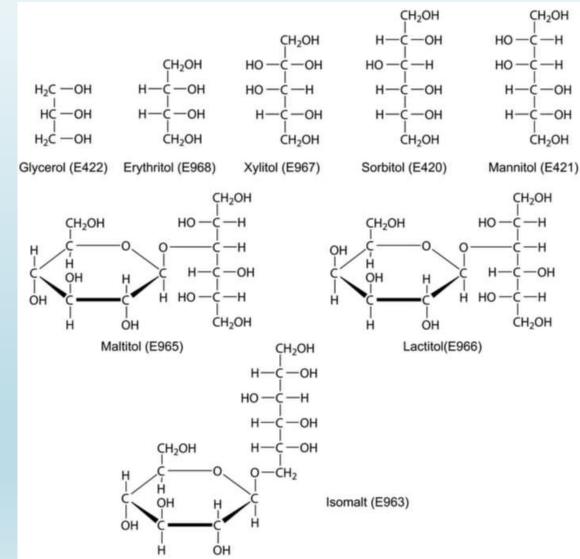
Preferred IUPAC name 1,6-Dichloro-1,6-dideoxy-β-Dfructofuranosyl-4-chloro-4deoxy-α-D-galactopyranoside

- Is x 600-700 times sweeter than sugar
- Is produced by selective chlorination of 3 OHgroups of sucrose
- Suitable for foods that are submitted to high temperatures & large ranges of pH
- Better taste, sweetener capability, stability & safety than other synthetic sweeteners
- In small ones quantities there is no indication of toxicity - it is extremely insoluble in fat unlike most chlorinated compounds
- Does not break down neither is dechlorinated below 120 °C – not suitable for higher temperatures
- EFSA proposed an ADI of 5 mg per kg bw (body weight) while FDA an ADI of 15 mg per kg bw (350–1050 mg per day for a person of 70 kg).

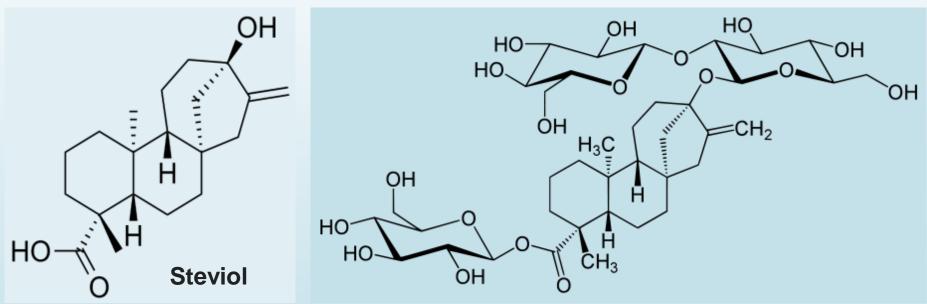
- Smaller or equal sweetness with sucrose
- Suitable for diabetics and prevention of tooth decay
- •Generally considered safe causing diarrhea in large doses

Compound	Sweetness %	Glycemic index	Kcal/g
Sucrose	100	60	4
Maltitol syrup	75	52	3
Maltitol	75	36	2.7
Xylitol	100	13	2.5
Sorbitol	60	9	2.5
Lactitol	35	6	2
Mannitol	60	0	1.5

## Sugar alcohols (polyols)



#### **Steviol glycosides**



- Steviol glycosides are chemical compounds responsible for the sweet taste of the leaves of the S. American plant *Stevia rebaudiana* (*Asteraceae*)
- Are the main ingredients of many sweeteners marketed under the generic name stevia
- Are x **30-320** times sweeter than sucrose
- Do do not induce a glycemic response because humans cannot metabolize stevia
- ADI for steviol glycosides, expressed as steviol equivalents, has been established to be 4 mg/kg bw/day.

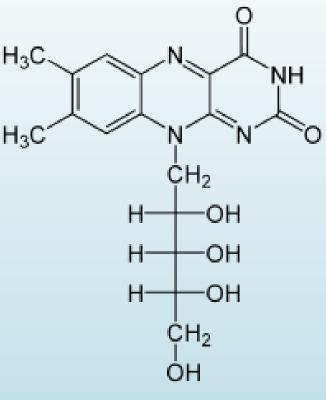
- Substances that are added to restore the color of food
- They include natural food ingredients and natural substances not normally consumed as food and they are not used usually as components of food, e.g.:
  - E 100 Curcumin
  - E 101 Riboflavin & 5-P-riboflavin (Vitamin B2)
  - E 102 Tartrazine
  - E 104 Quinoline Yellow
  - E 120 Cochineal, carminic acid, carmines
  - E 122 Azorubin
  - E 123 Amaranth
  - E 124 Ponceau 4R, cochineal red A
  - E 129 Allura Red AC
  - E140-141 Chlorophylls, chlorophyllins
  - E150a,b,c,d Caramel colors
  - E163 Anthocyanins
  - E170 CaCO 3
  - E171 TiO<sub>2</sub>
  - E174 Ag
  - E175 Au
  - Etc.....



