5. SACCHARIDES

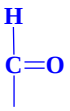
sugars
classification
according number of sugar molecules

- monosaccharides
- oligosaccharides (2-10 monosacharides)
- polysaccharides (> 10 monosacharides)
- conjugated (complex) saccharides

- free
- bound homoglycosides, heteroglycosides, aglycons (non-sugar components)

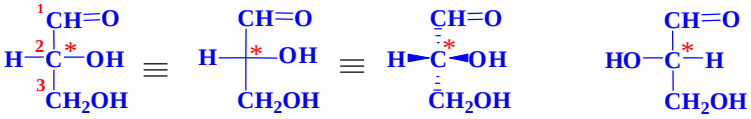
Monosaccharides
polyhydroxyalkyl substituted aldehydes a ketones and derived compounds
main nutrients, biological and sensory activites
content (book 1, tab. 4.4, 4.5)
structure and classification
according to type of carbonyl group

- aldoses
- ketoses

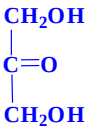



according to number of C atoms (3-8)

- trioses

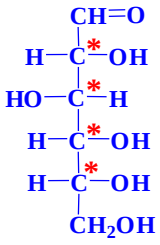
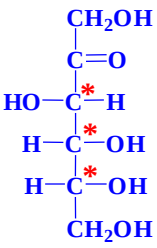


D-(+)-glyceraldehyde (D-*glycero*-triose) L-(-)-glyceraldehyde
optical isomers (enantiomers) D/L, *R/S* d/l, +/-



1,3-dihydroxyacetone (1,3-dihydroxypropane-2-one, glycerone)

- tetroses
- pentoses, hexoses

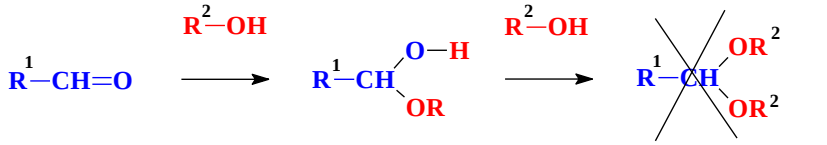



D-glucose (D-*gluko*-hexosa) D-fructose (D-*arabino*-hex-2-ulose)
dextrose, grape sugar levulose, fruit sugar

according to chain

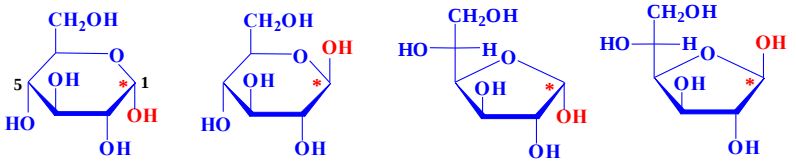
- linear chain

- branched chain
- **according to type of lactol**

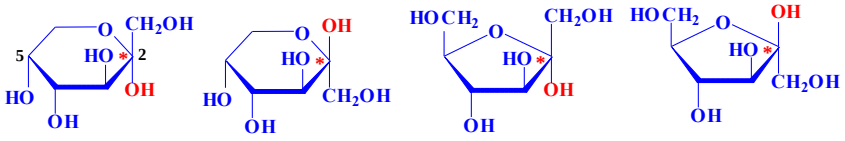


aldehyde semiacetal acetal

- furanose
- pyranose

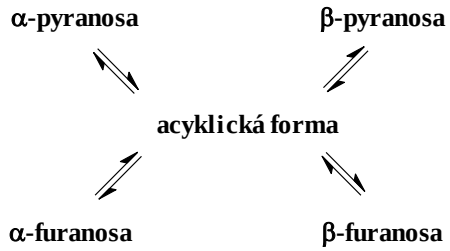


α-D-glukopyranosa β-D-glukopyranosa α-D-glukofuranosa β-D-glukofuranosa



α-D-fruktopyranosa β-D-fruktopyranosa α-D-fruktofuranosa β-D-fruktofuranosa

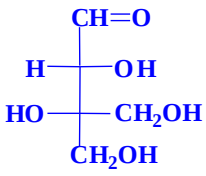
mutarotation
anomers, anomeric C, anomeric OH



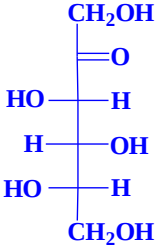
conformation

- furanoses (envelope *E*, twist *T*)
- pyranoses (chair $^4C_1$, $^1C_4$)
- acyclic forms (cik-cak)

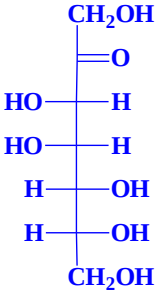
occurrence
present in all food
less typical monosaccharides



D-apiose
branched sugar
root vegetables



L-sorbose
rowanberries



D-*manno*-hept-2-ulose
ketoheptose
avokado

abbreviations

glucose	Glc	furanose	*f*
fructose	Fru	pyranose	*p*
mannose	Man	acid	A
apiose	Api		
sorbose	Sor		

