FOOD ADDITIVES

Introduction

- Food additives:
  - Intentional additives
  - Incidental additives

Intentional additives are added to food for specific purposes and are regulated by strict governmental controls.

Introduction

- A food additive is a substance (or a mixture of substances) which is added to food and is involved in its production, processing, packaging and/or storage without being a major ingredient.

- Additives or their degradation products generally remain in food, but in some cases they may be removed during processing.

FA Purposes

- To improve or maintain nutritional quality
  - Vitamins, minerals, amino acids & their derivatives
- To enhance quality
- To reduce wastage
- To enhance consumer acceptability – sensory value
  - Pigments, flavor enhancer, aroma compounds, polysaccharides, etc
- To prolong the shelf life of food
  - Antimicrobials, active agents (buffer to stabilize pH), thickening and gelling agents
- To make the food more readily available

In many food processing techniques, the use of additives is an integral part of the method.

FA should not be used:

- To disguise faulty or inferior processes
- To conceal damage, spoilage
- To deceive consumer
- If the use entails substantial reduction of important nutrients
- If the amount is greater than minimum necessary to achieve the desired effect.

Intentional FA

- Complex substances such as proteins or starches that are extracted from other foods (e.g. caseinates for sausages)
- Naturally occurring, well-defined chemical compounds such as salt, phosphates, acetic acid and ascorbic acid.
- Substances produced by synthesis which may or may not occur in nature, such as coal tar dyes, synthetic beta carotene, antioxidants, preservatives and emulsifiers.

Preservatives

- Increasing demand for convenience foods and reasonably long shelf-life of processed foods, therefore chemical food preservatives are indispensable.
- Elimination of microbes by physical methods is not always possible, therefore, antimicrobial agents are needed.
- Long history of use common preservatives, such as sulfites, nitrate, and salt-have been used for centuries in processed meats and wine.

Preservatives

- The choice of an antimicrobial agent is based on a knowledge of the antimicrobial spectrum of the preservative, the chemical and physical properties of both food and preservative, the conditions of storage and handling, and the assurance of a high initial quality of the food to be preserved.

- In the use of weak acids as preservatives, their pK value and the pH value of the food are very important for the application because only the undissociated molecule can penetrate into the inside of the microbial cell → weak acids are suitable preferably for acidic foods.

1. Benzoic Acid

- Benzoic acid (C_6H_5COOH) occurs naturally as a glycoside (in cranberry, bilberry, plum and cinnamon trees and cloves).
- As an additive, it is used as benzoic acid or benzoate. The sodium benzoate is used more often because it is more soluble than benzoic acid, which is sparsely soluble in water.
- Once in the product, some of the salt converts to the active form which is most active against yeast and bacteria, and least active against molds.

1. Benzoic Acid

- The undissociated form of benzoic acid (pKa = 4.19) is more effective antimicrobial agent. The optimum pH range from 2.5 to 4.
- Benzoic acid activity is directed both to cell walls and to inhibition of citrate cycle enzymes/ Krebs cycle (α-ketoglutaric acid dehydrogenase, succinic acid dehydrogenase) and of enzymes involved in oxidative phosphorylation.

1. Benzoic Acid

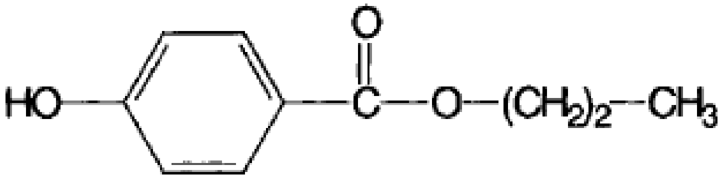
- Benzoic acid is an effective antimicrobial agent in high-acid foods, fruit drinks, cider, carbonated beverages, and pickles. It is also used in margarines, salad dressings, soy sauce and jams.
- Often benzoic acid is used in combination with sorbic acid or parabens.
- Level of use usually range from 0.05-0.1% by weight.
- Benzoate does not accumulate in the body but is converted, by condensation with glycine into hippuric acid (N-benzoylglycine), which is excreted in the urine.

1. Benzoic Acid

- Esters of p-hydroxybenzoic acid with methanol, propanol, and other alcohols, known collectively as ‘parabens’, are also commonly used in most of the same situations as benzoic acid and present similarly little problem of toxicity.

2. Parabens

- Parabens are alkyl esters of *p*-hydroxybenzoic acid.



- The alkyl groups may be methyl, ethyl, propyl, butyl and heptyl.
- Parabens are colorless, tasteless, odorless (except the methyl paraben), non-volatile and non-hygroscopic.
- Their solubility in water depends on the nature of alkyl group. → it decreases with increasing alkyl chain length (methyl → butyl).
- They have antimicrobial activity in both acid and alkaline pH regions.

2. Parabens

- The antimicrobial activity of parabens is proportional to the chain length of the alkyl group. The shorter chain is often used due to their solubility.
- Parabens are more active against moulds and yeasts (0.5-1% by weight) than against bacteria, and more active against Gram-positive than Gram-negative bacteria.
- Unlike benzoic acid, the esters can be used over a wide pH range since their activity is almost independent of pH

2. Parabens

- Parabens are used in fruitcakes, pastries, and fruit fillings. Methyl and propyl parabens can be used in soft drinks. Various combinations of several parabens can also be used in these and other foods.

3. Sorbic Acid

- Sorbic acid (C-C=C-C=C-COOH) is a straight chain, *trans-trans* unsaturated fatty acid, 2,4-hexadienoic acid.
- As an acid, it has low solubility in water at room temperature. The salts, sodium or potassium are more soluble in water.
- Sorbates are stable in the dry form; in aqueous solutions they decompose through oxidation.
- Sorbic acid and sorbates are effective against yeast and moulds.

3. Sorbic Acid

- The antimycotic effect of straight chain carboxylic acids has long been known. In particular the unsaturated acids, for example crotonic acid and its homologues, are very active.
- Sorbic acid (2-trans, 4-trans-hexadienoic acid; pK = 4.76) has the advantage that it is odorless and tasteless at the levels of use (0.3% or less). At such levels, sorbates do not affect food flavor. When used at higher levels, they may be detected by some people as unpleasant flavor.