https://www.linkedin.com/pulse/food-color-benefits-safety-dipali-patil/

#### E 101 - Riboflavin & 5-P-riboflavin

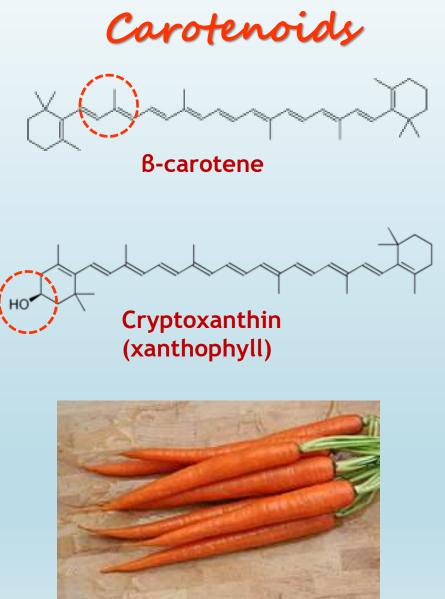
- Part of the flavino-coenzymes FAD & FMN
- Yellow-orange pigment
- Is produced biotechnologically from microorganisms such as Ashbya gossypii, Candida famata & C. flaveri, Corynebacterium ammoniagenes, Bacillus subtilis, modified genetically or not
- It holds up at heating but is destroyed with exposure to light or in alkaline environment
- It is used for coloring children foods, breakfast cereals, pasta, sauces, processed cheese, drinks, fruit, enriched milk products, and energy drinks
- Adding it to aqueous foods is difficult because it has small solubility, so it is used in the 5'-phosphateriboflavin (E101a) form, which is more expensive but more stable



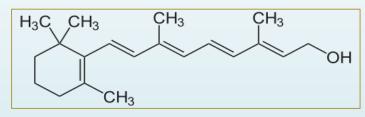


## **21. Colorings (natural and synthetic pigments)** E 160 – Carotenoids

- Yellow, orange, red pigments
- They are found in all photosynthetic cells, but are covered by chlorophyll and stand out during autumn when chlorophyll decomposes
- They are linear molecules with conjugate systems of doubles bonds, who are responsible for the color
- There are over 600 carotenoids
- which belong to two categories: <u>hydrocarbons (carotenes)</u> and <u>oxygenated</u> <u>hydrocarbons (xanthophylls)</u> with chains of 40 C atoms
- They are all tetraterpenoids [8 units of isoprene (2-methyl-1,3-butadiene)]

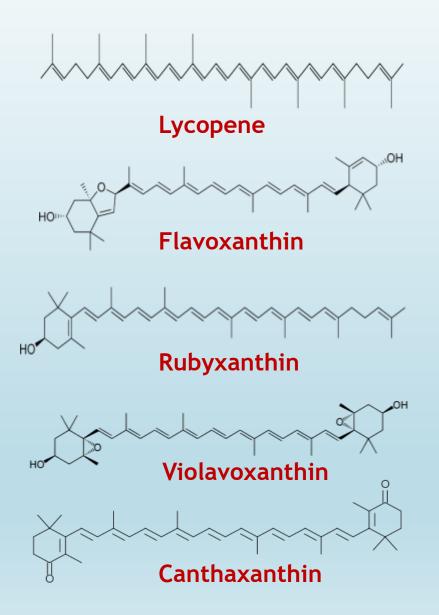


#### E 160 – Carotenoids



Vitamin A (retinol)

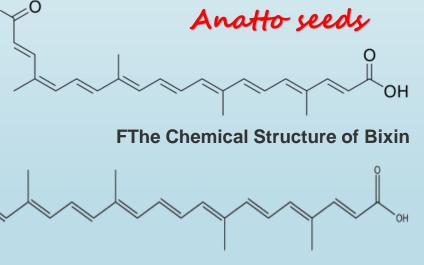
- In humans, carotenoids (mainly βcarotene, the more abundant at foods) have a vitamin action, as they are converted in retinol
- They have antioxidant action
- They are mainly produced in plants, algae, photosynthetic bacteria and some fungi
- Animals do not produce carotenoids, and must receive them from food



### **21. Colorings (natural and synthetic pigments)** E160b - Annatto, Bixin & Norbixin

- Annatto is an orange-red food coloring derived from the seeds of the achiote tree (*Bixa orellana*), native to tropical America.
- It is often used to impart a yellow or orange color to foods, but sometimes for its flavor and aroma (slightly peppery slightly nutty).
- The color of annatto comes from various carotenoid pigments, mainly **bixin** and **norbixin**, found in the reddish waxy coating of the seeds.
- Annatto and its extracts are now widely used as a coloring agent in processed food such as cheeses, dairy spreads, butter, margarine, baked goods, snacks foods, breakfast cereals, sausages etc.
- It has been linked to rare cases of food-related allergies.

