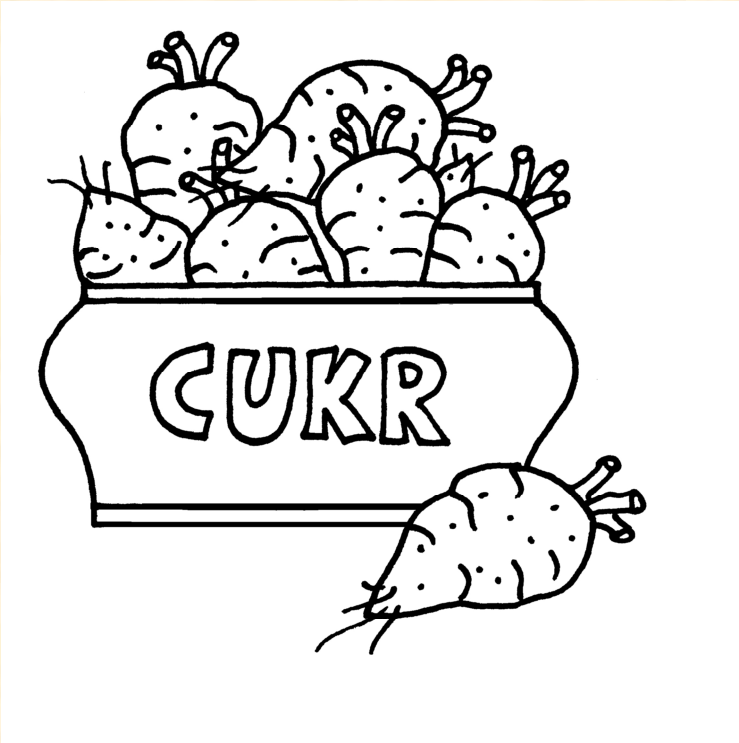
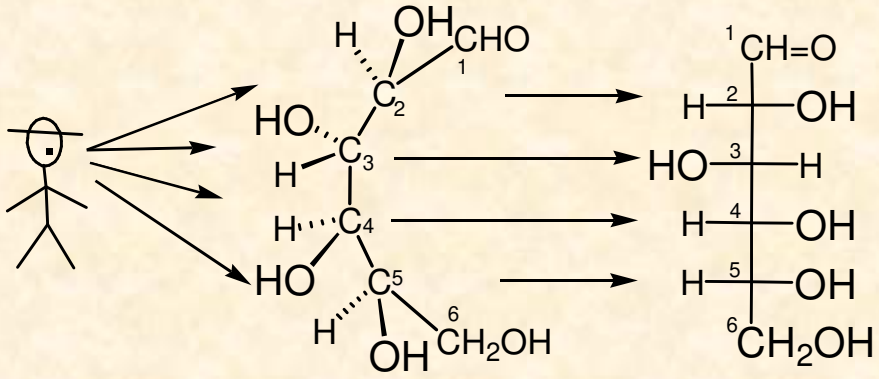
SACCHARIDES 1.

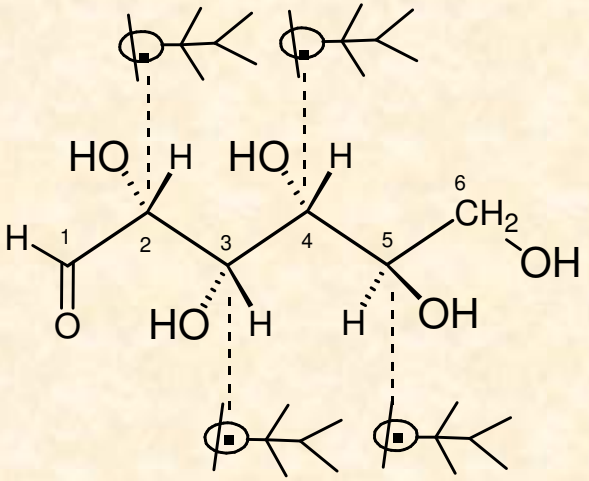


Biological importance of saccharides

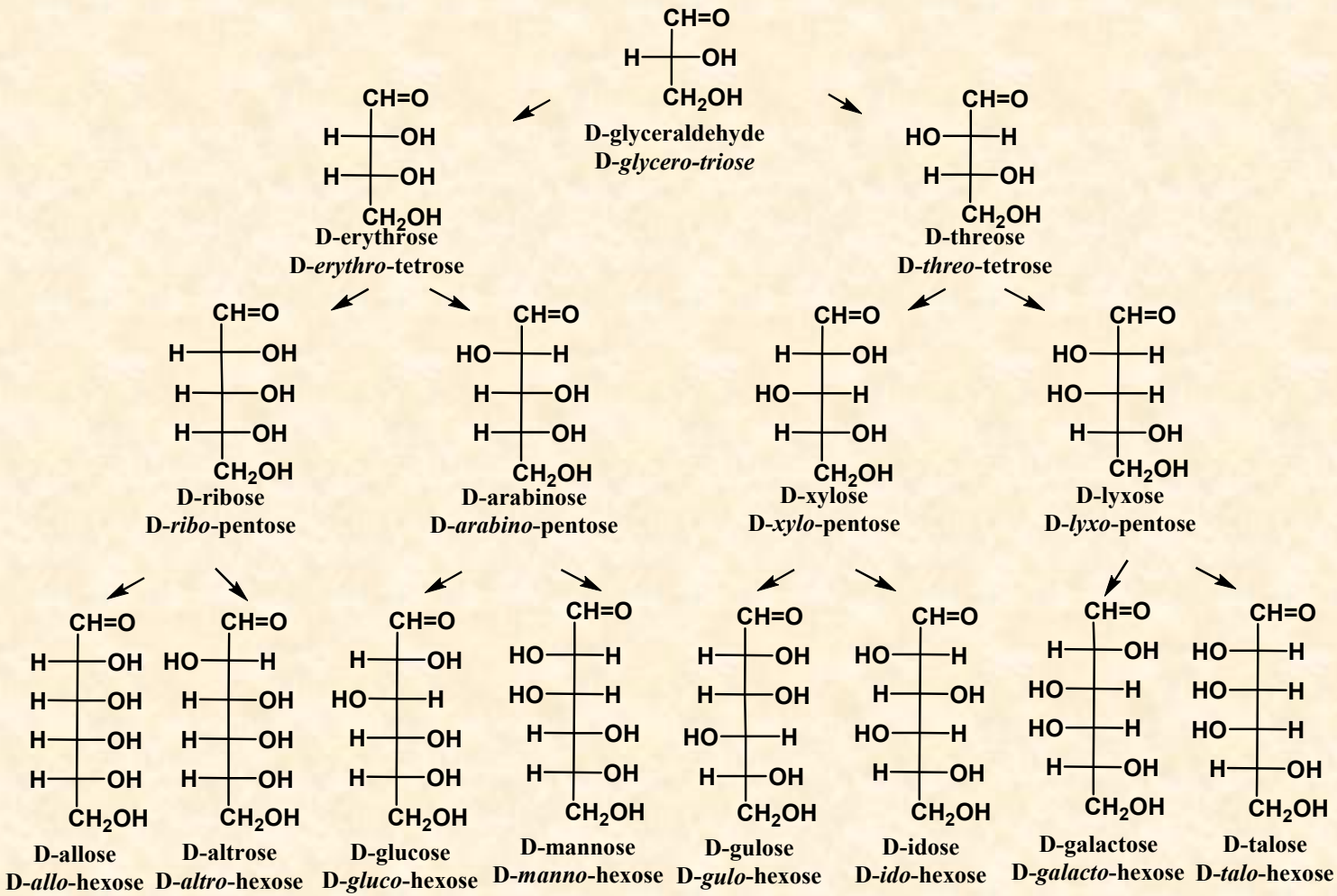
- They comprise a building material of all plant cells and tissues
- They represent nourishment and source of energy for animals and plants
- They represent key compounds for the biosynthesis of proteins and lipids.
- They are the components of glycoproteins, glycolipids and nucleic acids.
- They are used in medicine as drugs and diagnostics.