3. Sorbic Acid

- The activity is pH dependent.
- Its utilization is possible up to pH 6.5, the proportion of undissociated acid being still 1.8%.
- Sorbates inhibit yeast growth in wine, fruit juice, dried fruit, cottage cheese, meat and fish products. Sorbates are usually used in sweetened wines or wines that contain residual sugars to prevent re-fermentation.
- Sorbates may also be degraded by certain microorganisms to produce off-flavors.

3. Sorbic Acid

- Some microorganisms, such as *Penicillium roqueforti*, have the ability to decarboxylate sorbic acid and thus convert it into 1,3-pentadiene, which has no antimicrobial activity and in addition may contribute to an off-flavor in cheeses.

4. Sulfites

- Sulfur dioxide and sulfites have long been used as preservatives, serving both as antimicrobials and as antioxidants (used in wine in Roman times).
- Sulfur dioxide also can inhibit nonenzymatic browning and certain enzyme-catalyzed reactions.
- It dissolves to form sulfurous acid.
- Instead of sulfur dioxide solutions, a number of sulfites can be used when dissolved in water, they all yield active SO_2.

4. Sulfites

- The commonly used forms in foods: sulfur dioxide gas, Na/K/Ca salts of sulfite (SO_3^{2-}), bisulfite (HSO^{3-}) or metabisulfite ($S_2O_5^{2-}$).
- The most widely used are sodium or potassium metabisulfite → because they exhibit good stability toward autoxidation.
- All of water dissolved sulfur are known as free sulfur dioxide. The bisulfite ion (HSO_3^-) can react with aldehydes, dextrins, pectic substances, proteins, ketones, and certain sugars.

4. Sulfites

- The activity of these preserving agents covers yeasts, molds and bacteria.
- The activity increases with decreasing pH and is mostly derived from undissociated sulfurous acid, which predominates at a pH < 3.
- Toxicity is negligible at the levels usually applied.
- Sulfite reacts with a series of food constituents, e. g., proteins with cleavage of disulfide bonds, with various cofactors like NAD$^{\oplus}$, folic acid, pyridoxal, and thiamine.

4. Sulfites

- SO_2 is used in the production of dehydrated fruits and vegetables, fruit juices, syrups, concentrates or purée.
- SO_2 is added in wine making prior to fermentation to eliminate interfering microorganisms.
- The form of application is SO_2, Na_2SO_3, K_2SO_3, $NaHSO_3$, $Na_2S_2O_5$ and $K_2S_2O_5$ at levels of 200 ppm or less.
- During wine fermentation with selected pure yeast cultures, SO_2 is used at a level of 50–100 ppm, while 50–75 ppm are used for wine storage.

5. Nitrates & Nitrites

- They are known as curing agents, which produce the characteristic color and flavor of products such as bacon, ham.
- Nitrate can be reduced to nitrite, which is not desired in food.
- Both nitrates and nitrites have antimicrobial agents.
- Nitrate is used in the production of cheese to prevent gas formation by butyric acid-forming bacteria.
- Nitrite inhibits toxin formation by *C. botulinum*.

5. Nitrates & Nitrites

- The activity is dependent on the pH and is proportional to the level of free HNO_2.
- Indeed, 5–20 mg of nitrite per kg are considered sufficient to redden meat, 50 mg/kg for the production of the characteristic taste, and 100 mg/kg for the desired antimicrobial effects.
- Nitrite, which may react with secondary amines in food to form nitrosamines.
- The nitrosamines are powerful carcinogens, and they may be mutagenic and teratogenic.

6. Hydrogen Peroxide

- H_2O_2 is a strong oxidizing agent and is also useful as a bleaching agent. For example: in crude soya lecithin.
- H_2O_2 is used for the preservation of cheese milk.
- H_2O_2 decomposes slowly into water and oxygen. This process is accelerated by increased temperature and the presence of heavy metals and enzymes such as catalase and lactoperoxidase.
- Its antimicrobial action increases with temperature.

6. Hydrogen Peroxide

- When H_2O_2 is used for cheese making, the milk is treated with 0.02% H_2O_2 followed by catalase to remove H_2O_2.
- H_2O_2 is also used as component of the lactoperoxidase system, which generates antimicrobial compounds through the oxidation of thiocynate (SCN^-), naturally present in milk.
- H_2O_2 can be used for sterilizing food processing equipment and for sterilizing packaging material used in aseptic food packaging systems.

7. Propionic Acid

- Propionic acid is found in nature where propionic acid fermentation occurs, e. g., in Emmental cheese, in which it is present up to 1%.
- Its antimicrobial activity is mostly against molds, less so against bacteria.
- Propionic acid has practically no effect against yeast.
- Its activity is pH dependent. It is recommended and used up to pH 5 and only occasionally up to pH 6.

7. Propionic Acid

- Propionic acid is practically nontoxic.
- It is used as an additive in baked products for inhibition of molds, and to prevent ropiness caused by the action of *Bacillus mesentericus*.
- It is added to flour at 0.1–0.2% as its Ca-salt and is used in cheese manufacturing by dipping the cheese into an 8% solution of the acid.

8. Acetic Acid

- The preserving activity of vinegar has been known from ancient times.
- The acid has a two-fold importance: as a preservative and as a seasoning agent.
- It is more active against yeasts and bacteria than against molds.
- It is used as the free acid, Na- and Ca-salts, or as Na-diacetate ($CH_3COOH·CH_3COONa·1/2H_2O$), in ketchup, mayonnaise, acid-pickled vegetables, bread and other baked products.

Sweeteners

- Sweeteners are natural or synthetic compounds which imprint a sweet sensation and possess no or negligible nutritional value (“nonnutritive sweeteners”) in relation to the extent of sweetness.