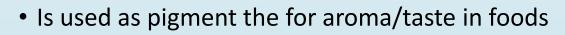




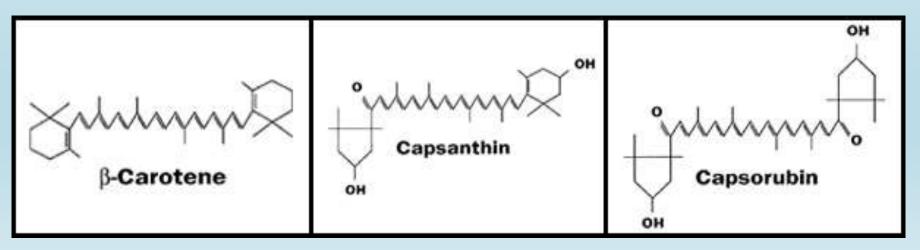
The Chemical Structure of Norbixin

https://www.differencebetween.com/what-is-thedifference-between-bixin-and-norbixin/

- E160c Paprica pigments, Capsanthin & Capsorubin (Di-hydroxy, keto-carotenoids)
- Paprika is the fat-soluble extract of the fruits of Capsicum Annum Linn the *Capsicum frutescens* (Indian origin red peppers)



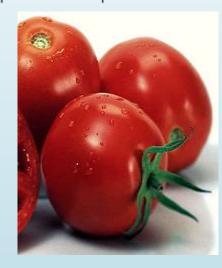
- The main flavoring substance is capsaicin, while the pigments are **capsanthin** and **capsorubin**, among other carotenoids
- Extraction is done with solvents such as hexane

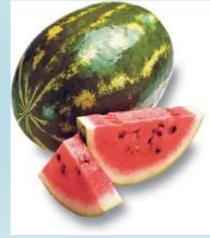




# **21. Colorings (natural and synthetic pigments)** E160d - Lycopene

- Carotenoid pigment an intermediate of the biosynthesis of many carotenoids
- It is a shiny red pigment of tomato (from where it is commonly isolated), red carrots, red peppers, watermelon, papaya etc., but not strawberries and cherries (their colors are due to anthocyans)
- Although a carotenoid, it does not have vitamin A action
- It is the strongest carotenoid antioxidant (100 times stronger than Vit. E)
- It has antiaging, anticancer, cardioprotective properties and other health benefits
- Not toxic, it accumulates in liver and other organs or glands, and extensive use may result in discoloration of the skin (lycopenodermia)
- However, rare cases have been reported of allergy or intolerance (diarrhea, nausea, loss of appetite etc.)

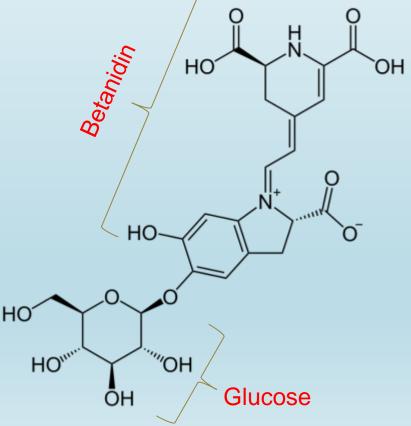




#### E162 – Betanin or Beetroot red

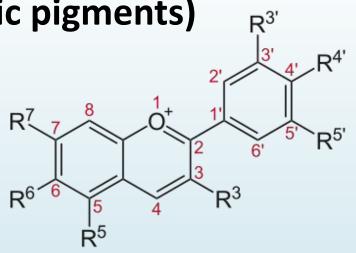
- Is a red glycosidic pigment of beets, from which it is produced by extraction
- The aglycone part is called betanidin
- It breaks down when exposed to light, the heat and the oxygen
- Used in dried or frozen products with small duration life, and in foods with added antioxidants and appropriate packaging (meat products, ice cream, soft drinks, confectionery, coatings, soups, etc.)
- No allergenic effect has been reported and it has antioxidants properties





