FOOD CHEMISTRY

Chapter 7 : Additives

7.1 DEFINITIONS AND CLASSIFICATION
The components of food

A composite food can contain or result from the use of :

INGREDIENTS ⟶ Food or part of a food.

Examples : vegetable oil, whey proteins, salt

PROCESSING AIDS ⟶ Substances which are used to process or transform raw materials or foodstuffs and are usually extracted from the resulting product.

Examples : PVPP, bentonite, pectinases

ADDITIVES ⟶ Substances that are added to foodstuffs for technological purposes and become a component of the finished product .

Examples : saccharine, benzoïc acid, potassium sulphite

7.1 DEFINITIONS AND CLASSIFICATION

The role of food additives

To improve product conservation

- Prevention of bacterial and fungal growth
- Delaying of spoilage
- Extension of the shelf life
- Delaying of rancidity or lipid oxidation
- Enhancement of stability

To improve sensory characteristics

- Improvement of texture
- Enhancement of flavor (odour and taste)
- Improvement, modification or stabilization of color

To modify nutritional properties

- Lowering of energy contents

7.1 DEFINITIONS AND CLASSIFICATION

The Codex Alimentarius classes of food additives

- Acids
- Acidity regulators
- Anticaking agents
- Antifoaming agents
- Antioxidants
- Bulking agents
- Food colors
- Colour retention agents
- Emulsifiers
- Emulsifying salts
- Firming agents
- Flavour enhancers
- Foaming agents
- Gelling agents
- Glazing agents
- Humectants
- Preservatives
- Propellants
- Raising agents
- Stabilizers
- Sweeteners
- Thickeners

7.1 DEFINITIONS AND CLASSIFICATION
The European Union numbering scheme

Class	***Type of additives***	***Number of additives***
E100 – E199	Colors	65
E200 – E299	Preservatives	57
E300 – E399	Antioxidants, acidity regulators	76
E400 – E499	Thickeners, stabilizers, emulsifiers	93
E500 – E599	Acidity regulators, anti-caking agents	70
E600 – E699	Flavor enhancers	22
E700 – E799	Antibiotics	16
E900 – E999	Miscellaneous	66
E1000 – E1599	Additional chemicals	49

7.1 DEFINITIONS AND CLASSIFICATION

Additives and swiss food law

About 40 legal texts describing how food should be produced and marketed

Available at https://www.blv.admin.ch/blv/fr/home/lebensmittel-und-ernaehrung/rechts-und-vollzugsgrundlagen/gesetzgebung-lme.html

Examples :

817.0	Loi fédérale sur les denrées alimentaires et les objets usuels
817.022.41	Ordonnance sur les arômes
817.022.16	Ordonnance concernant l'information sur les denrées alimentaires
817.022.31	**Ordonnance sur les additifs**
817.023.31	Ordonnance sur les cosmétiques
817.024.1	Ordonnance sur l'hygiène

7.1 DEFINITIONS AND CLASSIFICATION

The swiss food law structure

Parlement

Loi fédérale sur les denrées alimentaires et les objets usuels LDAI

Conseil fédéral

Ordonnance sur les denrées alimentaires et les objets usuels ODAIOUs	**Ordonnance concernant l'abattage d'animaux et le contrôle des viandes** OAbCV	**Ordonnance sur le plan de contrôle national de la chaîne alimentaire et des objets usuels** OPCN	**Ordonnance sur l'exécution de la législation sur les denrées alimentaires** OELDAI

Le Département fédéral de l'intérieur DFI

Ordonnance du DFI sur les limites maximales applicables aux résidus de pesticides présents dans ou sur les produits d'origine végétale ou animale OPOVA	**Ordonnance du DFI sur les résidus de substances pharmacologiquement actives et d'additifs pour l'alimentation animale dans les denrées alimentaires d'origine animale** ORésDAlan	**Ordonnance sur les additifs** OAdd	**Ordonnance du DFI sur l'hygiène** OHyg
Ordonnance sur les arômes	**Ordonnance du DFI sur les procédés et les auxiliaires technologiques utilisés pour le traitement des denrées alimentaires** OPAT	**Ordonnance sur les contaminants** OCont	**Ordonnance du DFI sur les nouvelles sortes de denrées alimentaires**
Ordonnance du DFI sur l'adjonction de vitamines, de sels minéraux et de certaines autres substances aux denrées alimentaires OASM	**Ordonnance du DFI concernant l'information sur les denrées alimentaires** OIDAI	**Ordonnance du DFI du 23 novembre 2005 sur les denrées alimentaires génétiquement modifiées** ODAIGM	**Ordonnance du DFI concernant l'hygiène lors de l'abattage d'animaux** OHyAb
Ordonnance du DFI sur les denrées alimentaires d'origine végétale, les champignons et le sel comestible ODAIOV	Ordonnance du DFI sur les denrées alimentaires d'origine animale ODAIAn	Ordonnance du DFI sur l'eau potable et l'eau des installations de baignade et de douche accessibles au public OPBD	Ordonnance sur les matériaux et objets
Ordonnance du DFI sur les boissons	Ordonnance du DFI sur les denrées alimentaires destinées aux personnes ayant des besoins nutritionnels particuliers OBNP	Ordonnance du DFI sur les cosmétiques OCos	Ordonnance sur les objets destinés à entrer en contact avec le corps humain XXXXXXXX
Ordonnance du DFI sur les compléments alimentaires OCAI		Ordonnance sur les jouets OSJo	Ordonnance du DFI sur les générateurs d'aérosols

Office fédéral de la sécurité alimentaire et des affaires vétérinaires OSAV

Ordonnance de l'OSAV sur l'importation de denrées alimentaires originaires ou en provenance du Japon	**Ordonnance de l'OSAV régissant l'importation de gomme de guar originaire ou en provenance d'Inde**	**Ordonnance Tchernobyl**

Aliments — Objets usuels

7.1 DEFINITIONS AND CLASSIFICATION

Examples of additives limitations

Product	*Code*	*Additive*	*Limit*	*Remarks*
Table salt	E535	Sodium ferrocyanide	20 mg/kg	Alone or sum of E 535, 536 and 538. Expressed as anhydrous sodium ferrocyanide
	E536	Potassium ferrocyanide	20 mg/kg	
	E538	Calcium ferrocyanide	20 mg/kg	
	-	Flavouring preparations	GMP	
	-	Flavours	GMP	
Meat	E129	Allura red AC	GMP	Only for marking and stamping
	E133	Brilliant blue FCF	GMP	
	E155	Brown HT	GMP	

7.2 FOOD FLAVORS

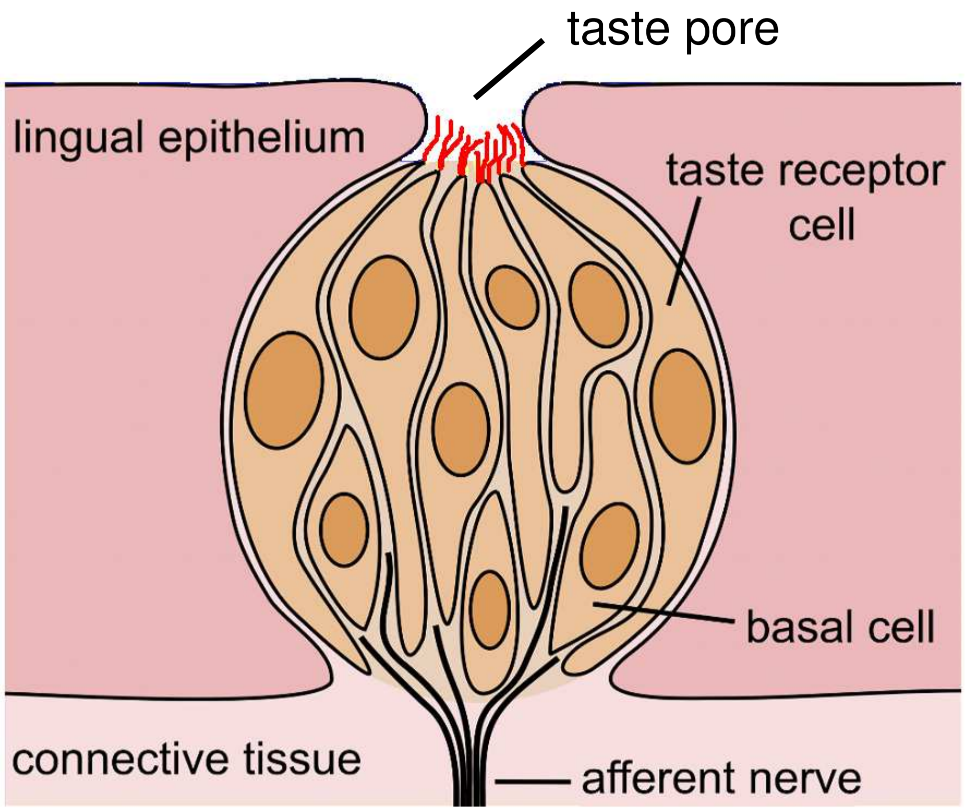
Flavor perceptions

Taste	Sweet	Smell	Natural flavoring substances
	Sour		Nature-identical flavoring substances
	Bitter		Artificial flavoring substances
	Salty		Process flavoring substances (Maillard)
	Umami		Smoke flavoring substances (Liquid smoke)

Further perceptions	Coolness (menthol, camphor)
	Dryness (tannins, oxalates)
	Spicyness (chillies, pepper, ginger)

7.2 FOOD FLAVORS
Taste physiology

Taste is due to ~ 5’000 taste buds, on the tongue and the palate.
Lifetime of a receptor cell : 2-3 weeks



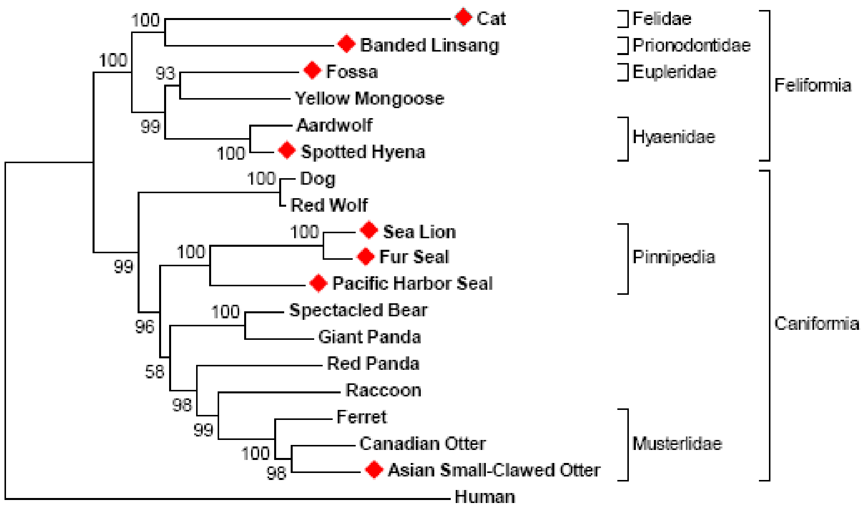
The plasma membrane of chemoreceptors sensitive to salinity and acidity have ion channels that these ions can penetrate . The entry of these species causes a depolarization of the receptor cell.

For umami, bitterness and sweetness receptors, the binding of tasty molecules opens the sodium or potassium channels and the Na^+ or K^+ ions diffuse into the cell, leading to depolarization.

7.2 FOOD FLAVORS
Taste and evolution

Cats and other meat-or fish-eaters lack taste receptor gene Tas1r2

They are insensitive to sweet carbohydrates, which are not part of their diet

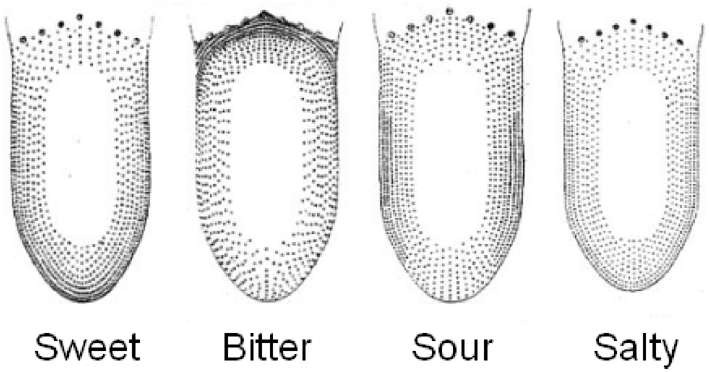


*Major taste loss in carnivorous mammals. G.K. Beauchamp & al. PNAS **109,** 4956-4961 (2012)*

7.2 FOOD FLAVORS
The tongue map myth (I)

In the early 20th century, a german physiologist published a paper on taste sensitivity (inverse detection threshold) :

D.P. Hänig, Zur Psychophysik des Geschmackssinnes
*Philosophische Studien, **17**, 576-623 (1901)*



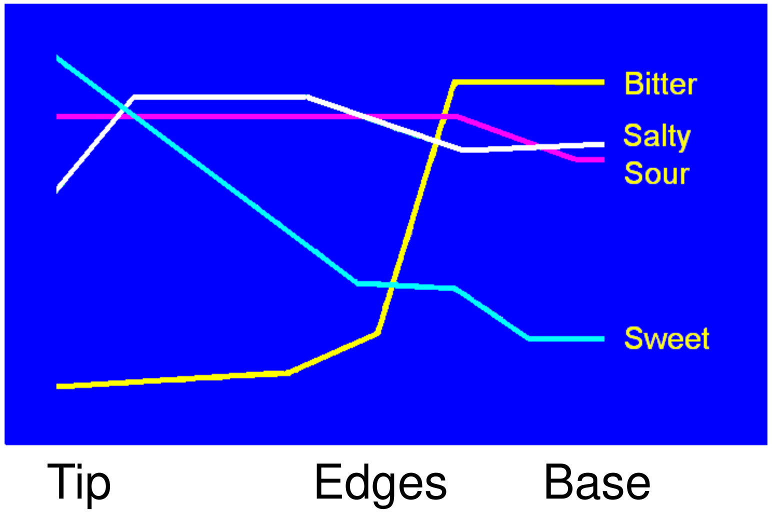
He showes that chemoperception thresholds were unequally distributed across the tongue. However :

- The threshold differences were small
- The differences between individuals were high
- Taste perception also existed in the middle of the tongue

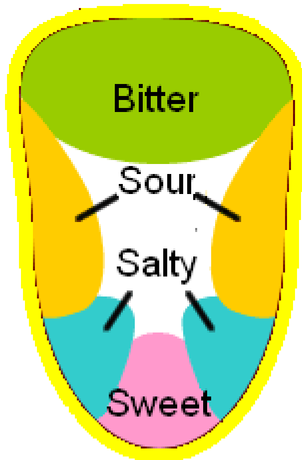
7.2 FOOD FLAVORS
The tongue map myth (II)

During World War II, the experimental psychologist Edwin Boring took Hänig's raw data and calculated real numbers for the levels of sensitivity.