Sweeteners

- The search for new sweeteners is complicated by the facts:
    - the relationship between chemical structure and sweetness perception
    - the safety of suitable compounds has to be certain
    - the compound must be adequately soluble and stable over a wide pH and temperature range
    - have a clean sweet taste without side or post-flavor effects
    - provide a sweetening effect as cost-effectively as does sucrose

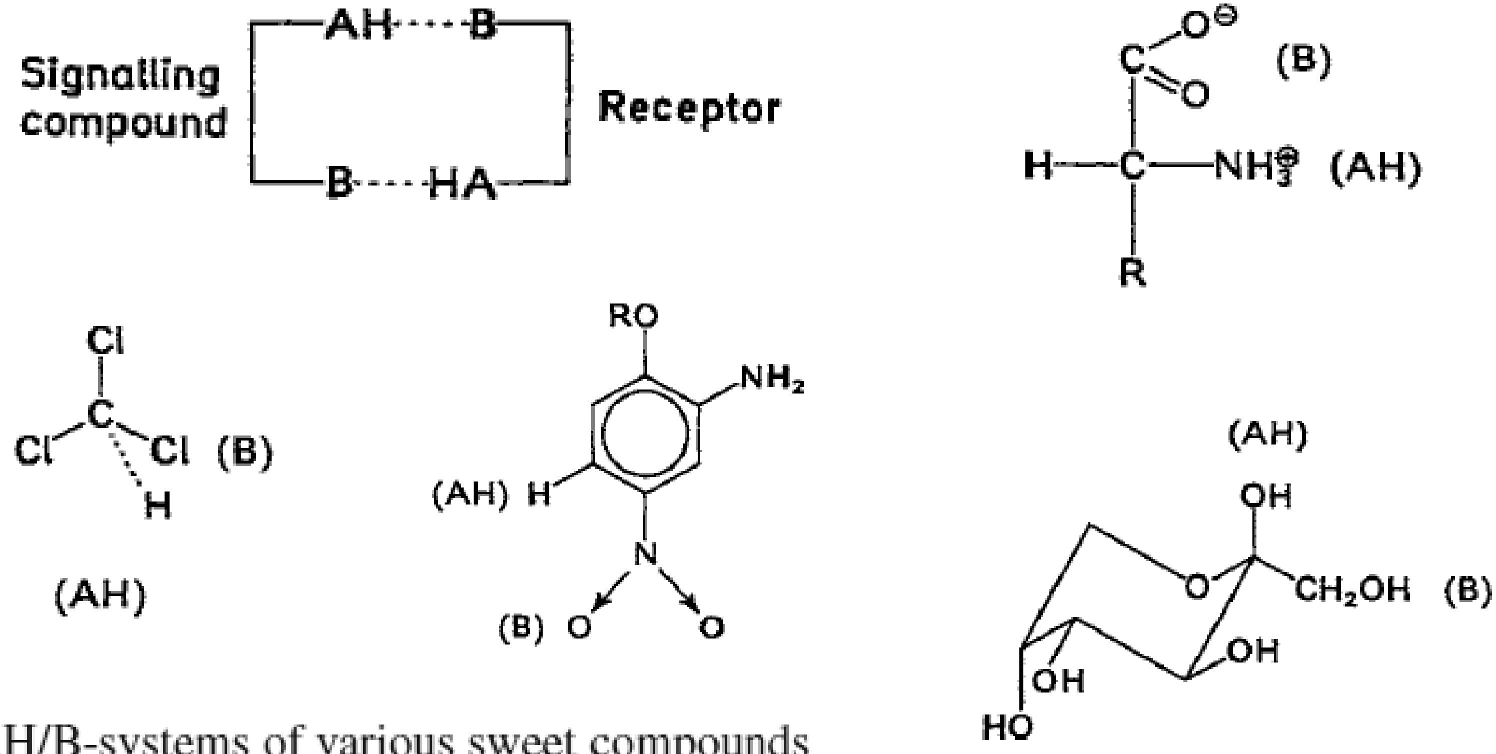
Sweeteners

- The same taste and functional characteristics as sucrose
- Low caloric density on a sweetness equivalency basis.
- Non-cariogenicity
- Metabolized normally or excreted unchanged
- No allergenic, mutagenic, carcinogenic or other toxic effects in the body.
- Chemical and thermal stability
- Compatibility with other food ingredients
- Economically competitive with existing sweeteners.

Sweeteners

- Sweeteners may be nutritive, as they are the hydrogenated sugars, also known as sugar alcohols or polyols, or can be non-nutritive as are the intense sweeteners.
- They can be synthesized or extracted form natural sources.
- Intense sweeteners contribute no bulk, viscosity or texture to foods and beverages, and must be mixed with nutritive sweeteners, or some other bulking agent when these properties are required.

- A sweet taste can be derived from compounds with very different chemical structures.
- A compound must contain a proton donor/acceptor system (AHs/Bs-system), which has to meet some steric requirements and which can interact with a complementary receptor system (AHr/Br-system) by involvement of two hydrogen bridges



AH/B-systems of various sweet compounds

Sweeteners

- In mixtures of sweet tasting substances, synergistic intensification of taste occurs, i. e., the sweetness intensity is higher than the calculated value.
- An example is the intensification of sweetness in acesulfame–aspartame mixtures

1. Polyols

- Sugar alcohols, which are functionally similar to sucrose, and are bulking agents.
- Sorbitol, mannitol and xylitol are naturally occuring like sucrose.
- They have technical benefits including increased chemical stability and affinity for water, without altering the sweetening power, and a reduced tendency to crystallise.
- The physiological benefits are that sugar alcohols have low cariogenicity. They are suitable for inclusion in products for diabetics.

1. Polyols

- Xylitol has about the same sweetness as sucrose.
- The other sugar alcohols are less sweet and need supplementation with intense sweeteners to be comparative to sucrose.
- Sugar alcohols add texture and mouth feel properties to foods and drinks since they are bulking agents.
- Many sugar alcohols, xylitol and sorbitol particularly, impart a cooling sensation in the mouth because they absorb heat as they dissolve.
- All have pleasant, sweet taste profile with no after-taste.

2. Saccharine

- Sachharine ($C_7H_5NO_3S$) was accidentally discovered in 1879.
- Saccharin is an important sweetener ($f_{sac, g}(10) = 550$) and is mostly used in the form of the water-soluble Na salt, which is not so sweet ($f_{sac, g}(10) = 450$).
- At higher concentrations, this compound has a slightly metallic to bitter after-taste.
- It is usually available as the sodium salt and sometimes as calcium salt.
- It is the most widely used sugar due to its high stability, and low cost.

