Reactions of saccharides

complex of enzymatic and nonenzymatic reactions

carbonyl, anomers OH, primary OH, secondary OH

nonenzymatic browning reactions

- reaction of saccharides
- Maillard reaction

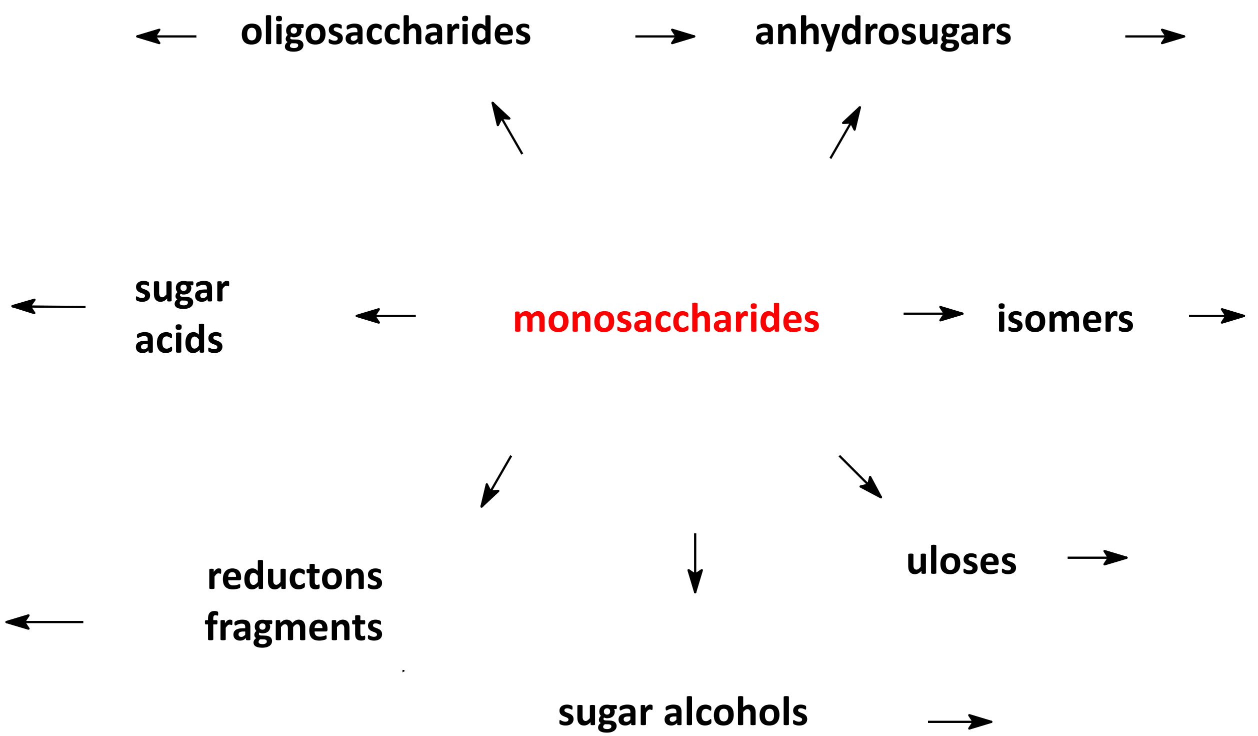
  (reaction with proteins, amino acids)
- caramelisation

Reaction of saccharides themselves

reactants

- reducing mono- and oligosaccharides
- non-reducing oligo- and polysaccharides after hydrolysis

main reactions of monosaccharides



acid-basic catalysed reactions

in acid medium | in alcali medium

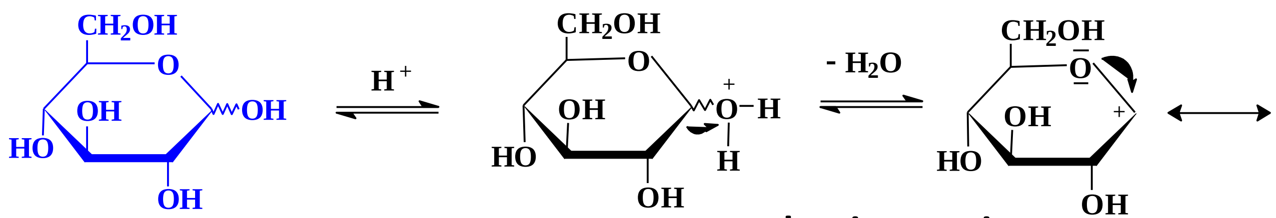
(further factors: temperature, time)

mutarotation

in acid medium	in alcali medium
formation (hydrolysis) of glycosides	isomeration
dehydration	rearrangement
reductone formation	fragmentation
	oxidation

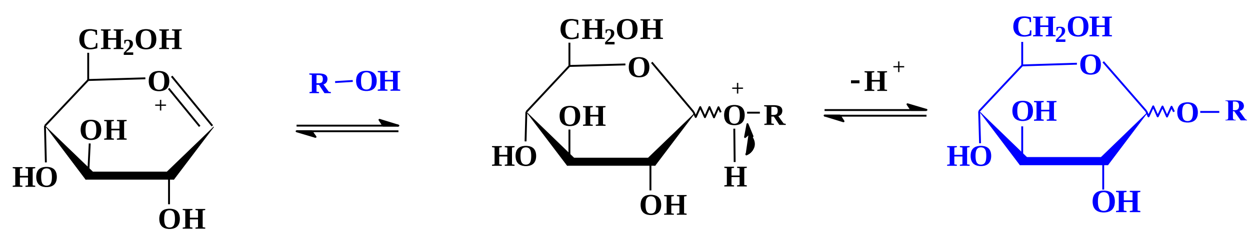
formation and hydrolysis of glycosides

reaction of poloacetals OH



monosaccharide

carbenium cation



glycoside (hetero- or homo glycoside)

hydrolysis (inversion)

- production of starch syrups
- invert sugar
- galactose

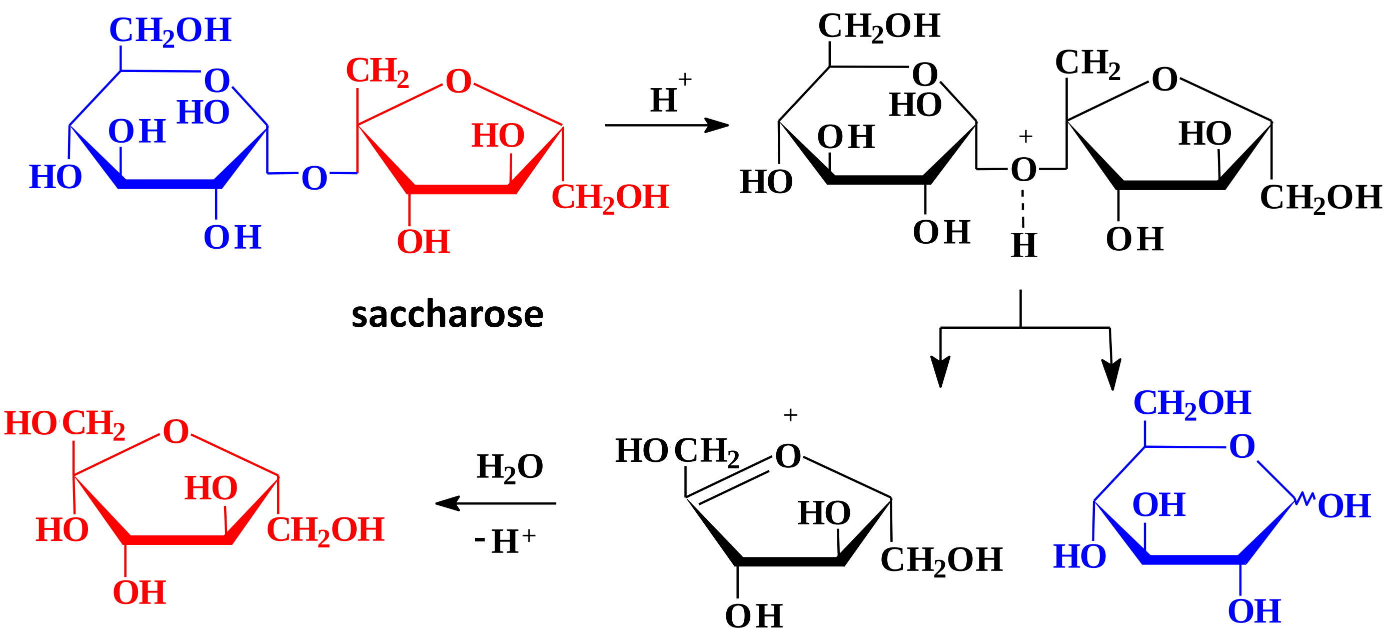
formation (reverse, Fischer reaction)

side products of inversion (starch syrup: 5-6%)

side products of caramelisation

preferably (1→6) bonds, less (1→4) and other bonds

mechanism of hydrolysis of saccharose



D-fructose

D-glucose

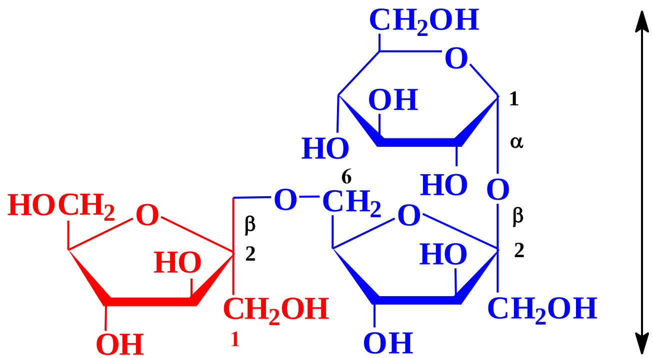
pH (5.2-5.8)