Acyclic forms of monosaccharides

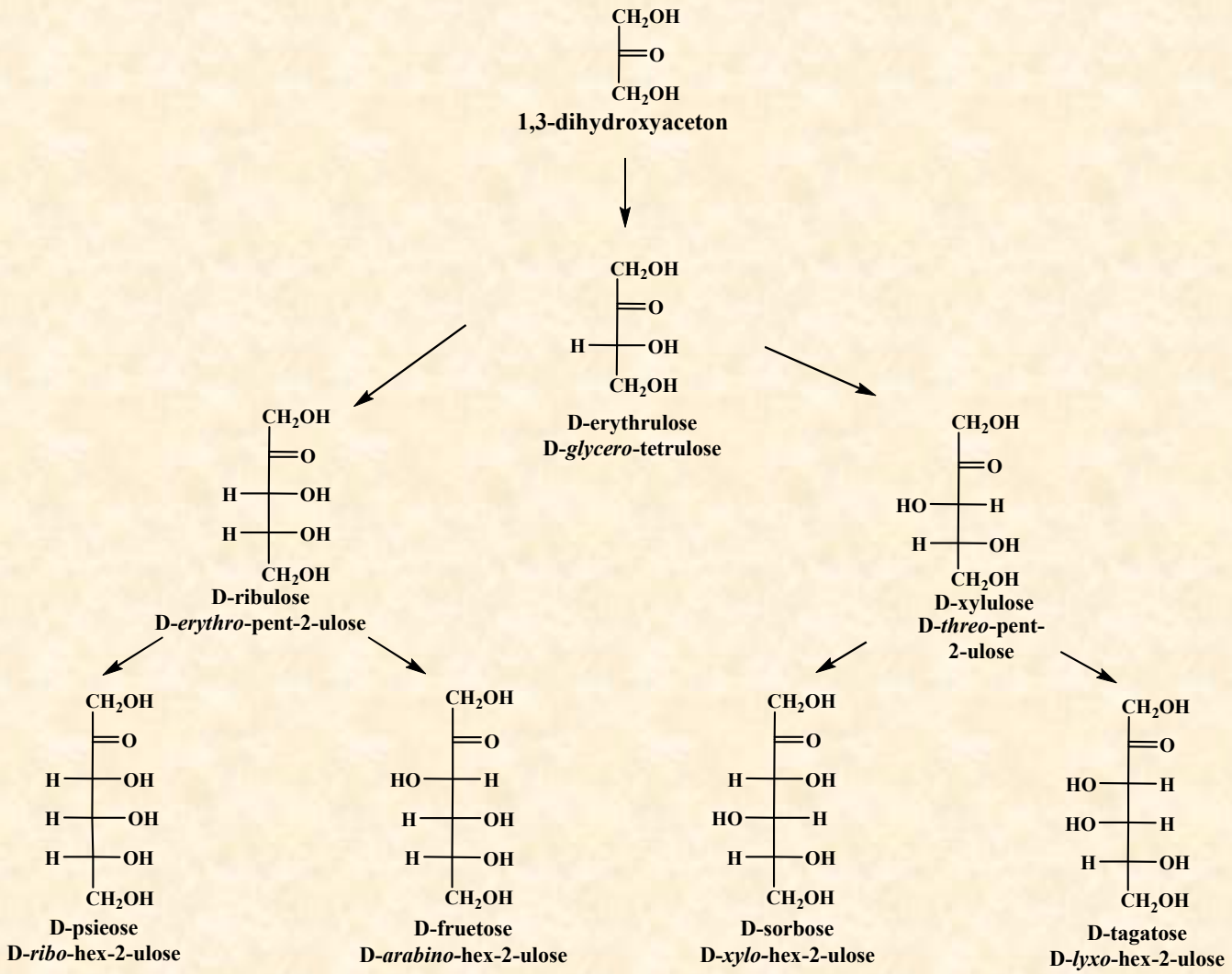




D-aldoses

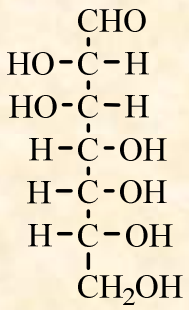

D-glyceraldehyde
D-glycero-triose
D-erythrose
D-erythro-tetrose
D-threose
D-threo-tetrose
D-ribose
D-ribo-pentose
D-arabinose
D-arabino-pentose
D-xylose
D-xylo-pentose
D-lyxose
D-lyxo-pentose
D-allose
D-allo-hexose
D-altrose
D-altro-hexose
D-glucose
D-gluco-hexose
D-mannose
D-manno-hexose
D-gulose
D-gulo-hexose
D-idose
D-ido-hexose
D-galactose
D-galacto-hexose
D-talose
D-talo-hexose

D-ketoses

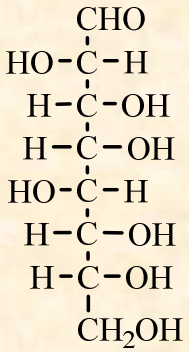

CH2OH
O
CH2OH
1,3-dihydroxyaceton
CH2OH
O
H OH
CH2OH
D-erythrulose
D-glycero-tetrulose
CH2OH
O
H OH
H OH
CH2OH
D-ribulose
D-erythro-pent-2-ulose
CH2OH
O
HO H
H OH
CH2OH
D-xylulose
D-threo-pent-2-ulose
CH2OH
O
H OH
H OH
H OH
CH2OH
D-psieose
D-ribo-hex-2-ulose
CH2OH
O
HO H
H OH
H OH
CH2OH
D-fruetose
D-arabino-hex-2-ulose
CH2OH
O
H OH
HO H
H OH
CH2OH
D-sorbose
D-xylo-hex-2-ulose
CH2OH
O
HO H
HO H
H OH
CH2OH
D-tagatose
D-lyxo-hex-2-ulose

Configurational prefixes

Trioses	*glycero-*
Tetroses	*erythro-, threo-*
Pentoses	*arabino-, lyxo-, ribo-, xylo-*
Hexoses	*allo-, altro-, galacto-, gluco-, gulo-, ido-,manno-, talo-*