E.G. Boring, Sensation and Perception in the History of Experimental Psychology
Academic Press, New York, 1942



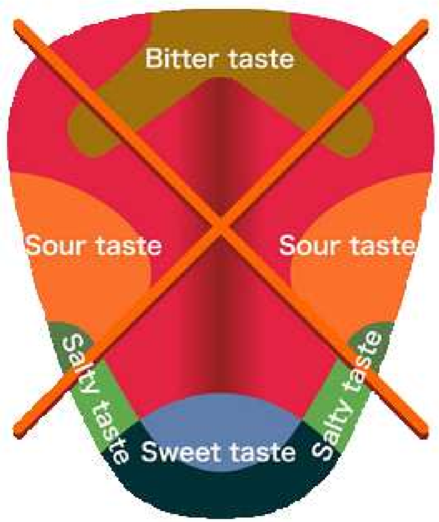
Data were plotted on a graph such that scientists assumed areas of lower sensitivity indicated no sensitivity at all. The tongue map was born!



7.2 FOOD FLAVORS
The tongue map myth (III)

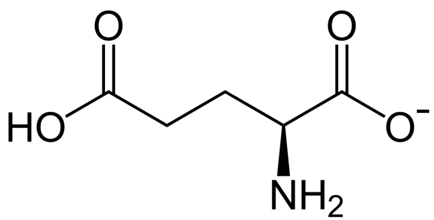
In 1974, Virginia Collings reinvestigated the topic, and concluded that all the tastes exist on all parts of the tongue. The tongue map was a urban legend !

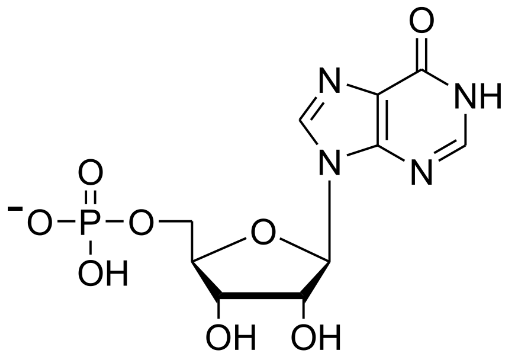
*V.B. Collings, Human Taste Response as a Function of Locus of Stimulation on the Tongue and Soft Palate. Perception & Psychophysics, **16**, 169-174 (1974)*



7.2 FOOD FLAVORS
The umami taste

Umami represents the taste of the amino acid L-glutamate and 5'-ribonucleotides such as inosine monophosphate.



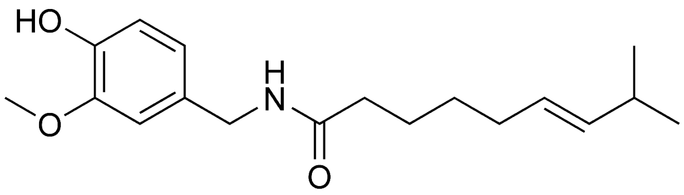


Kikunae Ikeda (1908)

Japanese broth *dashi* (miso) gives a very pure umami taste sensation because it is not based on meats. In dashi, glutamate comes from sea kombu (Laminaria japonica) and inosinate from dried bonito flakes.

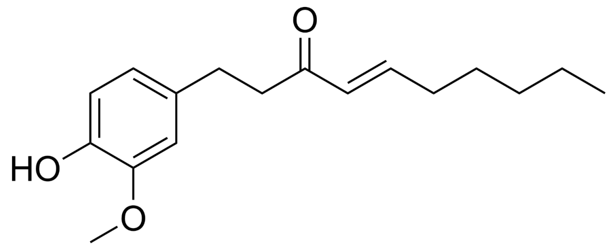
7.2 FOOD FLAVORS
The burning taste

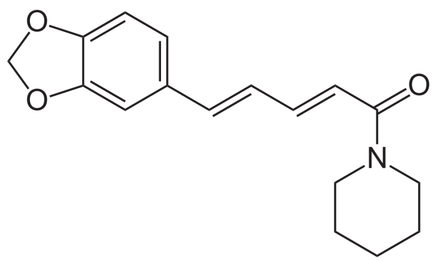
Mechanical, thermal, and chemical stimuli are detected by nerve endings called nociceptors, which are found in the skin and on internal surfaces such as the mucosae. All nociceptors are free nerve endings.



Capsaïcine (chili peppers)

Shogaol (ginger)





Piperine (black pepper)

7.2 FOOD FLAVORS

The Scoville scale

An alcohol extract of the product is added to a solution of sugar in water until the heat is just detectable. The degree of dilution gives its measure on the Scoville scale.

The American Spice Trade Association (ASTA) pungency units is an HPLC measure of the heat-producing chemicals .

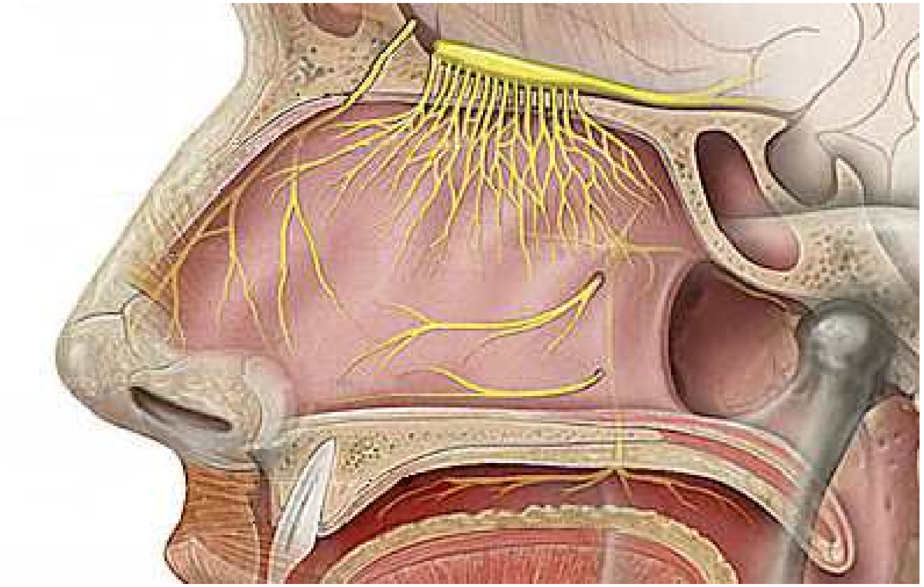
Wilbur Scoville

1912

16'000'000	Capsaïcine
1'500'000	Naga jolokia chili
600'000	Habanero chili
160'000	Shogaol
100'000	Thaï chili
60'000	Gingerol
40'000	Cayenne pepper
15'000	Serrano chili
2'000	Espelette chili
1'5000	Poblano chili
500	Paprika
0	Green pepper

7.2 FOOD FLAVORS

The nasal cavity



Olfactory receptors are directly connected to the brain !

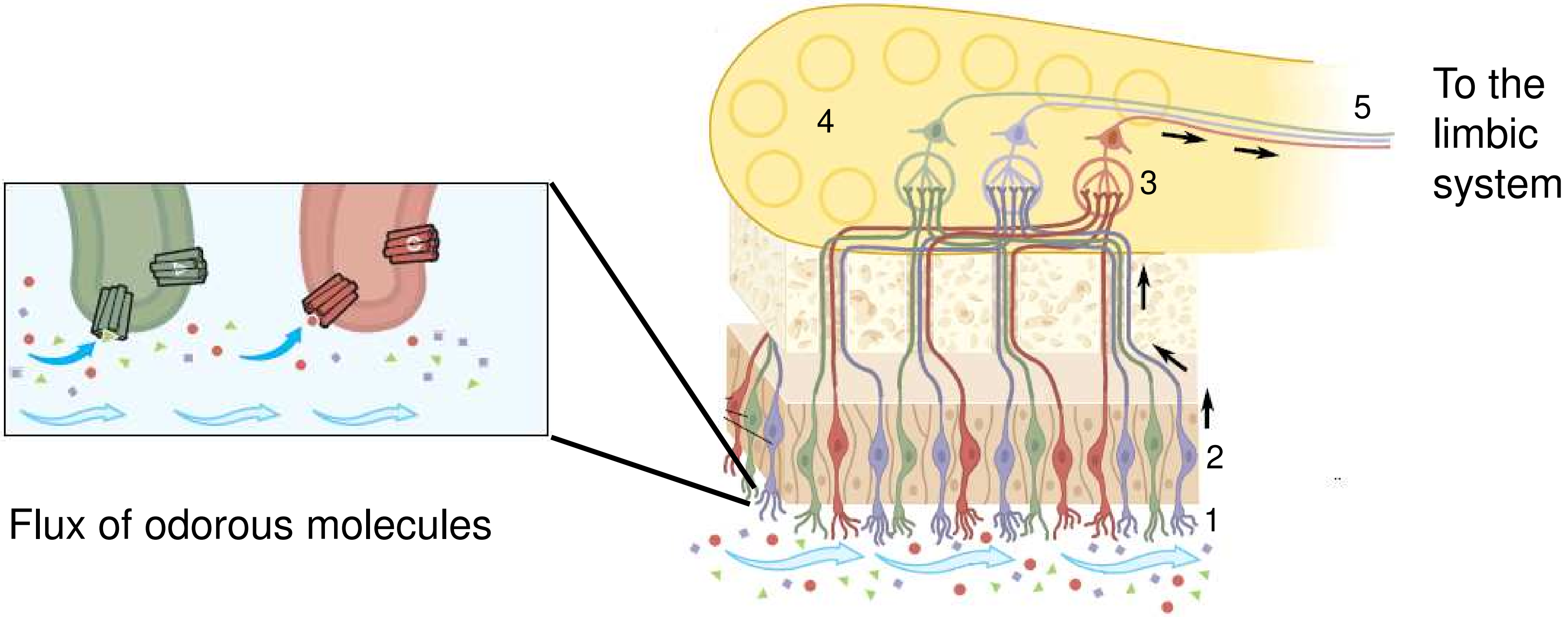
The olfactory membrane covers 4 – 6 cm^2 in each nostril.

The human olfactory system contains an estimated 10^8 receptor cells.

On average, olfactory receptors renew themselves every 30 days.

7.2 FOOD FLAVORS

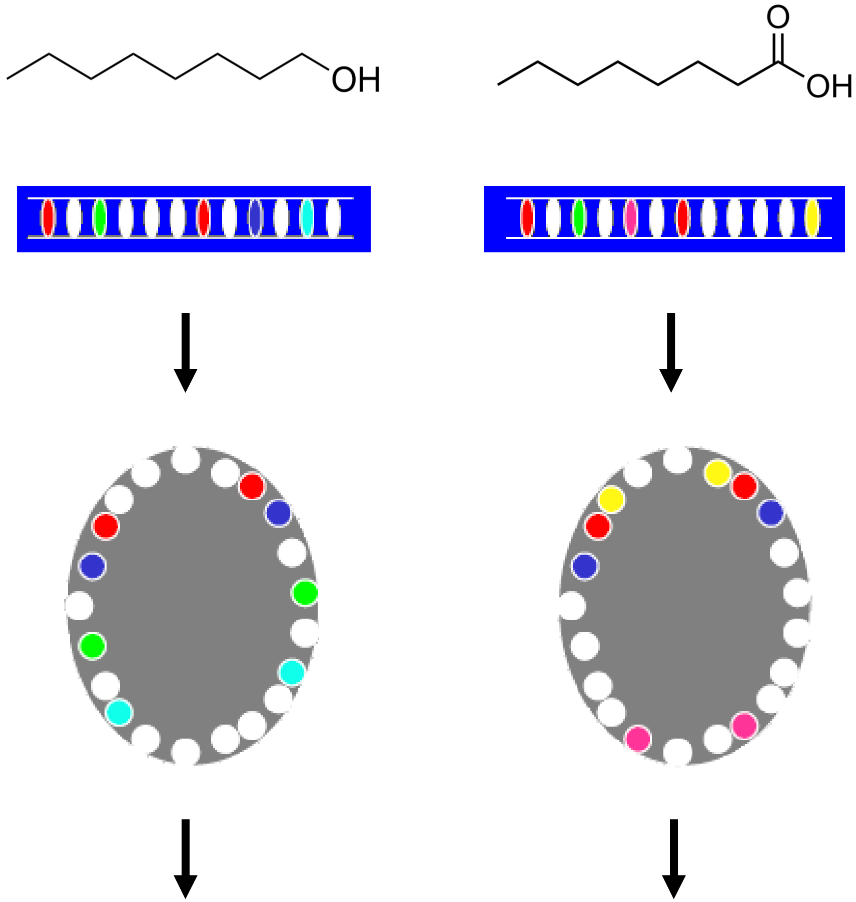
The olfactory system



1 Olfactory hairs
2 Cell neurons
3 Glomeruli
4 Olfactory bulb
5 Olfactory tracts

7.2 FOOD FLAVORS

Odor responses



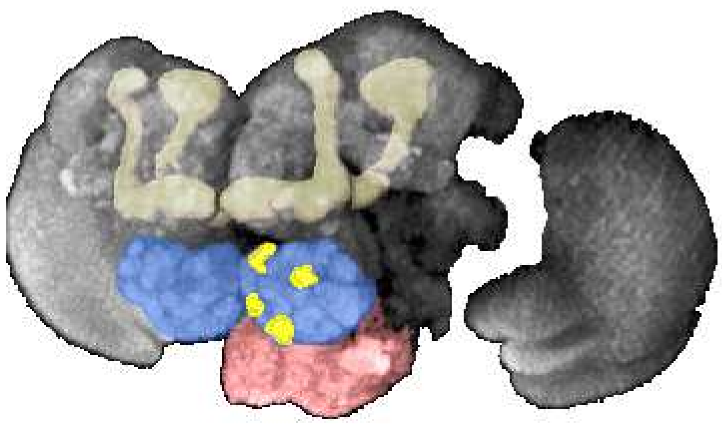
Epithelium — Signal creation

Olfactory bulb — Signal treatment

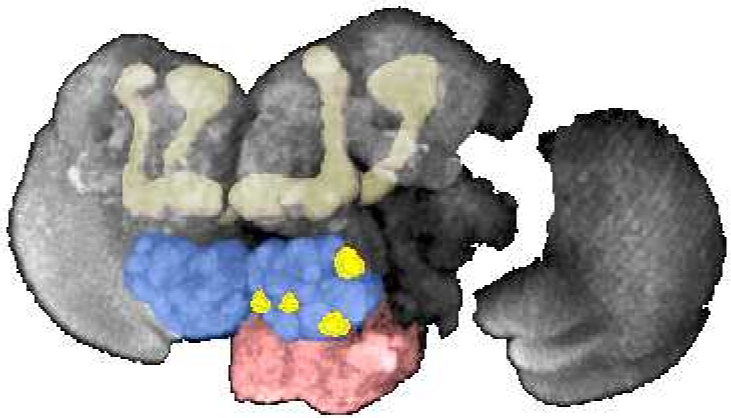
Limbic system — Rose — Rance — Signal interpretation