- enzymatic hydrolysis, hydrolases, inactivation 80 °C
- chemical hydrolysis, losses 0.5% /h

pH 8.4

- $Ca(OH)_2$
- Maillard reaction

glucose →	isomaltose	α-D-Glc*p*-(1→6)-D-Glc*p*	68-70%
(disaccharides)	genciobiose	β-D-Glc*p*-(1→6)-D-Glc*p*	17-18%
	maltose	α-D-Glc*p*-(1→4)-D-Glc*p*	
	cellobiose	β-D-Glc*p*-(1→4)-D-Glc*p*	
saccharose →	kestose	β-D-Fru*f*-(2→6)-β-D-Fru*f*-(2↔1)-α-D-Glc*p*	
(trisaccharides)	kelose	α-D-Fru*f*-(2→6)-β-D-Fru*f*-(2↔1)-α-D-Glc*p*	



saccharose

levanbiose

kestose

low energy foods

indicators of adulteration

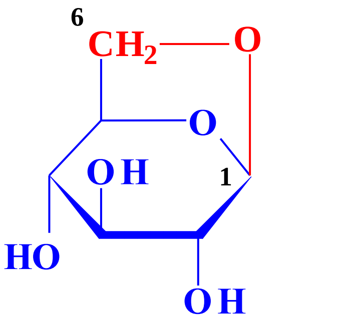
dehydration reaction

reaction of semiacetal OH and other OH

semiacetal OH / and other OH → anhydrosugars (glycosans)

other OH / other OH → deoxysugars

anhydrosugars

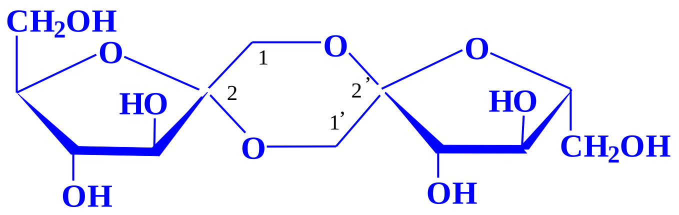


β-D-Glc*p* → 1,6-anhydro-β-D-Glc*p* (β-glucosan)

β-D-Man*p* → 1,6-anhydro-β-D-Man*p* (β-mannosan)

β-D-Gal*p* → 1,6-anhydro-β-D-Gal*p* (β-galactosan)

ketoses → dimeric anhydrides (tricyclic compounds)



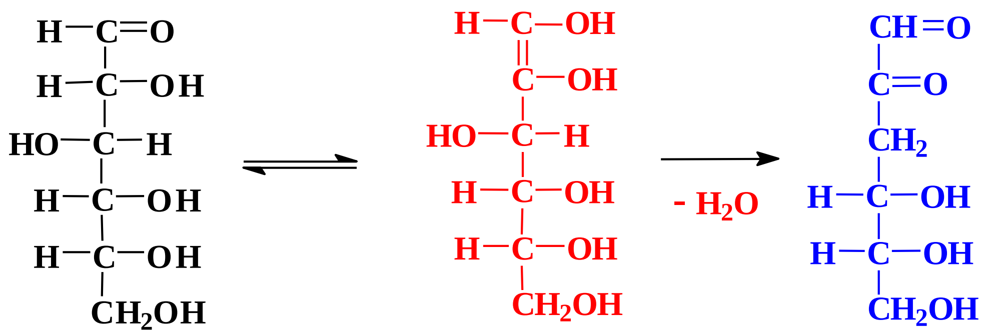
formation

byproducts of inversion (glucose: < 1%)

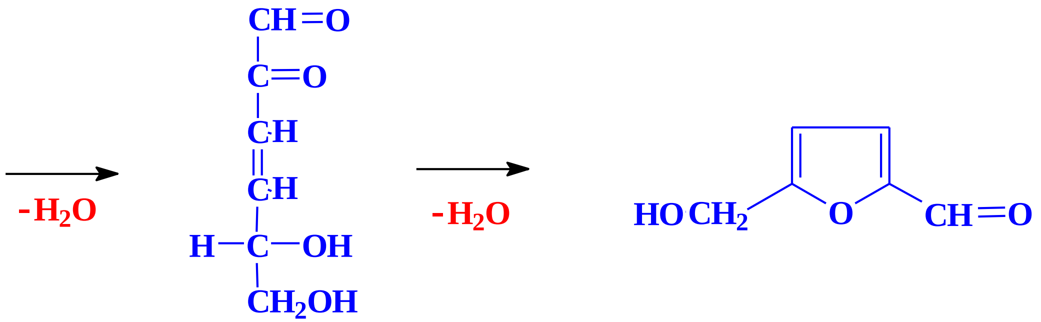
by-products of caramelization (higher amount)

deoxysugars

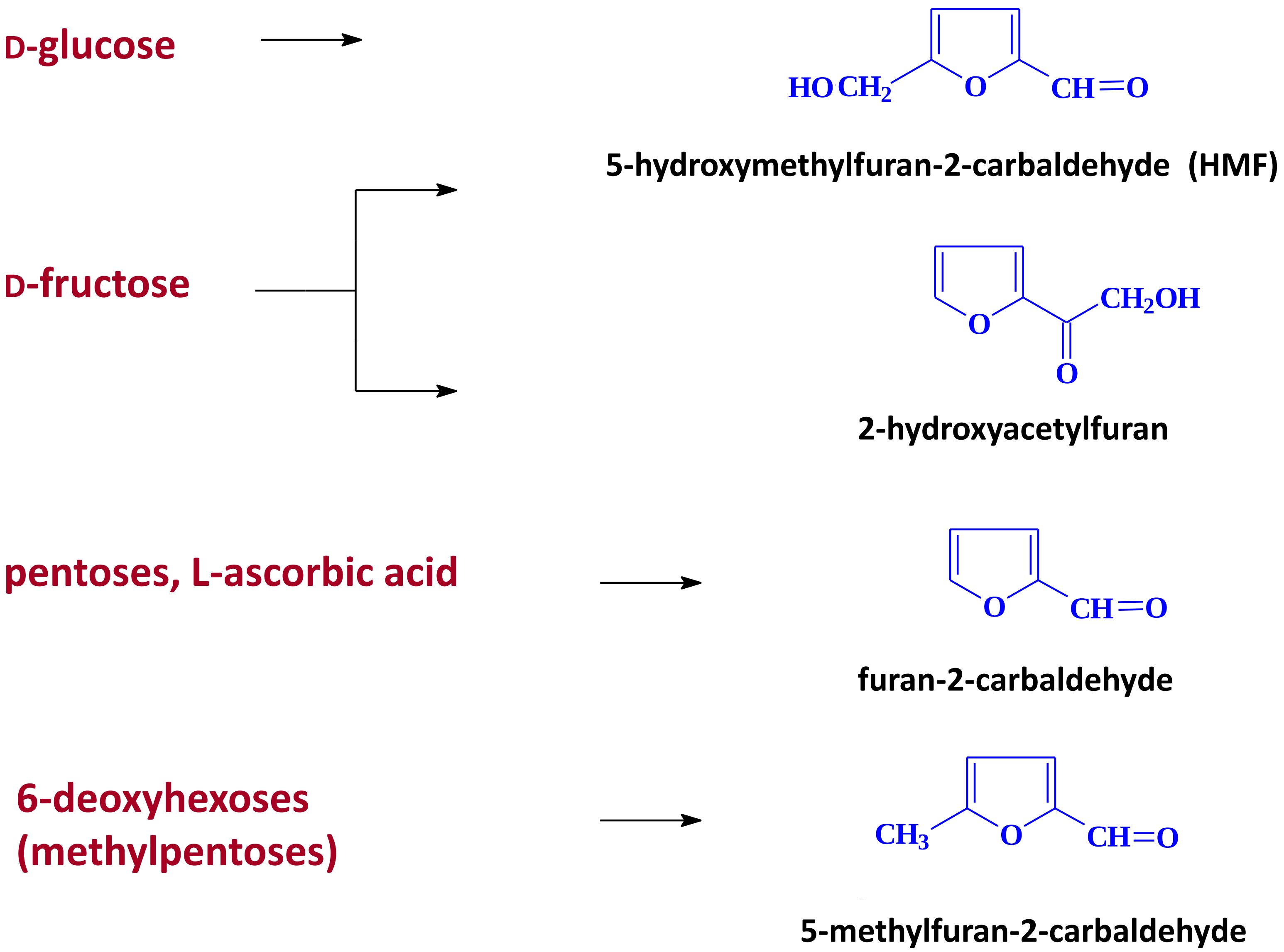
1,2-enolisation (series of isomeration and dehydratation)