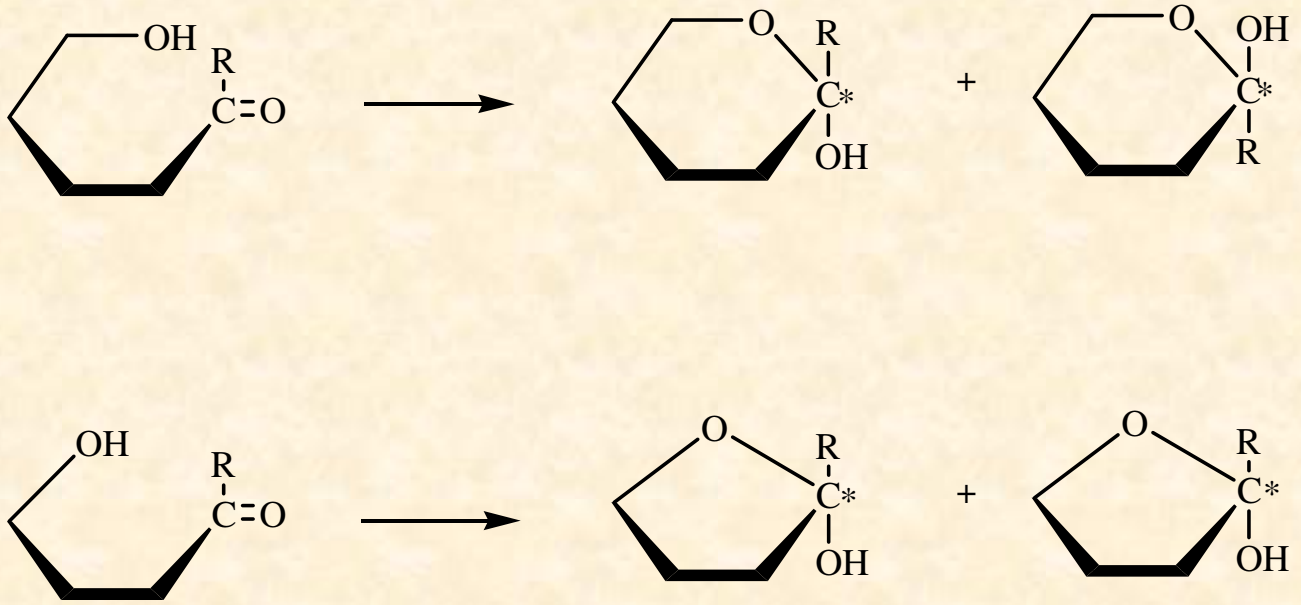


D-*glycero*-a-D-*manno*-heptose

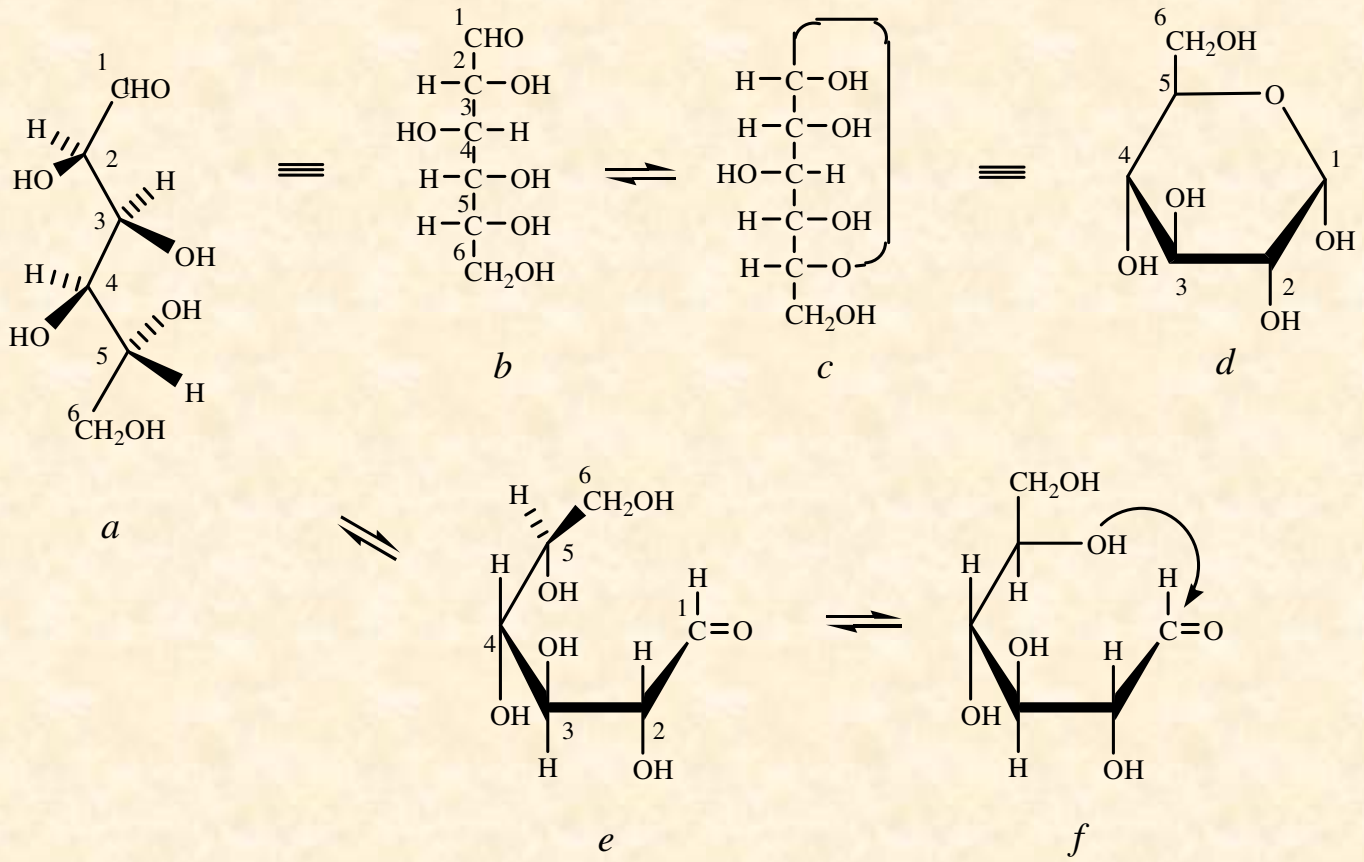


D-*erythro*-L-*galacto*-octose

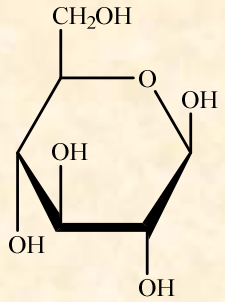
Cyclization of monosaccharides



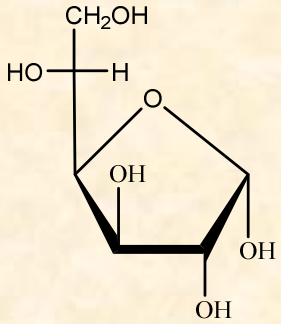
Cyclic structure of monosaccharides



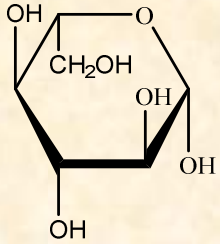
Haworth projection of monosaccharides



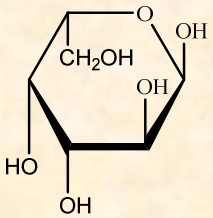
β-D-glucopyranose



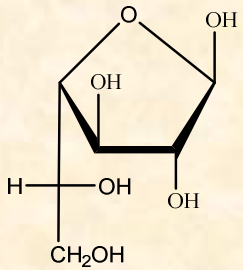
α-D-glucofuranose



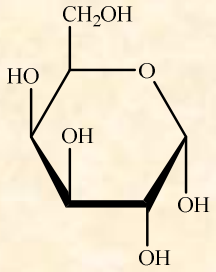
β-L-glucopyranose



α-L-galactopyranose

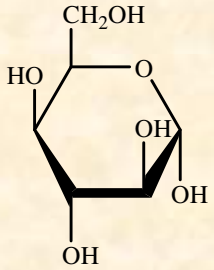


β-D-galactofuranose

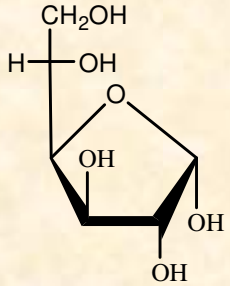


α-D-galactopyranose

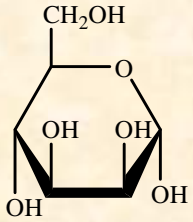
Sacharides in Haworth projection



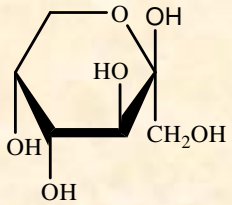
α-D-idopyranose



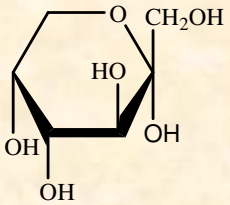
β-L-idofuranose



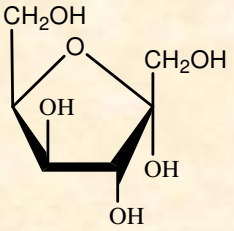
α-D-mannopyranose



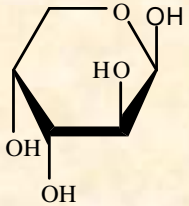
β-D-fructopyranose



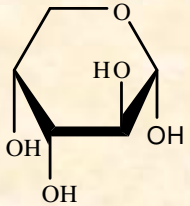
α-D-fructopyranose



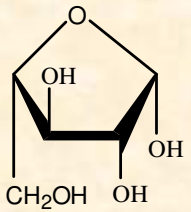
α-D-fructofuranose



β-D-arabinopyranose

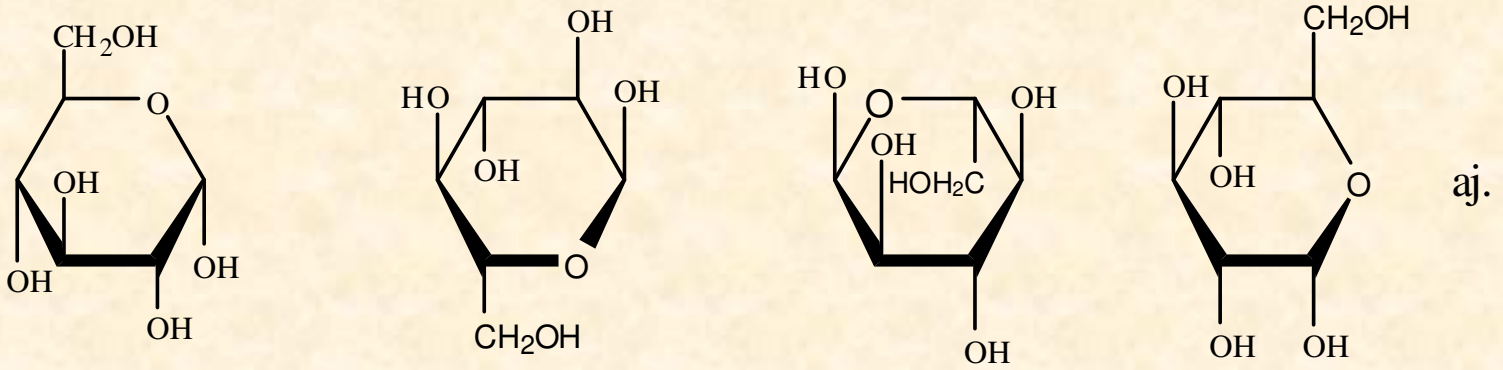


α-D-arabinopyranose



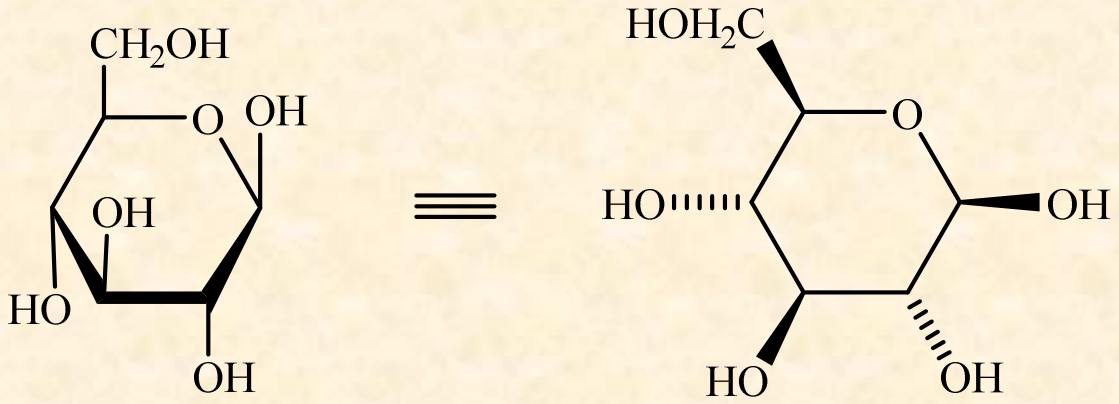
β-L-arabinofuranose

Another possibilities of drawing of Haworth formulas



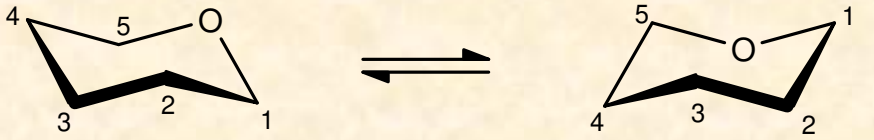
aj.

Mills formulas

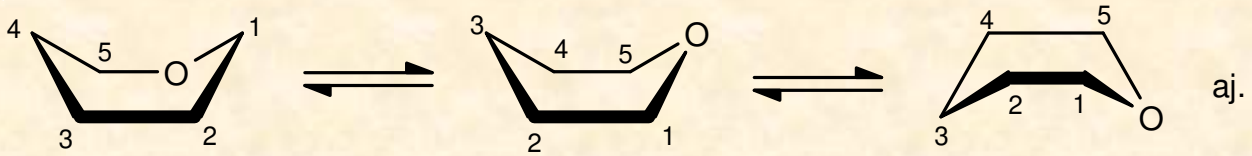


β-D-glucpyranose

Conformation of monosaccharides



$^{4}C_{1}$ $^{1}C_{4}$

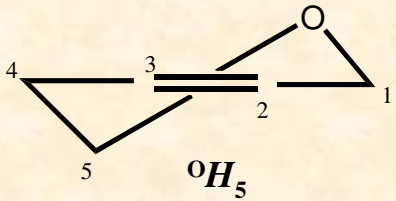


aj.