β-D-glukopyranose β-D-Glc*p*

derivatives of monosaccharides

formation

- oxidation (or rearrangement) — sugar acids, ketoaldoses, diketoses
- reduction — suger alcohols, deoxysugars
- dehydration — anhydrosugars
- reaction with other compounds — glycosides, ethers, esters, amino sugars

sugar acids

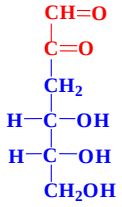
content in malt and chicory (book 1, tab. 4.10)

- aldonic
  Ca-gluconan (medicine), δ-laktone (fermented salami, 0,1 %)
- alduronic
  polysaccharidy: D-GlcA6 (glycoproteins), D-GalA6 (pectins), D-ManA6 a L-GulA6 (alginates)
- aldaric, for example tartaric and malic acids

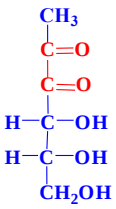
ketoaldoses, diketoses

main products of Maillard reaction and oxidation

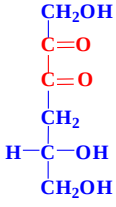
- 3-deoxyglycosuloses
- 1-deoxyglycodiuloses
- 4-deoxyglycodiuloses



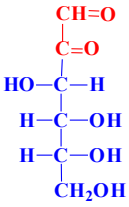
3-deoxy-D-*erythro*-hexos-2-ulosa



1-deoxy-D-*erythro*-hexo-2,3-diulosa



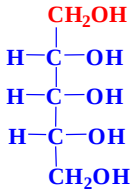
4-deoxy-D-*glycero*-hexo-2,3-diulosa



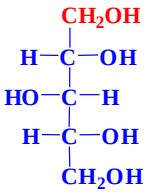
D-*arabino*-hexos-2-ulosa

sugar alcohols

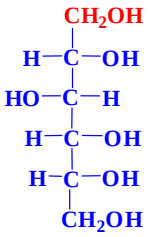
alditols, glycitols (homologues of glycerol)
reduction
content (book 1, tab. 4.7 a 4.8)



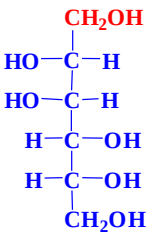
ribitol



xylitol



D-glucitol



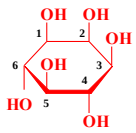
D-mannitol

- natural components of food

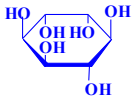
ribitol	riboflavin
arabinitol	mushrooms
xylitol	mushrooms
D-glucitol	plums, rowanberries, pears
D-mannitol	mushrooms, rowanberries, celery, green coffee
galactitol	mushrooms, fermented milk products

- synthetic (reduction H_2/catalyst., $NaHg_x$, sweetners)
  xylitol, D-glucitol

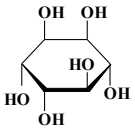
cyclitols
content (book 1, tab. 4.9)
cyclohexane-1,2,3,4,5,6-hexols (inositols, cycloses)



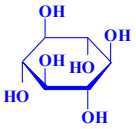
***myo*-inositol (*meso*-inositol)**



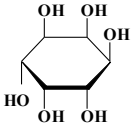
1D-(+)-*chiro*-inositol



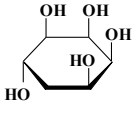
1L-(-)-*chiro*-inositol



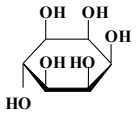
***scyllo*-inositol (scyllitol)**



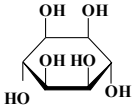
***neo*-inositol**



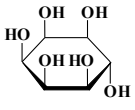
***allo*-inositol**



***epi*-inositol**

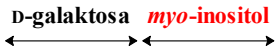


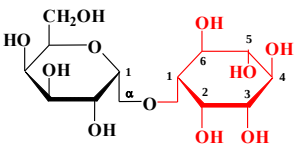
***muko*-inositol**



***cis*-inositol**

- *myo*-inositol — widespread" phospholipids, fytates
- pseudooligosaccharides — pulses





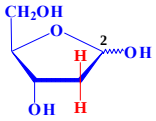
galaktinol

deoxysugars
reduction of primary / secondary hydroxyl

- natural

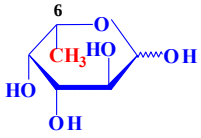
- Maillard reaction

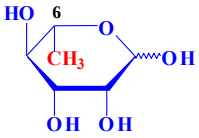
2-deoxysugars

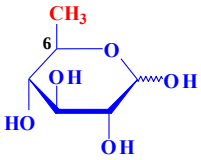


2-deoxy-D-ribose (thyminose)
deoxyribonucleic acids

6-deoxysugars (6-deoxyhexose = methylpentose)