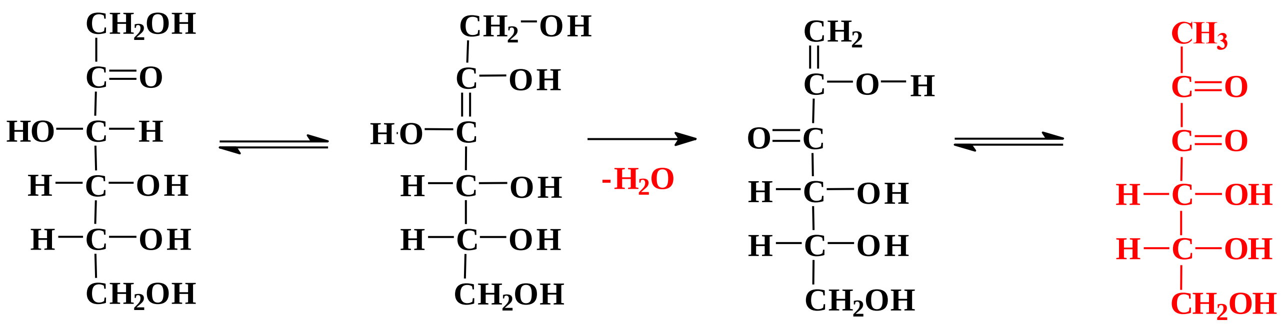
D-glucose   1-en-1,2-diol   3-deoxy-D-*erythro*-hexos-2-ulosa



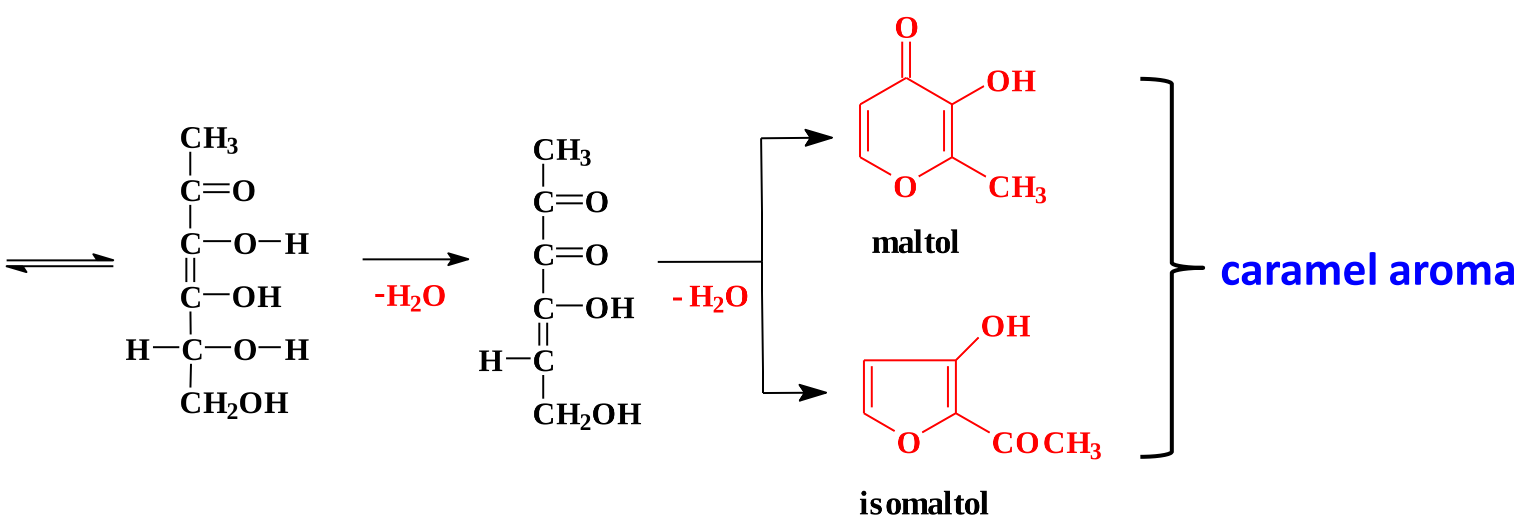
3,4-dideoxy-D-*glycero*-hex-3-enos-2-ulosa   5-hydroxymethylfuran-2-carbaldehyde (HMF)

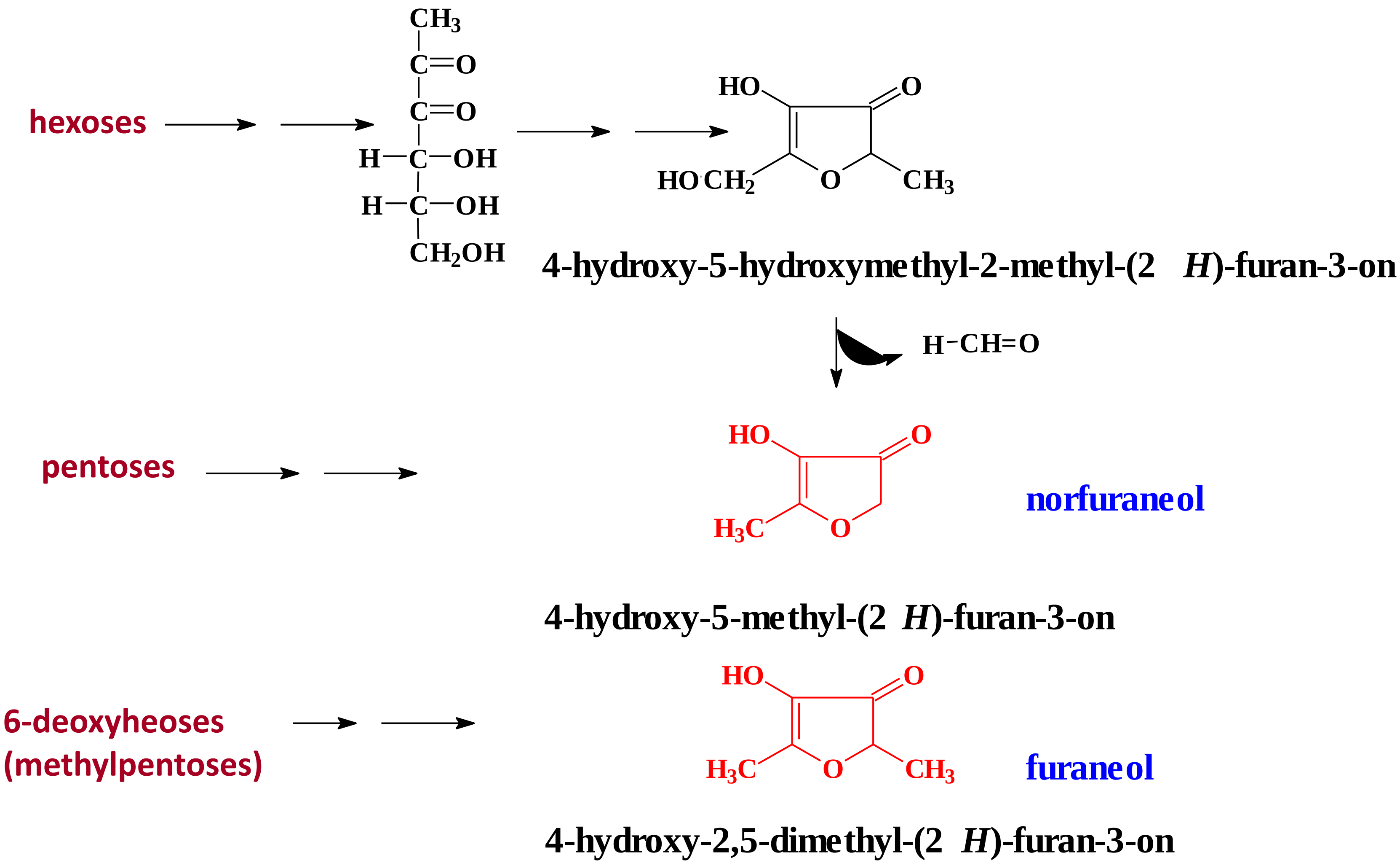

D-glucose
HOCH2
O
CH=O
5-hydroxymethylfuran-2-carbaldehyde (HMF)
D-fructose
O
CH2OH
O
2-hydroxyacetylfuran
pentoses, L-ascorbic acid
O
CH=O
furan-2-carbaldehyde
6-deoxyhexoses
(methylpentoses)
CH3
O
CH=O
5-methylfuran-2-carbaldehyde