### E163 – Anthocyanins

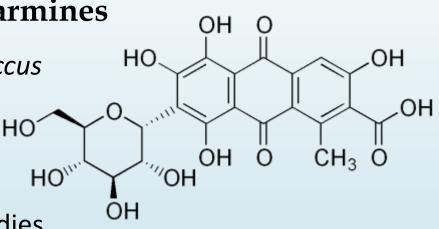
- Red, purple & blue pigments (flavonoids, glycosides of anthocyanidins)
- They are present in large quantities in mature dark olives
- Hybridization techniques and genetic engineering have created plants with unusually large amounts of anthocyanins (e.g. tomatoes)
- They are powerful antioxidants with anti-aging, anticancer, anti-inflammatory, antidiabetic, and antimicrobial properties.
- The antioxidant properties decrease drastically with digestion
- Commercial anthocyanins are usually extracted from grapes or red cabbage with water, ethanol or ethanol
- Their color is affected by pH so they are unsuitable for some types of food





#### E 120 Cochineal, carminic acid, carmines

- It is extracted from dried *Dactylopius coccus* insects
- It causes strong allergic reactions
- Is used in juices, ice cream, yoghurt, candies
- Other names: Crimson lake, Natural Red 4
- It is produced from its carminic acid aluminum (AI) salt:
- The insects are collected, dried and powdered, boiled with ammonia solution or sodium carbonate, the solid residue is removed by filtration, and Al is added for precipitation of carminic acid

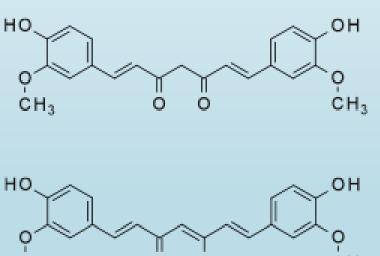




#### E 102 - Curcumin

- It is used as a pigment or for the protection of food from spoilage due to exposure to light
- Is used in cheeses, butter, margarines, in combination with annatto, in pickles, broths, mustards etc. as a cheap substitute of Saffron
- It is an antioxidant but at the same time suspected of carcinogenesis
- May cause nausea, diarrhea, hypotension
   & anemia due to complexation of iron



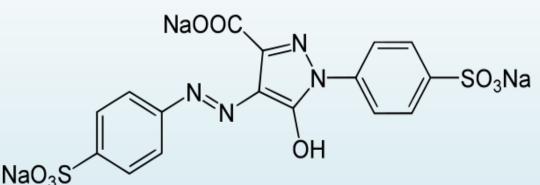


Curcumin keto- & enol- form

 $CH_2$ 

## **21. Colorings (natural and synthetic pigments)** E 100 - Tartrazine NaOOC

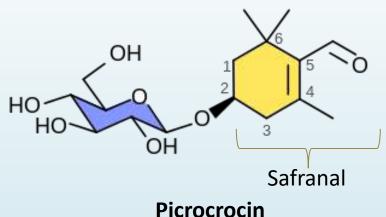
Synthetic, water-soluble, yellow
 azo dye, used in combination
 with blue pigments for
 production of green shades



- The trend is to avoid it or replace it with anatto
- It is contained in food with synthetic green or yellow color such as ice creams, sweets, candies, jellies, pasta, cookies, soft drinks, snacks, chewing gum, jams, mustards, pickles, sauces, cereals, etc.
- Has the most allergic reactions among all azo dyes
- Causes anxiety, migraines, depression, blurred vision, feeling of suffocation, insomnia, asthma, childish aggressiveness and hyperactivity, tumors of thyroid, chromosomal anomalies etc.
- Affects people with aspirin allergy and intolerance to gluten



- Saffron taste and iodoform- or hay-like fragrance result from the phytochemicals picrocrocin and safranal. It also contains a carotenoid pigment, crocin.
- Saffron contains some 28 volatile and aroma compounds, dominated by ketones and aldehydes. Its main aroma-active compounds are safranal – the main compound responsible for saffron aroma – 4-ketoisophorone, and dihydrooxophorone
- Saffron and specifically the dried red stigmata are a product of great aroma value used to correct the color, the smell and the taste of foods





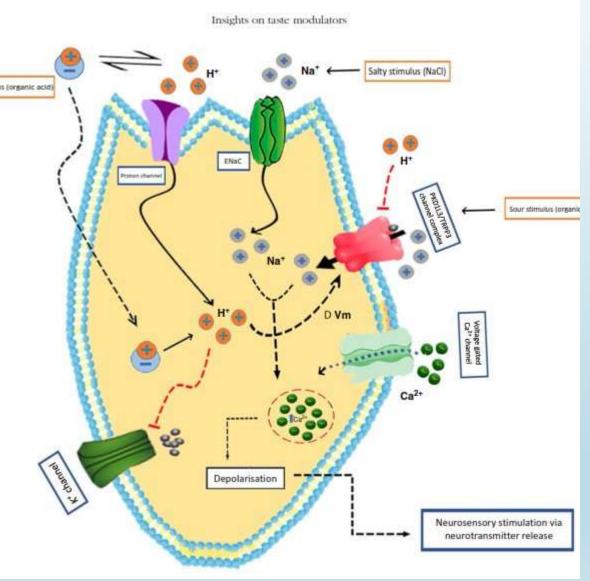
Crocus sativus L.