2. Saccharine

- Saccharin is not metabolized in the body, but it is excreted unchanged.
- Bladder tumor have been associated with saccharine intake.
- The present stipulated ADI value is 0–2.5mg/kg of body weight.
- The synthesis of saccharin usually starts with toluene process, or sometimes with the methyl ester of anthranilic acid.

3. Aspartame

- It is discovered accidentally in 1965, while synthesizing a product for ulcer therapy.
- Aspartame is dipeptide methyl ester, composed of two amino acids (phenylalanine and aspartic acid).
- It has a very agreeable sweet taste but is unstable under certain conditions.
- It is one of the most thoroughly tested FA.
- The safety of aspartame’s component amino acids, and of its metabolite (methanol) has been questioned.

3. Aspartame

- However, toxicity is always dose-related and large safety margins has been reported with regard to amounts likely to be consumed in the human diet.
- Analysis of adverse reactions and clinical data suggests that aspartame is remarkably safe.
- Warning on product packaging are necessary to alert sufferers of phenylketonuria who have to control the amount of phenylalanine in their diets.

4. Acesulfame -K

- It is a potassium salt derived from acetoacetic acid, with a chemical formula of $C_4H_4NO_4KS$ and has molar mass of 201.2.
- This sweet-tasting compound was discovered accidentally in 1967.
- No adverse reactions in the body to the consumption of acesulfame-K have been found.
- The Join FAO/WHO Expert Committee on Food Additives (JECFA) allocated an ADI of 0.9 mg/kg of bw in 1983, having found that acesulfame-K was neither mutagenic nor carcinogenic, and with no other toxicological problems.

4. Acesulfame -K

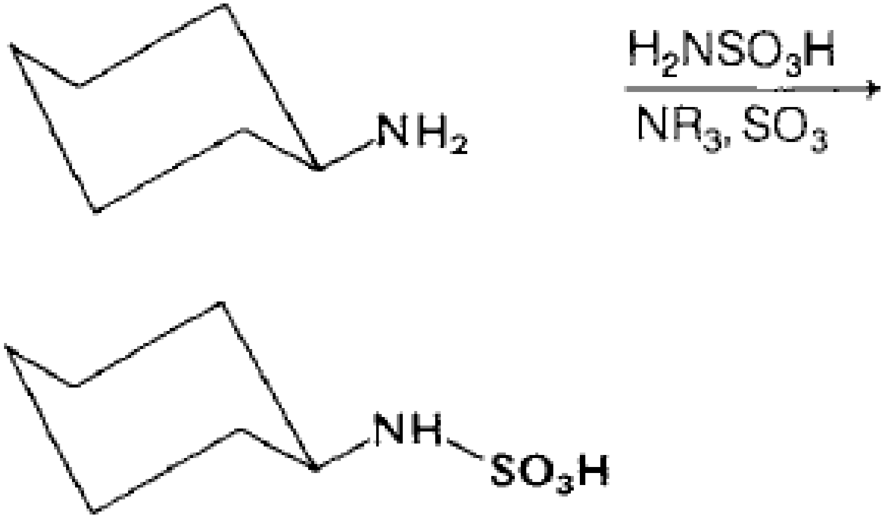
- It is not metabolized in the body, is excreted rapidly and completely, and thus has no caloric value and it is suitable for diabetics.
- It is also considered to be non-cariogenic, since the acute oral toxicity of acesulfame-K use is extremely low.

5. Cyclamate

- Cyclamate is a widespread sweetener and is marketed as the Na- or Ca-salt of cyclohexane sulfamic acid.
- The sweetening strength is substantially lower than that of saccharin and is f_{sac}, g(10) = 35. It has no bitter after-taste.
- Overall, the sweet taste of cyclamate is not as pleasant as that of saccharin.
- The present stipulated ADI value of the acid is 0−11 mg/kg of body weight.

5. Cyclamate

- The synthesis of the compound is based on sulfonation of cyclohexylamine



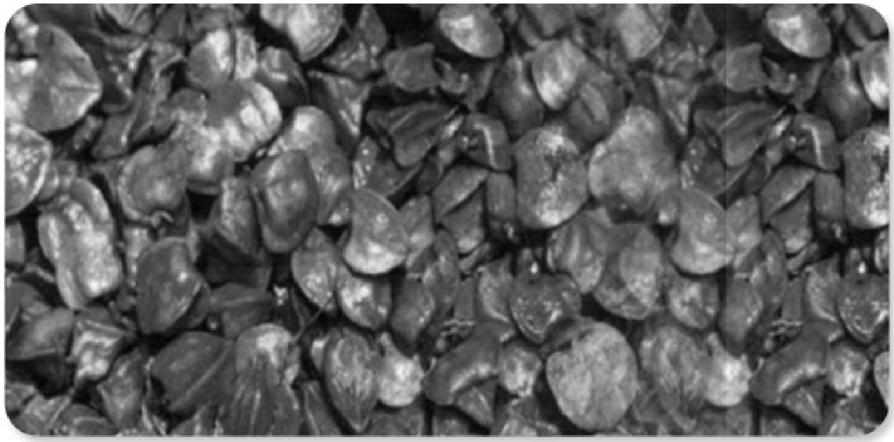
6. Monellin

- The pulp of *Dioscoreophyllum cumminsii* fruit contains monellin, a sweet protein with a molecular weight of 11.5 kdal. It consists of two peptide chains, A and B, which are not covalently bound.
- The threshold value is f_{sac}, g = 3000.
- Based on its low stability, slow triggering and slow fading away of taste perception, monellin probably will not succeed as a commercial sweetener.

Inunurin

7. Thaumatin

- The fruit of *Thaumatococcus daniellii* contains two sweet proteins: thaumatin I and II, with f_{sac}, g ~2000.
- Thaumatin which is regarded as toxicologically safe is used, e. g., in chewing gum and milk products.
- Synergistic effects have been observed when thaumatin is used in combination with saccharin and acesulfame.