L-fucose
6-deoxy-L-galactose
milk oligosaccharides

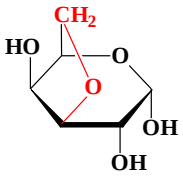
L-rhamnose
6-deoxy-L-mannose
heteroglycosides

D-chinovose
6-deoxy-D-glucose
heteroglycosides

anhydrosugars

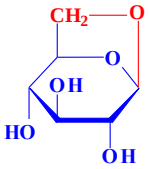
sugar anhydrides, glycosans
water elimination, mostly poloacetal and other OH

- natural components of polysaccharides



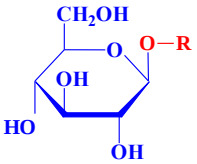
3,6-anhydro-α-D-galactopyranose (carageenan)
3,6-anhydro-α-L-galactopyranose (agar)

- products of thermal reactions

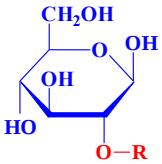


1,6-anhydro-β-D-glucopyranose (β-glucosan, levoglucosan) (caramel)

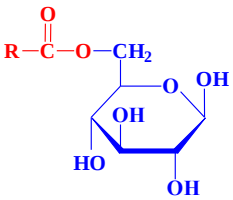
glykosides, ethers, esters and other derivatives



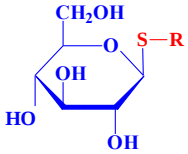
***O*-glykosid**



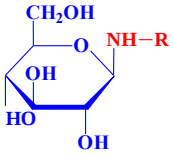
ether



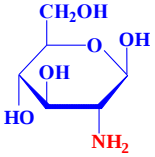
ester



***S*-glykosid**

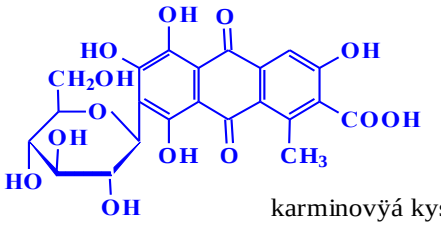


***N*-glykosid**



2-amino-2-deoxycukr

O-glykosides	widespread
ethers	4-*O*-methyl-D-Glc*p*A (hemiceluloses)
	2-*O*-methyl-D-Xyl*p* (pectins)
esters	natural (phosphates, acetates, benzoates etc.), synthetic (fatty acids, emulgators)
S-glycosides	glucosinolates in brassica vegetables
N-glycosides	natural (ATP, NADH), Maillard reaction (glycosylamines)
aminodeoxysugars	natural (chitosamine), Maillard reaction (Amadori products)
C-glycosides	



karminovÿá kyselin
(anthrachinony)

carminic acid

Oligosaccharides
homoglycosides
pentoses, hexoses, sugar acids and other derivatives
furanoses, pyranoses

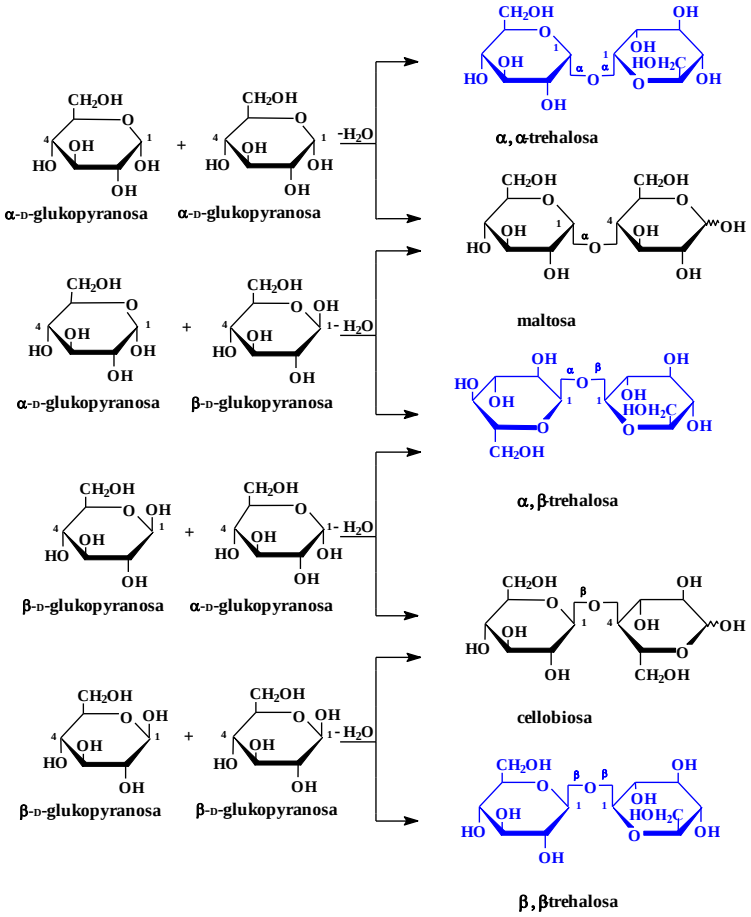
classification
according to number of monosaccharides (2-10)
- disaccharides (bioses) – decasacharides (decaoses)