2,3-enolisation



D-fructose 2-en-2,3-diol 1-deoxy-D-*erythro*-hexo-2,3-diulosa




hexoses
CH3
C=O
C=O
H—C—OH
H—C—OH
CH2OH
HO
O
HOCH2
O
CH3
4-hydroxy-5-hydroxymethyl-2-methyl-(2H)-furan-3-on
H−CH=O
pentoses
HO
O
H3C
O
norfuraneol
4-hydroxy-5-methyl-(2H)-furan-3-on
6-deoxyheoses
(methylpentoses)
HO
O
H3C
O
CH3
furaneol
4-hydroxy-2,5-dimethyl-(2H)-furan-3-on

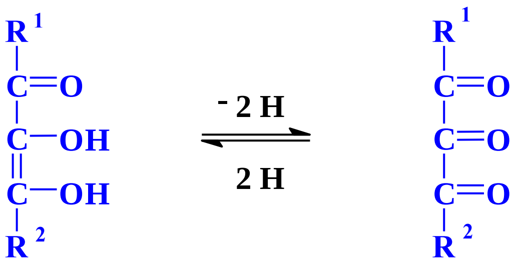
reductone formation

- **antioxidants**

reduction of organic substances, metal ions

pH < 6 monoanions

pH > 6 dianions

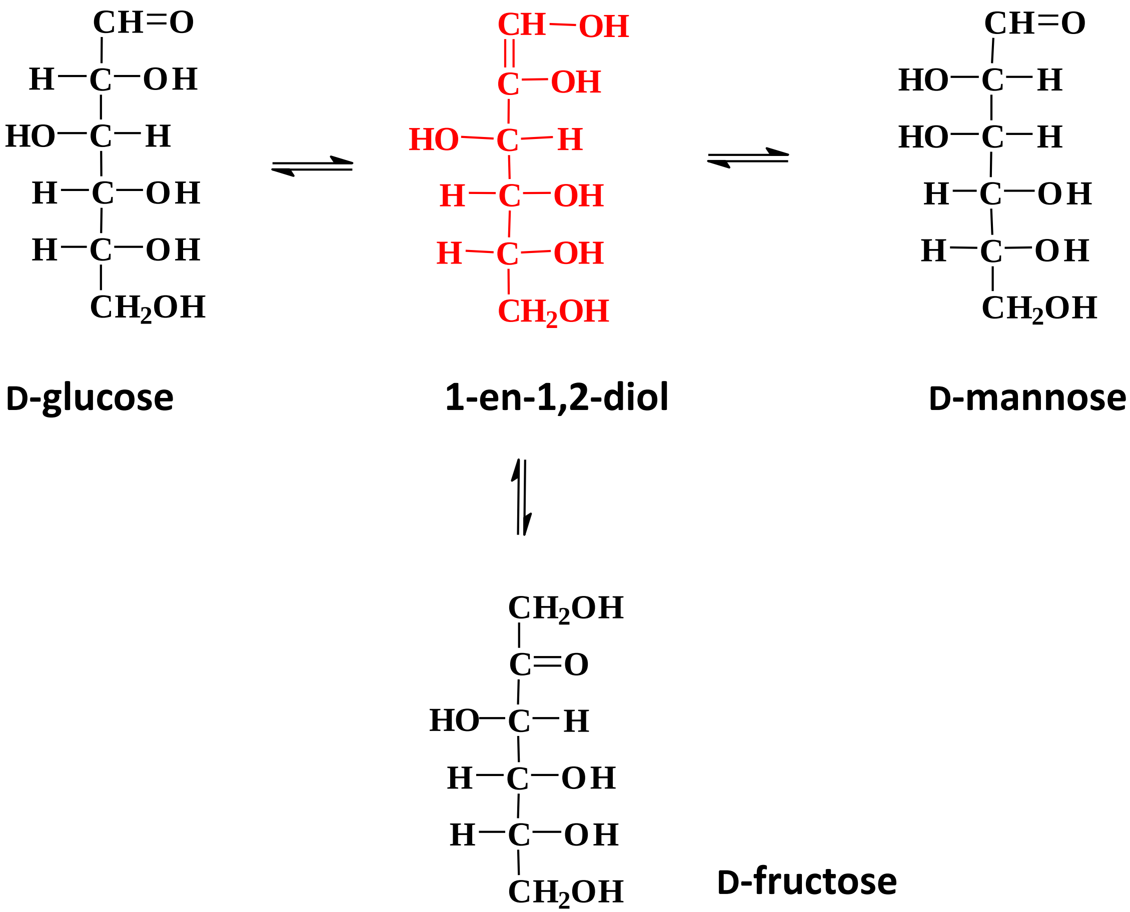


reductone **triulose**

isomeration

aldose → ketose

aldose → aldose (epimeration)



example

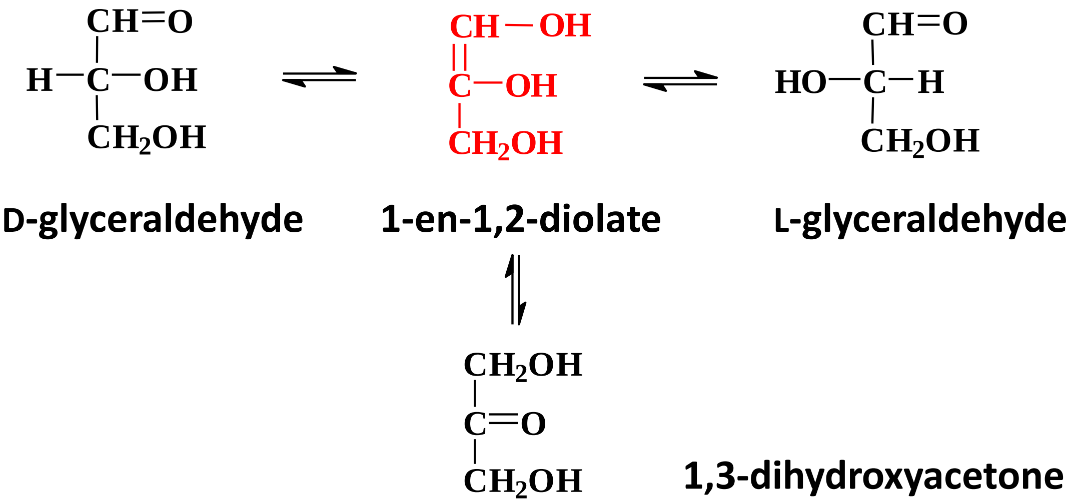
Glc / pH 10 /35 °C	Glc	64%
	Fru	31%
	Man	3%

further isomerization - other aldoses and ketoses

disaccharides isomeration

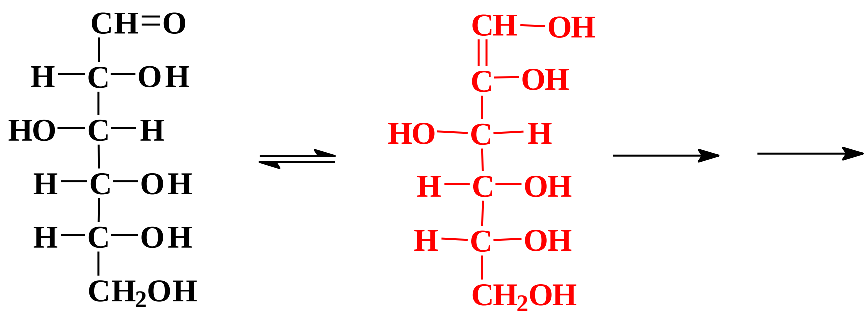
lactose	lactulose	epilactose
β-D-Gal*p*-(1→4)-D-Glc*p*	β-D-Gal*p*-(1→4)-D-Fru*f*	β-D-Gal*p*-(1→4)-D-Man*p*