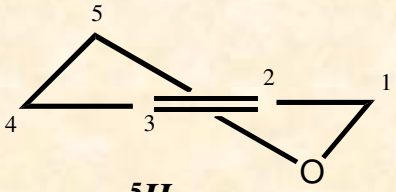
$^{1,4}B$ $^{O,3}B$ $B_{O,3}$

$^{2}S_{o}$ $^{O}S_{3}$

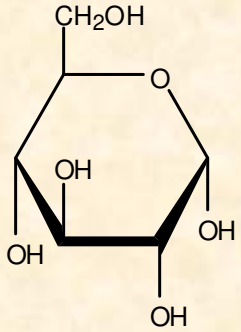
Conformation of monosaccharides



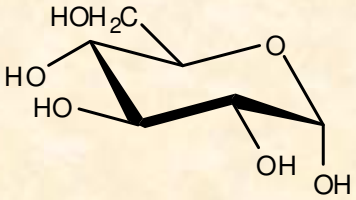
$^{O}H_{5}$



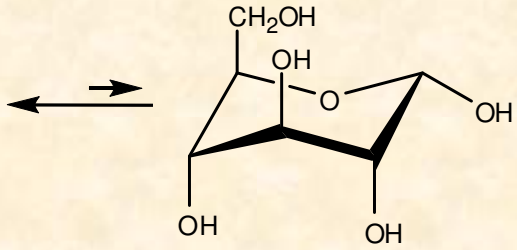
$^{5}H_{O}$



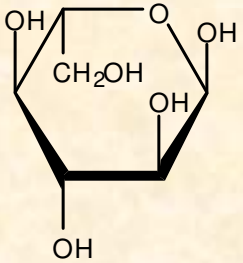
α-D-glucopyranose



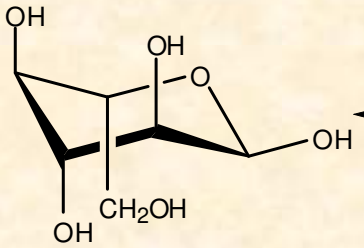
α-D-glucopyranose-$^{4}C_{1}$



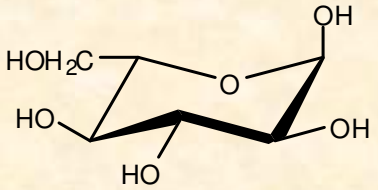
α-D-glucopyranose-$^{1}C_{4}$



α-L-glucopyranose

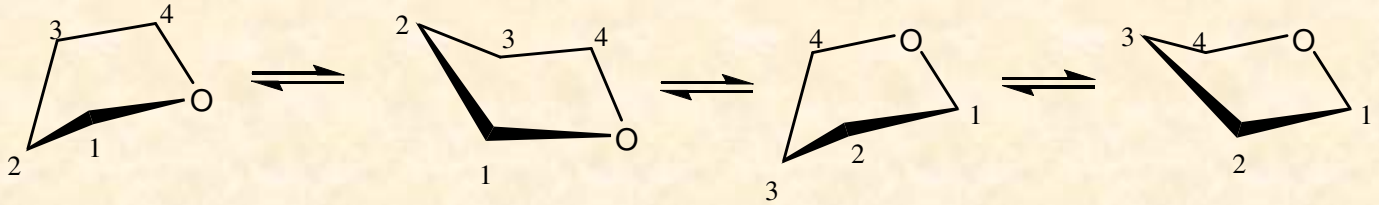


α-L-glucopyranose-$^{4}C_{1}$

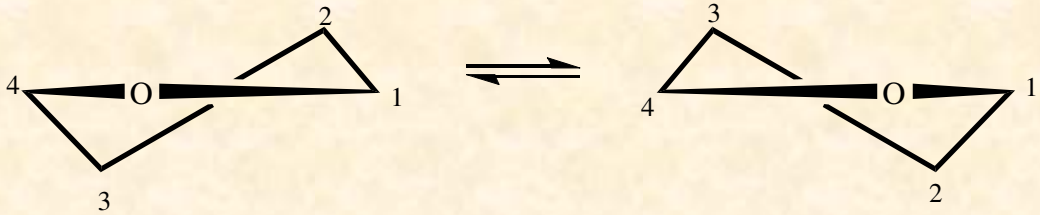


α-L-glucopyranose-$^{1}C_{4}$

Conformation of pentoses

- 

E_2 ^2E E_3 ^3E



$^2T_3$ $^3T_2$

Anomeric effect

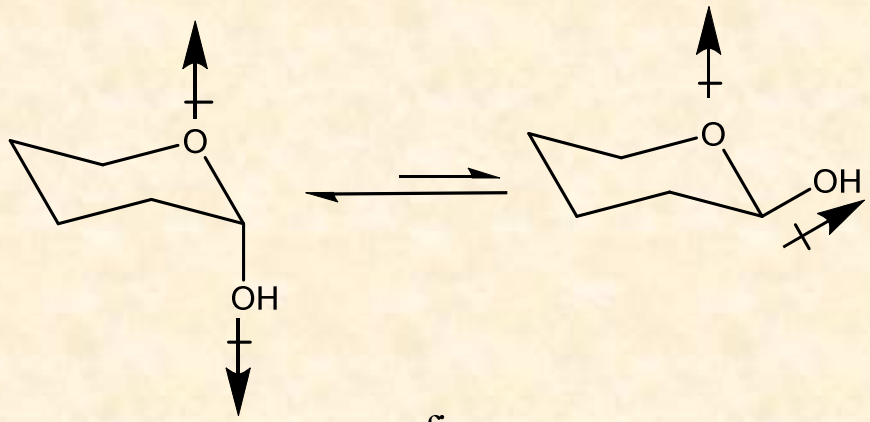


fig.a

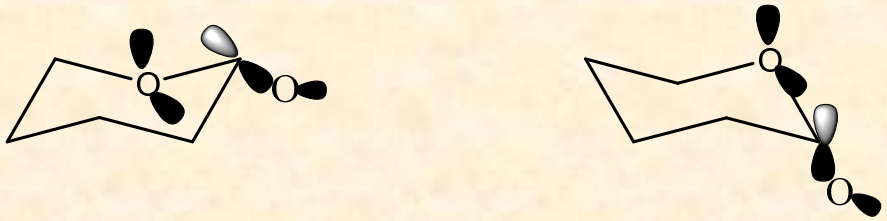
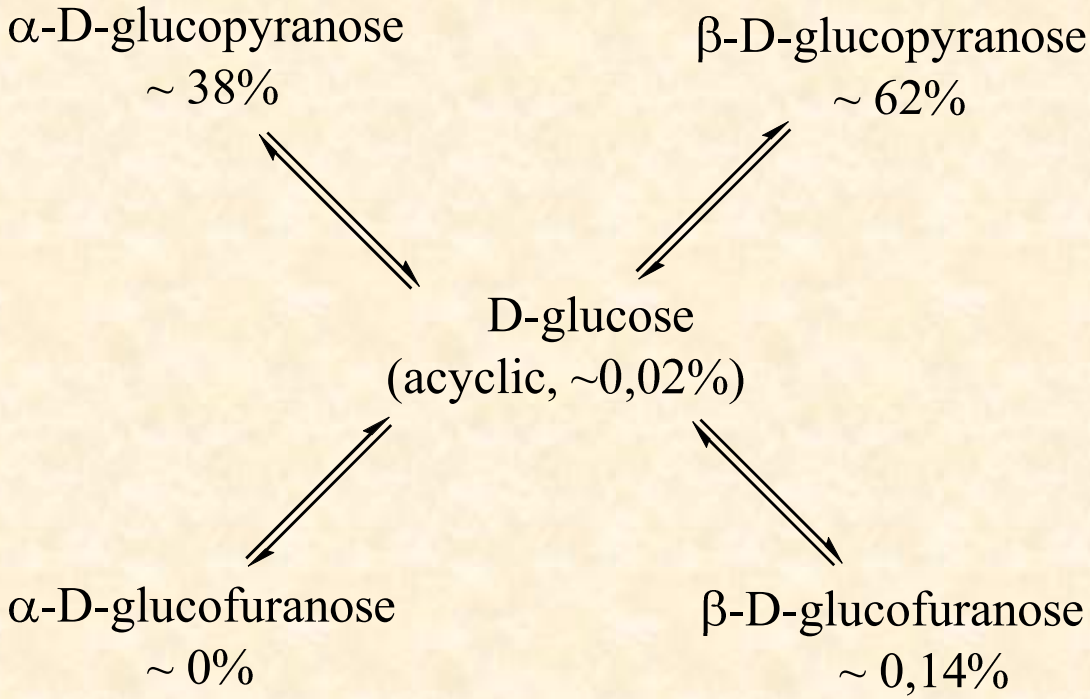


fig.b

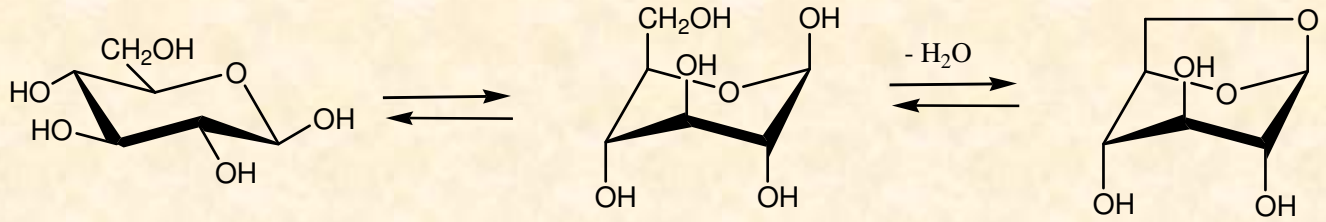
Properties of monosaccharides

- Chiral
- Crystalline
- Soluble in the water and polar solvents
- Insoluble in nonpolar solvents
- Hydroxy groups of sugars are more acidic (pK_a 12 až 14)
- They are substrates of enzymes oxidases, isomerases, kinases, aldolases
- They form complexes with metal ions Cu^{2+}, Ca^{2+}, Mg^{2+} Fe^{3+}, Mn^{2+}, Al^{3+}
- The equilibrium is established after dissolving in the water between cyclic and acyclic form – this effect is called „mutarotation“

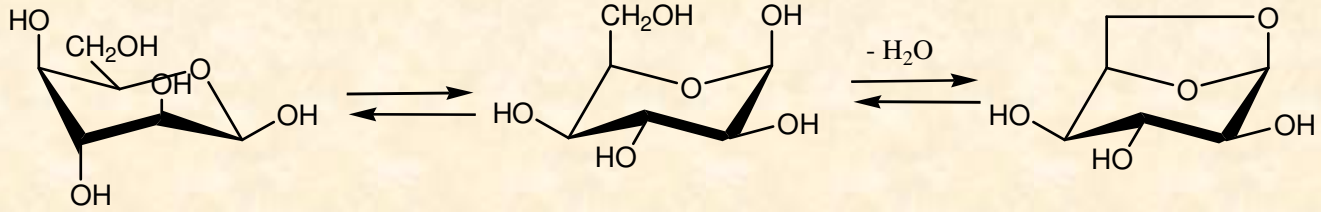
Mutarotation



Intramolecular dehydration of aldohexoses

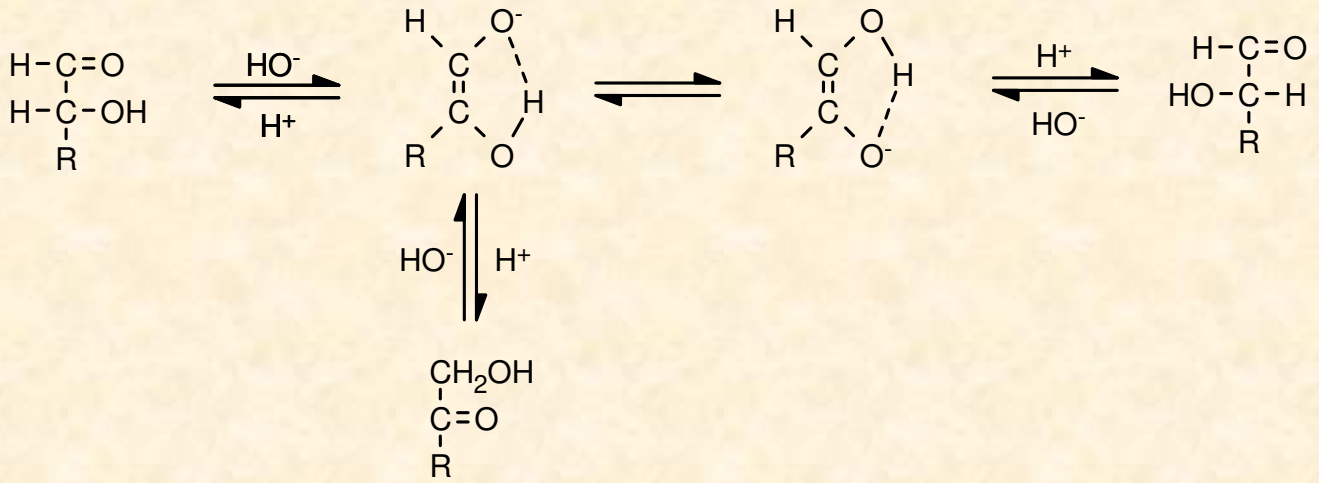


β-D-glucopyranose-$^4C_1$ β-D-glucopyranose-$^1C_4$ 1,6-anhydro-β-D-glucopyranose-$^1C_4$



