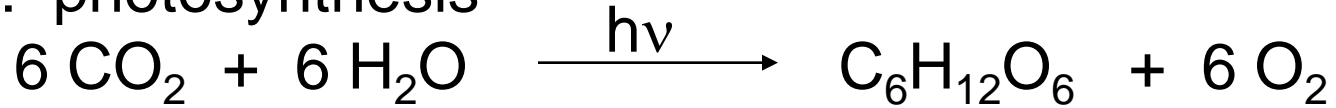


Carbohydrates

hydrates of carbon: general formula $C_n(H_2O)_n$

Plants: photosynthesis



Polymers: large molecules made up of repeating smaller units
(monomer)

Biopolymers:

carbohydrates (Chapter 25)

peptides and proteins (Chapter 27)

nucleic acids (Chapter 28)

Monomer units:

monosaccharides

amino acids

nucleotides

25.1: Classification of Carbohydrates.

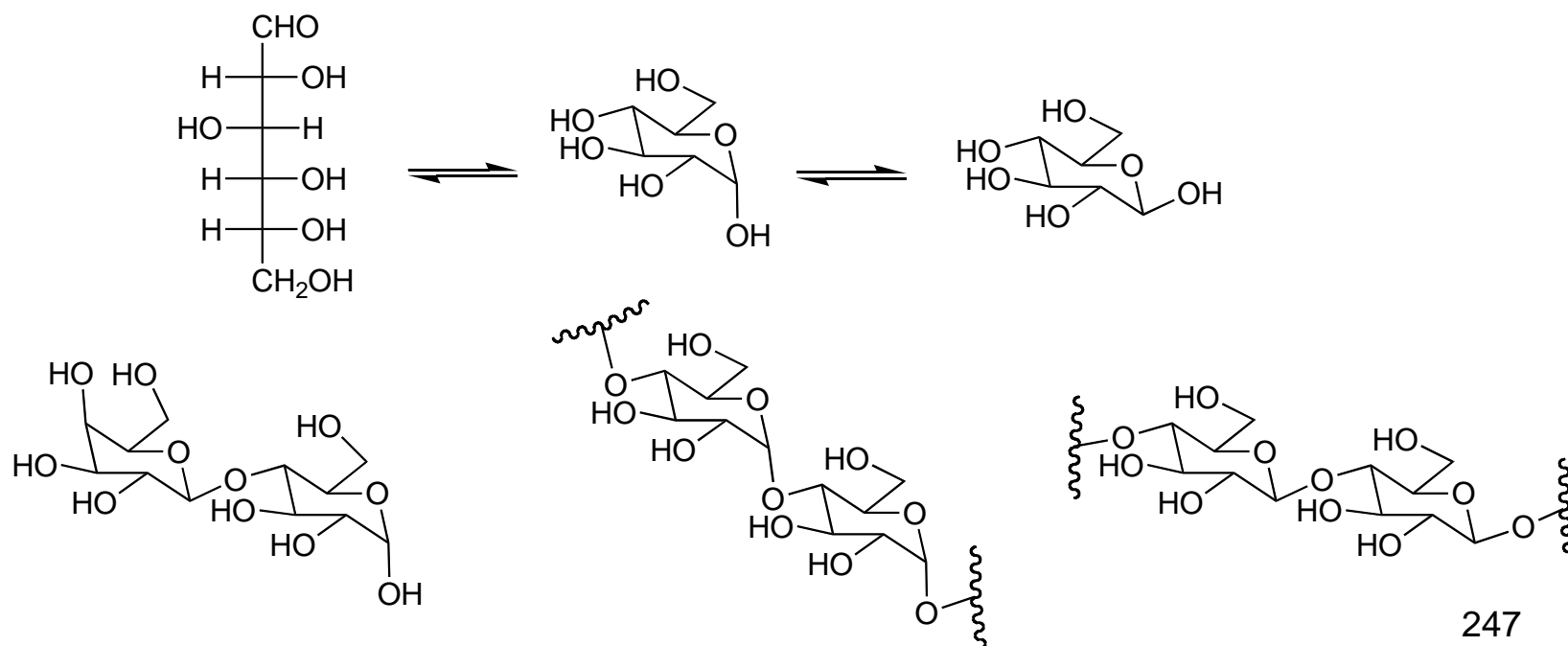
I. Number of carbohydrate units

monosaccharides: one carbohydrate unit
(simple carbohydrates)