trioses isomerisation



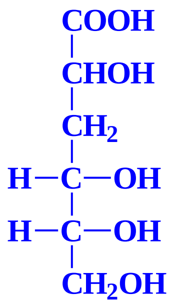
rearrangement to acids

1-en-1,2-diol, Cannizzaro reaction, benzyl rearrengement

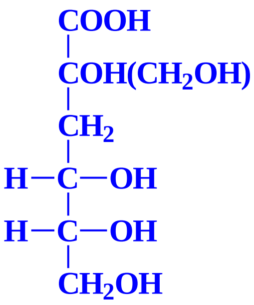


D-glucose

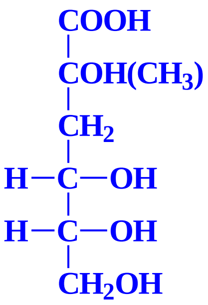
1-en-1,2-diol



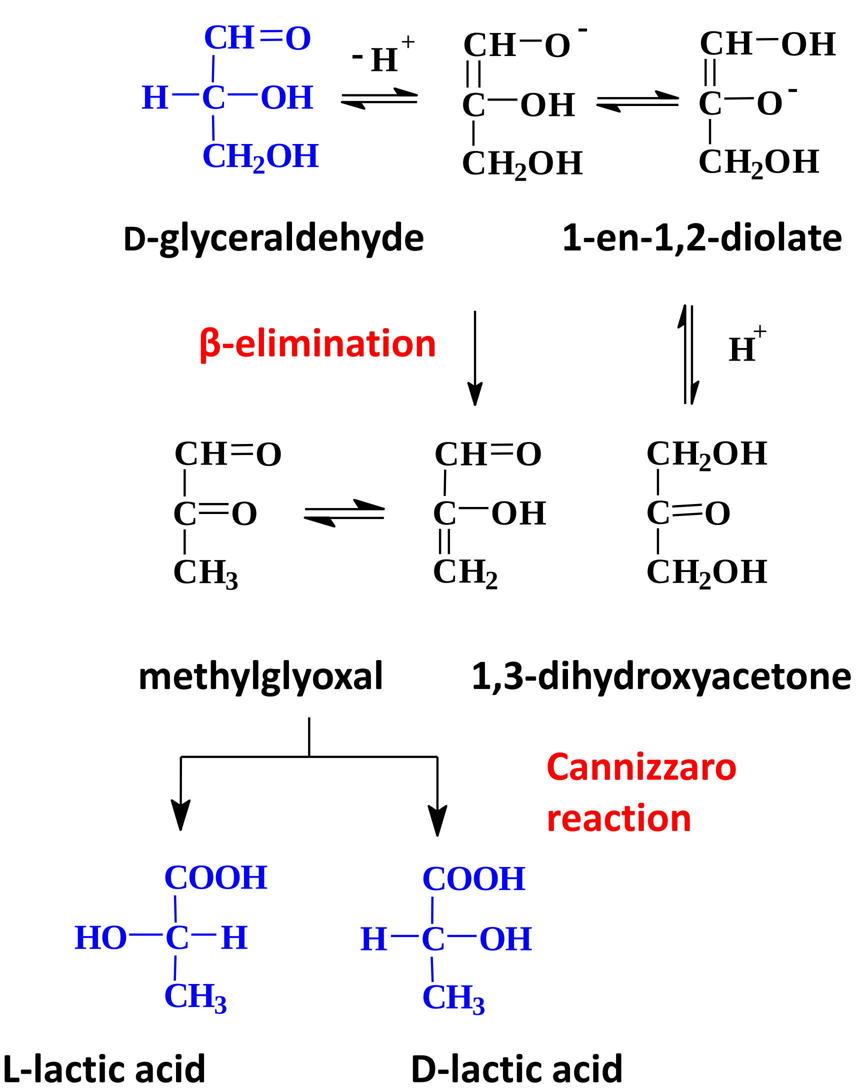
meta sugar acids



iso sugar acids



sugar acids

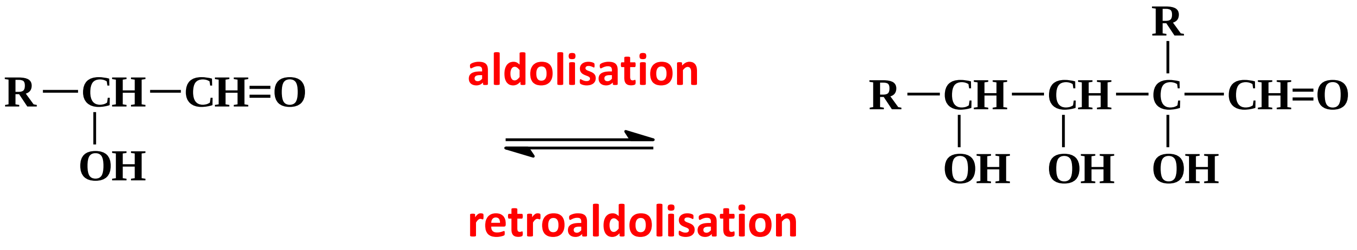


D-glyceraldehyde
1-en-1,2-diolate
β-elimination
methylglyoxal
1,3-dihydroxyacetone
Cannizzaro reaction
L-lactic acid
D-lactic acid

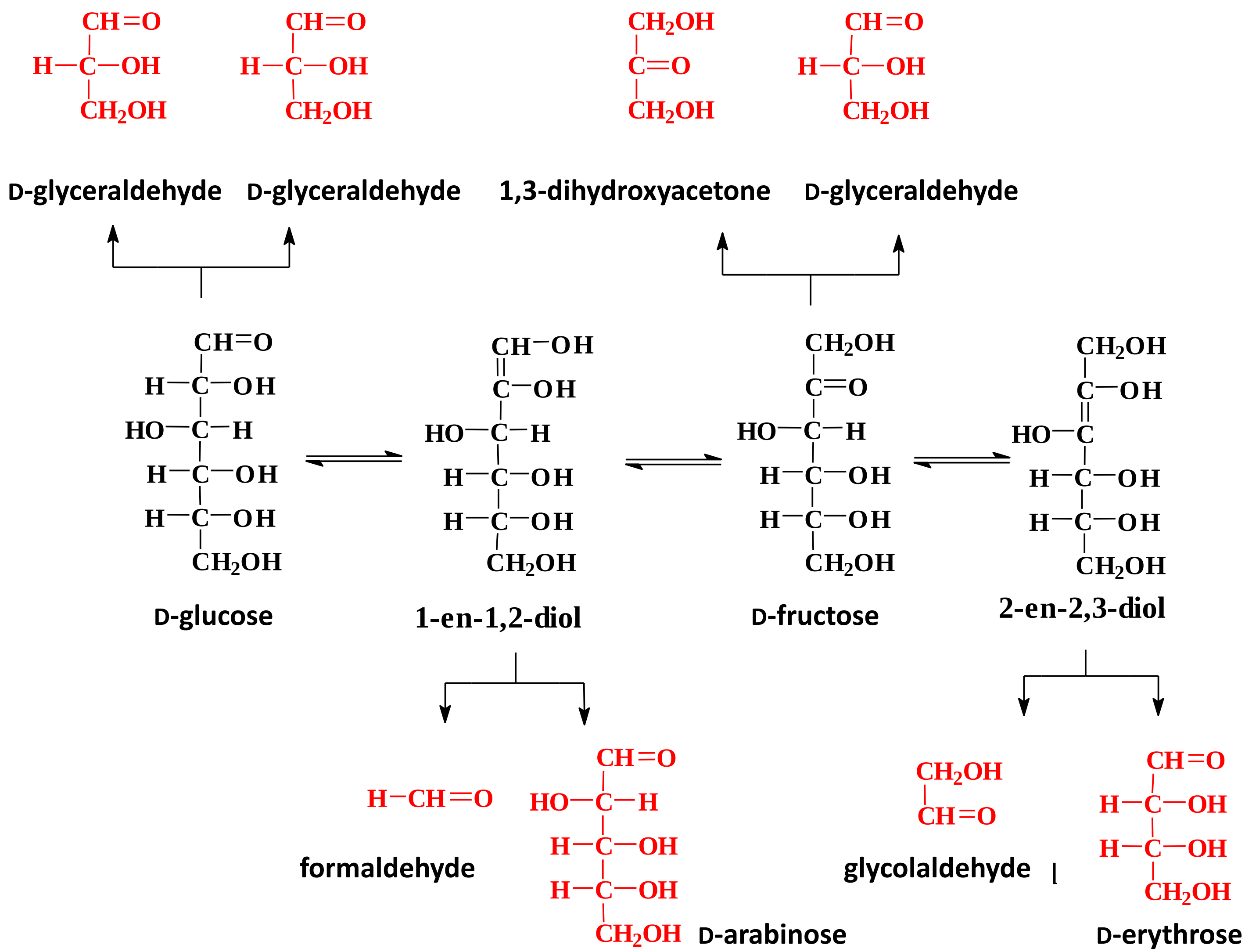
fragmentation

formation of reactive componds

- retroaldolisation



oxidadation (after isomeration, dehydration)



glyoxal 2C | hydroxyacetone 3C | methylglyoxal 3C

1,3-dihydroxyacetone 3C | laktaldehyde 3C | hydroxymethylglyoxal 3C

Maillard reaction

non-enzymatic browning reaction

French pronunciation : [majaʁ], Engl.: /maɪˈjɑr/

reactants

- **sugars (carbonyl compounds)**

  monosaccharides and reducing oligosaccharides

  (nonreducing oligosaccharides, polysaccharides, glycosides)

  triose > …. > pentose > hexose (acyclic form)

  aldose > ketose

  α-dikarbonyls > aldehydes > ketones > saccharides

proteins (aminocompounds)