7.2 FOOD FLAVORS
Olfactory representations in fruit fly

Signal representations in olfactory bulb



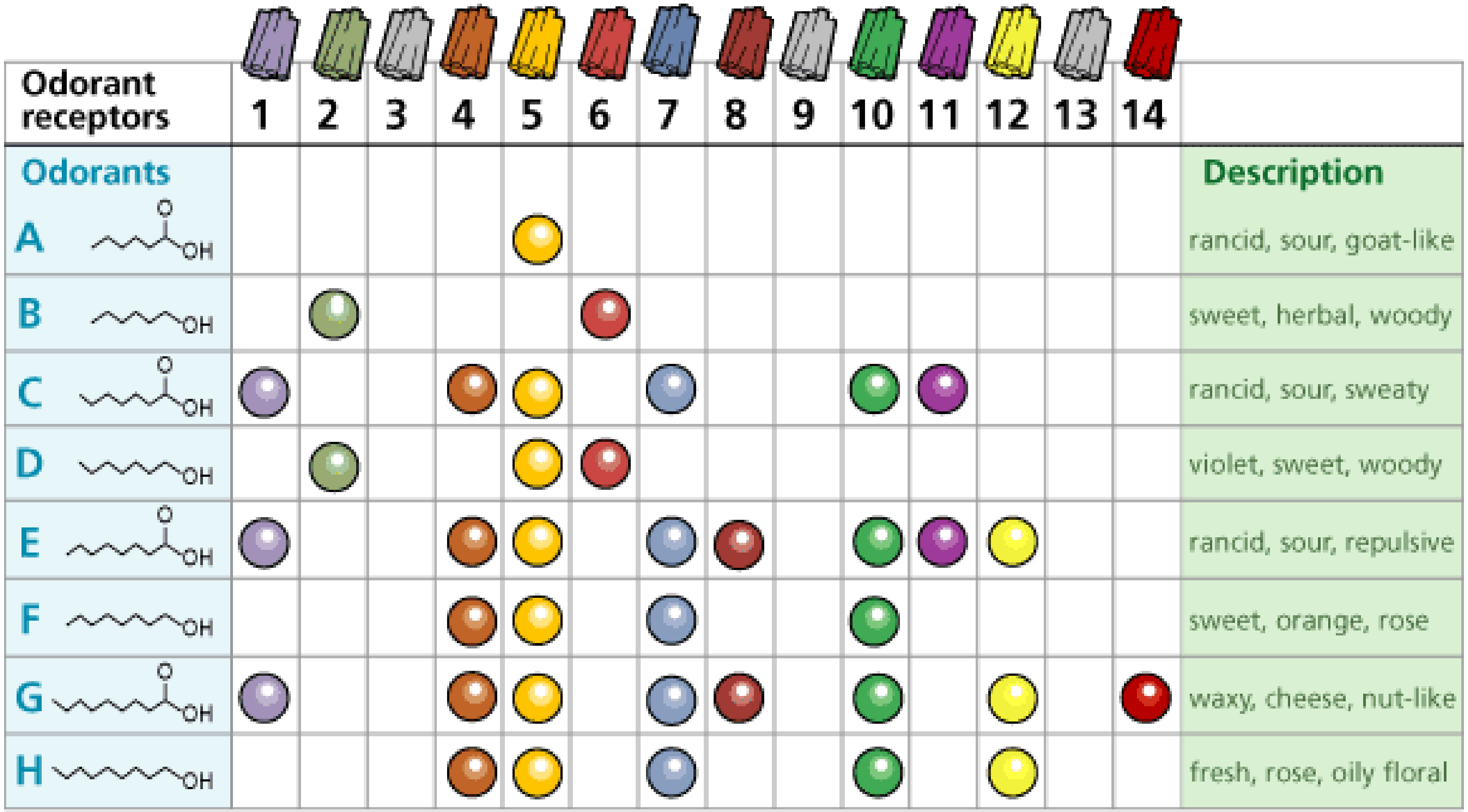
Banana



Cherry

7.2 FOOD FLAVORS

Combinatorial identification of flavors

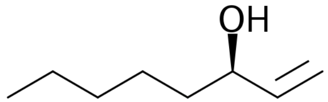


7.2 FOOD FLAVORS
Flavor typology : Group 1a

Only one compound determines the aroma (« Character impact compound »)

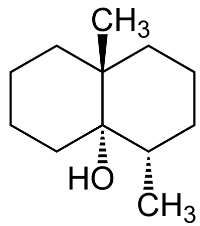
Mushrooms

1-Octene-3-ol



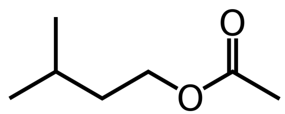
Beetroot

Geosmine



Banana

Isopentyl acetate



7.2 FOOD FLAVORS

Flavor typology : Group 1b

A limited number of compound determine the aroma

Blue cheese	2,3-Butanedione
	Acetaldehyde
	Dimethyl-disulfure
	2-Heptanone
	2-Nonanone

Tangerine	Methyl anthranylate
	Thymol
	γ-Tepinene
	α-Pinene

7.2 FOOD FLAVORS
Flavor typology : Groups 2 and 3

Group 2

The aroma can only be simulated or reproduced with a large number of compounds

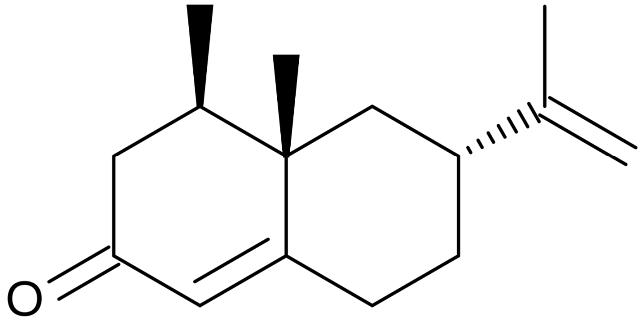
Examples : Coffee, tea, bread, apricot

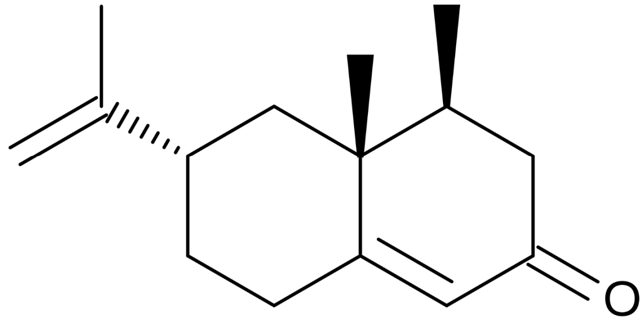
Group 3

The aroma can not be satisfactorily reproduced even with a large number of compounds

Examples : Cocoa, beer, strawberry

7.2 FOOD FLAVORS
Effect of chirality on flavor perception





(+)-Nootkatone

Woody smell

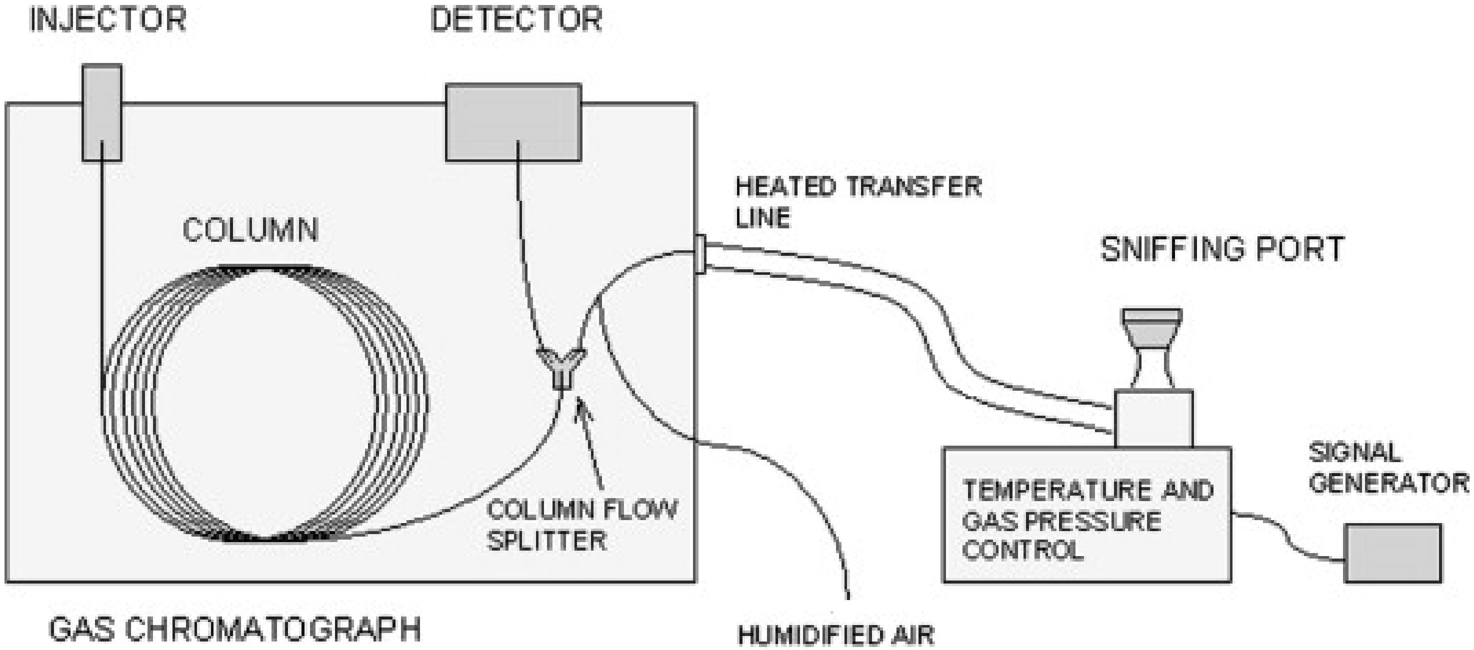
LD = 600 mg/kg

(-)-Nootkatone

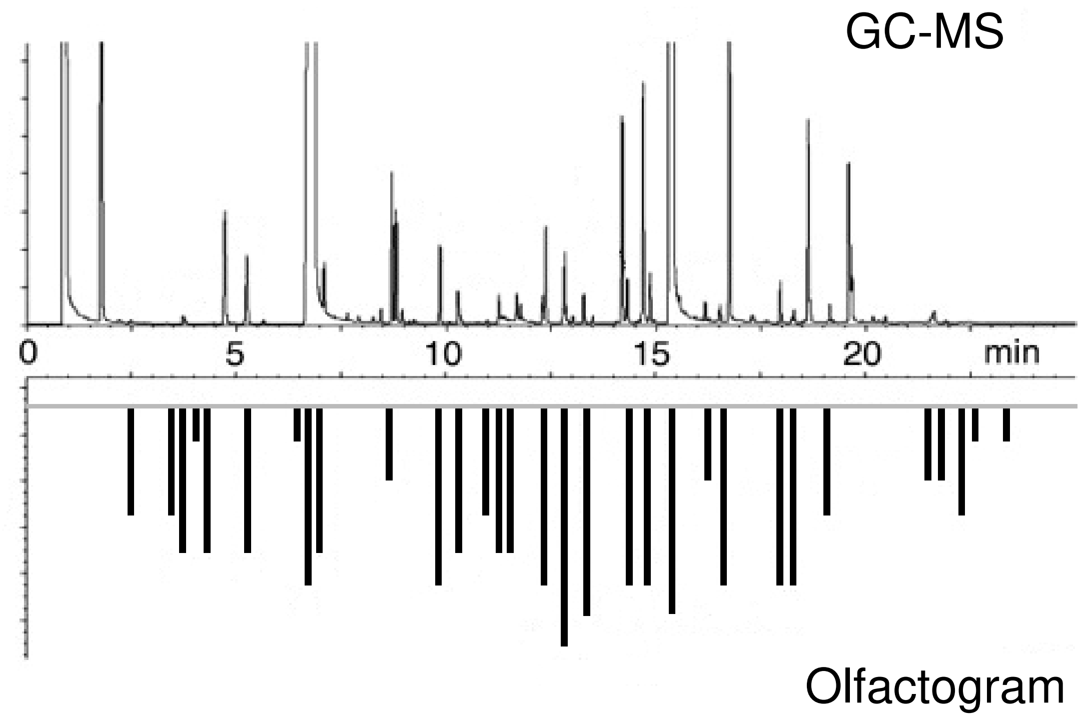
Grapefruit flavor

LD = 0.8 mg/kg

7.2 FOOD FLAVORS
Olfactometric chromatography

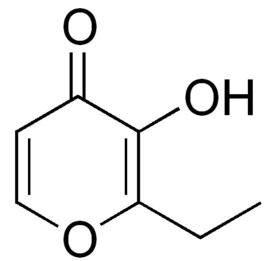


7.2 FOOD FLAVORS
Olfactometric analysis

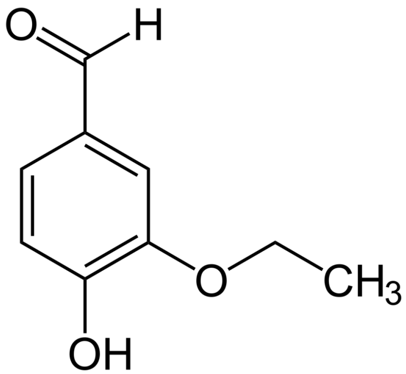


Olfactometric evaluation of a Riesling – Sylvaner wine

7.2 FOOD FLAVORS
Artificial aromas



Ethyl-maltol Caramelized sugar, cooked fruits



Ethyl-vanillin Vanilla, chocolate

7.2 FOOD FLAVORS
Odor threshold values

The lowest concentration of a compound that is just enough for its recognition

Compound	***Aroma***	***OTV (mg/l) at 20°C in water***
Maltol	Caramel	35
Vanillin	Vanilla	0.02
4-Hydroxyphenyl-butan-2-one	Raspberry	0.01
(+)-Nootkatone	Grapefruit	0.001
(-)-Nootkatone	Grapefruit	1.0
Filbertone	Hazelnut	0.00005
2-Isobutyl-3-methoxypyrazine	Green pepper	0.000002
1-Menthen-8-thiol	Grapefruit	0.00000005

7.2 FOOD FLAVORS
Chemical interactions and food liking

Panel tasting showed that flavor intensity is related to 12 cpds, with 8 major contributors :