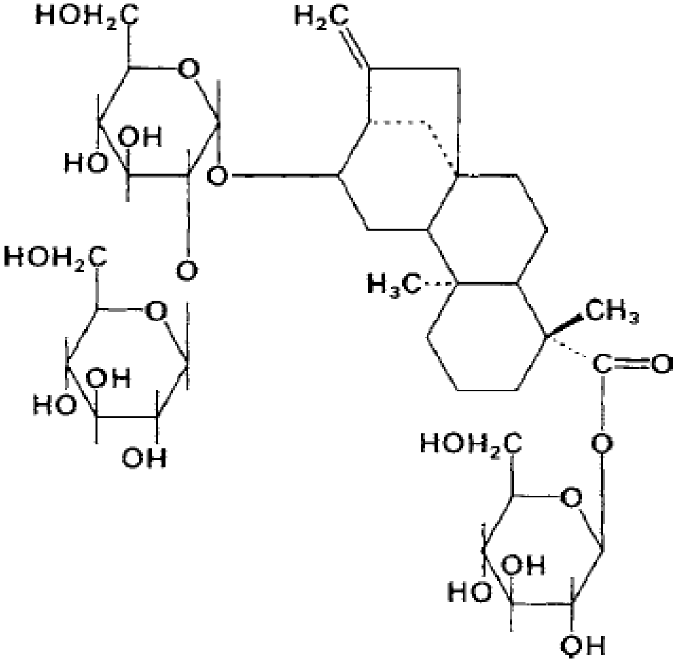
8. Curculin

- Curculin is a sweet protein ($f_{sac,\ g}(6.8) = 550$) of known sequence.
- It occurs in the fruit of *Curculigo latifolia*. The sweet taste induced by this protein disappears after a few minutes, only to reappear with the same intensity on rinsing with water.
- It is assumed that Ca^{2+} and/or Mg^{2+} ions in the saliva suppress the sweet taste.
- Rinsing with citric acid (0.02 mol/l) considerably enhances the impression of sweetness ($f_{sac,\ g}(12) = 970$). Thus, like miraculin, curculin acts as a taste modifier.

9. Miraculin

- Miraculin is a glycoprotein present in the fruit of *Synsepalum dulcificum* (a tropical fruit known as miracle berry).
- Although it is tasteless, it has the property of giving sour solutions a sweet taste and therefore it is called a taste modifier.
- Thus, lemon juice seems sweet when the mouth is first rinsed with a solution of miraculin.
- The molecular weight of this taste modifier is 42–44 kdal.

10. Stevioside

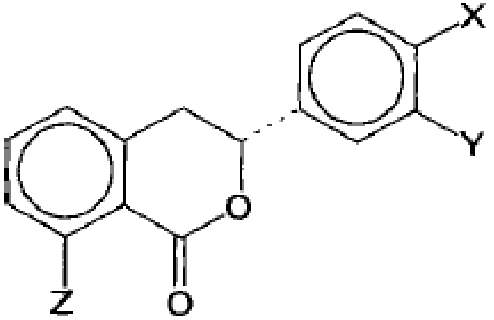


- Leaves of *Stevia rebaudiana* contain approx. 6% stevioside ($f_{\text{sac, g}}(4)$ ~300).
- This compound is of interest as a sweetener, however its toxic properties are unclear.

11. Phyllodulcin

- The leaves of *Hydrangea macrophylla* contain a 3,4-dihydroisocoumarin derivative, phyllodulcin.
- Its sweetness matches that of dihydrochalcones and of licorice root.
- The taste perception builds relatively slowly and also fades away slowly.
- The sweetening strength is $f_{sac}(5) = 250$.
- A study of a number of related isocoumarin derivatives shows that taste quality and strength are very much dependent on the substitution pattern of the molecule

11. Phyllodulcin



Z = OH, X = OMe, Y = OH

Sensory properties of some 2,3-dihydro-isocoumarins

Compound[a]			
X	Y	Z	Taste
OMe	OH	OH	very sweet
OMe	OMe	OH	bitter
OMe	OMe	OMe	no taste
OMe	OAc	OAc	slightly sweet
OH	OH	OH	no taste
OH	H	OH	no taste
OH	OH	H	no taste
OMe	OH	H	very sweet
OH	OMe	H	no taste

Hydrocolloids

- A group of polysaccharides and to some extent proteins (notably gelatin) which are obtained from a variety of sources including trees, plants, seaweeds, animals and bacteria.
- Hydrocolloids are water-soluble polymers with an ability to thicken or gel aqueous systems (thickening and gelling agents).
- They can be classified according to origin, isolation method, function, texture, gelling time.

Hydrocolloids

- The function of hydrocolloids:
  - Control rheology and texture (thickening and gelling agents)
  - Stabilize emulsions (prevent coalescence and flocculation)
  - Prevent sedimentation and creaming
  - Control the organoleptic properties (mouthfeel and flavor release)
  - Inhibit ice crystal growth

Table 1 *Functionalities of hydrocolloids*

Function	Example
Adhesive	Glazes, icings, frostings
Binding agent	Pet foods
Bodying agent	Dietetic beverages
Crystallization inhibitor	Ice cream, sugar syrups, frozen foods
Clarifying agent (fining)	Beer, wine
Cloud agent	Fruit drinks, beverages
Coating agent	Confectionery, fabricated onion rings
Dietary fibre	Cereals, bread
Emulsifier	Salad dressings
Encapsulating agent	Powdered flavours
Film former	Sausage casings, protective coatings
Flocculating agent	Wine
Foam stabiliser	Whipped toppings, beer
Gelling agent	Puddings, desserts, confectionery
Moulding	Gum drops, jelly candies
Protective colloid	Flavour emulsions
Stabiliser	Salad dressings, ice cream
Suspending agent	Chocolate milk
Swelling agent	Processed meat products
Syneresis inhibitor	Cheese, frozen foods
Thickening agent	Jams, pie fillings, sauces
Whipping agent	Toppings, marshmallows

Hydrocolloids

Structure	Characteristics	Examples
Substituted linear	Numerous short branches often consisting of only one sugar unit in length	Guar gum
Branch on branch	Slide chains on side chains. More viscous than linear. Typically, two or more types of sugar make up the polysaccharides. Excellent adhesive properties.	Amylopectin, gum arabic