  ε-NH_2 Lys, N-ending NH_2, guanidyl Arg, SH Cys

  free amino acids, amines, ammonia

  ε-NH_2 > …. > β-NH_2 > α-NH_2

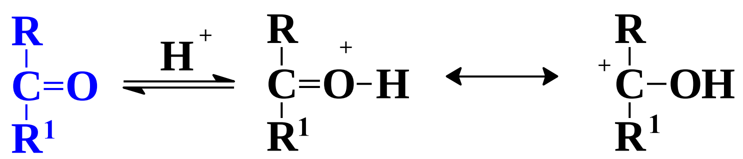
  NH_3 > R-NH_2 > aminoacid (reactivity is related to their basicity)

Réaction générale des acides aminés sur les sucres. Journal de Physiologie, 1912 tome 14 page 813

reaction conditions

- water activity (a_w 0,3-0,7)
- pH (5-9)
- others (temperature, time of reaction, other components)

formation of cations →



carbonyl compound

protonation of the carboxyl group **increases** its reactivity

$$NH_3 \underset{}{\overset{HX}{\rightleftharpoons}} \overset{+}{N}H_4X^-$$

ammonia — ammonium salt

$$R{-}NH_2 \overset{HX}{\rightleftharpoons} R{-}\overset{+}{N}H_3X^-$$

primary amine — salt of amine

protonation of the amino group **reduces** its reactivity

concequences

positive, negative

- formation of aroma compounds
- formation of yelow, brown, black pigments → **melanoidins**

  + bread crust, coffee, fried products

  - dried foods (milk), fruits

- decrease of nutritive value → reaction with Lys
- formation of potentially toxic products

reaction *in vivo* (glykosylation of proteins)

mechanism of reactions

3 stages

- **initial stage**

formation of glykosylamines (Amadori rearrangement) and formation of aminodeoxysugars (Amadori products)

- **middle stage**

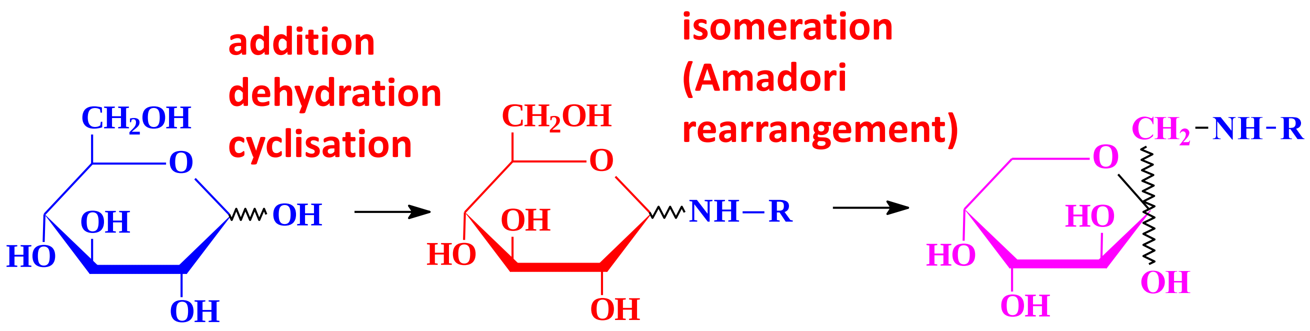
decomposition of saccharides, glycosylamines, aminodeoxysugars (dehydratation, fragmentation)

decomposition of amino acids (Strecker degradation)

- **final stage**

reaction of degradation products, formation of aroma, taste and colour products (melanoidins)

glycosylamines and aminodeoxysugars



D-glucose

D-glucosylamine

D-fructosamine
1-amino-1-deoxy-D-fructose

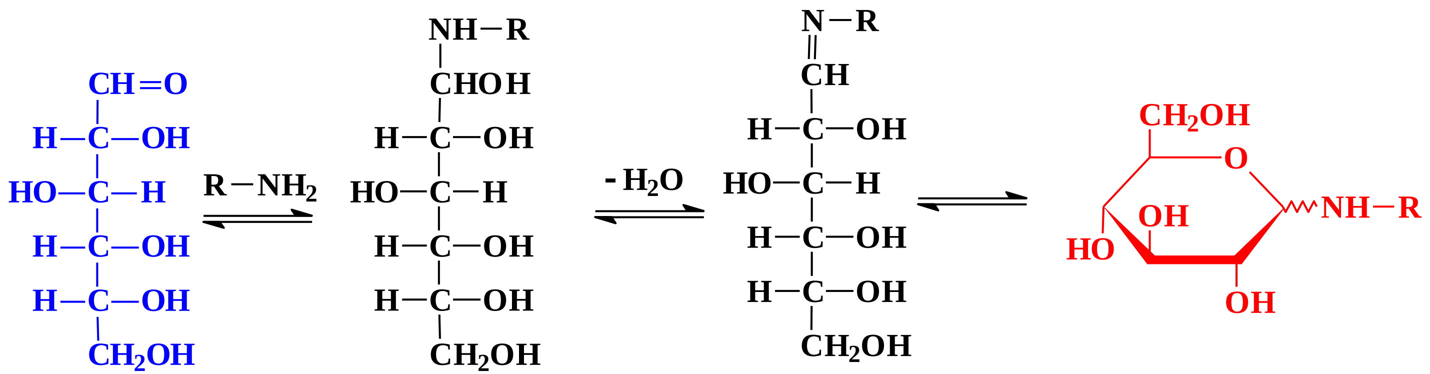
totally utilisable form

non-utilisable form

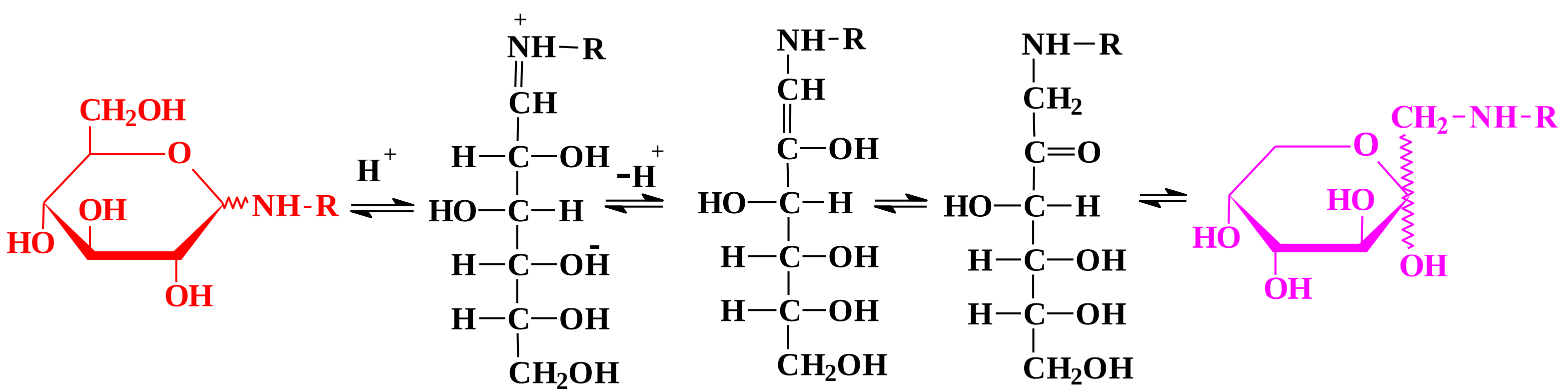
aldose → aldosylamine → ketosamine(1-amino-1-deoxyketose) Amadori rearrangement

ketose → ketosylamine → aldosamine (2-amino-2-deoxyaldose) Heyns rearrangement

mechanisms (reaction of acyclic forms)



D-glucose | carbinolamine | imine (Schiff´s base) | D-glucosylamine



D-glucosylamine | cation of Schiff´s base | D-fructosamine (1-amino-1-deoxy-D-fructose)