disaccharides: two carbohydrate units
(complex carbohydrates)

trisaccharides: three carbohydrate units

polysaccharides: many carbohydrate units



II. Position of carbonyl group

at C1, carbonyl is an aldehyde: aldose

at any other carbon, carbonyl is a ketone: ketose

III. Number of carbons

three carbons: triose

four carbons: tetrose

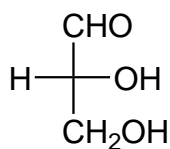
five carbons: pentose

six carbons: hexose

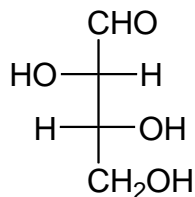
seven carbons: heptose

etc.

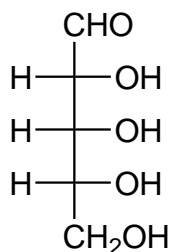
IV. Cyclic form (chapter 25.6 and 25.7)



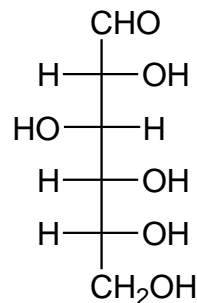
glyceraldehyde
(triose)



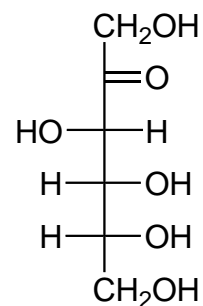
threose
(tetrose)



ribose
(pentose)



glucose
(hexose)
(aldohexose)

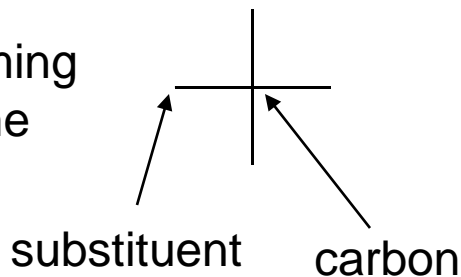


fructose
(hexose)
(ketohexose)

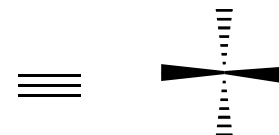
25.2: Fischer Projections and the D-L Notation.

Representation of a three-dimensional molecule as a flat structure. Tetrahedral carbon represented by two crossed lines:

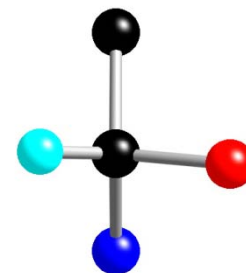
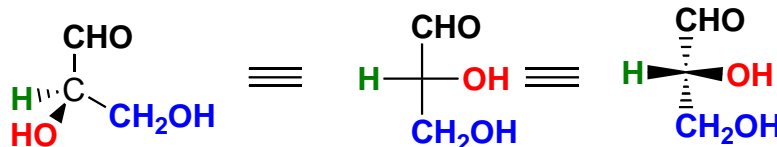
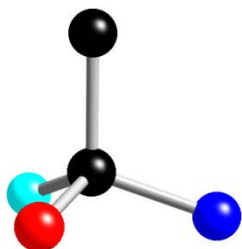
horizontal line is coming out of the plane of the page (toward you)



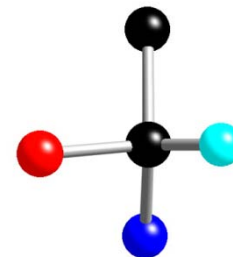
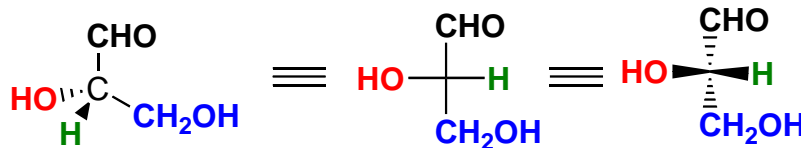
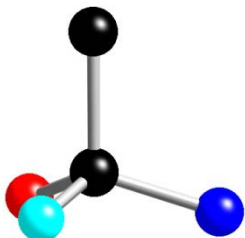
vertical line is going back behind the plane of the paper (away from you)