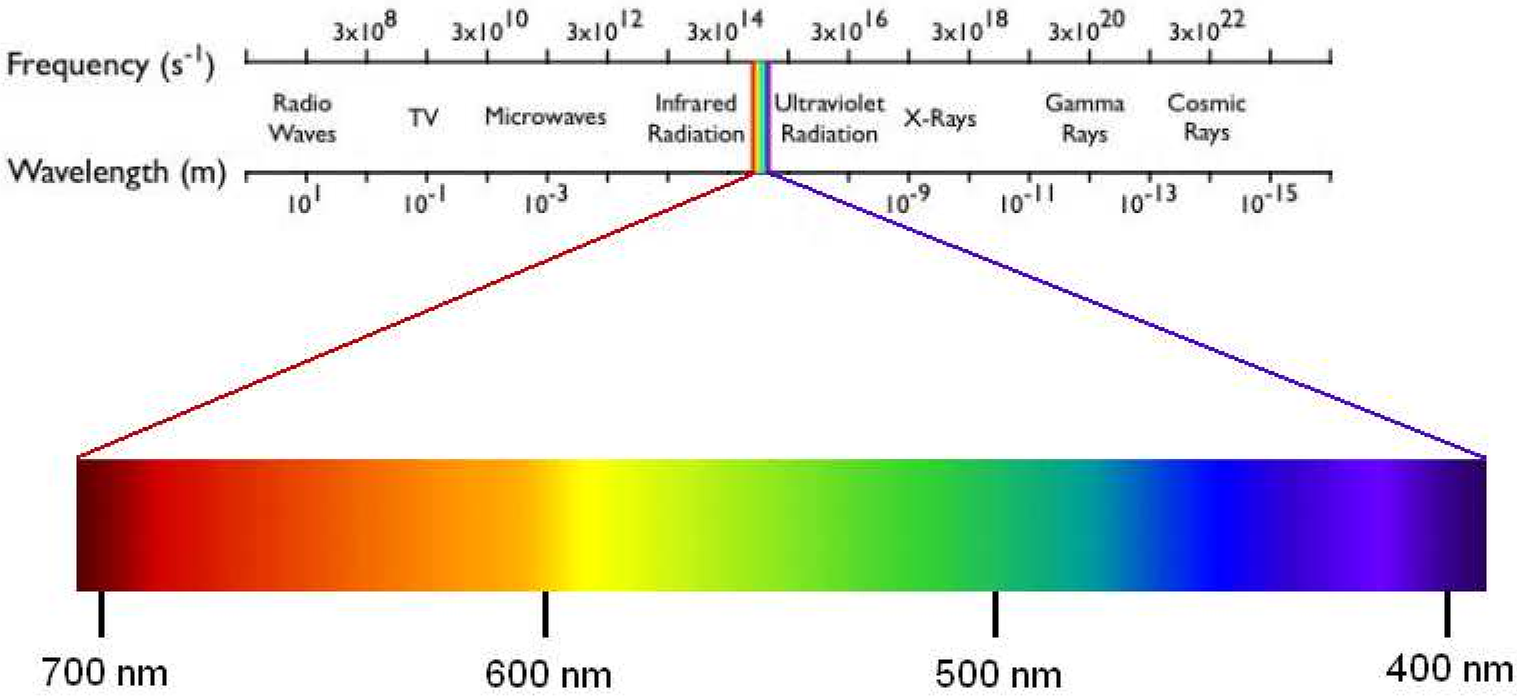
Fructose, isobutyl acetate, hexenol, citric acid, methyl butanol, methyl butanal, octenone, decadienal

→ There is an interaction between retronasal olfaction and taste: volatile compounds enhance the sweet taste of tomatoes

The Chemical Interactions underlying Tomato Flavor Preferences
D. Tieman & al., Current Biology ***22****, 1-5 (2012)*

7.3 FOOD COLORS

The electromagnetic spectrum

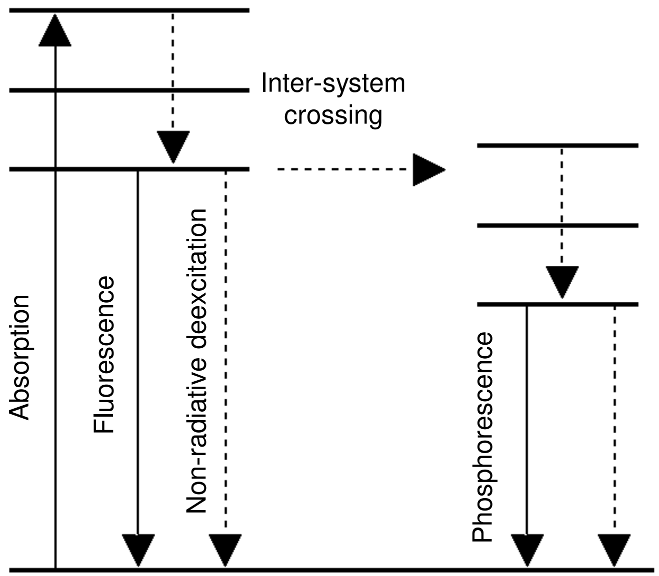


7.3 FOOD COLORS
The origins of the colors

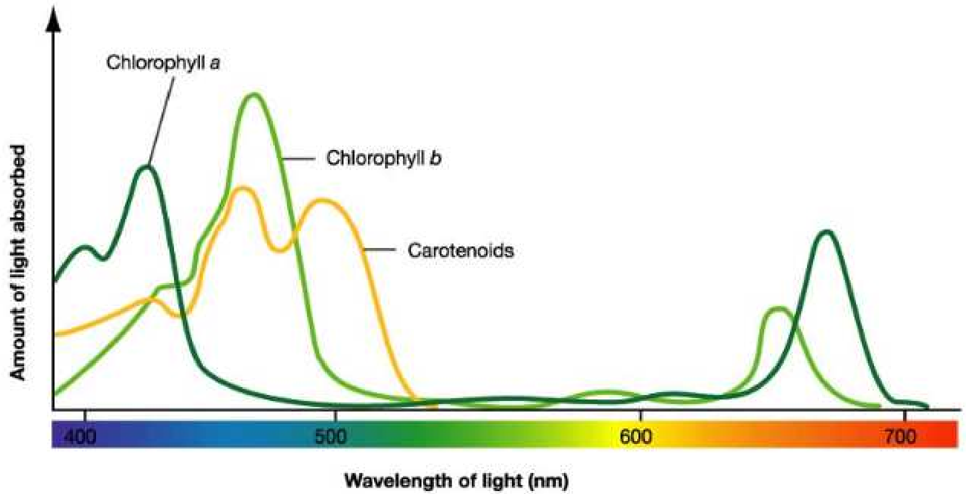
True light sources — Light emission

Fluorescence

Phosphorescence



Jablonsky diagram



Color of an object — Reflectance

Diffraction

7.3 FOOD COLORS
The natural colors

xanthophylls
and chlorophylls

β-carotene

α-carotene

Porphyrins	Meat, vegetables, leaves
Quinoïds	Barks, roots, trees
Carotenoïds	Vegetables, seafood
Anthocyans	Flowers, fruits
Betalaïns	Red beets, berries

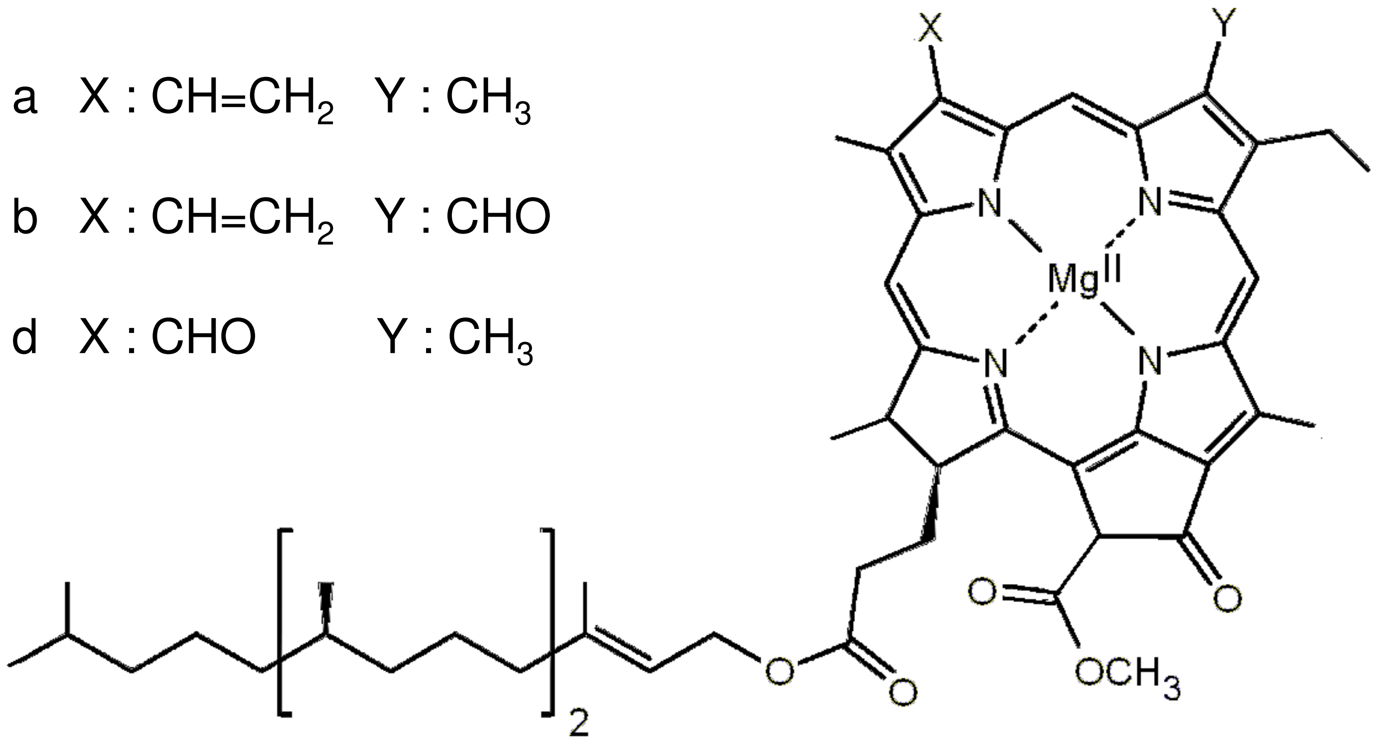
7.3 FOOD COLORS

Porphyrins : the structure of chlorophylls

Chlorophyll a X : $CH=CH_2$ Y : CH_3

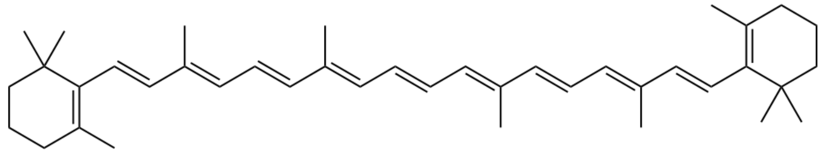
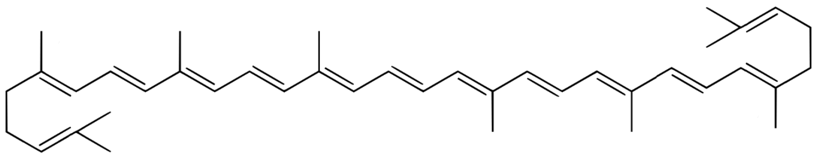
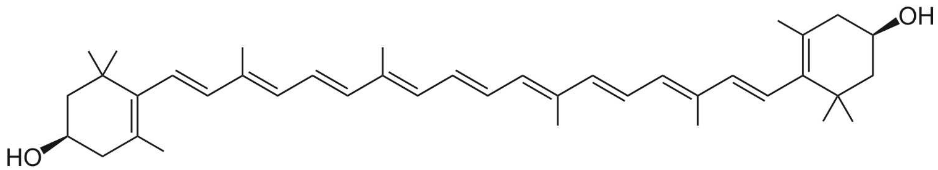
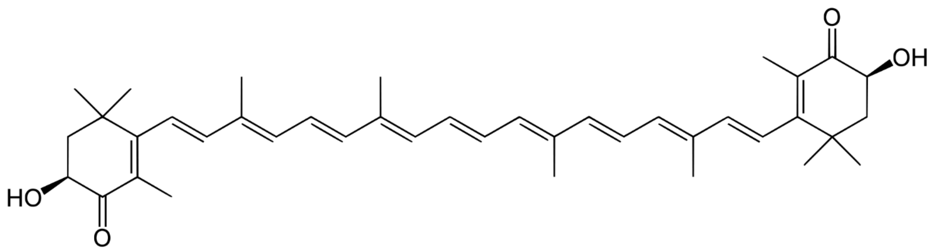
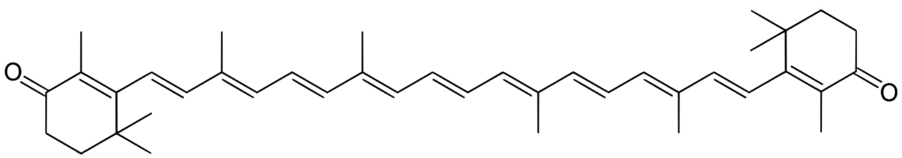
Chlorophyll b X : $CH=CH_2$ Y : CHO

Chlorophyll d X : CHO Y : CH_3



7.3 FOOD COLORS

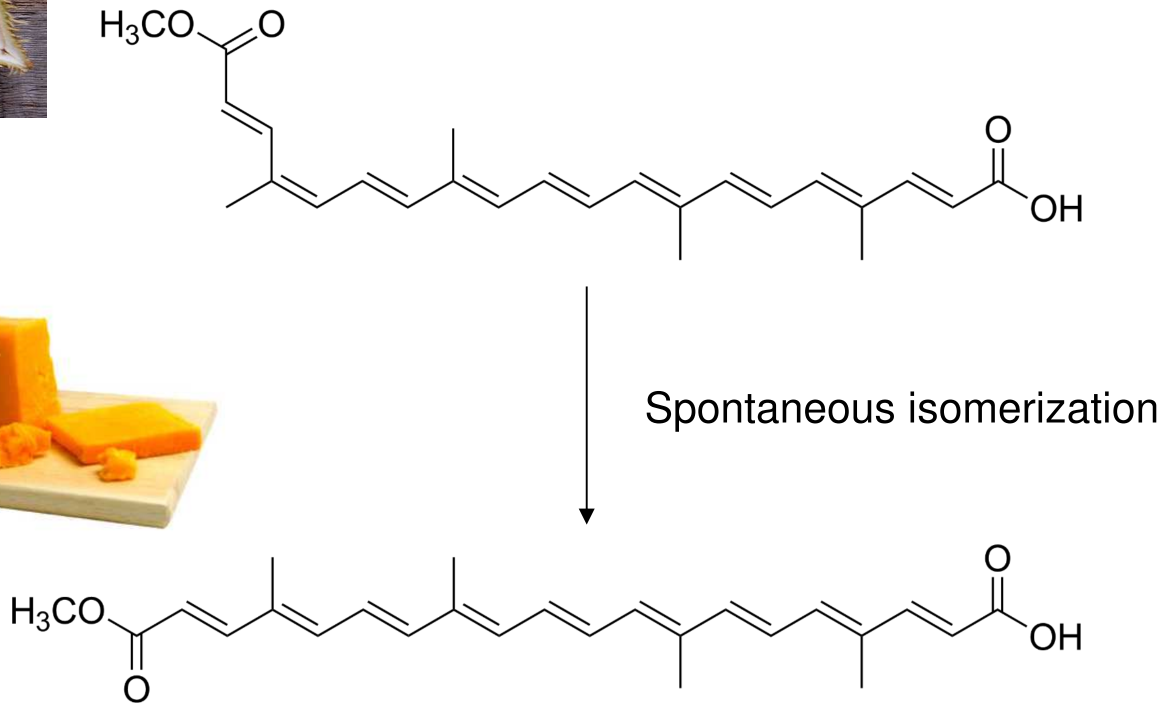
The carotenoïds

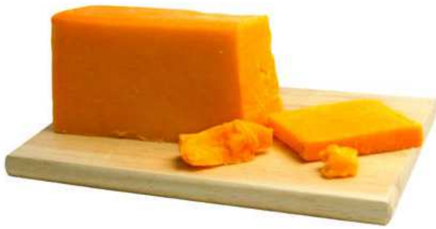
	β-carotene	Carrot, pumpkin, apricot
	Lycopene	Tomato, watermelon, papaya
	Zeaxanthin	Paprika, corn, saffron
	Astaxanthin	Salmon, shrimp, crayfish
	Cantaxanthin	Mullet, pacific salmon

7.3 FOOD COLORS
Annatto

Bixa orellana (rocou)

Wax from dried seeds is extracted to obtain an extract rich in carotenoids, mainly α-bixin



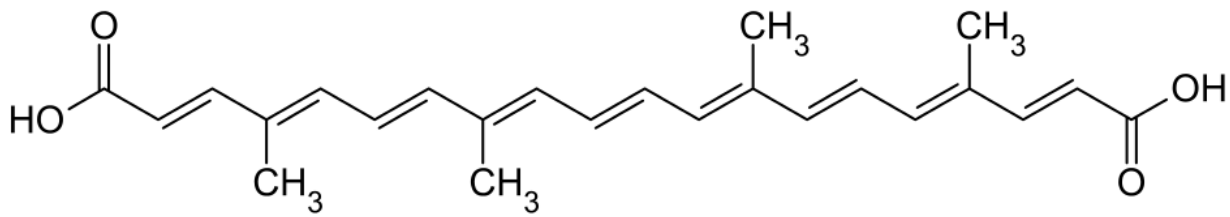


β-bixin
(E160b)

Water insoluble !