according to semiacetal OH
- reducing (glycosides)
- non-reducing (glycosylglycosides)

according to major monosaccharids (backbone)
- glucooligosaccharides
  maltose, maltooligosaccharides
- fructooligosaccharides
  saccharose
- galactooligosaccharides
  lactose, α-galactosides

according to digestability
- digestible
- non-digestible

according to biological effects
- prebiotic effects
  (stimulate growth and metabolisms of desirable microorganisms)
- probiotic effects
  (with fibre influence and regulate peristaltic activity)
- symbiotic effects (simultaneously prebiotic and probiotic effects)

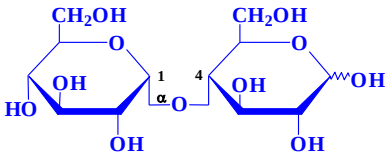


terminology

maltose	α-D-glucopyranosyl-(1→4)-D-glucopyranose
	4-*O*-α-D-glucopyranosyl-D-glucopyranose
	α-D-Glc*p*-(1→4)-D-Glc*p*
α,α-trehalose	α-D-glucopyranosyl-α-D-glucopyranoside
	α-D-Glc*p*-(1↔1)-α-D-Glc*p*

glucooligosaccharides

maltose α-D-Glc*p*-(1→4)-D-Glc*p* malt sugar



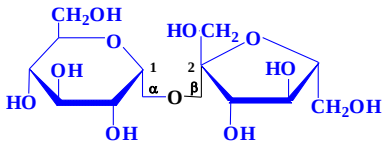
occurrance (book 1, tab.4.11 a 4.12)
product of starch hydrolysis, reversion of glucose
malt, bread (1,7-4,3 %), honey (2,7-16 %)

production

- maltose sirups (85 %), glucose sirups (acids, enzymes)
- maltose
- isomeration on maltulose, α-D-Glc*p*-(1→4)-D-Fru*f*
- reduction on maltitol, α-D-Glc*p*-(1→4)-D-glucitol

fructooligosaccharides

saccharose α-D-Glc*p*-(1↔2)-β-D-Fru*f*



occurrance (book 1, obr. 4.14)

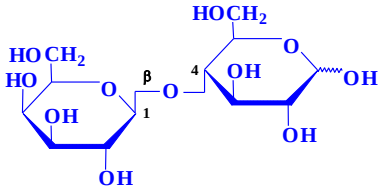
fruits	up to 8 %	
vegetables	0,1-12 %	
green coffee (roasted)	6-7 % (0,2 %)	
sugar beet	15-20 %	saccharose
sugar cane	12-26 %	saccharose
maple sirup		
date sirup		

production (from sugar beet)

- extraction of sugar beet slices (diffusion)
- cleaning (epuration) of crude juice, clarification by $Ca(OH)_2$
- saturation by CO_2
- filtration, light juice
- thickening
  heavy juice (61-67 % saccharose, 68-72 % dry matter)
- crude (brown) sugar
  96 % saccharose, 2-3 % non-sugars, 1-2 % water
  (1,0-1,2 % organic, 0,8-1,0 % inorganic matters)
- afinade
- rafinade
  molasses (folder, substrat for fermentation processes)
  production of invert suger, other products

galactooligosaccharides

lactose β-D-Gal*p*-(1→4)-D-Glc*p* milk sugar



occurrance (book 1, tab.4.15, 4.16)

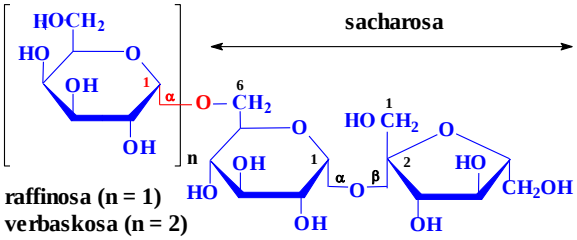
cow milk	4-5 %
human milk	5,5-7 %

production (from whey)

- ultrafiltration
- thickening, crystalisation
- production of galactose, galactitol, lactulose, lactitol

other β-galactooligosaccharides of milk

α-galactooligosaccharides of pulses
content (book 1, tab.4.17)



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

reactants

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

main reactions of monosaccharides

(acid-basic catalysed)

in acid medium
(futher factors: temperature, time)