Hydrocolloids

Structure	Characteristics	Examples
Linear	Not more than two copolymerized sugar units. High viscosity. Unstable solutions. Difficult to dissolve. Risk of precipitation after gelation.	Cellulose, amylose, pectin, carrageenan, alginate, agar.
Single branch	Sugar units condensed with carbon groups other than C1 or C4	Dextrane

Thickeners

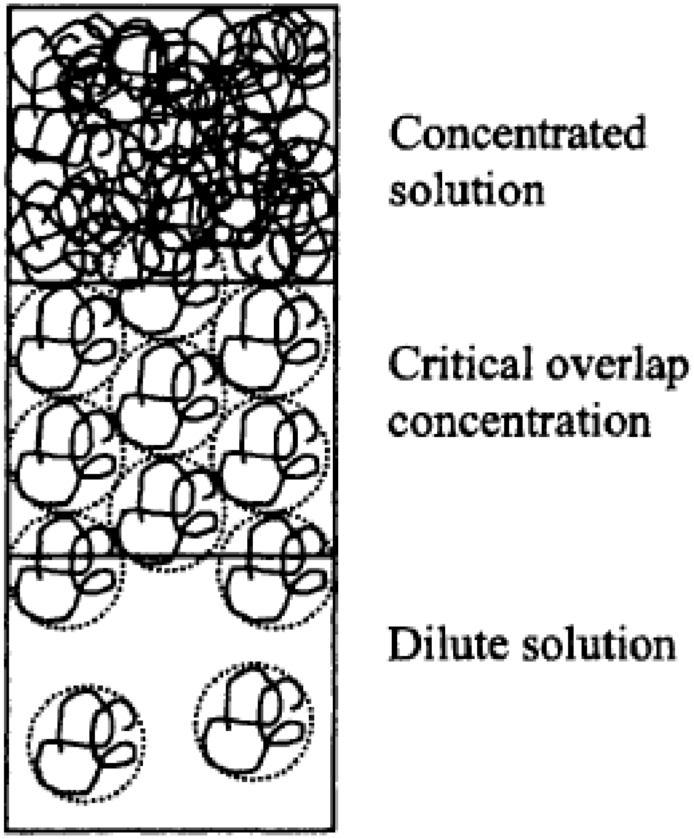
- Within the food industry, stabilizers, thickeners and gelling agents are often more simply referred to as food hydrocolloids.
- The hydrocolloids traditionally used in food thickening and gelling include, but are not limited to, the following:
    - agar, alginates, arabic, carrageenan, cassia tora, carboxymethyl cellulose, gelatin, gellan, guar, karaya, konjac, locust bean gum, methyl cellulose, hydroxypropylmethyl cellulose, microcrystalline cellulose, pectin, starches, tara, tragacanth and xanthan.

Thickeners

Hydrocolloid	Characteristic
Modified starch	Form viscous solutions
Xanthan gum	Solutions have a high low-shear viscosity (apparent yield stress) and is not significantly influence by temperature, addition of salts or to pH changes.

Sodium carboxymethyl cellulose	Viscous solutions are formed but the viscosity decreases on addition of salts and at low pH
Methylcellulose and hydroxymethylcellulose	Viscous solutions are formed which are not influenced by salts or pH. Solutions gel on heating
Galactomannans (guar, locust bean, and tara gum)	Viscous solutions are formed which are not influences by addition of salts or changes in pH
Konjac maanan	Forms highly viscous solutions which are not influenced by the addition of salts; however will form thermally irreversible gels in alkali.

- Hydrocolloid thickeners can be considered **as** entanglement networks and properties are very much related to the size and number of molecules in solution, i.e. molecular weight and concentration.
- In dilute solution the individual molecules (random coils), are free to move independently and hence do not contribute significantly to the viscosity.
- **As** concentration is increased, the molecules begin to come into contact with one another.
- This transition from free moving molecules to an entangled network is accompanied by a change in the concentration dependence of the viscosity.



The application of thickener in food:

- **Guar gum:** drinks, sauces, soups, ketchups, dressings
- **Locust bean gum:** ice cream, soups, ketchups, dressings
- **Tara gum:** soups, ketchups, dressings
- **Karaya:** coatings, fillings, toppings, chewing gum
- **Konjac:** dessert, surimi, frozen desserts, sauces
- **Xanthan gum:** sauces, dressings, drinks, fruit preparations, meat products
- **Gum arabic:** drinks, confectionery gums
- **Sodium alginate:** salad dressings, ice cream, low fat spreads, bakery filling creams
- **Pectin:** jams, confectionery, bakery fillings, glazes, sorbets, yoghurt drinks

Gelling agents

- The most important hydrocolloid food gelling agents are gelatine, starch, pectin, carrageenan and alginate, but also agar, celluloses, gellan gum, konjac, milk proteins and soy proteins can be used as gelling agents.
- In high-moisture foods, hydrocolloids are more or less dissolved in water, whereas in low-moisture foods water has a completely different role: that of plasticiser.
- Gel properties are important for flavour release from gelled foods, whereas the clarity and surface smoothness of gels mainly depend on the presence and structure of insoluble components.

Gelling agents

- Gel is a continuous network of particles or molecules in a continuous liquid phase (water or oil).
- Hydrocolloids can form molecular gels through association of parts of the molecules forming ‘junction zones’.
- The type of binding in the junction zone and the amount of molecules forming the junction zones are the most important factors determining the rheological and thermal properties of the gel.

- Gelling agents’ molecules have structures that allow them to form ordered structures, which in turn can form ordered structures together with other molecules.
- The ordered structures of two or more molecules are called ‘junction zones’.
- The number of molecules that form a junction zone is an important gel property determinant.