• Although a red dye, it is classified as yellow, because at the small concentrations usually applied in food it gives yellow shades

- Taste perception refers to those sensations that are elicited by the stimulation of the gustatory receptors on the tongue — sweet, sour, salty, bitter and umami.
- Smell (olfactory) perception is a process that starts in the nose with the stimulation of olfactory sensory neurons and terminates in higher cerebral centers which, when activated, make us consciously aware of an odor.

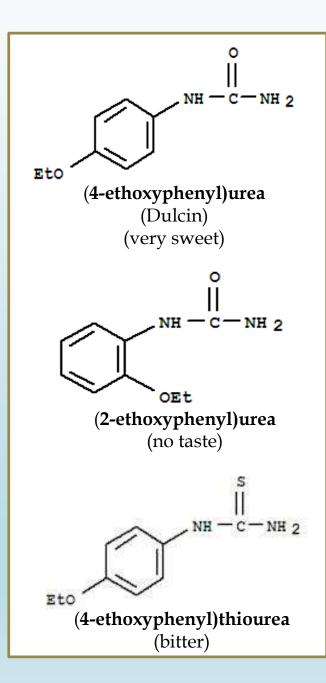


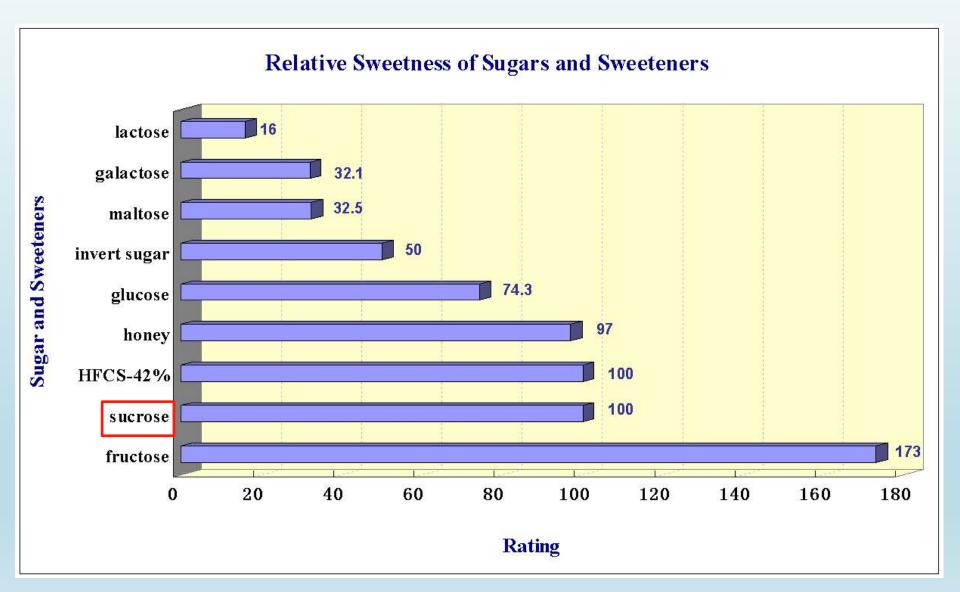
- The salty taste: It is due to the electrolytes , mainly cations
- Sodium & lithium are exclusively salty
- Potassium and other cations are salty & bitte
- The anions (except of chlorine) affect & obstruct the salty taste
- Complex anions give different tastes than salty (e.g. fatty acids: taste soapy)
- Today efforts are made to understanding the salty taste in order to make products low in sodium but equally tasty



https://www.researchgate.net/publication/334293427\_Insights\_on\_modulator s\_in\_perception\_of\_taste\_modalities\_A\_review/figures?lo=1

- Sweet taste perception of a substance is a complicated phenomenon, affected by physical and psychological factors
- Approximate sweetness of substance, relative to sucrose (100%), is estimated by specialized individuals (panel) under controlled conditions,
- Sweetness is affected by the presence of other substances, temperature, and the balance between anomeric structures of sugars
- The relationship between sweet taste & chemical structure is under investigation
- Minor differences affect radically the sweetness of compounds (Figure)