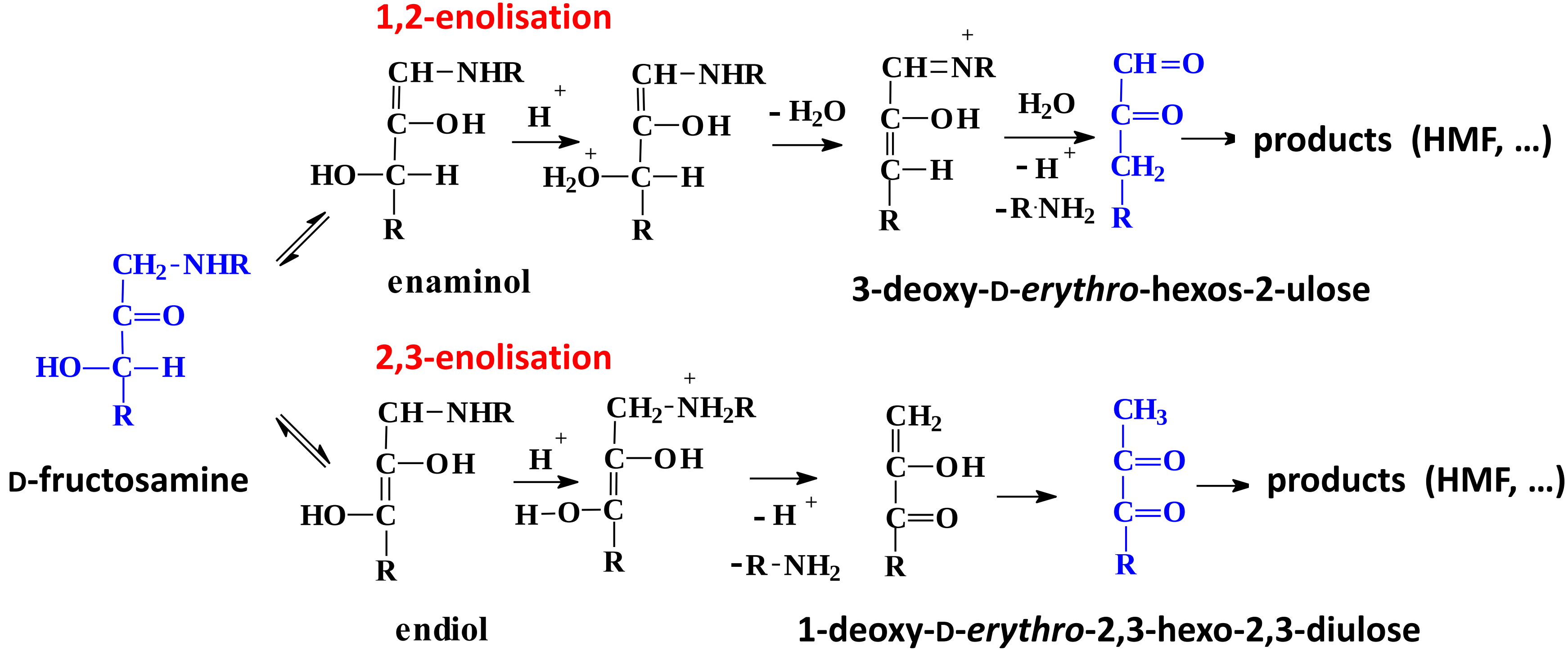
enol form | oxo form | cyclic form

decomposition of aminodeoxysugars

1,2-enolisation acidic medium

2,3-enolisation neutral and alkaline medium

formation of glycosuloses and glycodiuloses (aldoketoses and diketoses)



analogy with the reactions of sugars themselves

- **lower activation energy**

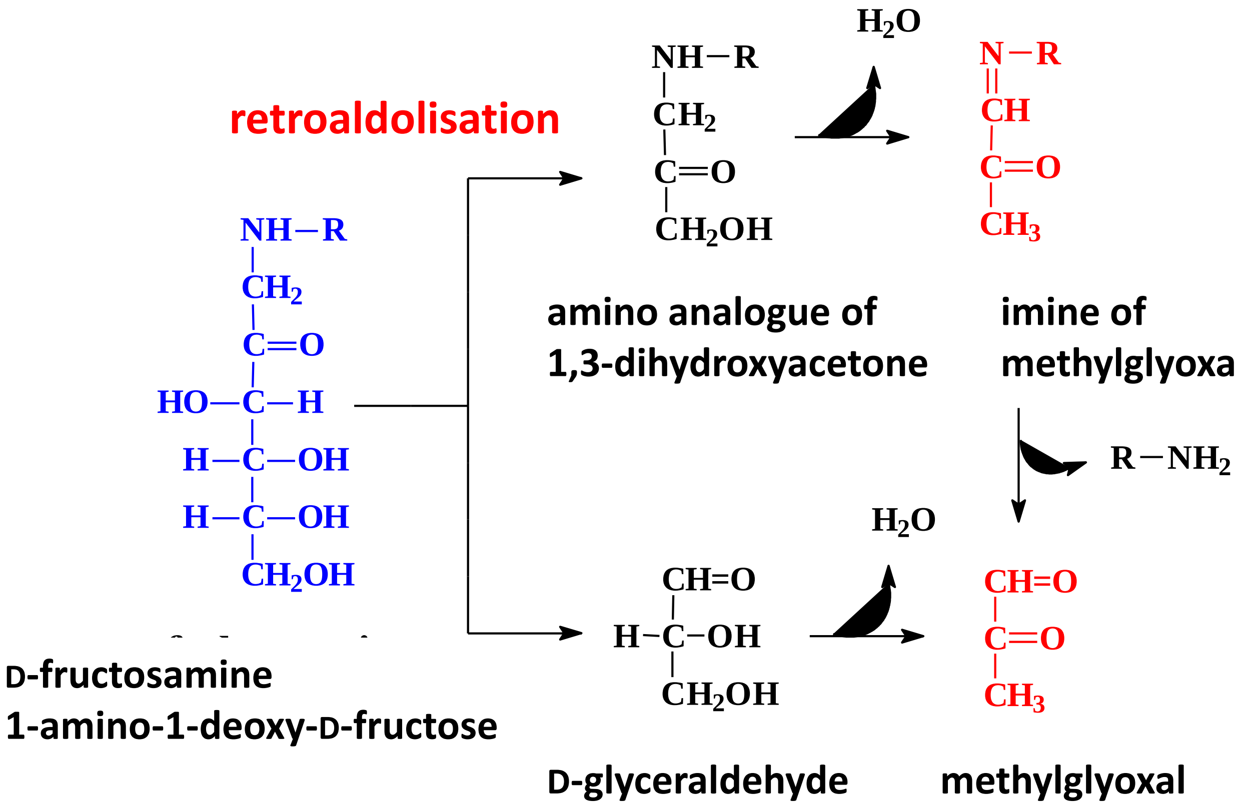
  unlike reactions of carbohydrates themselves these are running already at ambient temperatures and pH 4-7

- **products contain N and S**
- **qualitatively and quantitatively more products**

in parallel - decomposition of sugars and aminoacids themselves

examples

formation of methylglyoxal and 2,5-dimethylpyrazine from fructosamine

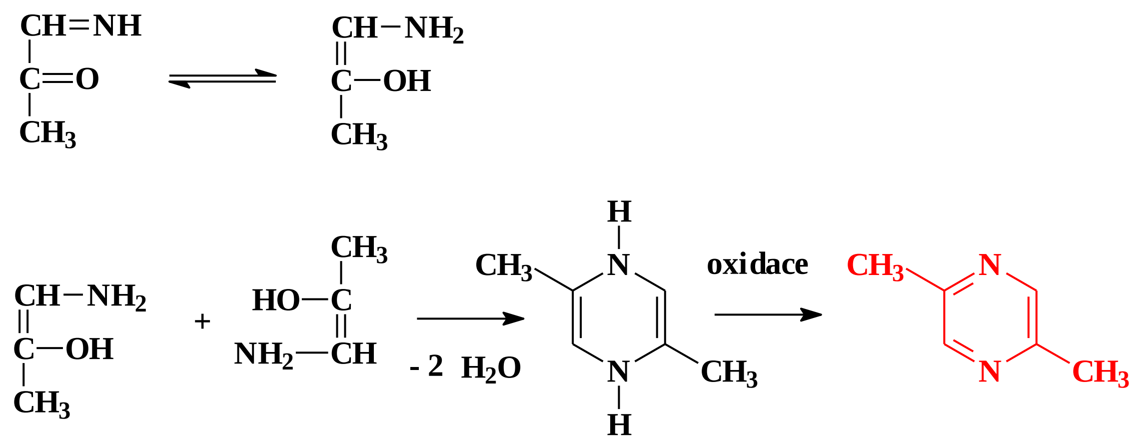


R = H

(Strecker´s degradation of amino acids)