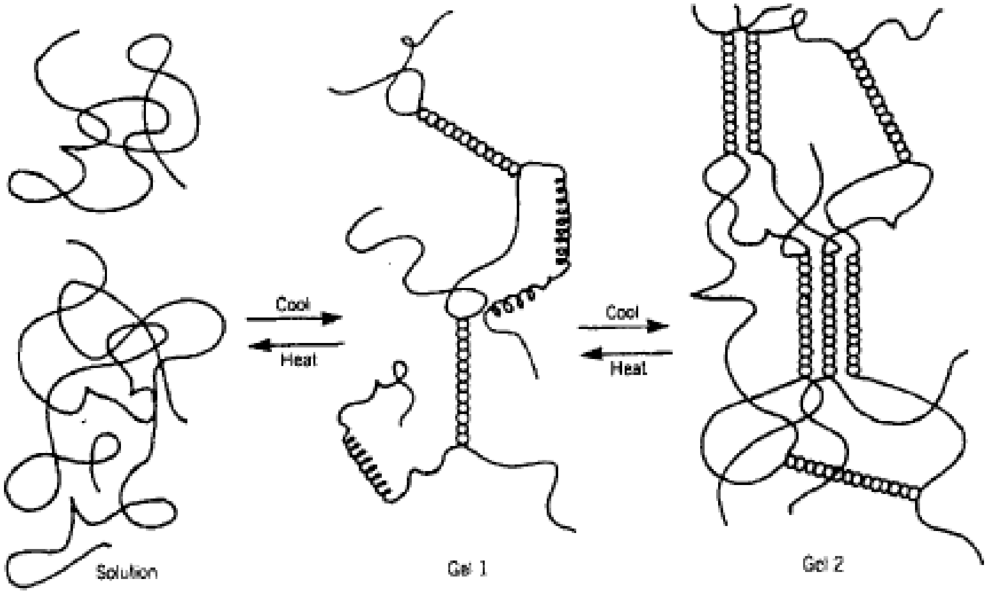
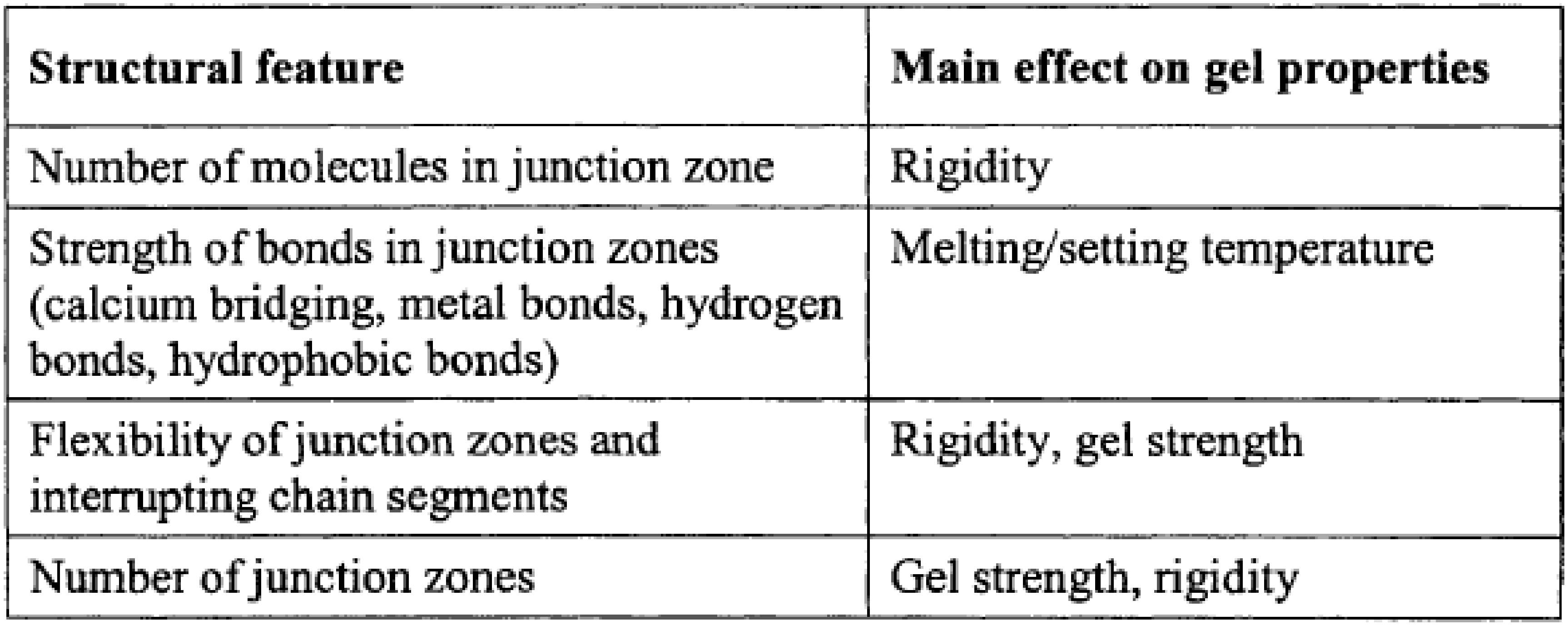


Figure 1: Schematic representation of kappa carrageenan gelling.

- In kappa carrageenan some 6-10 molecules form a junction zone, whereas in iota carrageenan only two molecules are involved.
- This is the reason why iota carrageenan gels have much more ‘flexible’ textures and are less shear sensitive: the multi-molecule junction zones of kappa carrageenan are more rigid and less easily rebuilt when disturbed by shear.

- The thermal behaviour of gels depends on the strength of the bonds holding the junction zones together.
- Gelatine melts at much lower temperatures because the junction zones are only bound by weak hydrogen bonds.



Structural feature	**Main effect on gel properties**
Number of molecules in junction zone	Rigidity
Strength of bonds in junction zones (calcium bridging, metal bonds, hydrogen bonds, hydrophobic bonds)	Melting/setting temperature
Flexibility of junction zones and interrupting chain segments	Rigidity, gel strength
Number of junction zones	Gel strength, rigidity

Table 3: Main gel characteristic determining features of gelling agent molecules.

Application of gelling agents:

- **Carrageenans**
    - They are used in dairy desserts and chocolate milk because they form gels in milk at much lower concentrations compared with any other gelling agent.
    - The second-most important application for carrageenan is injected meat, in which only carrageenans can be dispersed in brine without too high viscosity and simultaneous gel formation when the ham has been cooked.
    - In acidic environments (pH <4) carrageenans are degraded at high temperatures.

- **Pectins**
  - Pectins are acid stable and need acid/sugar/calcium for gelling.
  - They are therefore the preferred gelling agents for acidic (fruit) gels, jams and sugar confectionery products with a ‘short’ texture.
- **Alginates**
  - Alginate is the only gelling agent that can form gels without prior heating (because sodium alginate is cold soluble), and those cold-formed gels are heat stable.
  - This makes alginate the preferred gelling agent for re-structured foods (centre fillings for jarred olives) and for cold-prepared instant bakery custard that is to be bake stable.