β-D-idopyranose-$^4C_1$ β-D-idopyranose-$^1C_4$ 1,6-anhydro-β-D-idopyranose-$^1C_4$

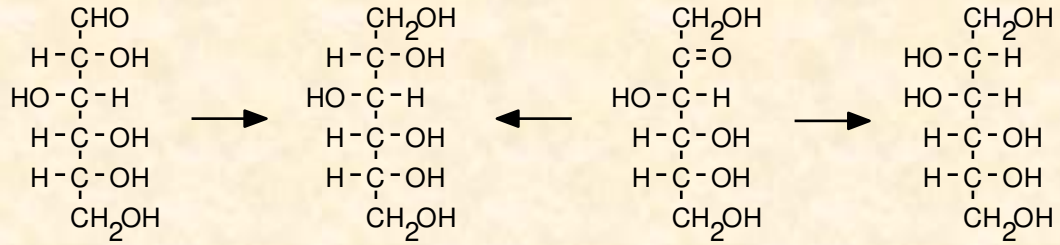
Mechanism of alkaline isomerization I.



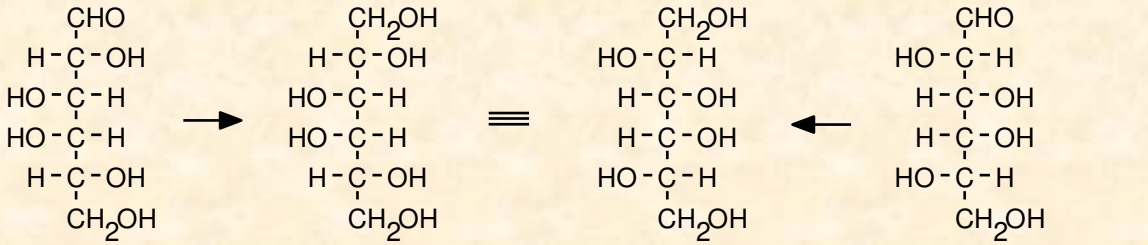
for example:

D-mannose ~4% ⇌ D-glucose ~62% ⇌ D-fruktosa ~32%

Reaction of carbonyl group
Reduction - alditols

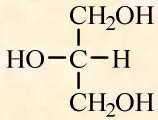


D-glucose D-glucitol D-fructose D-mannitol

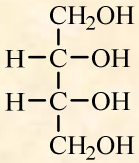


D-galactose galactitol L-galactose

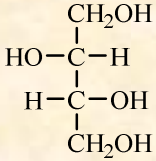
Reaction of carbonyl group
Reduction - alditols



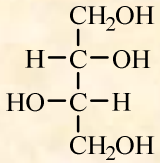
glycerol



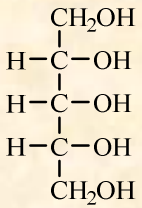
erythritol



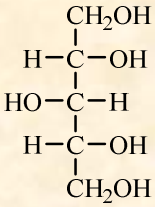
D-threitol



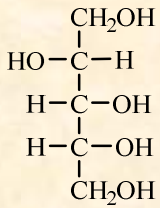
L-threitol



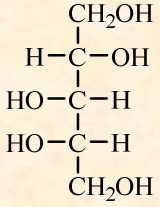
ribitol



xylitol

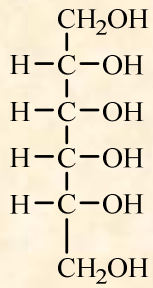


D-arabinitol

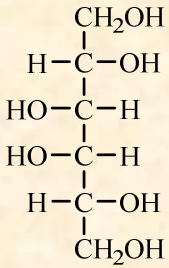


L-arabinitol

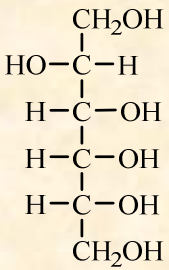
Reaction of carbonyl group
Reduction - alditols



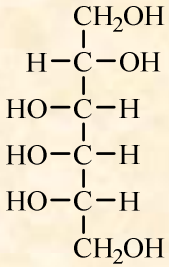
allitol



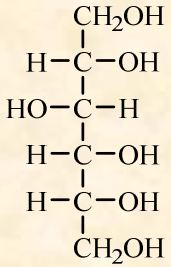
galactitol



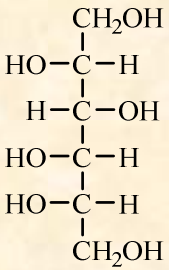
D-altritol



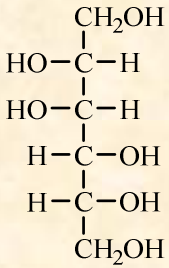
L-altritol



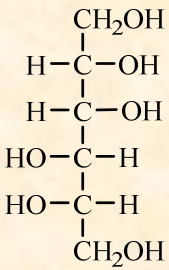
D-glucitol



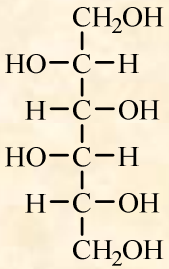
L-glucitol



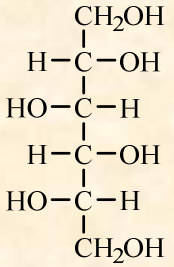
D-mannitol



L-mannitol

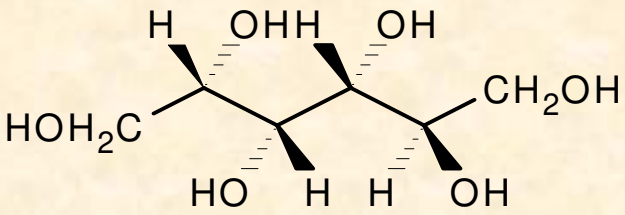


D-iditol

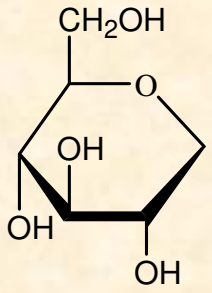


L-iditol

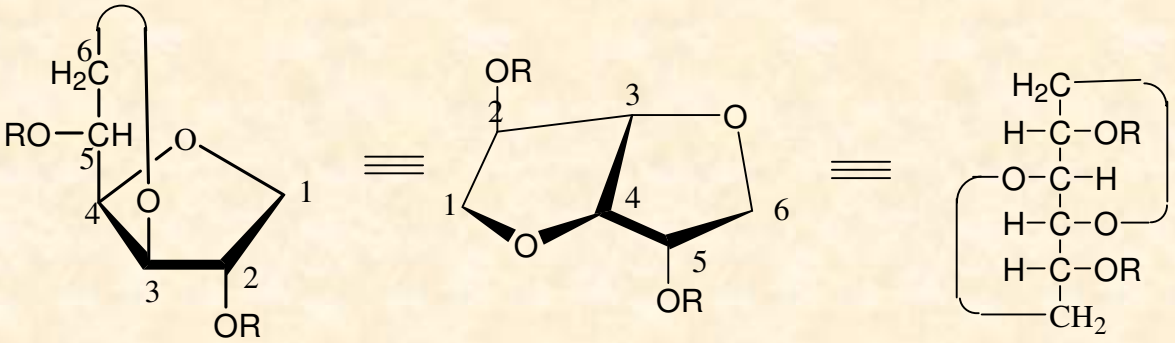
Reaction of carbonyl group
Reduction - alditols



D-glucitol,

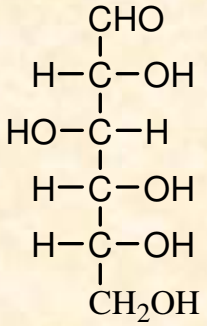


polygalitol

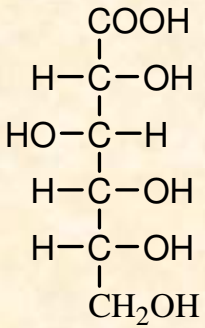


isosorbide (R = H)
isosorbid dinitrate (R = NO_2)

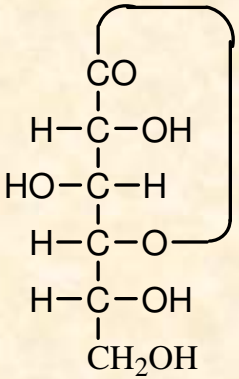
Oxidation
Aldonic acids and their lactones