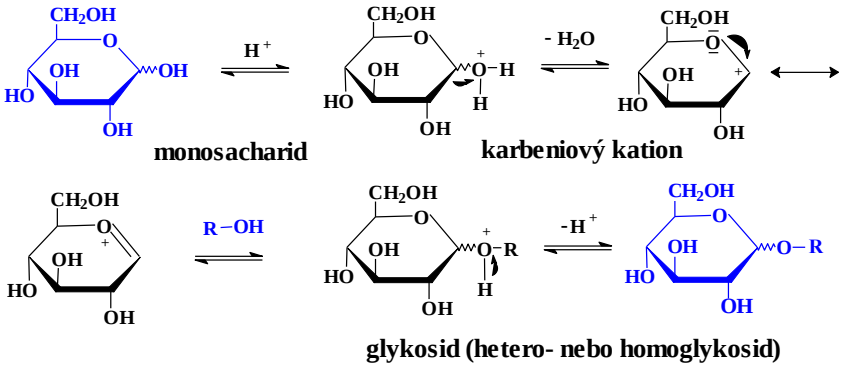
mutarotation
formation (hydrolysis) of glycosides
dehydration
reductone formation

in alcali medium

mutarotation
isomeration
fragmentation
rearrangement
oxidation

formation and hydrolysis of glycosides

reaction of poloacetals OH



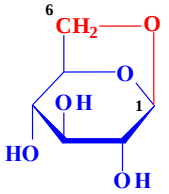
hydrolysis (inversion)

- production of starch hydrolysates
- invert sugar
- galactose
-

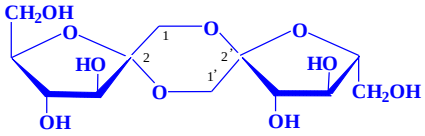
formation (reverse, Fischer reaction)
side products of inversion (starch sirup: 5-6 %)
side products of caramelisation
low energy products
indicaters of edulteration

dehydratation reactions
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)

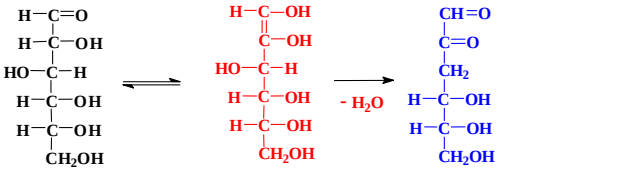


ketoses → dimericanhydrides (tricyclic compounds)

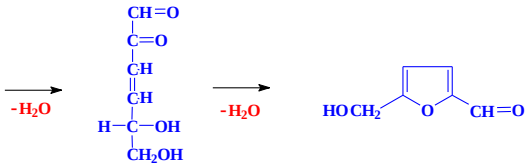


(α-D-fruktofuranosa)-(α-D-fruktofuranosa)-1,2´:1´,2-dianhydrid

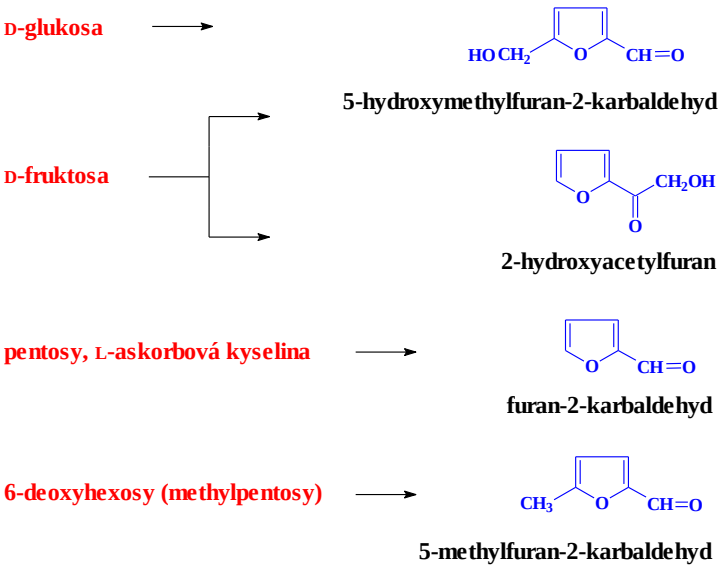
deoxysugars
1,2-enolisation (series of isomeration and dehydratation)



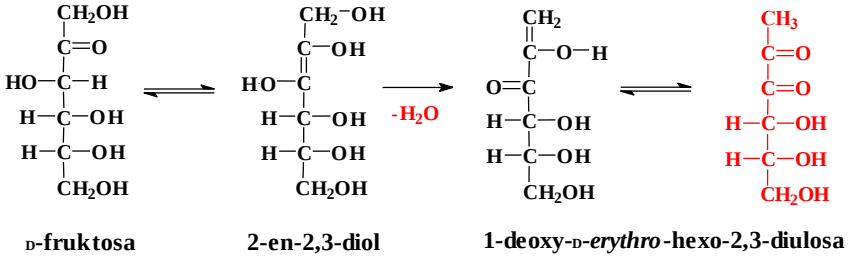
D-glukosa **1-en-1,2-diol** **3-deoxy-D-*erythro*-hexos-2-ulosa**