- **Gelatine**
  - Gelatine gels melt at relatively low temperatures (melt-in-mouth), they are slow setting (no gelling above approx. 15°C when cooling).
  - These features make gelatine the preferred gelling agent in yoghurt products, dairy mousse, low-fat spreads and sugar confectionery (marshmallows and wine gums in which the elastic gel characteristics and the clarity are also appreciated).
  - The clarity is the main reason for use in aspic and table jellies.
- **Agar**
  - Agar gives very brittle gels, and if this is a desirable feature agar is the preferred gelling agent (e.g. confectionery products, table jellies, milk gels in Asian countries).
  - The high melting temperature of agar gels is used in some icings.

Emulsifiers-Classification

- Based on charge:
  - Anionic: surfactants that carry a negative charge on the active portions of the molecule.
  - Cationic: surfactants that carry a positive charge on the active portions of the molecule.
  - Non-ionic: Uncharged molecule having lipophilic and hydrophylic parts.
  - Amphoteric: surfactant species that can be either cationic or anionic.
  - Zwitterionic: both positive and negative charge may be present in the surface active portion.

Emulsifiers-Classification

- Based on hydrophylic – lipophylic balance (HLB)
- Based on solubility
- Based on functional groups: saturated/ unsaturated acids, alcohols, ethylene oxide, etc.

Emulsifiers-Emulsification

- All emulsifiers are surface active agents, which can promote emulsification of oil and water phases because they possess both hydrophilic and lipophilic groups within the same molecule.
- Emulsifiers with low hydrophilic to lipophilic ration value (HLB value) stabilize water in oil emulsions, whereas emulsifiers with high HLB value stabilize oil in water emulsions.
- Each system requiring an emulsifier has an optimum HLB value.

Emulsifiers-Emulsification

- This HLB value can be used as an indicator of the most suitable emulsifier for that particular system.
- However, the chemical type of the emulsifier also is important in achieving emulsion stability.

Emulsifiers-Dispersion

- Dispersions of solids, liquids and gasses depend on the reduction of interfacial energy by a surface – active agent. The disperse systems can involve all three principle phases.

Type	Internal phase	External phase
Emulsion	Liquid	Liquid
Foam	Gas	Liquid
Aerosol	Liquid / Solid	Gas
Suspension	Solid	Liquid

Emulsifiers

Behavior of surfactant in water	HLB range
No dispersibility in water	1 – 4
Poor dispersion	3 – 6
Milky dispersion after vigorous agitation	6 – 8
Stable milky dispersion	8 – 10
Translucent to clear dispersion	10 – 13
Clear solution	13+

Emulsifiers

- Sorbitan monostearate
- Polysorbate 60
- Lecithin
- Polyglyserol ester of FA
- Mono and di-glyceride lactylated
- Milk proteins

Fat Replacers

Natural (fat mimetics)

- **Microparticulated Proteins**
  - Protein particles with a diameter of more than 8 µm are experienced as sandy, those in the range of 3–8 µm as powdery, 0.1–3 µm as creamy, and less than 0.1 µm as watery.
  - Therefore, protein particles with diameter 0.1–3 µm is possible to achieve the melt-in-the-mouth feeling produced by fat globules.
  - Examples: ovalbumin, casein, whey protein.

  - These substitutes are suitable for milk products (ice cream, desserts etc.) which are not strongly heated.
  - In fact, 3 g of fat can be replaced by 3 g of swollen substitute (1 g of protein +2 g of water) or 27 kcal by 4 kcal.
- **Carbohydrates**
  - Polymeric carbohydrates (fiber) are non-digestible in the small intestine.
  - These substances are degraded by the bacteria in the large intestine with the formation of short-chain acids (2:0, 3:0, 4:0), which are absorbed and gain in energy at 2 kcal/g.
  - The carbohydrate based fat substitutes include the resistant starches, fructose polymers, pectin, modified starch and cellulose, e. g., carboxymethyl cellulose

Synthetic (fat substitute, fat replacer)

- **Roles:**
  - replacement of glycerol with other alcohols,
  - replacement of the usual fatty acids with branched, polybasic or especially long-chain carboxylic acids,
  - introduction of inverse ester bonds (retrofats),
  - use of ether instead of ester bonds.

- Mono-, oligo- and polysaccharides yield fatlike products when esterified with fatty acids.
- In the best known product, *Olestra*, 6–8 OH groups are esterified with fatty acids 8:0–12:0. This product is tasteless and thermally stable so that it can be as strongly heated as an edible fat during baking and frying.
- Retrofats are esters of polybasic acids (e. g., malonic acid, citric acid, propane 1,2,3-tricar-boxylic acid, butane 1,2,3,4-tetracarboxylic acid) with long-chain alcohols.

Chelating Agents (Sequestrans)

- Chelating agents have ability to bind metal ions has contributed significantly to stabilization of food color, aroma and texture.
- Traces of heavy metal ions can act as catalysts for fat or oil oxidation.
- Their binding by chelating agents increases antioxidant efficiency and inhibits oxidation of ascorbic acid and fat-soluble vitamins.
- The stability of the aroma and color of canned vegetables is substantially improved.

Table 8.14. Chelating agents used as additives in food processing. (Compounds given in brackets are utilized only as salts or derivatives)

(Acetic acid)	Na-, K-, Ca-salts
Citric acid	Na-, K-, Ca-salts, monoisopropyl ester, monoglyceride ester, triethyl ester, monostearyl ester,
EDTA	Na-, Ca-salts
(Gluconic acid)	Na-, Ca-salts
Oxystearin	
Orthophosphoric acid	Na-, K-, Ca-salts
(Pyrophosphoric acid)	Na-salt
(Triphosphoric acid)	Na-salt
(Hexametaphosphoric acid, 10–15 residues)	Na-, Ca-salts
(Phytic acid)	Ca-salt
Sorbitol	
Tartaric acid	Na-, K-salts
(Thiosulfuric acid)	Na-salt