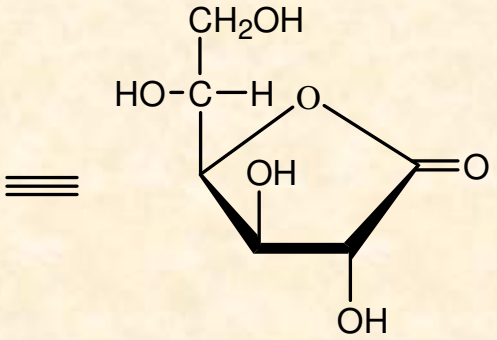


D-glucose



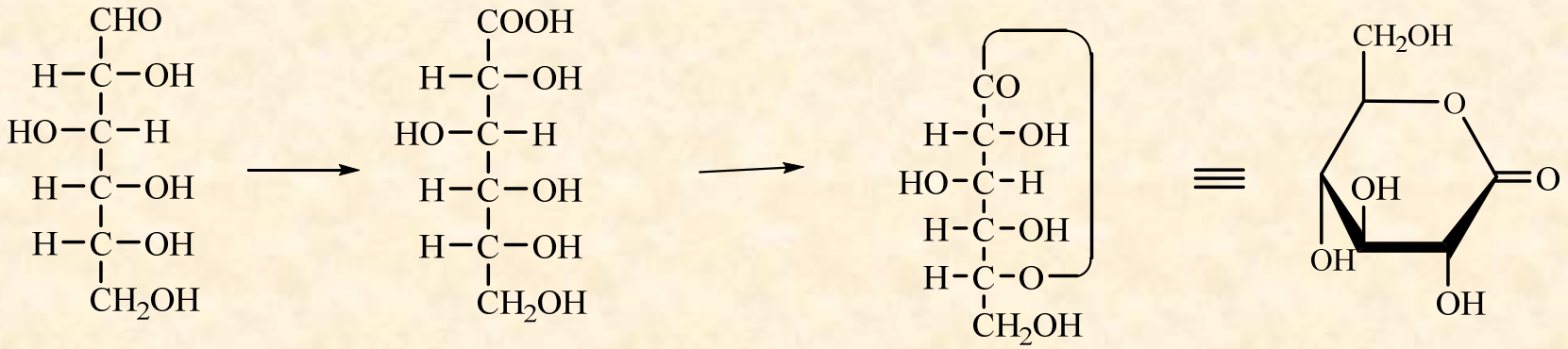
D-gluconic acid





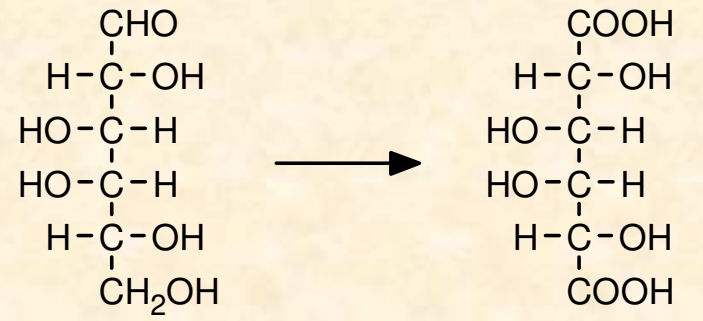
D-glucono-1,4-lacton

Oxidation
Aldonic acids and their lactones



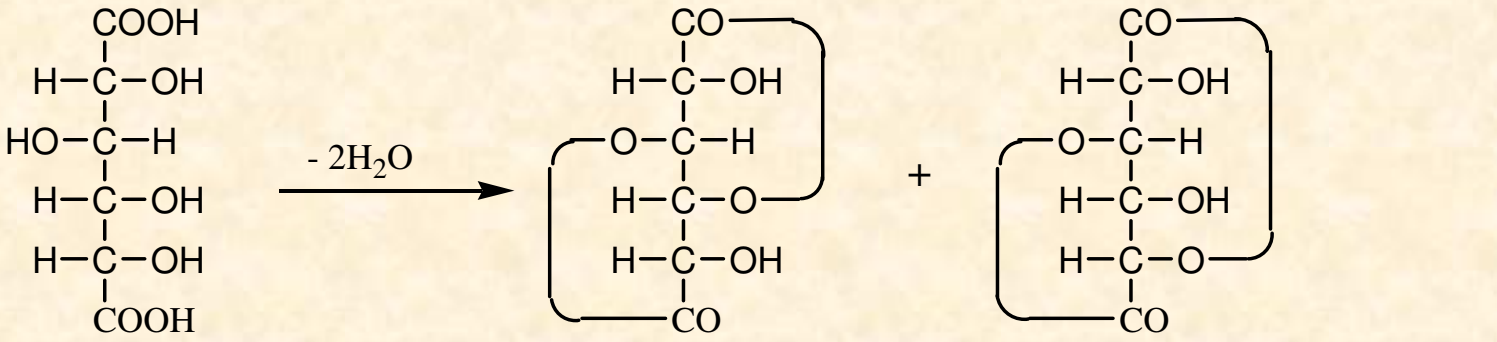
D-glucose D-gluconic acid D-glucono-1,5-lakton

Oxidation
Aldaric acids and their lactones



D-galactose galactaric acid

Oxidation
Aldaric acids and their lactones

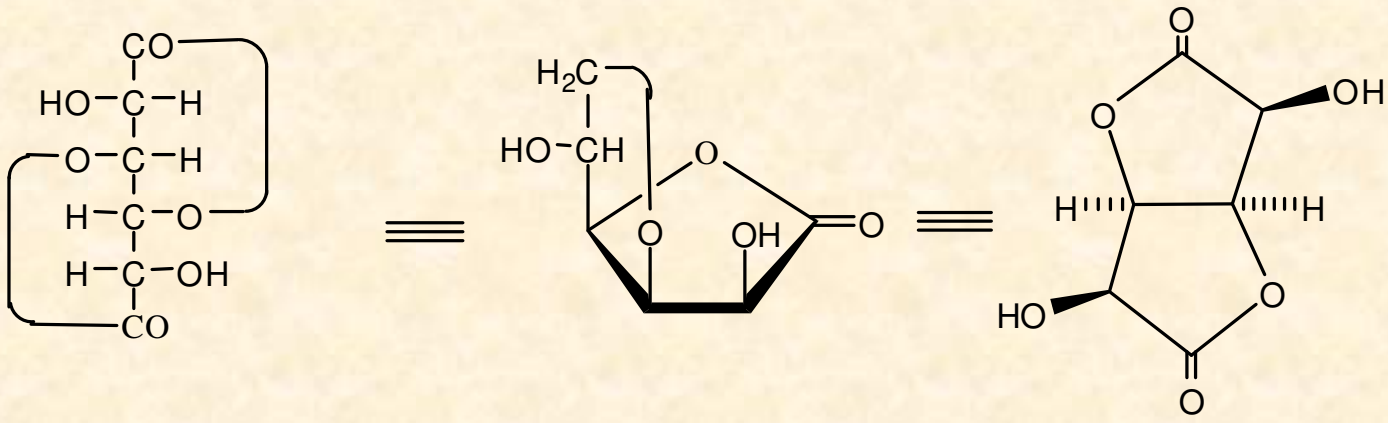


D-glucaric acid

D-glucaro-1,4:6,3-dilactone

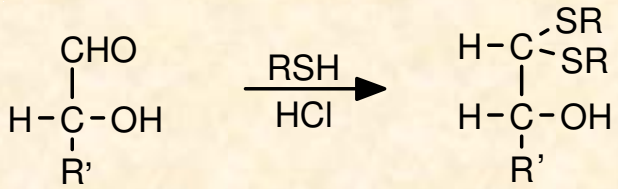
D-glucaro-1,5:6,3-dilactone

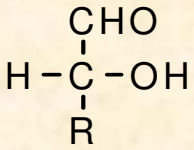
Oxidation
Aldaric acids and their lactones

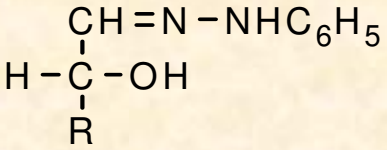


D-mannaro-1,4:6,3-dilakton

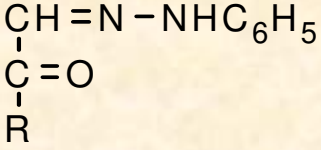
Dithioacetals, hydrazones, osazones, oximes