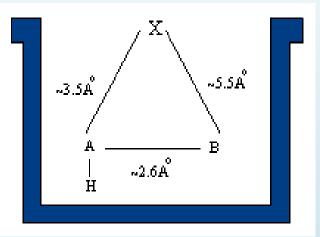




Sweetener	Commonly Reported Relative Sweetness (Sucrose = 1)	
Advantame	20,000	
Neotame	8,000	
Sucralose	600	
Sodium Saccharin	300	
Steviol Glycosides	200-300	
Aspartame	200	
Acesulfame Potassium	200	
Fructose	1.3	
Sucrose	1	
Glucose	0.6	
Mannitol	0.4	

#### Sweet taste: triangle of sweetness

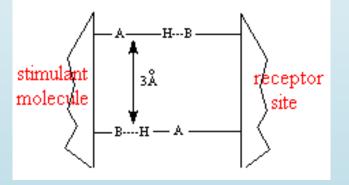
- The theoretical model of sweetness is the multipointattachment theory, which involves multiple binding sites between a sweetness receptor and a sweet substance.
- For sweetness to be perceived, a molecule needs to be soluble in the chemical environment of the receptor site on the tongue.



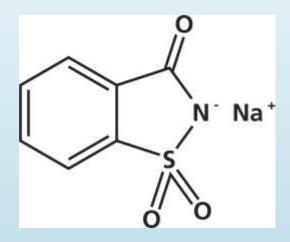
- It must also have a certain molecular shape that will allow it to bond to the protein in the taste bud. Lastly, the sugar must have the proper electronic distribution. This electronic distribution is often referred to as the AH, B system.
- An AH, B, and X site are present and the three sites are often represented as a triangle. The A and B regions of a molecule represent higher regions of electronegativity. Certain atoms represent these regions and the distance between them is greater than 2.4 Å and less than 4.0 Å. If the distance between the atoms are not in this range then molecule becomes bitter.

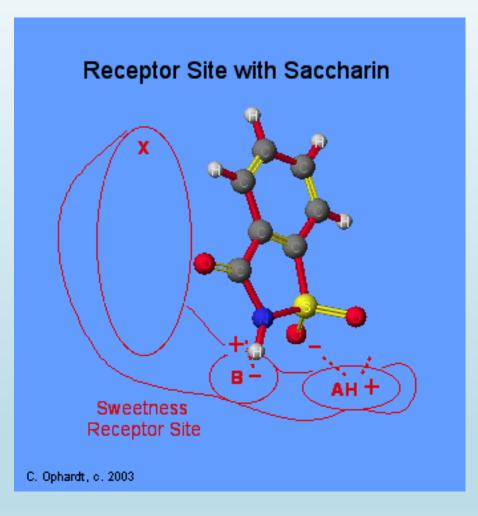
#### Sweet taste: triangle of sweetness

- The A part in the molecule becomes less electronegative because of the addition of a H atom that is bonded to the atom in the A region and thus is referred to as AH and it becomes an electron acceptor. The second region, B, is an electron donor. The third part of this triangle is named X, which represents the hydrophobic and lipophilic region of the molecule. X is represented as a region, not as an atom, and does not bond to the receptor site.
- AH and B regions are also present in receptor sites; the AH region of a sweetener H-bonds to the B region of a receptor site, the B region of a sweetener H-bonds to the AH region of the receptor site. The bonded protein and sugar is released and triggers a response by cells in the taste bud. The cells send electrical impulses to the brain creating the perception of sweetness.