7.3 FOOD COLORS
Norbixin

Obtained through hydrolysis of bixin.



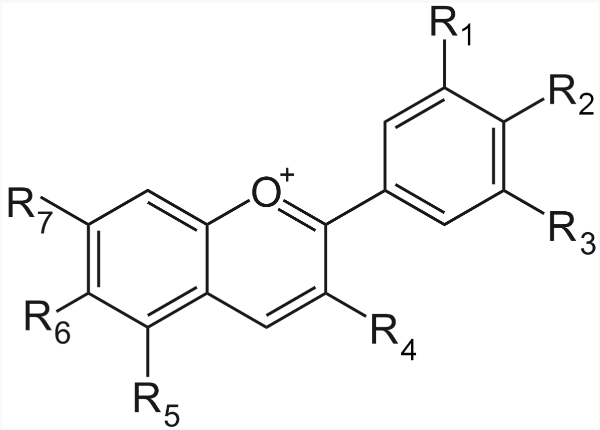
Salts are water soluble, whereas the dicarboxylic acid is insoluble.

Cereals for breakfeast are uniformly coloured with norbixin salts. After pH lowering, norbixin is formed *in situ* and cannot leach into added milk.

7.3 FOOD COLORS

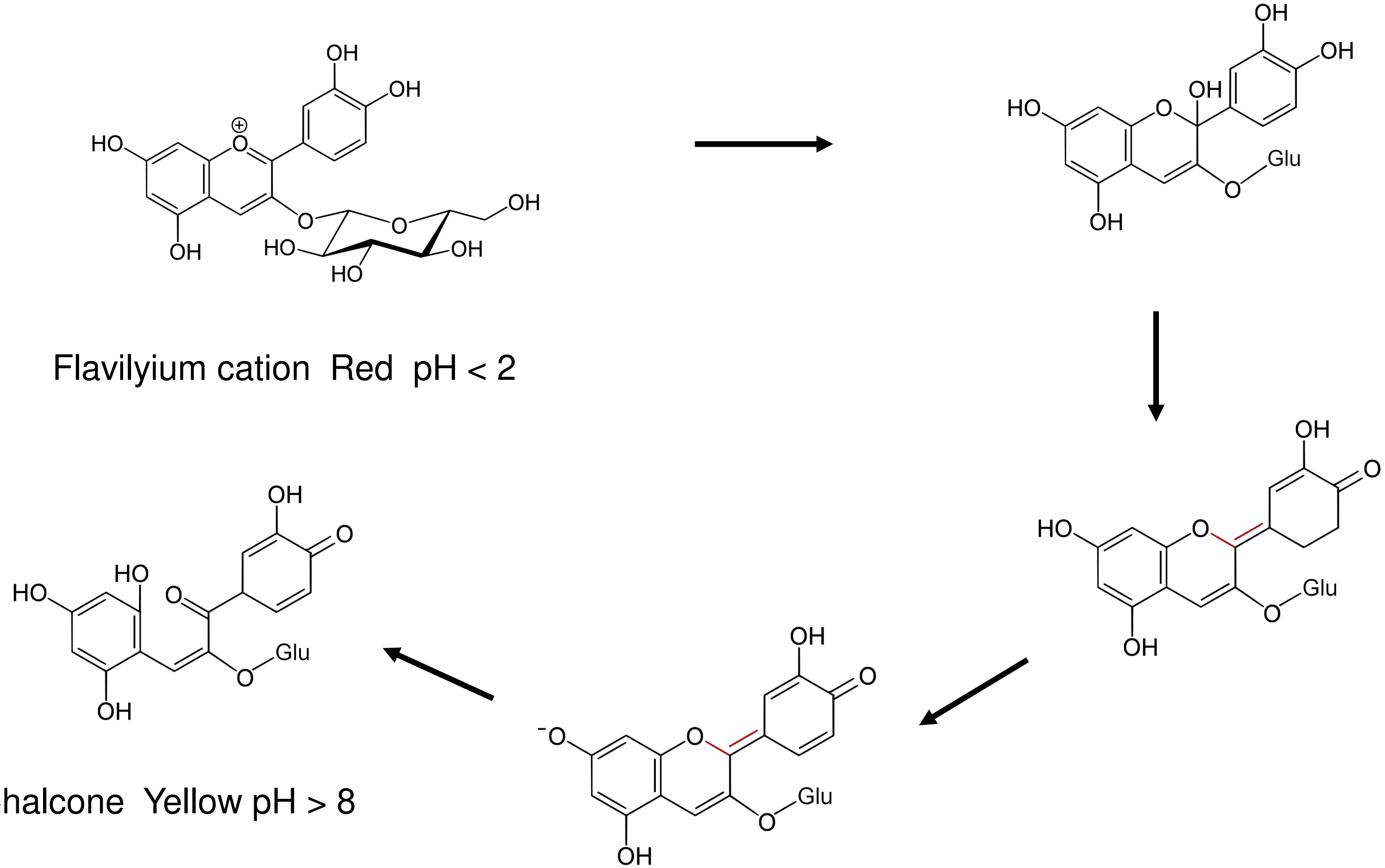
The anthocyanins

The anthocyanins are glucosides of the anthocyanidins

<table>
<tr><th>Anthocyanidin</th><th>Basic structure</th><th>R_1</th><th>R_2</th><th>R_3</th><th>R_4</th><th>R_5</th><th>R_6</th><th>R_7</th></tr>
<tr><td>Aurantinidin</td><td rowspan="10">
</td><td>−H</td><td>−OH</td><td>−H</td><td>−OH</td><td>−OH</td><td>−OH</td><td>−OH</td></tr>
<tr><td>Cyanidin</td><td>−OH</td><td>−OH</td><td>−H</td><td>−OH</td><td>−OH</td><td>−H</td><td>−OH</td></tr>
<tr><td>Delphinidin</td><td>−OH</td><td>−OH</td><td>−OH</td><td>−OH</td><td>−OH</td><td>−H</td><td>−OH</td></tr>
<tr><td>Europinidin</td><td>$-OCH_3$</td><td>−OH</td><td>−OH</td><td>−OH</td><td>$-OCH_3$</td><td>−H</td><td>−OH</td></tr>
<tr><td>Luteolinidin</td><td>−OH</td><td>−OH</td><td>−H</td><td>−H</td><td>−OH</td><td>−H</td><td>−OH</td></tr>
<tr><td>Pelargonidin</td><td>−H</td><td>−OH</td><td>−H</td><td>−OH</td><td>−OH</td><td>−H</td><td>−OH</td></tr>
<tr><td>Malvidin</td><td>$-OCH_3$</td><td>−OH</td><td>$-OCH_3$</td><td>−OH</td><td>−OH</td><td>−H</td><td>−OH</td></tr>
<tr><td>Peonidin</td><td>$-OCH_3$</td><td>−OH</td><td>−H</td><td>−OH</td><td>−OH</td><td>−H</td><td>−OH</td></tr>
<tr><td>Petunidin</td><td>−OH</td><td>−OH</td><td>$-OCH_3$</td><td>−OH</td><td>−OH</td><td>−H</td><td>−OH</td></tr>
<tr><td>Rosinidin</td><td>$-OCH_3$</td><td>−OH</td><td>−H</td><td>−OH</td><td>−OH</td><td>−H</td><td>$-OCH_3$</td></tr>
</table>

7.3 FOOD COLORS

The red cabbage cyanidin-3-glucoside as pH indicator



Flavilyium cation Red pH < 2

Carbinol
Colorless
pH 4 – 5

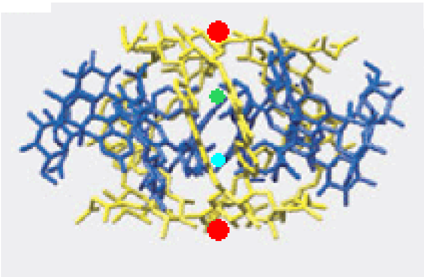
Quinone
Purple
pH 6 – 7

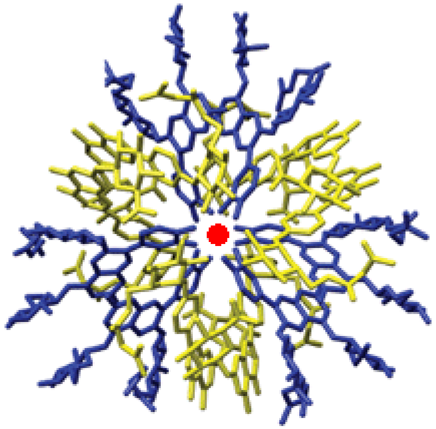
Anhydro base   Deep blue pH 7-8

Chalcone Yellow pH > 8

7.3 FOOD COLORS
Anthocyanin supramolecular pigments

Willstätter (1915) : red roses and blue cornflowers contain the same anthocyanin !





Dark blue : antocyanin
(cyanidin 3,5 diglycoside)

Yellow : flavone
(apigenin 7 glycoside)

Red : Ca^{2+}

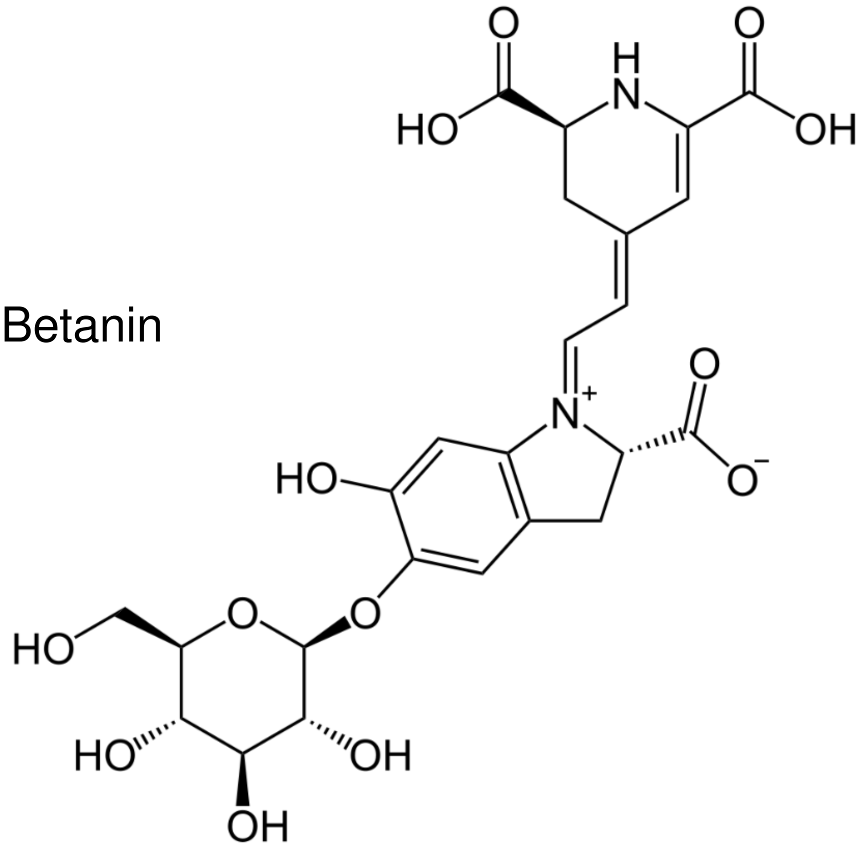
Green : Fe^{3+}

Light blue : Mg^{2+}

M. Shiono & al., Phytochemistry : Structure of the blue cornflower pigment
*Nature **436**, 791 (2005)*

7.3 FOOD COLORS
The betalaïns

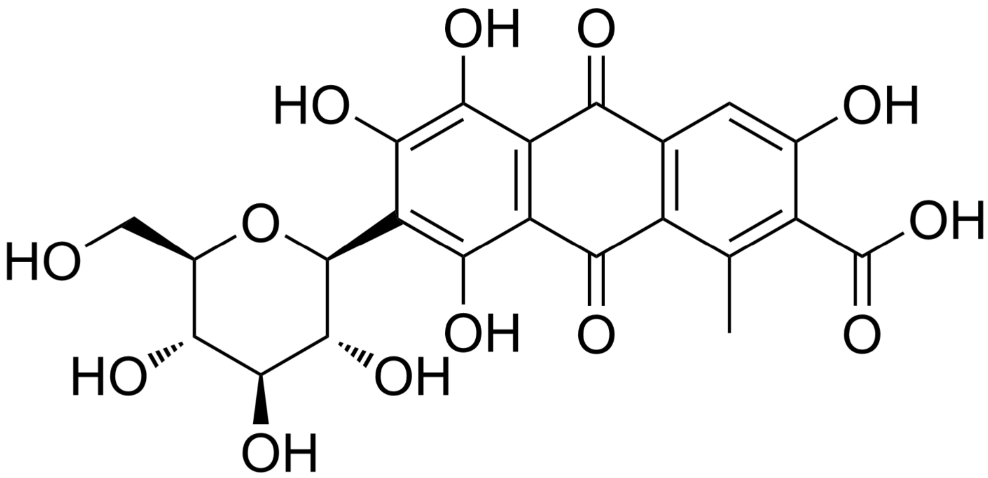
Betanin



Zur Konstitution des Randenfarbstoffes Betanin
*H. Wyler, A.S. Dreiding & al., Helv. Chim. Acta **42**, 1696-1698 (1959)*

7.3 FOOD COLORS

The quinoïds



Carminic acid E120

~ 20 % of the weight of dry cochineals !