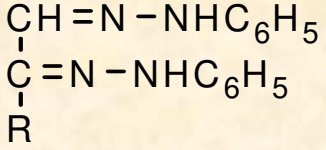






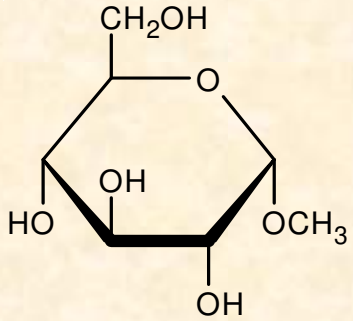
hydrazone



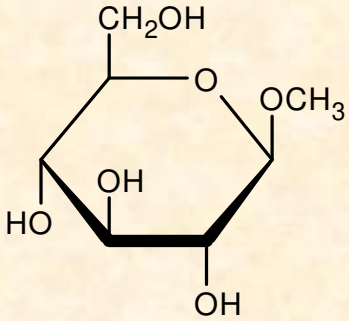


osazone

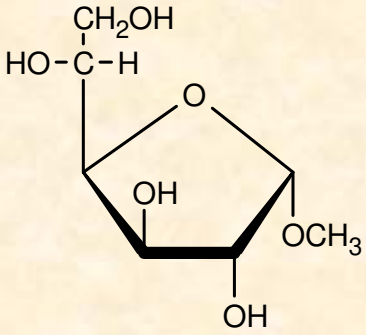
Glycosides



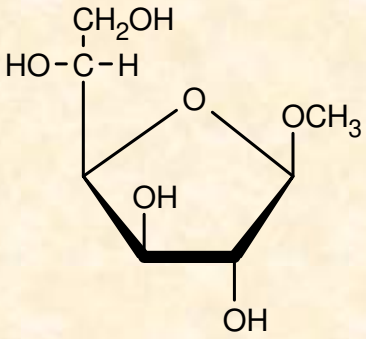
methyl-α-D-glucopyranoside



methyl-β-D-glucopyranoside



methyl-α-D-glucofuranoside

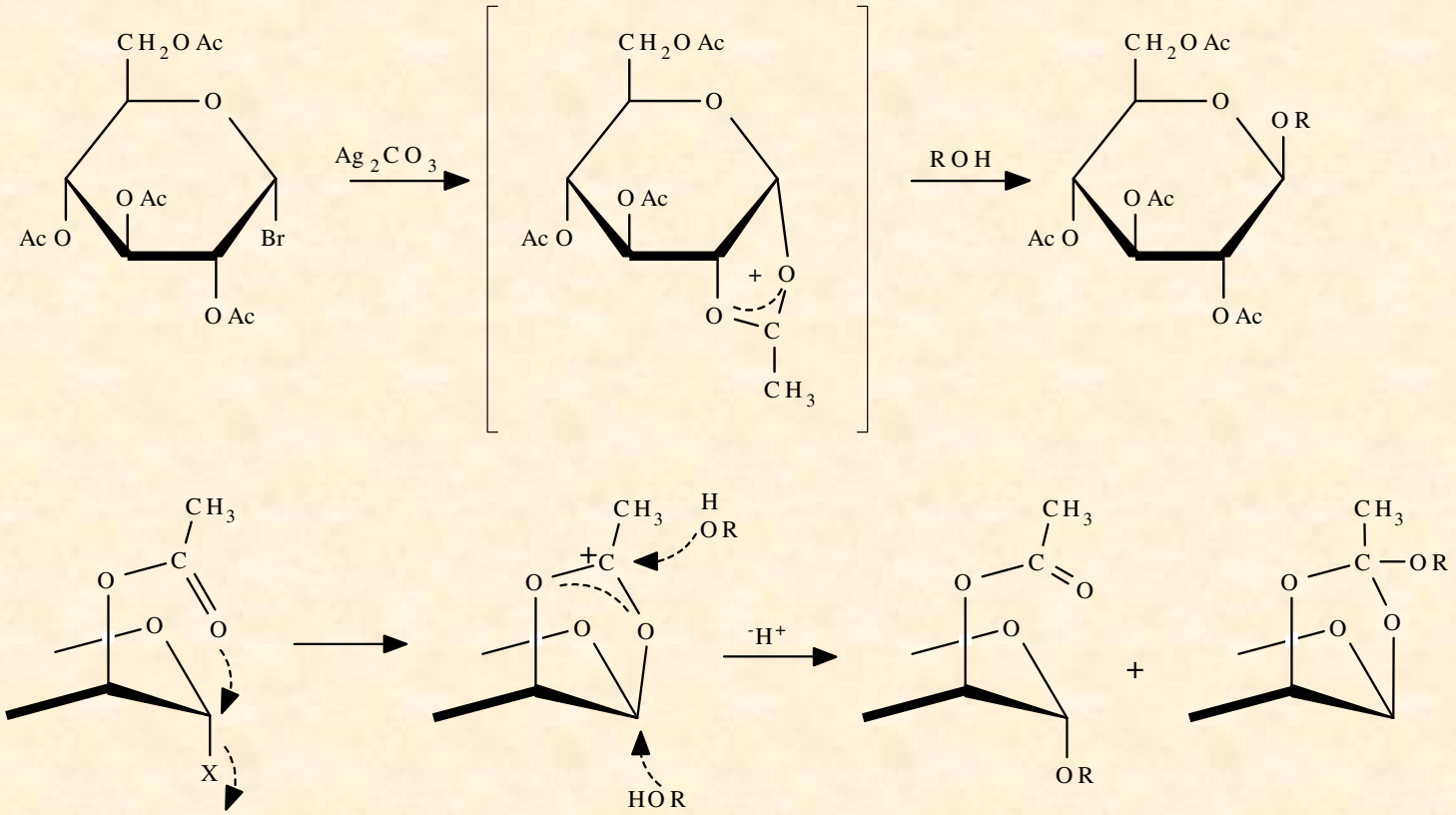


methyl-β-D-glucofuranoside

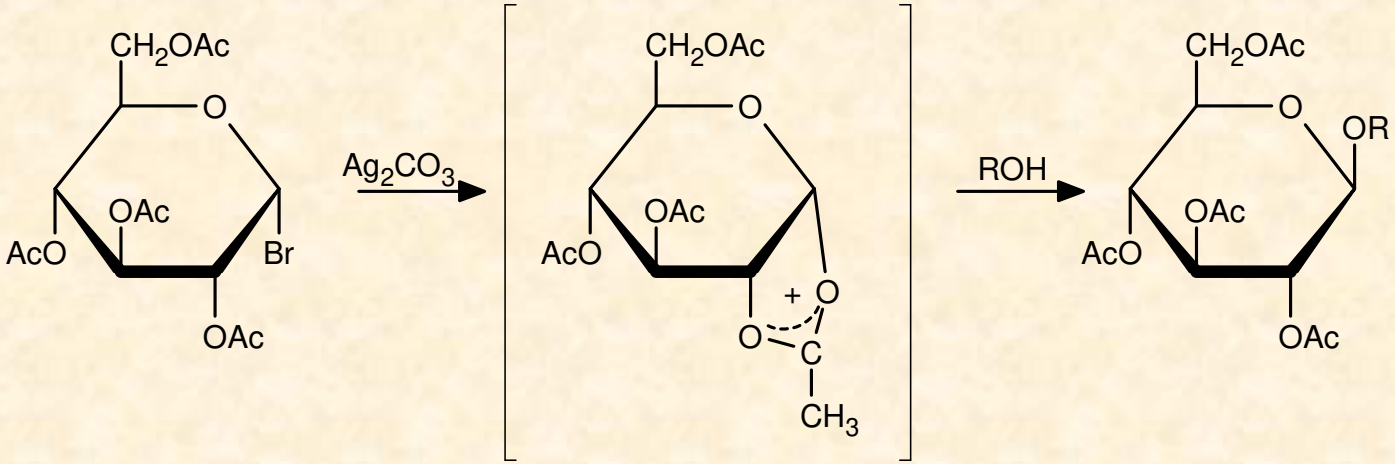
Composition (%) of equilibrium mixture of methylglcosides in methanol (35°C, 1% HCl)

Methylglycoside	Furanoside		Pyranoside	
	α	β	α	β
D-ribose	5	17	12	66
D-arabinose	22	7	24	47
D-mannose	0,74	0	94	5,3
D-gluckose	0,6	0,9	66	32,5
D-galactose	6	16	58	20