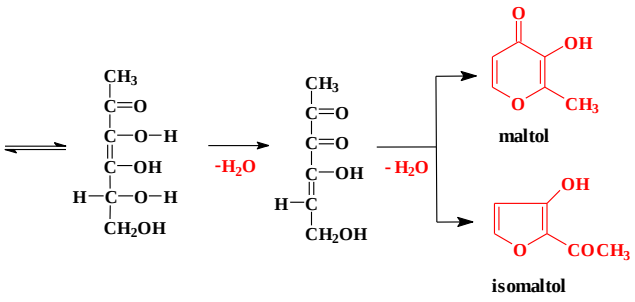


3,4-dideoxy-D-*glycero*-hex-3-enos-2-ulosa **5-hydroxymethylfuran-2-karbaldehyd**



2,3-enolisation

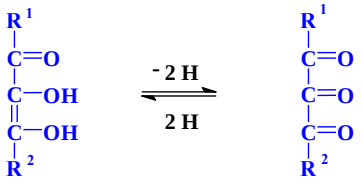




caramel aroma

reductone formation

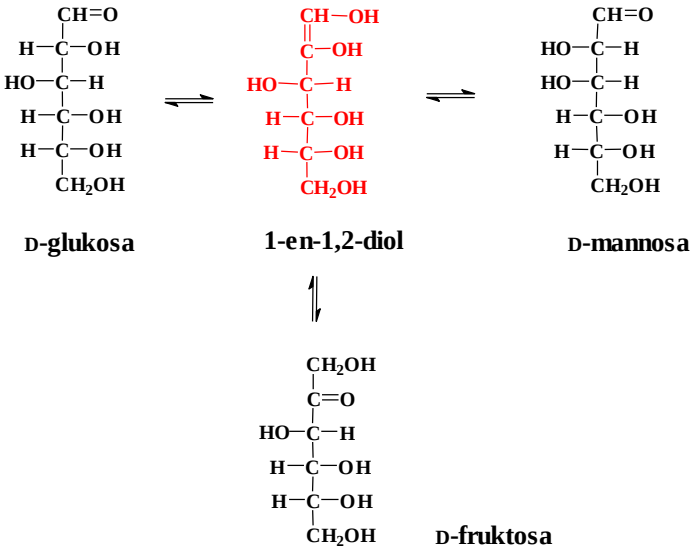
- Antioxidants (reduction of organic substances, metal ions)



isomerisation

aldose → ketose

aldose → aldose (epimeration)