7.3 FOOD COLORS

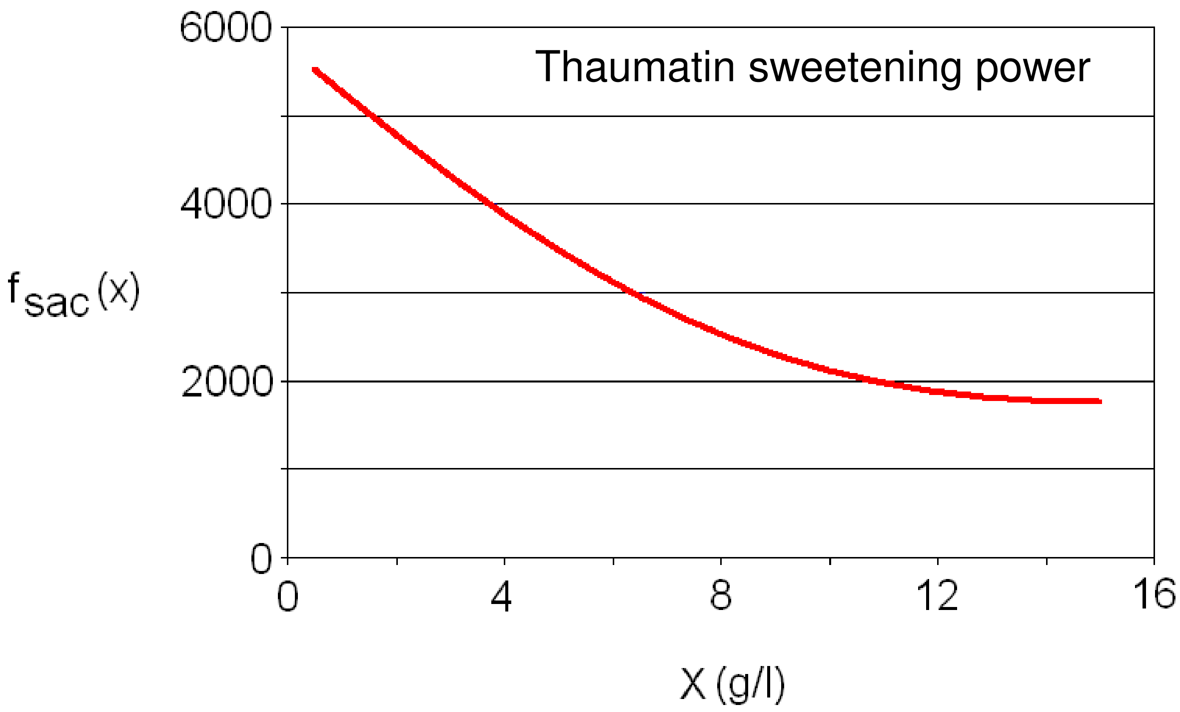
The artificial colors

Common name	US Number	EU Number	Color Index
Brilliant Blue FCF	FD&C Blue Nr 1	E133	42090
Indigotine	FD&C Blue Nr 2	E132	73015
Fast Green FCF	FD&C Green Nr 3	E143	42043
Erythrosine B	FD&C Red Nr 3	E127	45430
Allura Red AC	FD&C Red Nr 40	E129	16035
Tartrazine	FD&C Yellow Nr 5	E102	19140
Sunset Yellow	FD&C Yellow Nr 6	E110	15985
Quinoline Yellow WS	Banned	E104	47005
Azorubin	Banned	E122	14720
Ponceau 4R	Banned	E124	16255
Amaranth	Banned	E123	16185
Patent Blue V	Banned	E131	42051
Green S	Banned	E142	44090
Brilliant Black BN	Banned	E151	28440
Brown HT	Banned	E155	20285
Litholrubine BK	Banned	E180	15850

7.4 FOOD SWEETENERS

Sweetening power of sugar substitutes

The sweetening power is usually compared to saccharose.



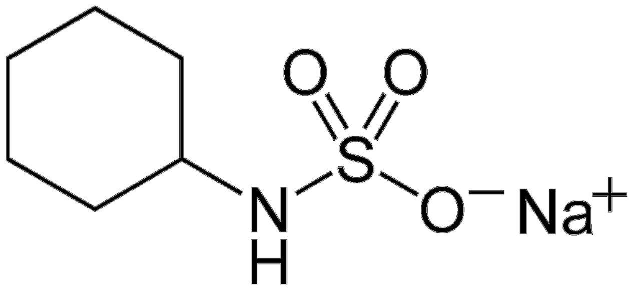
$f_{sac,g}(10)$: sweetening power compared to a 10 g/l saccharose solution

7.4 FOOD SWEETENERS

Some examples

Compound	***$f_{sac,g}$(10)***	***DJA (mg/kg)***	***EU Nr***
Saccharin	550	5	954
Cyclamate	35	7	952
Acesulfame-K	200	15	950
Sucralose	650	15	955
Aspartame	135	40	951
Neotame	> 7'000	2	961
Steviosides	300	4	-
Rebaudiosides	350	4	-
Hernandulcin	1'800	-	-
Thaumatin	2'000	GMP	957
Xylitol	1.0	GMP	967
Sorbitol	0.5	0.15 (laxative)	420

7.4 FOOD SWEETENERS
Artificial sweeteners(I)

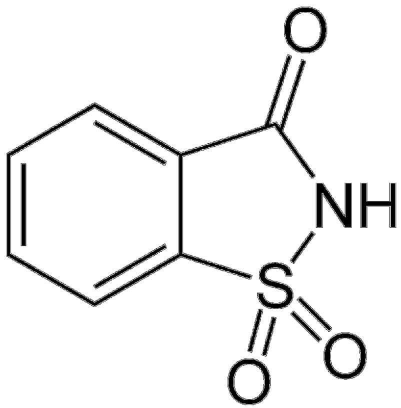


Saccharin (discovered 1879)

Stable at high temperatures and low pH

Has a metallic and bitter aftertaste

In 2010, EPA stated that it is not a potential hazard to human health



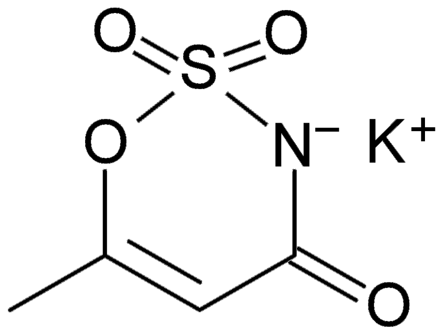
Cyclamate (discovered 1937)

Stable at high temperatures

Derived from sulfamic acid

7.4 FOOD SWEETENERS

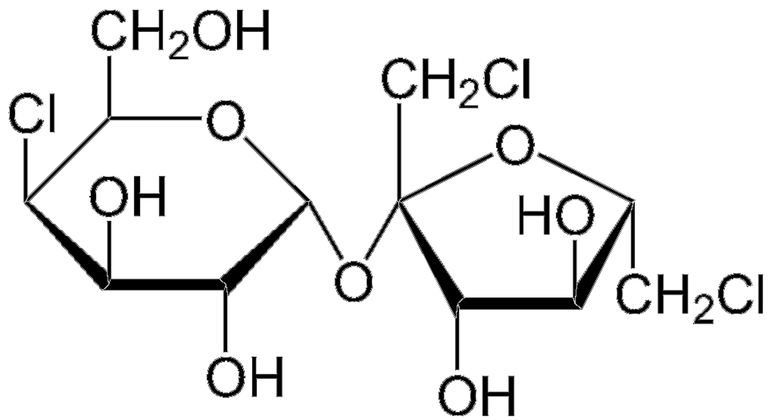
Artificial sweeteners (II)



Acesulfame (discovered 1967)

Stable at high temperatures and low pH

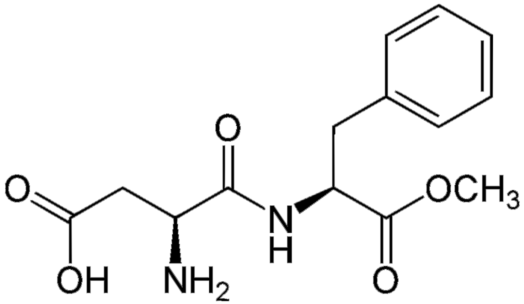
Slightly bitter after taste at high concentrations



Sucralose (discovered 1976)

Very stable at high temperatures and low pH

7.4 FOOD SWEETENERS
Artificial sweeteners (III)

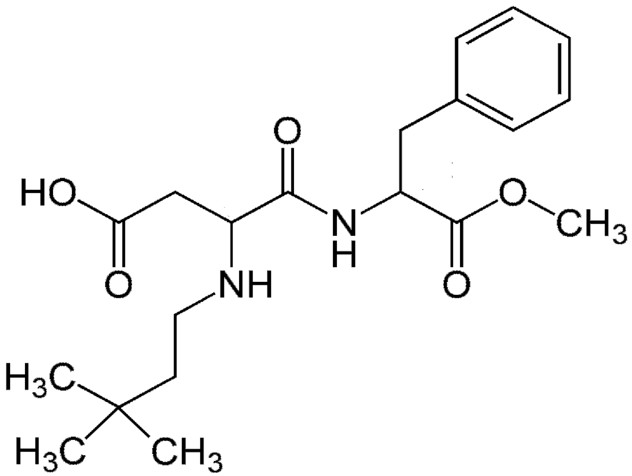


Aspartame (discovered 1965)

Methyl ester of aspartyl-phenylalanine

Must be avoided by people suffering from phenylketonuria

Unstable at high temperatures and pH ≠ 4.3



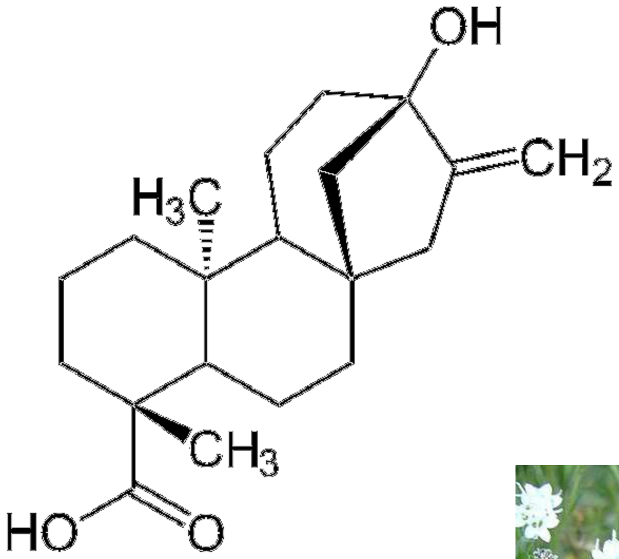
Neotame (discovered 1996)

neo-Hexyl group blocks peptidases activity

Most potent sweetener known

7.4 FOOD SWEETENERS

Natural sweeteners : Stevia rebaudiana Bert.



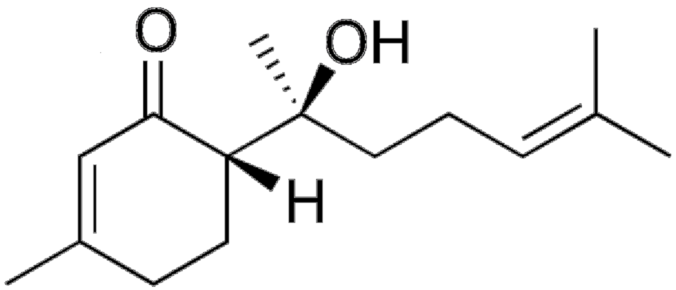
Steviol

Plant contains several steviol glycosides :

5–10%	stevioside
2–4%	rebaudioside A
1–2%	rebaudioside C
0–1%	dulcoside A.

For centuries, the Guaraní peoples of Paraguay used stevia as a sweetener in yerba mate and herbal teas.

7.4 FOOD SWEETENERS
Natural sweeteners : Lippia dulcis Trev.



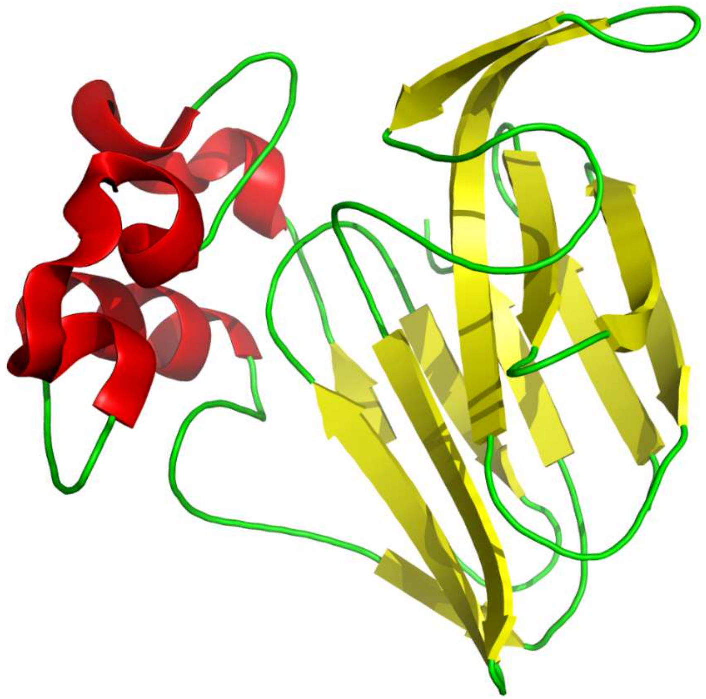
Hernandulcine (discovered in 1985)

Perennial herb native to Southern and Central America.

Two chemotypes of the plant were found, one with a significant amount of hernandulcine (hernandulcine chemotype), and one of camphor (camphor chemotype).

7.4 FOOD SWEETENERS

Natural sweeteners : Thaumatococcus danielli Benth.



Thaumatin I

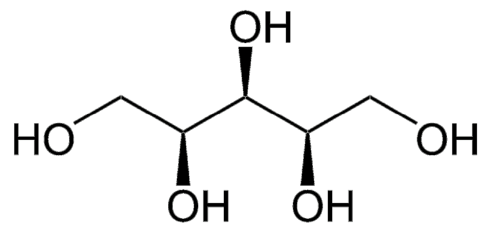
Highly water soluble, stable to heating and acidic conditions (numerous sulphur bridges).

Arils of rhizomatous flowering herb native to the african rainforests.

Sweetness of thaumatin builds very slowly and perception lasts a long time.

7.4 FOOD SWEETENERS

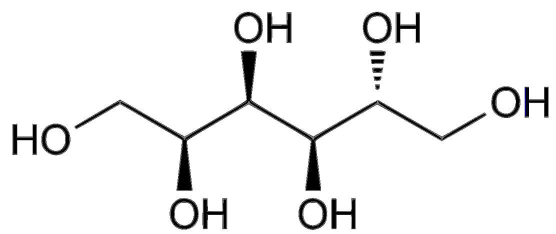
Natural sweeteners : polyols



Xylitol

Found in vegetable fibers

They produce a cooling sensation in the mouth, due to the strongly endothermic dissolution reaction.



Sorbitol

Found in fruits of the Rosaceae family (prunes)

They present a laxative effect because they are not fully broken down during digestion.