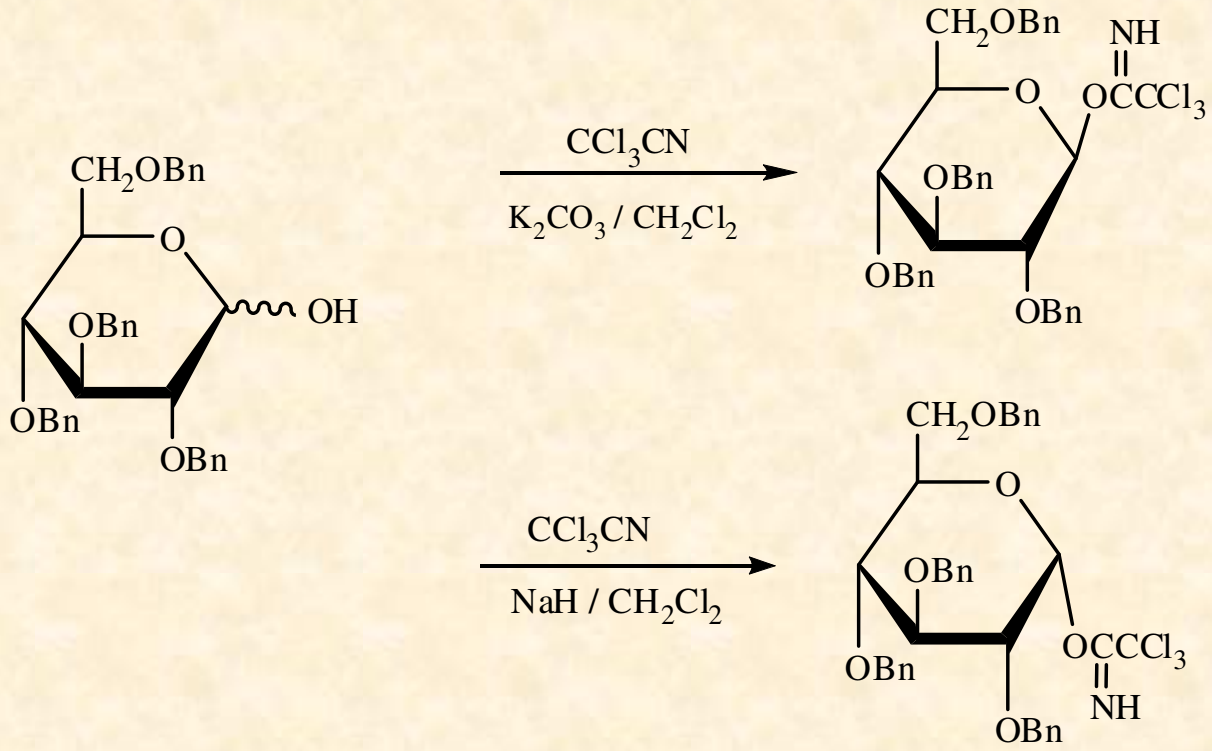
Koenigs – Knorr glycosylation



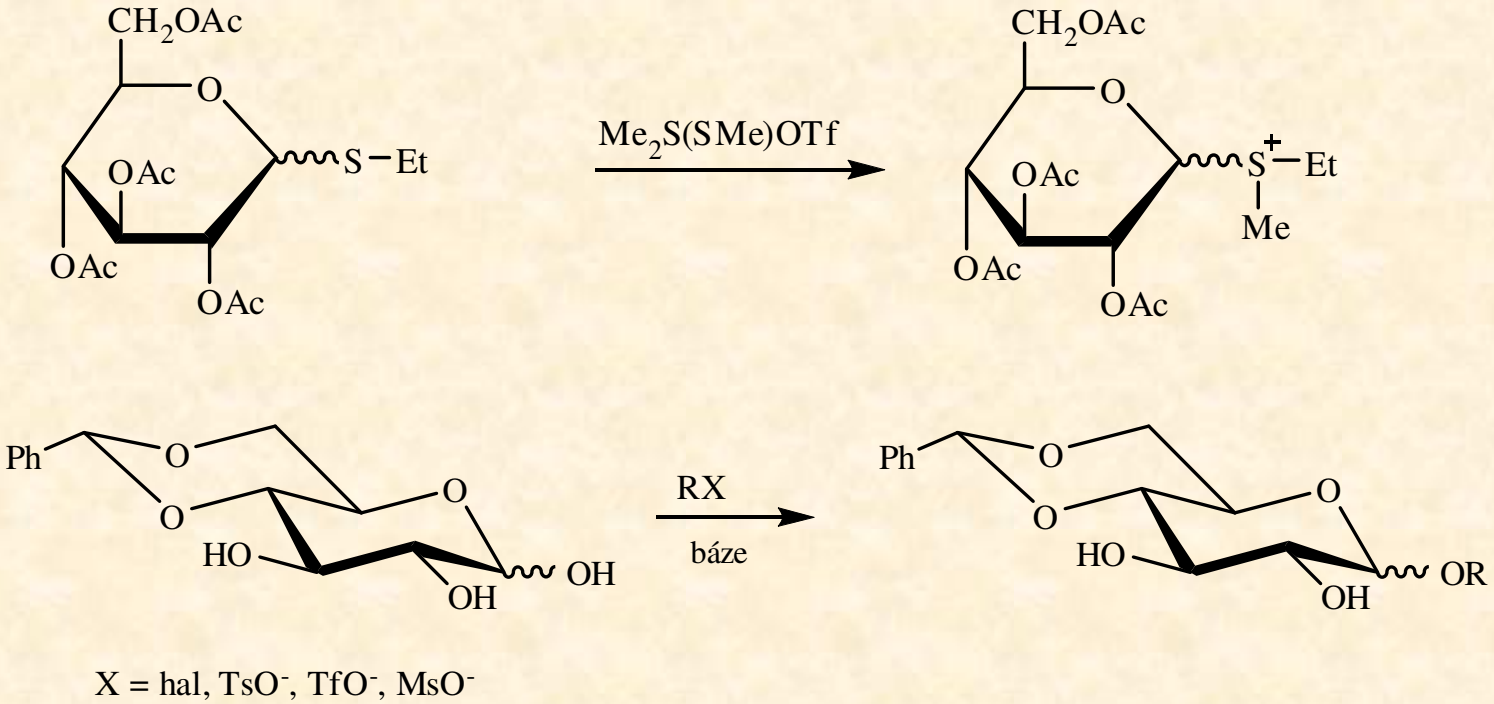
Neighbouring group participation



Glycosylation reaction - trichloroacetimidates

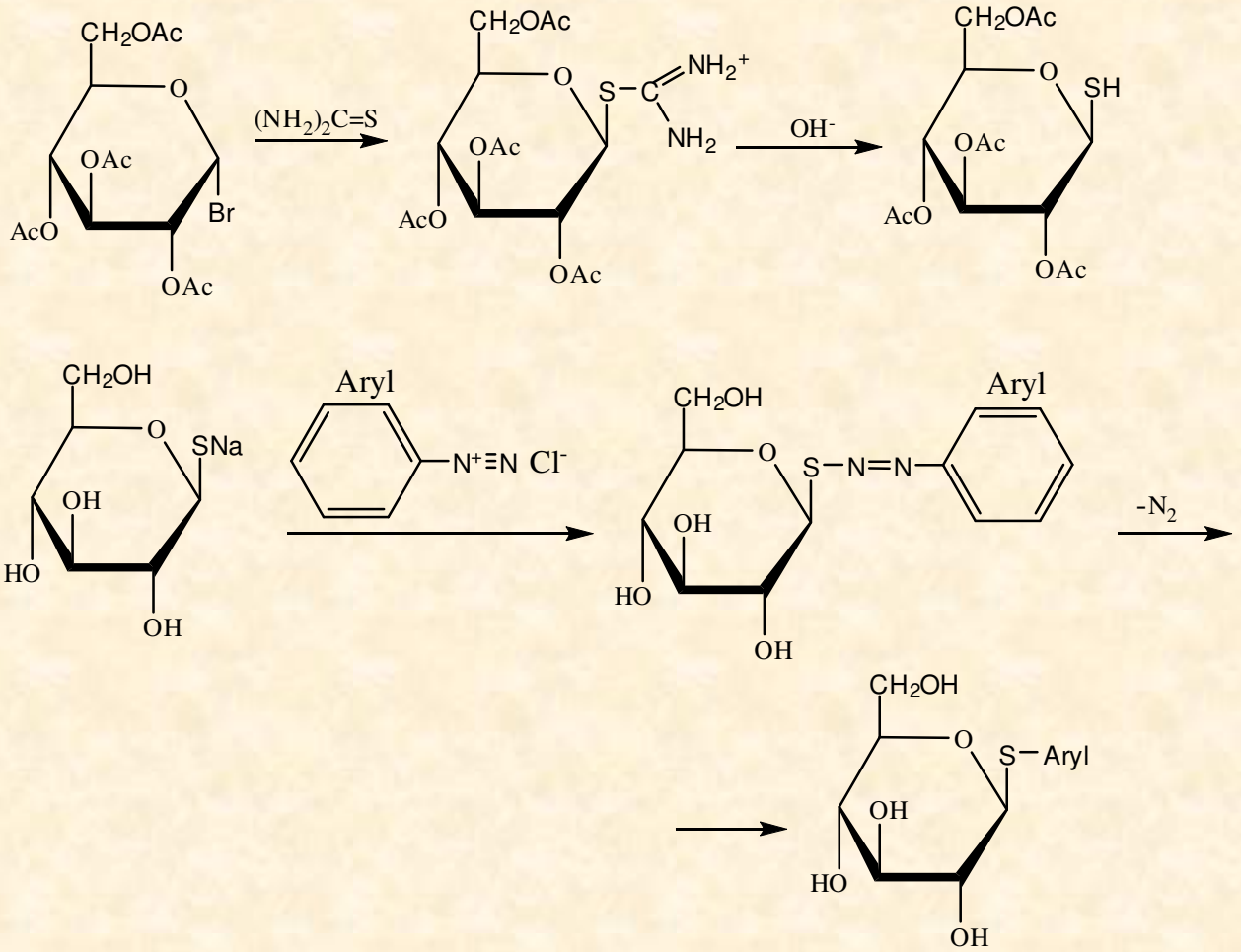


Glycosylation reaction - thioglycosides

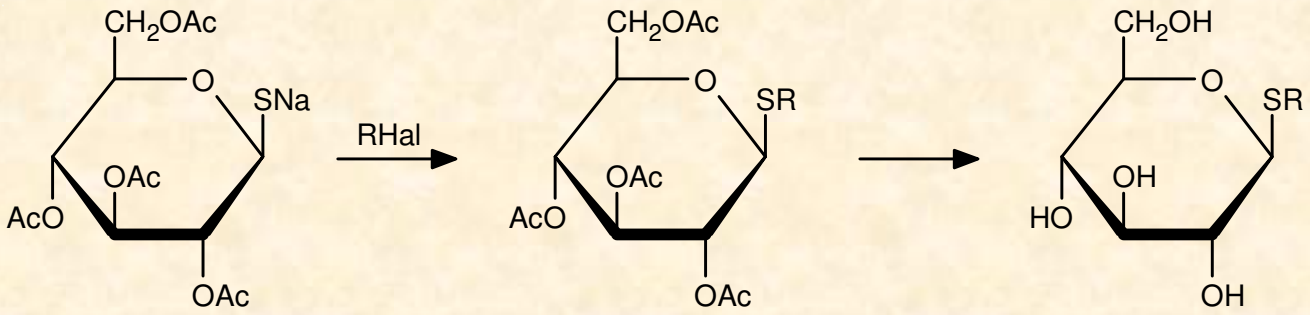


X = hal, TsO^-, TfO^-, MsO^-

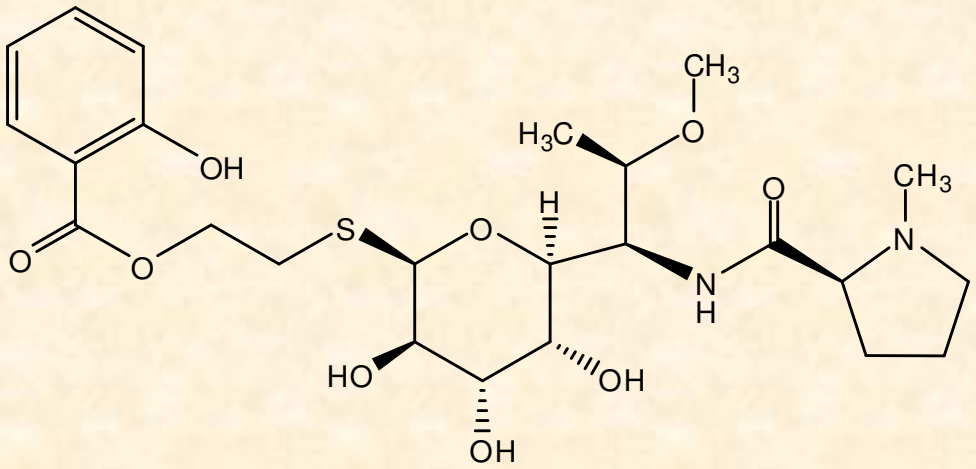
Thioglycoside - preparation



Thioglycosides - preparation

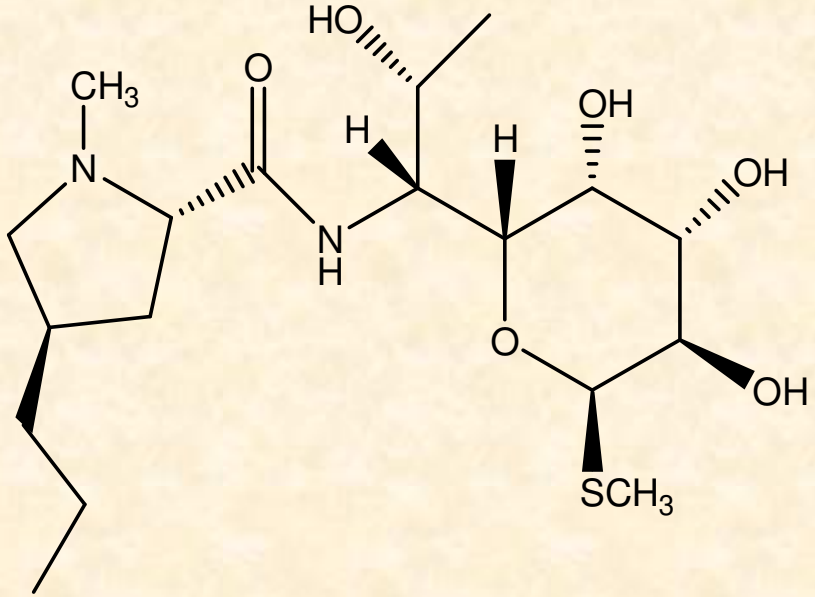


Thioglycosides



Celesticetin

Thioglycosides



Lincomycin