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*

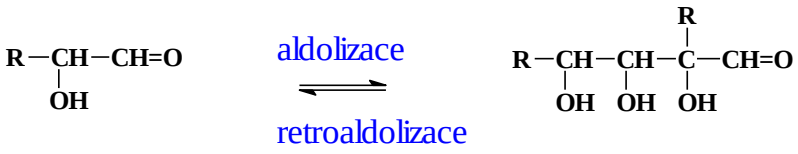
rearrangement to acids

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

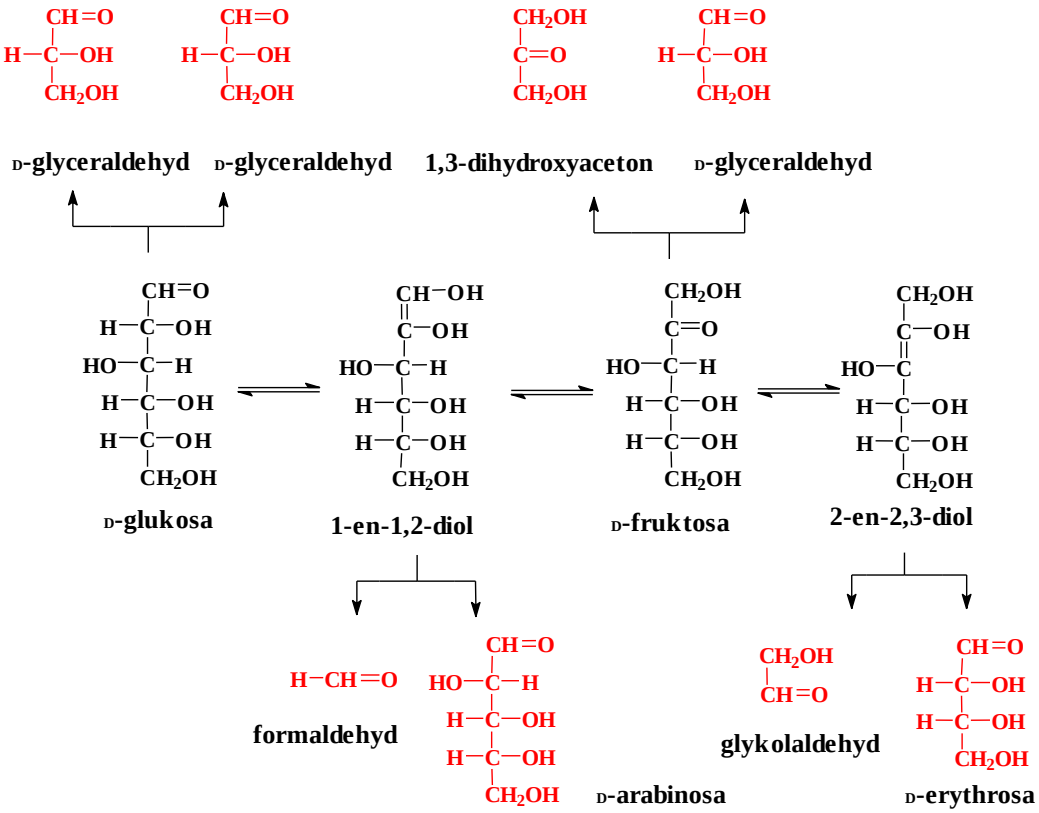
fragmentation

formation of reactive componds

- retroaldolisation



- oxidadation (after isomeration, dehydration)



MAILLARD REACTION
non-enzymatic browning reaction

reactants

- sugars (carbonyl compounds)
  monosaccharides and reducing oligosaccharides
  (nonreducing oligosaccharides, polysaccharides, glycosides)
  triose > …. > pentose > hexose (acyclic forms)
  aldose > ketose
  α-dicarbonyls > aldehydes > ketones > saccharides

- proteins (amino compounds)
  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 > amino acids

reaction conditions

- water activity (a_w 0,3-0,7)
- pH (9-10)
- others (temperature, time of reaction, other components)

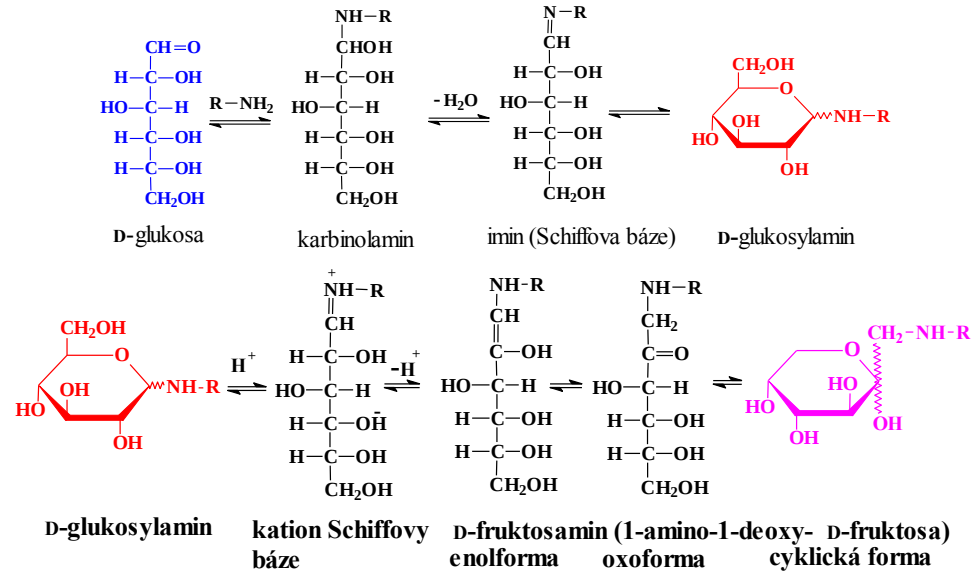
concequences: positive, negative

- formation of aroma compounds
- formation of yelow, brown, black pigments melanoidins
- decrease of nutritive value
- formation potentially toxic products
- reaction *in vivo* (glykosylation of proteins)

mechanism of reaction
3 stages

- initial stage
  formation of glykosylamines (Amadori rearrangement) and formation of aminodeoxysugars (Amadori products)
- central 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)