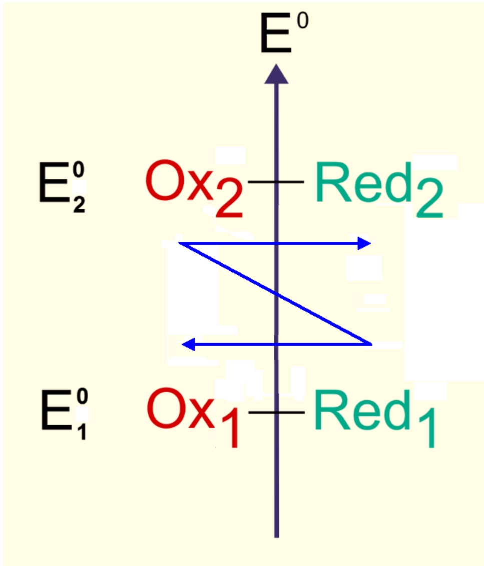
Polyols are added to chewing gums because they are not metabolized by mouth bacteria, so they do not contribute to tooth decay.

7.5 ANTIOXIDANTS

Definitions

The inverted-Z rule :

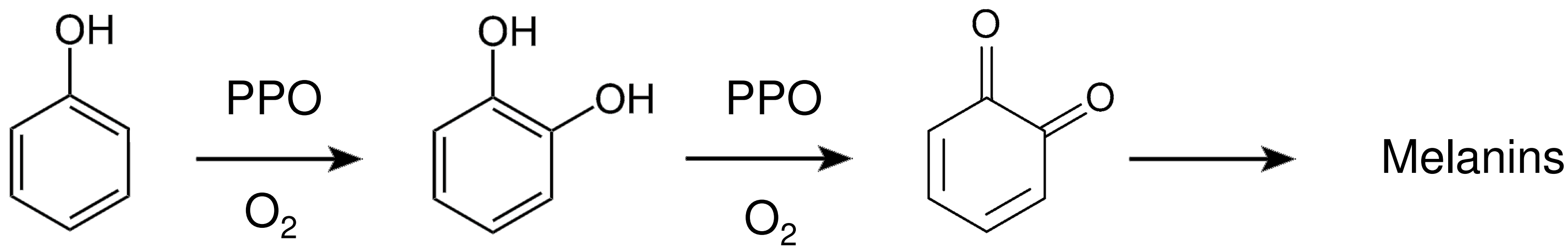
$$Ox_2 + Red_1 \longrightarrow Ox_1 + Red_2$$



In food :	*Antioxidants :*
Redox reactions (browning)	Ascorbic acid, sulfites
Radical reactions (fat oxydation)	Tocols, BHA, BHT, gallates

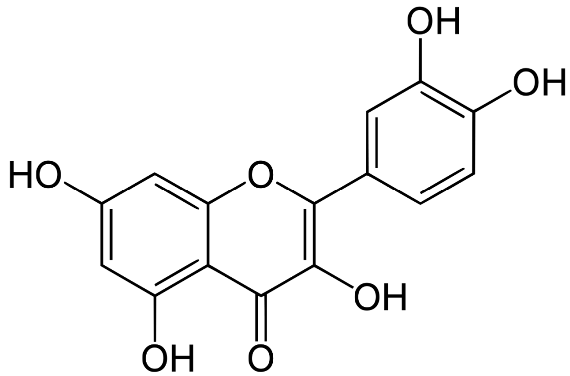
7.5 ANTIOXIDANTS
Enzymatic browning

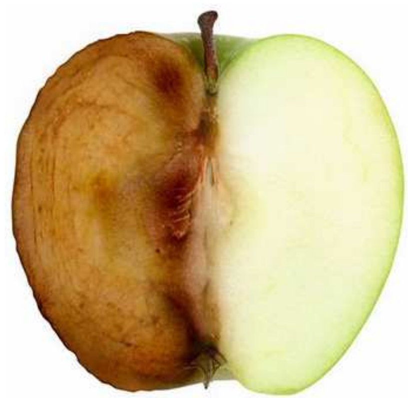
Polyphenoloxydase : copper-containing enzyme present in the membranes of vegetal cells (PPO)



Quercetin (flavonoid)

440 ppm in apples





7.5 ANTIOXIDANTS
Antioxidant properties of sulfites

$$SO_2 + \tfrac{1}{2} O_2 \rightleftharpoons SO_3$$

Oxygen scavenging

$$SO_3 + H_2O \longrightarrow HSO_4^- + H^+$$

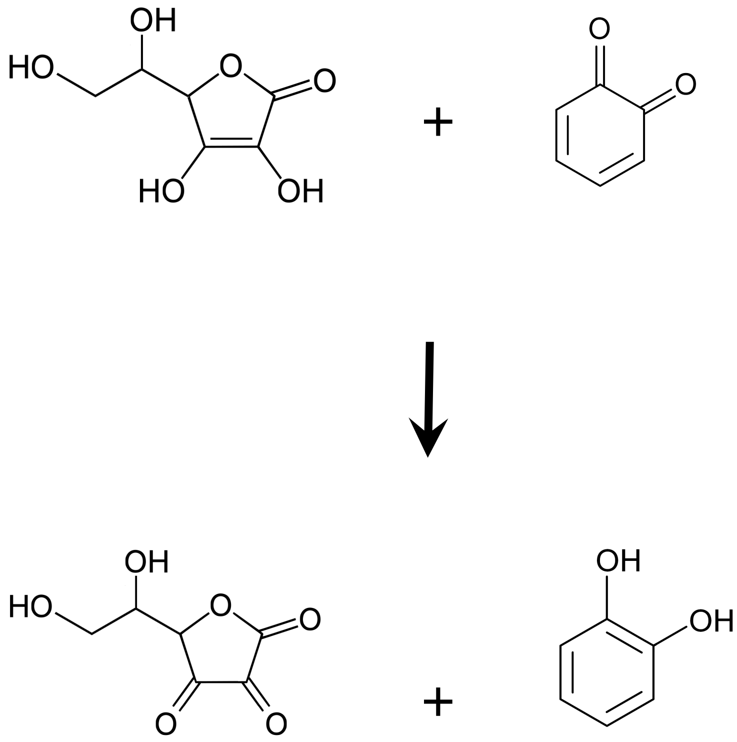
Reactions with carbonyl species

Oxidation products scavenging

Untreated organic dried apricots

SO_2 treated dried apricots

7.5 ANTIOXIDANTS
Antioxidant properties of ascorbic acid

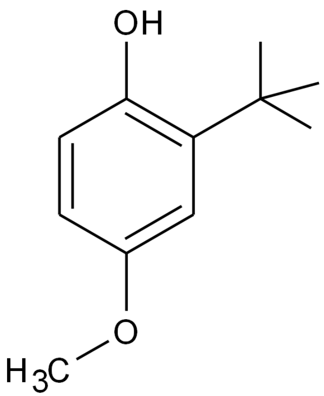


Oxidation products scavenging

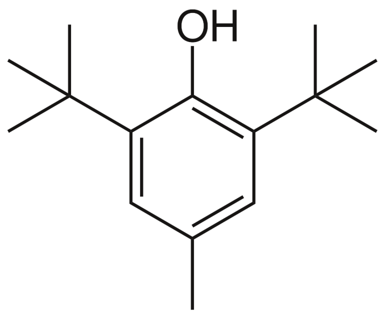
Dehydroascorbic acid

7.5 ANTIOXIDANTS

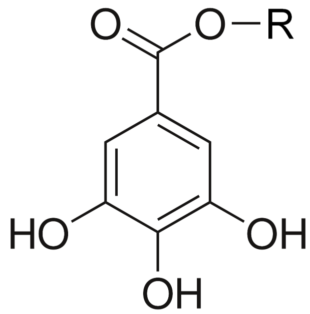
Antioxidant properties of substituted phenolic compounds



Butyl hydroxy anisol
(BHA)



Butyl hydroxy toluene
(BHT)



Alkyl gallates

$$RO^{\bullet} + ArOH \longrightarrow ROH + ArO^{\bullet}$$

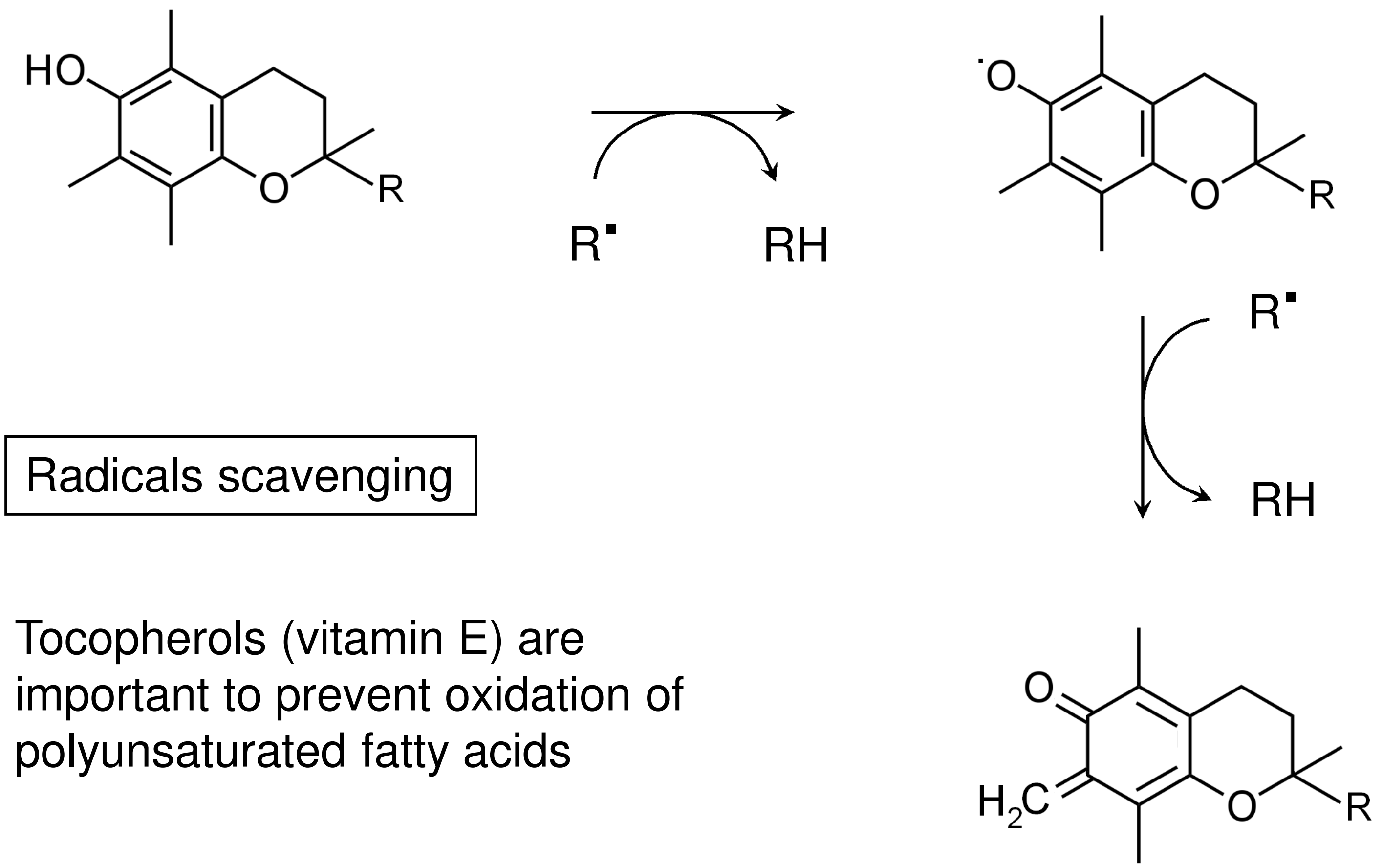
$$ROO^{\bullet} + ArOH \longrightarrow ROOH + ArO^{\bullet}$$

$$RO^{\bullet} + ArO^{\bullet} \longrightarrow ArOR$$

$$ROO^{\bullet} + ArO^{\bullet} \longrightarrow ArOOR$$

$\boxed{\text{Radicals scavenging}}$

7.5 ANTIOXIDANTS
Antioxidant properties of tocopherols

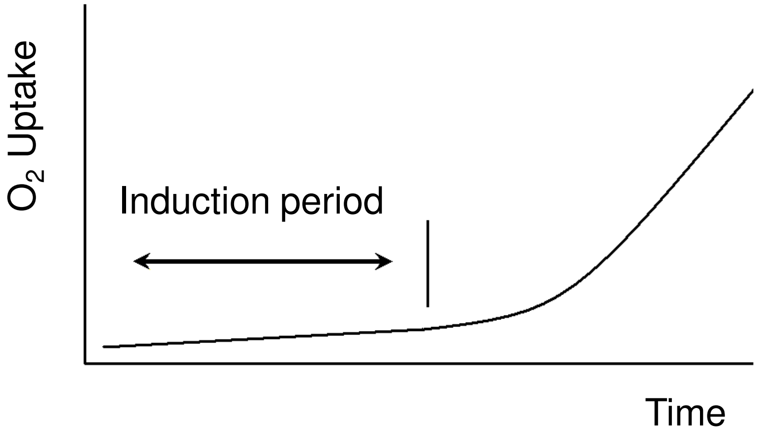


Radicals scavenging

Tocopherols (vitamin E) are important to prevent oxidation of polyunsaturated fatty acids

7.5 ANTIOXIDANTS

Antioxidative factors (AF)



$AF = I_A / I_0$

I_A : Induction period with antioxidant

I_0 : Induction period without antioxidant

Antioxidative factors of some antioxidants at 0.02% in refined lard

Antioxidant	*AF*
α - Tocopherol	5
γ - Tocopherol	12
BHA	10
BHT	6
Octyl gallate	6
BAH + BHT	12

7.5 ANTIOXIDANTS

Antioxidant supplements and health

Meta-analysis including 78 randomised clinical trials.

296,707 participants were randomised to antioxidant supplements (β-carotene, vitamin A, vitamin C, vitamin E, and selenium) vs. placebo or no intervention

Twenty-six trials included 215,900 healthy participants.
Fifty-two trials included 80,807 participants with various diseases.

➡ No statistical significance in terms of mortality !

➡ For the trials with low risks of bias, the increased mortality in supplemented participants was even more pronounced, 1.04 times as compared to the controls (RR = 1.05, IC 95 % 1.02-1.08).