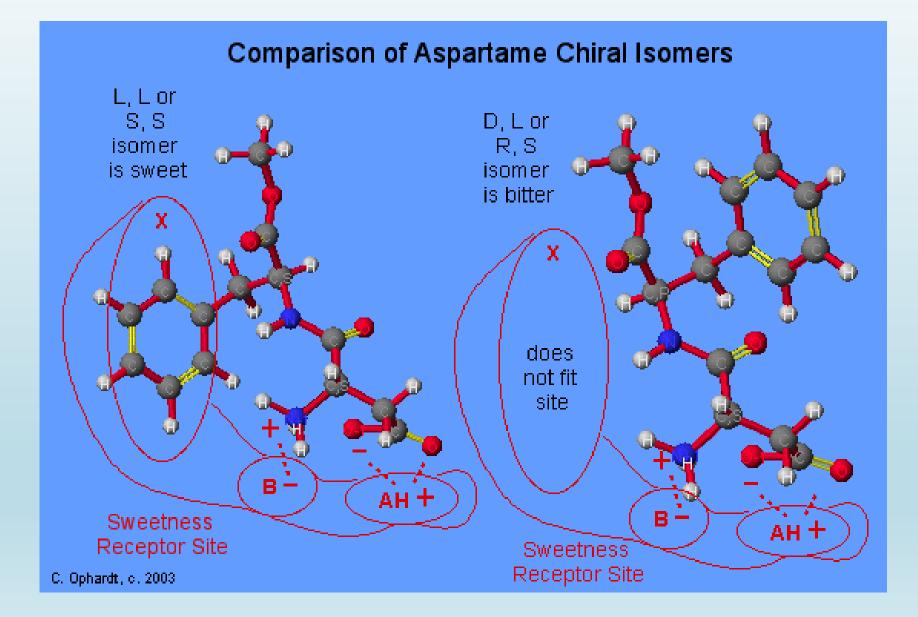


http://shodor.org/succeed-1.0/compchem/projects/fall00/sweetene rs/index.html



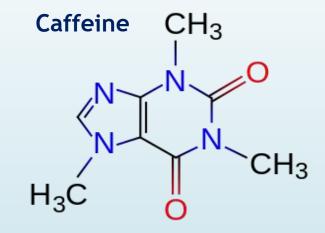


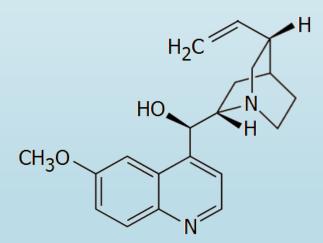
http://chemistry.elmhurst.edu/vchembook/549saccharin.html



#### The bitter taste:

- The bitter taste is also based on the stereochemistry of molecules like sweet taste.
- Bitterness can be desired or unwanted in foods.
- Bitter compounds with interest for food technology are salts, alkaloids, and some flavonoid glycosides.
- The bitterness of a salt depends on the ionic diameter: e.g. <6.5 Å the salt is salty (NaCl, 5.6 Å) and larger ones have increased bitterness (MgCl, 8.5 Å is extremely bitter).</li>
- Among alkaloids, quinine and caffeine are of technological interest because the=ir addition in food is allowed (e.g. Cola type drinks):

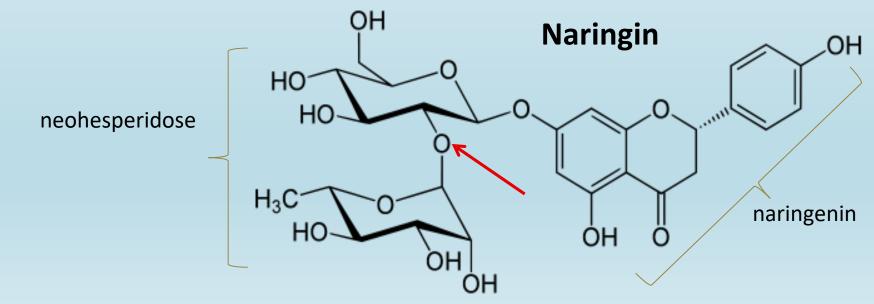




Quinine (alkaloid of cinchona tree *Cinchona pubescens*)

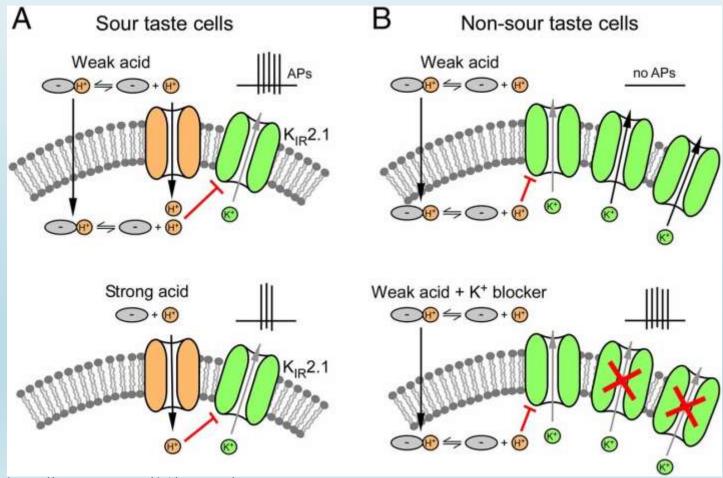
The bitter taste:

- An example of a flavonoid glycoside is naringin of citrus fruits (a flavanone-7-O-glycoside between the flavanone naringenin and the disaccharide neohesperidose).
- The bitterness of the citrus juices is due to the glycosidic bond between rhamnose and glucose moieties
- Debitternes of citrus juices is therefore done with the enzyme **naringinase**, which hydrolyzes this bond



The acidic (sour) taste:

- It is due to hydrogen ions (H<sup>+</sup>)
- It is not related absolutely with their acid strength but also with other characteristics such as the nature of the cation



https://www.pnas.org/doi/10.1073/pnas.1523319113

#### **Compensation and flavour enhancement**

- The perception of taste is affected from the composition, the physicochemical state (solution, foam, gel, etc.), but mainly from the effect of other taste components. E.g. salt reduce the sweetness of sucrose and vice versa
- The phenomenon where one ingredient reduces the intensity of perception of another is called **compensation**.
- Shifts in taste escalate the feeling. E.g. consuming juice after consumption of a sweet makes the juice feel more sour.
- Different individuals perceive the taste different than others or they may not taste certain substances (taste blindness); a property that is genetically inherited.

#### **Odor perception**

- The perception of smell is equally a complicated phenomenon as is taste, and up to a degree it is still inexplicable.
- As a chemical sense, olfaction relies on the sensory detection and perceptual interpretation of odorous molecules in the environment.
- In order to be perceived as odorous, a molecule must be volatile enough to evaporate and have specific solubility characteristics to pass through the (hydrophilic) nasal mucosa and bind to the (hydrophobic) olfactory receptors in the olfactory epithelium.
- In addition, some functional groups have been associated with characteristics of odor quality. E.g., esters are known for fruity odors and some aldehydes are associated with grassy odors.
- Physicochemical properties of odors presumably also influence the perceived intensity and concentration threshold at which an individual can detect them. Intensity is positively associated with vapor pressure.

#### Aroma compounds in food

- The main categories of chemical compounds that are important for the odor of food are:
- Fat acids of small MB (C1–C8): e.g. acetic, butyric, etc.
- Esters of fatty acids & alcohols: e.g. ethyl acetate, isoamyl acetate, etc.
- Alcohols of small and intermediate MB (C1–C10): e.g. ethanol, isobutyl alcohol, amyl alcohols, etc.
- Aldehydes: the small MB are unwanted but higher aldehydes have desired aromas. e.g. acetaldehyde, hexanal, benzaldehyde, phenylacetaldehyde, cinnamaldehyde, anisaldehyde, vanillin, etc.
- **Ketones:** diacetyl, ionones, menthone etc.
- **Terpenes and terpenic alcohols** : e.g. limonene, geraniol, nerol, etc.
- **Lactones**: e.g.  $\delta$ -decalactone and  $\delta$ -dodecalactone etc.
- Phenols: e.g. thymol, eugenol, etc.

#### Aroma compounds in food

• The main categories of chemical compounds that are important for the odor of food are:

Almond	Benzaldehyde	
Apple	Ethyl 2-methylbutyrate	
Banana	Acetic isoamyl ester	
Cabbage	Dimethyl sulfide	
Lemon	Citral	
Cloves	Eugenol	
Cloves	1-Propylene-disulfide	
Mushrooms	1-Octen-ol	
Chocolate	5-Methyl-2-phenylhexenal	
Butter	Diacetyl	
Green pepper	2-Methoxy-3-isobutylpyrazine	

Aroma compounds in food

 Chemical structures of some terpenoid flavouring compounds: HO a-Limonene Menthol p-Menthone Carvone Eucalyptol Linalool Nootkatone β-Damascenone β-Ionone Safranal a-Ionone Geranyl isobutyrate trans-Geranyl acetate

https://www.researchgate.net/profile/Lorenzo-Caputi-2/publication/49642213/figure/fig2/AS:60179928738 2026@1520491539843/Fig-2-Chemical-structures-ofsome-terpenoid-flavouring-compounds\_W640.jpg

#### **Question examples**

- Definitions of 1 or 2 food additives categories of food: e.g. (a) emulsifiers, (b) Gelling agents, (c) Taste enhancers, etc.
- Which ones is the main categories of chemicals compounds that have importance for the aroma of food?
- What is responsible for the colour of muscular tissue and how can it stabilized in processed meat;
- Mention an azo dye, a peptide dye and a terpenoid dye of food.
- To be able to recognized chemical structures.
- What is from a chemical point of view: (a) anthocyanins, (b) Flavonoids,
   (c) Saccharose, etc.

#### **Question examples**

• Multiple choice or matching. E.g. match between of two columns:

Compound	Category	Answer
1. Betanin	Flavor enhancer	3
2. Na cyclamate	Flavoring ingredient	4
3. Guanylic acid	Pigment	1, 5, 6
4. Limonene	Synthetic sweetener	2
5. Lycopene	Preservative additive	7
6. Tartrazine	Antioxidant additive	7
7. SO <sub>2</sub>	Terpenoid substance	4, 5



# Chemical additives in food

**Pigments** 

Flavor