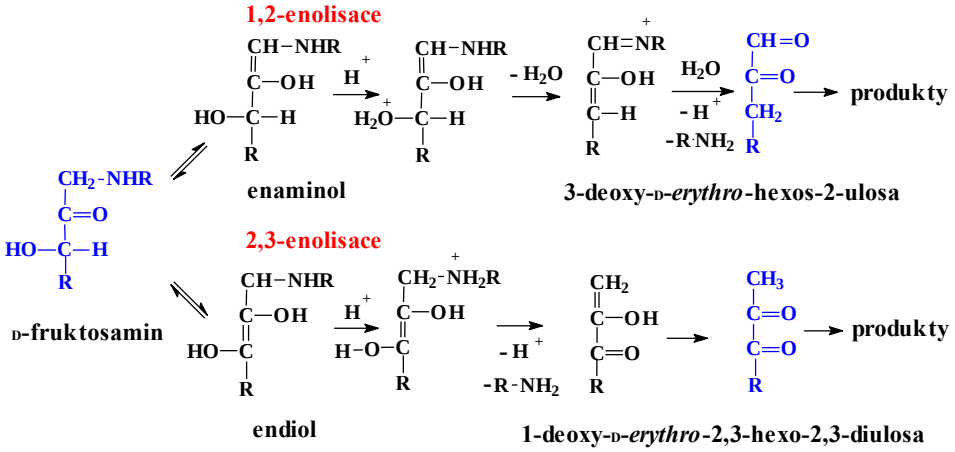
glycosylamines and aminodeoxysugars



totally utilisable form non-utilisable form

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

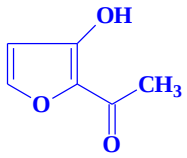
mechanisms (reaction of acyclic forms)
decomposition of aminodeoxysugars
1,2-enolisation in acidic medium
2,3-enolisation in neutral and alkali medium
formation of glycosuloses and glycodiuloses (aldoketoses a diketoses)



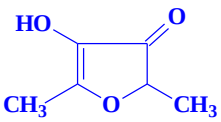
analogy with reaction of sugars but:

- lower activation energy
- products contain N a S
- qualitativelly and quantitativelly more products

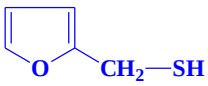
important heterocyclic products



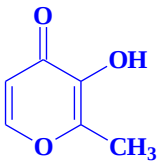
isomaltol
(caramel)



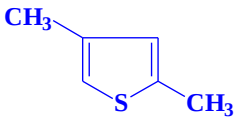
furaneol
(strawberry, pineapple)



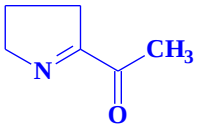
furfurylthiol
(coffee)



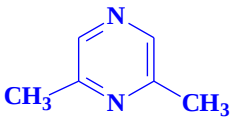
maltol
(caramel)



2,4-dimethylthiophene
(fried anion)



2-acetyl-1-pyrroline
(bread)



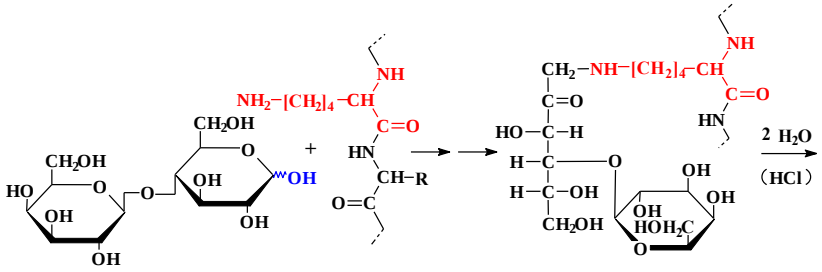
2,6-dimethylpyrazine
(chocolate, nuts)

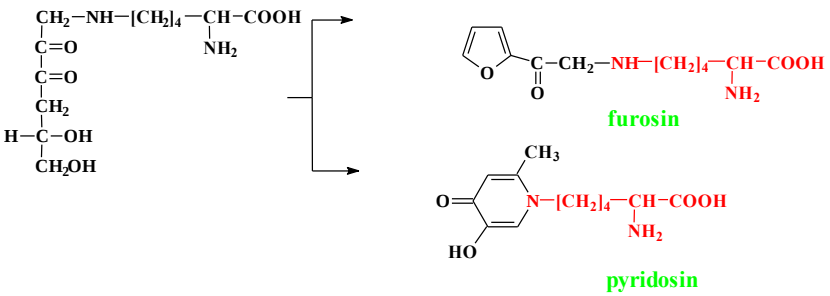
Maillard reaction in important food commodities
positive and negative consequences, desirable and undesirable reactions

technology (aroma, taste, colour, nutritive value)

- roasting
- boiling, frying , backing
- drying
- extrusion, microvawe heating
- milk, milk products
  Lys losses: 10-30 % traditional drying, 3 % sprey drying
- cereals, vcereal products
  Lys losses: 70 % bread crust, 10 % total
- meat, meat products
  mutagenes
- fruits, vegetables
- coffee, cocoa, nuts

reaction during processing of milk non-utilisable (blocked) Lys (example)



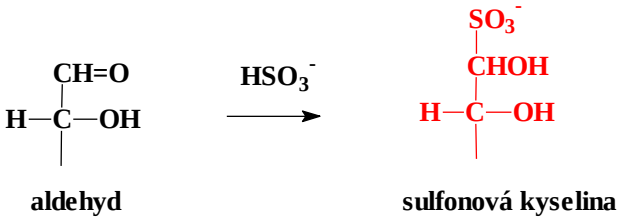


isomeration lactose → lactulose + epilactose
lysinoalanine

inhibition of Maillard reaction

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

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



aldehyd **sulfonová kyselina**

CARAMELISATION
sugars (saccharose, glucose, fructose, starch sirup, invert sugar)
temperature: 150-190°C (240°C)
reaction time: 5-10 hours
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 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