G. Bjelakovic & al., Antioxidant supplements for prevention of mortality in healthy participants and patients with various diseases.
Cochrane Database of Systematic Reviews 2012 (3), No. 7176

7.6 PRESERVATIVES

Definitions

Preservation prevents the growth of unwanted bacteria, yeasts, and fungi

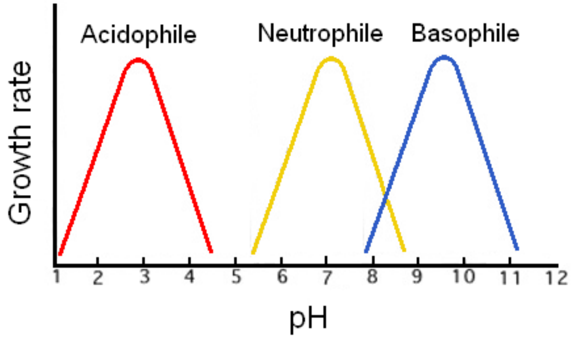
→ Physical or chemical treatment that kills microorganisms

→ Removal of nutrients needed by microorganisms

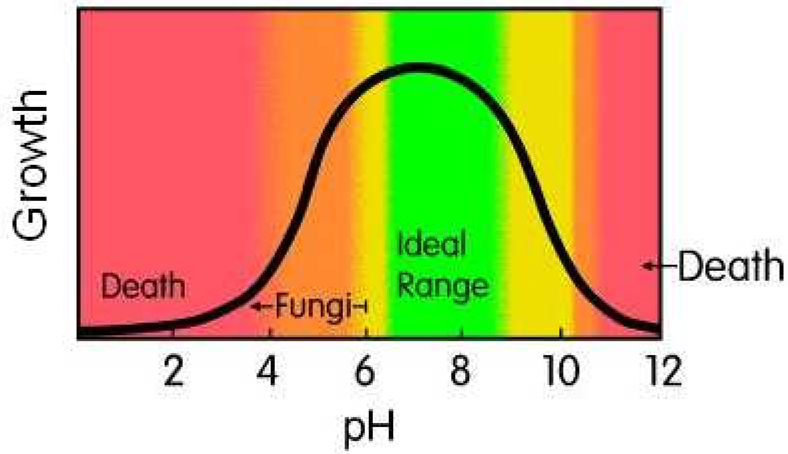
Parameter	*Application*
High temperature	Heating
Low temperature	Chilling, freezing
High pressure	Pascalization
Low water activity	Drying, curing, smoking, sugaring
High ionising radiations	Irradiation
High acidity	Acid addition, fermentation
Low oxygen concentration	Vacuum packing, controlled atmosphere
Cell perturbation	Chemical preservatives

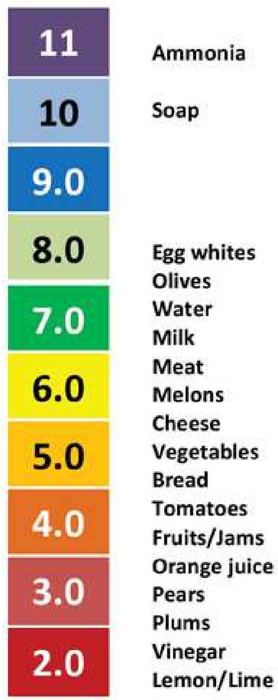
7.6 PRESERVATIVES

Natural preservatives : acetic acid



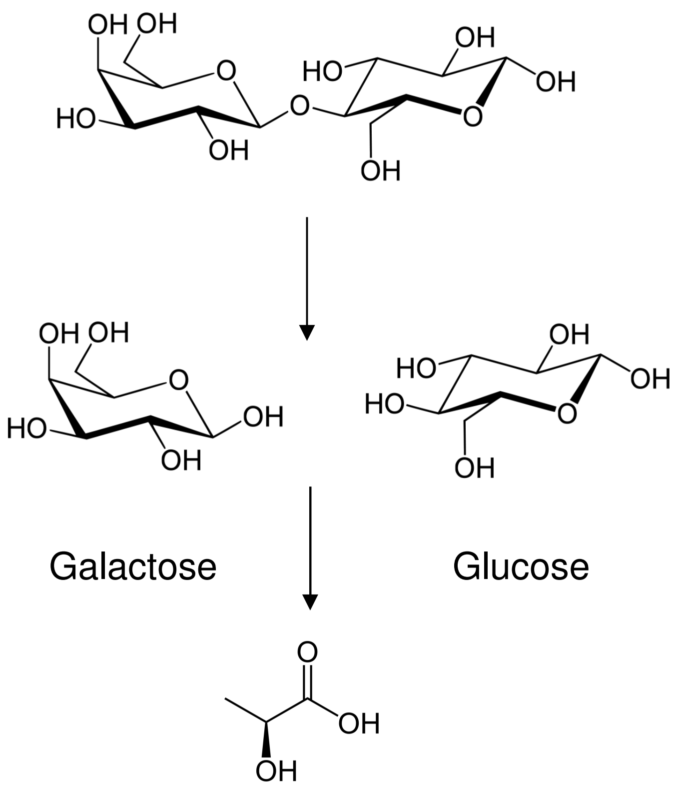
Growth of pathogenic bacteria





7.6 PRESERVATIVES
Natural preservatives : lactic acid

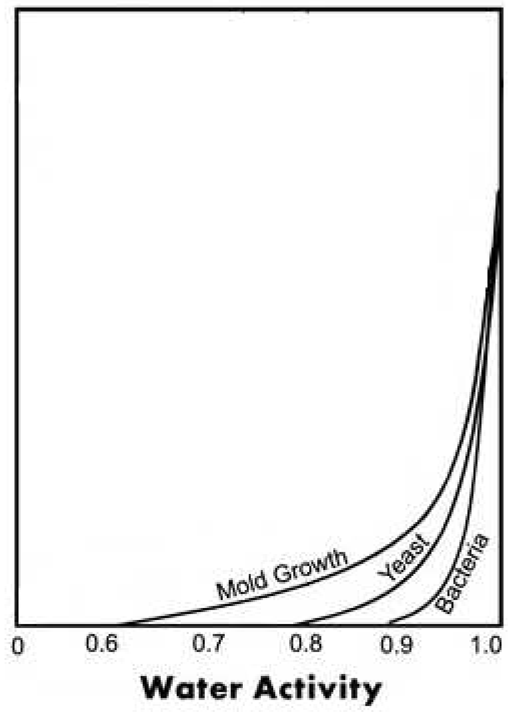
Lactose



Lactic acid

7.6 PRESERVATIVES

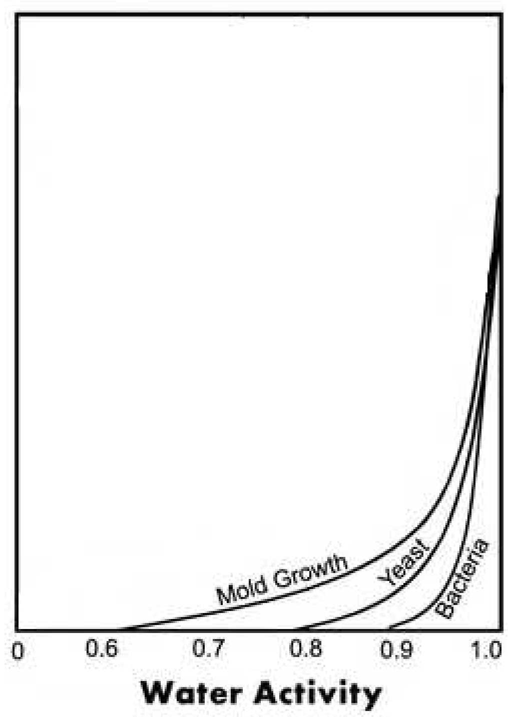
Natural preservatives : salt



NaCl (g)	Water (g)	% NaCl	A_w
0.9	99.1	0.9	0.995
1.7	98.3	1.7	0.99
3.5	96.5	3.5	0.98
7.0	93.0	7.0	0.96
10.0	90.0	10.0	0.94
13.0	87.0	13.0	0.92
16.0	84.0	16.0	0.90
22.0	78.0	22.0	0.86

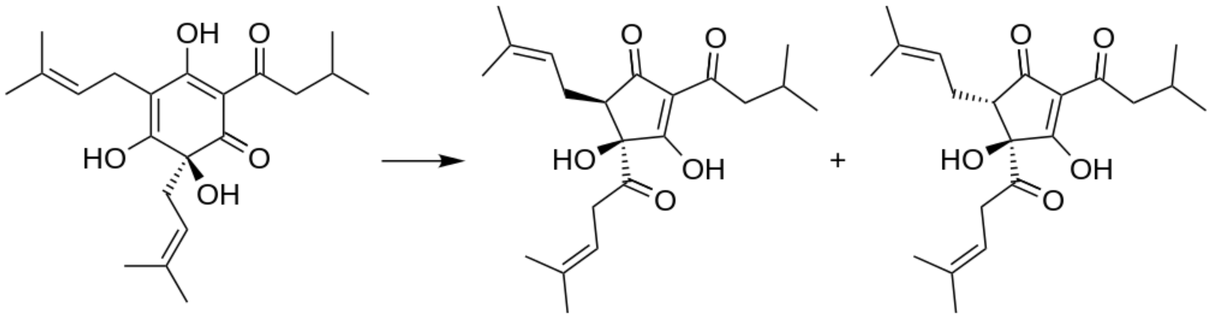
7.6 PRESERVATIVES

Natural preservatives : saccharose



Sucrose (g)	Water (g)	% Sucrose	A_w
0	100	0	1.00
20	100	16.7	0.998
40	100	28.6	0.969
60	100	37.5	0.955
80	100	44.4	0.941
100	100	50.0	0.927
120	100	54.5	0.913
140	100	58.3	0.900
160	100	61.5	0.888
180	100	64.3	0.876
200	100	66.7	0.860

7.6 PRESERVATIVES
Natural preservatives : hop extract



Humulone

Cis- and trans-isohumulones

Antimicrobial properties

Concentrated hop extracts were added to english beer to prevent spoilage during transport in the colonies (« India pale ale »)

7.6 PRESERVATIVES

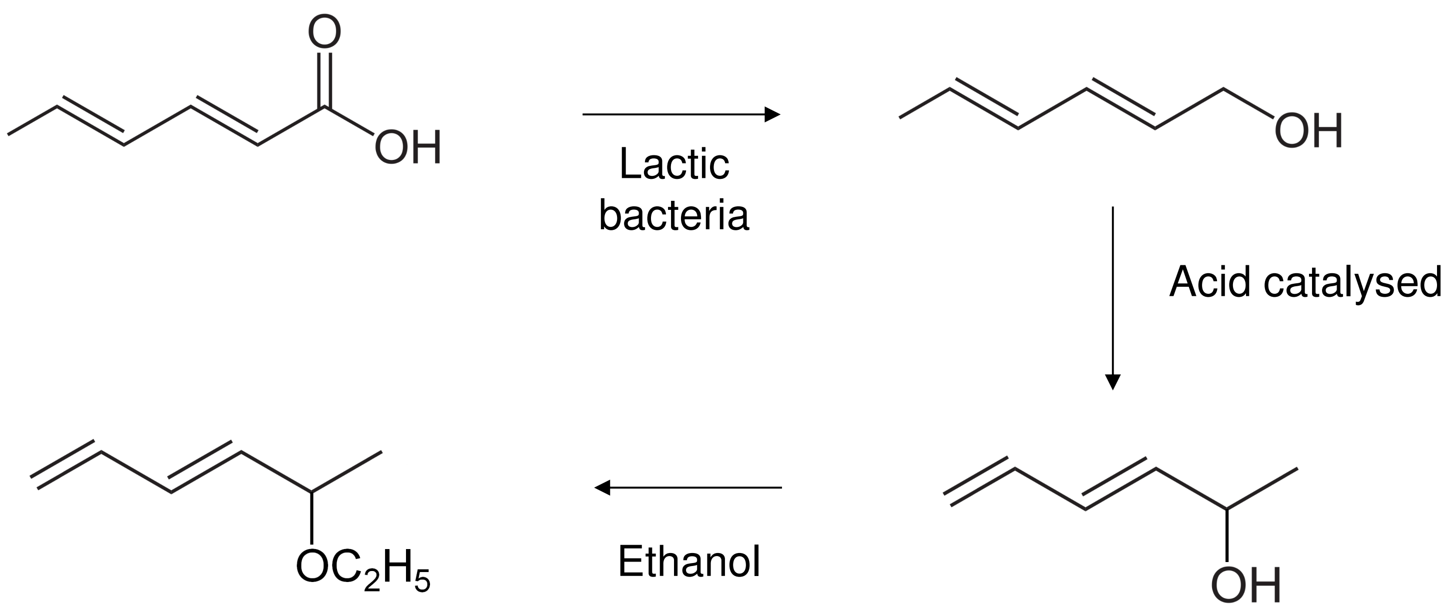
Preservatives allowed in the European union

Hexamethylenetetramine	Sorbic acid and salts
Ethanol	Benzoic acid and salts
Nisin	p-Hydroxybenzoic acid and salts and esters
Natamycin	Boric acid and salts
Lysozyme	Borax
Formic acid and salts	Nitrites and nitrates
Acetic acid and salts	Sulfur dioxide and related compounds
Propionic acid and salts	

7.6 PRESERVATIVES
Sorbic acid (I)

Inhibits the grows of molds and yeasts

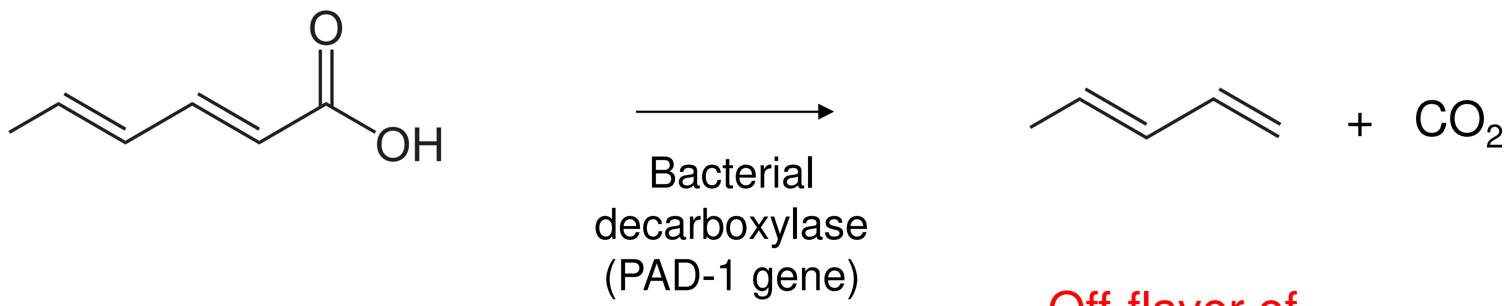
In wine, can produce a geranium leaf off-flavor



2-Ethoxy-hexadiene

7.6 PRESERVATIVES
Sorbic acid (II)

In presence of spoilage bacteria, can undergo a decarboxylation



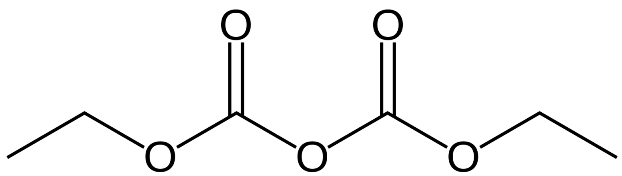
Off-flavor of petroleum, kerosene

7.6 PRESERVATIVES
Diethyl dicarbonate (DEDC)

In acidic media, causes complete destruction of yeasts in less than 60 minutes

Mainly used in beer, wine and fruit juices

Inactivates RNase enzymes (also used in biochemistry)



$$+\ 2\ H_2O \longrightarrow 2\ EtOH\ +\ 2\ CO_2$$