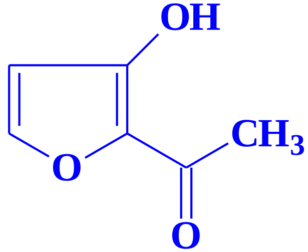
formation of 2,5-dimethylpyrazine

aroma of roasted nuts, potato chips

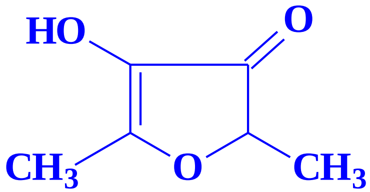


2,5-dimethylpyrazine

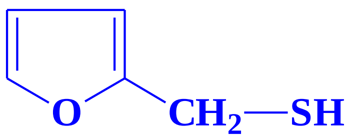
important heterocyclic products



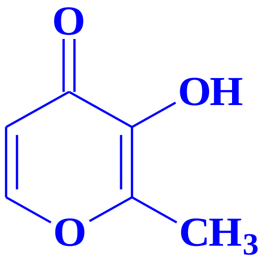
isomaltol
caramel



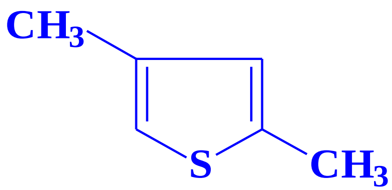
furaneol
strawberries, pineapple



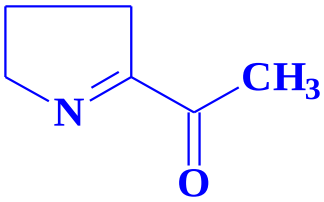
furfurylthiol
coffee



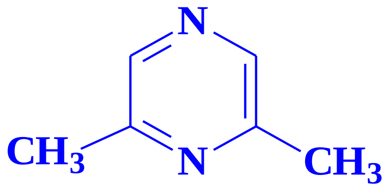
maltol
caramel



2,4-dimethylthiophene
fried onion



2-acetyl-1-pyrroline
bread



2,6-dimethylpyrazine
chocolate, roasted nuts

Maillard reaction in important food commodities

positive and negative consequences

desirable and undesirable reactions

technology (aroma, taste, colour, nutritive value)

- roasting
- cooking, baking, frying
- drying
- extrusion, microvawe heating

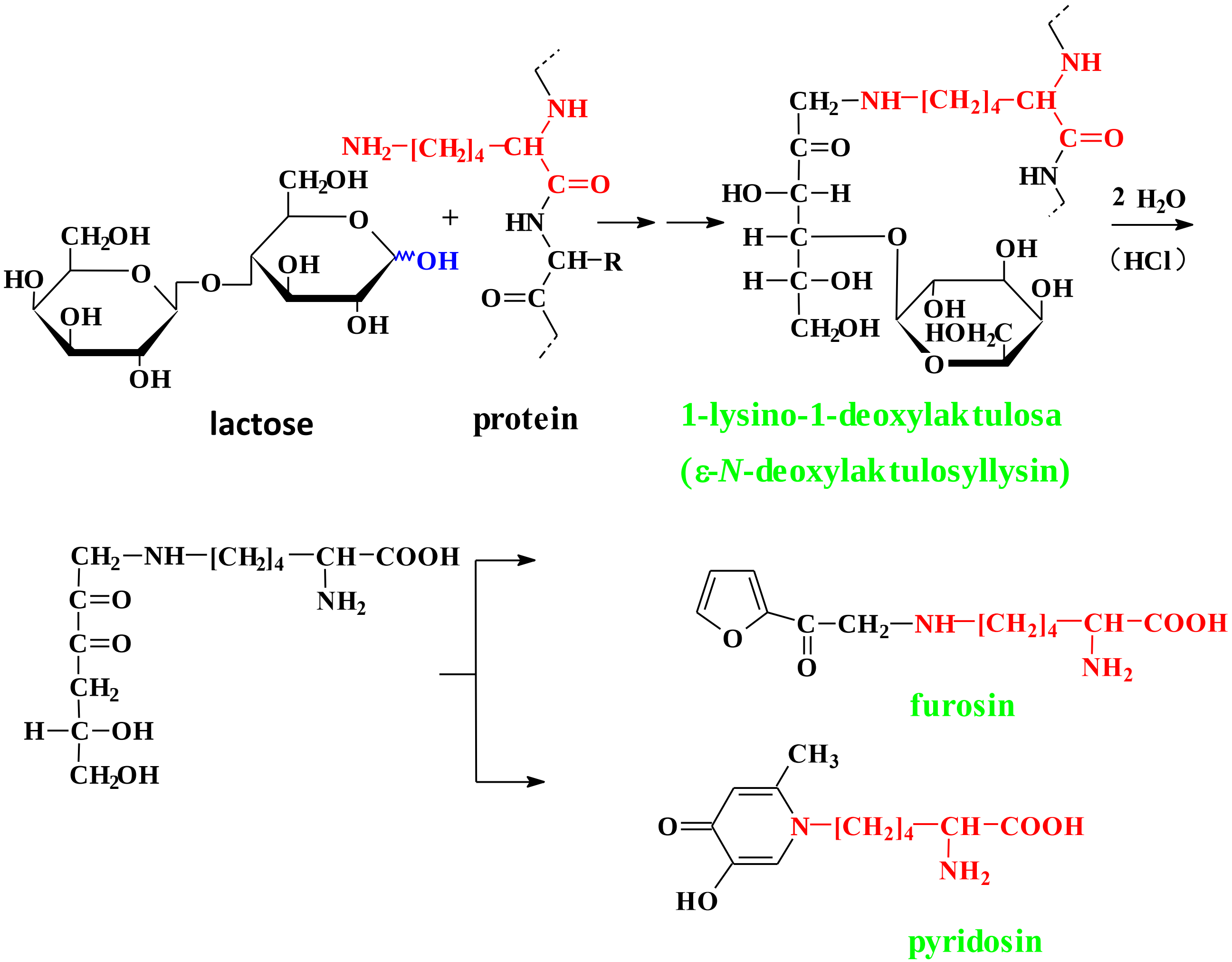
- **milk, milk products**

  Lys losses: 10-30% traditional drying, 3% sprey drying
- **cereals, cereal products**

  Lys losses: 70% bread crust, 10% total
- **meat, meat products**

  mutagenes (heterocyclic amines)
- **fruits, vegetables**
- **coffee, cocoa, nuts**

reactions in the processing of milk unavailable (blocked) Lys



isomeration lactose → lactulose + epilactose

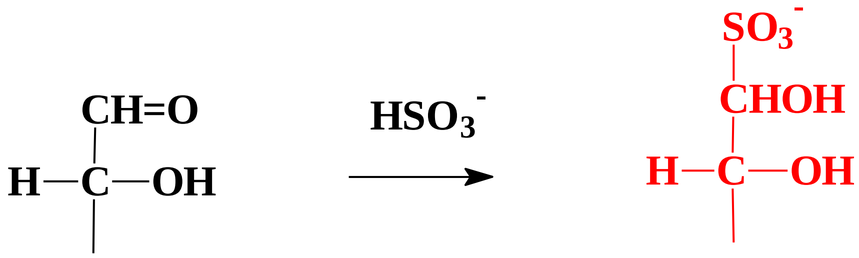
lysinoalanin

inhibition of Maillard reaction

- creating unfavorable conditions

  water content (activity), lower temperature, regulation of pH
- removal of one reaction partner
- use of inhibitors

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$



aldehyde

sulfonic acid

Caramelisation

sugars

sugars (saccharose, glucose, fructose, starch sirup, invert sugar

temperature

150-190 ^{o}C (240 ^{o}C)

reaction time

5-10 h

catalysts

caramel = solid product

couler = liquid product

class		name of couler	additives matter	utilisation
I	CP	caustic	Na_2CO_3, K_2CO_3, NaOH, KOH, H_2SO_4, acetic acid, citric acid	alcoholic beverages (high content of alcohol)
II	CCS	caustic sulphite	SO_2, H_2SO_4, Na_2SO_3, K_2SO_3, NaOH, KOH,	vinegar, beer, alcoholic beverages, aromatised wine
III	AC	ammonium	NH_3, $(NH_4)_2SO_4$, Na_2CO_3, H_2SO_4, NaOH, KOH	beer, alcoholic beverages, acid food
IV	SAC	ammonium-sulphite	NH_3, SO_2, $(NH_4)_2SO_3$, Na_2SO_3, K_2SO_3, Na_2CO_3, K_2CO_3, NaOH, KOH, H_2SO_4,	acid food, non-alcoholic beverages