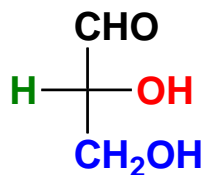
(*R*)-(+)-glyceraldehyde



(*S*)-(-)-glyceraldehyde



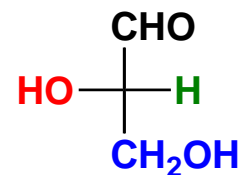
before the *R/S* convention, stereochemistry was related to (+)-glyceraldehyde



D-glyceraldehyde

R-(+)-glyceraldehyde

(+)-rotation = dextrorotatory = D



L-glyceraldehyde

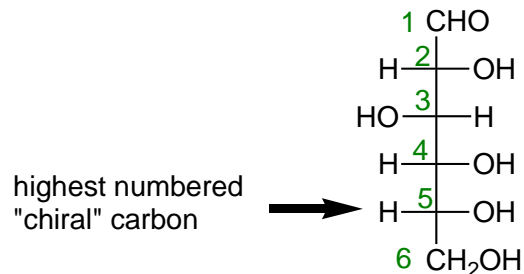
S-(-)-glyceraldehyde

(-)-rotation = levorotatory = L

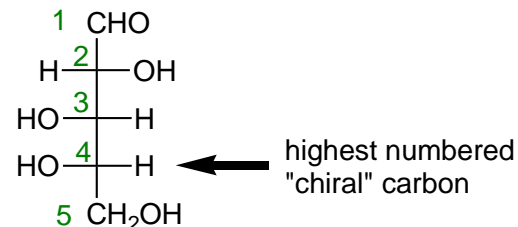
D-carbohydrates have the -OH group of the highest numbered chiral carbon pointing to the right in the Fischer projection as in *R*-(+)-glyceraldehyde

For carbohydrates, the convention is to arrange the Fischer projection with the carbonyl group at the top for aldoses and closest to the top for ketoses. The carbons are numbered from top to bottom.

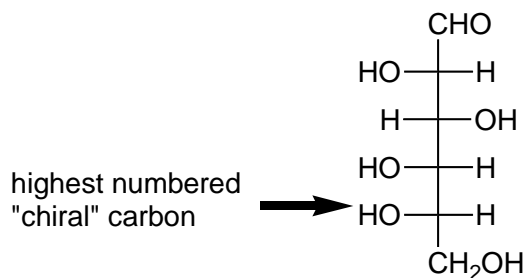
Carbohydrates are designated as D- or L- according to the stereochemistry of the highest numbered chiral carbon of the Fischer projection. If the hydroxyl group of the highest numbered chiral carbon is pointing to the right, the sugar is designated as **D** (*Dextro*: Latin for *on the right side*). If the hydroxyl group is pointing to the left, the sugar is designated as **L** (*Levo*: Latin for *on the left side*). Most naturally occurring carbohydrates are of the D-configuration.



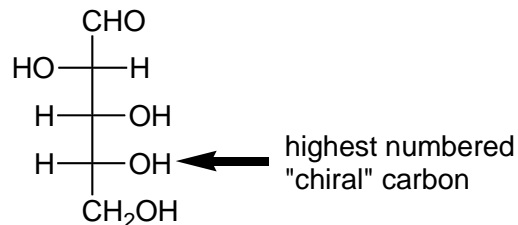
D-Glucose



L-Arabinose



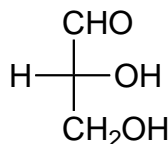
L- glucose



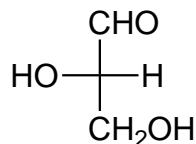
D-Arabinose

25.3: The Aldotetroses. Glyceraldehyde is the simplest carbohydrate (C₃, aldotriose, 2,3-dihydroxypropanal). The next carbohydrate are aldotetroses (C₄, 2,3,4-trihydroxybutanal).

aldotriose

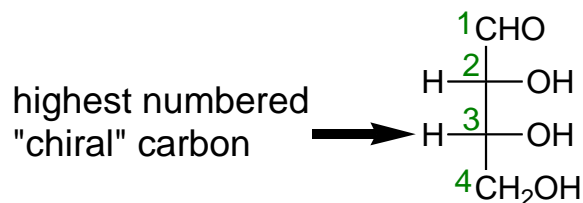


D-glyceraldehyde

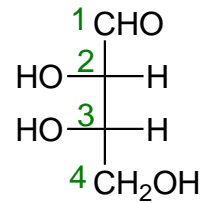


L-glyceraldehyde

aldotetroses

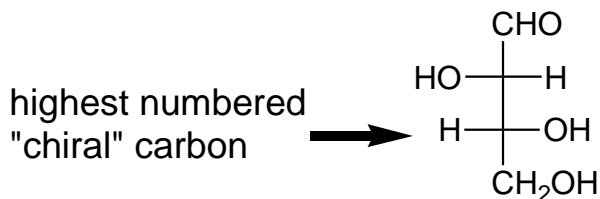


D-erythrose

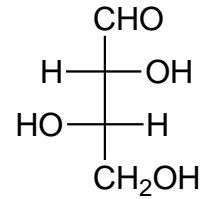


L-erythrose

← highest numbered "chiral" carbon



D-threose

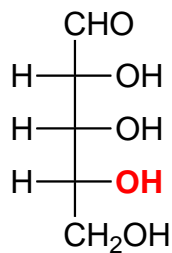


L-threose

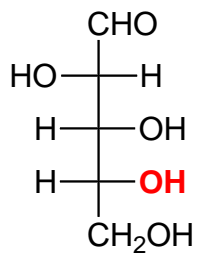
← highest numbered "chiral" carbon

25.4: Aldopentoses and Aldohehexoses.

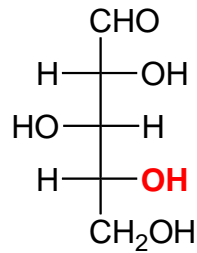
Aldopentoses: C_5 , three chiral carbons, eight stereoisomers



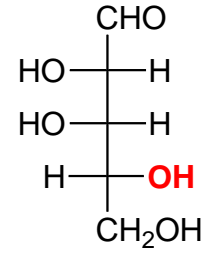
D-ribose



D-arabinose

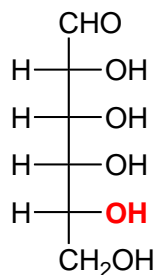


D-xylose

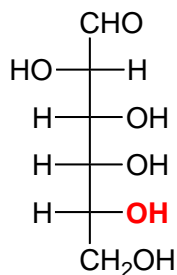


D-lyxose

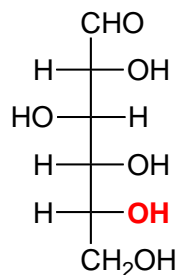
Aldohexoses: C_6 , four chiral carbons, sixteen stereoisomers



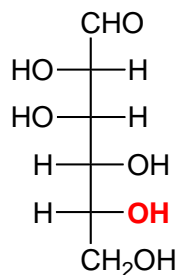
D-allose



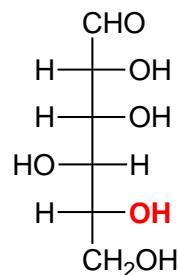
D-altrose



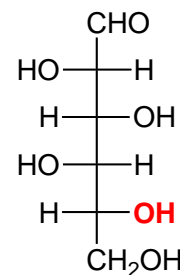
D-glucose



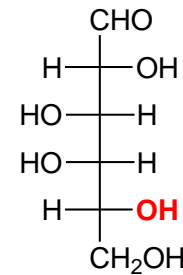
D-mannose



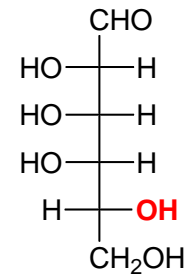
D-gulose



D-idose



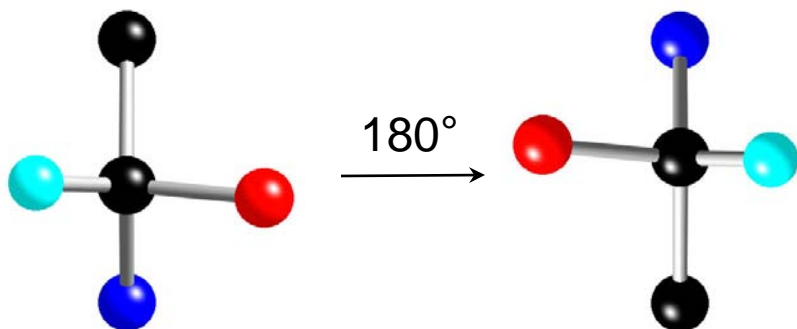
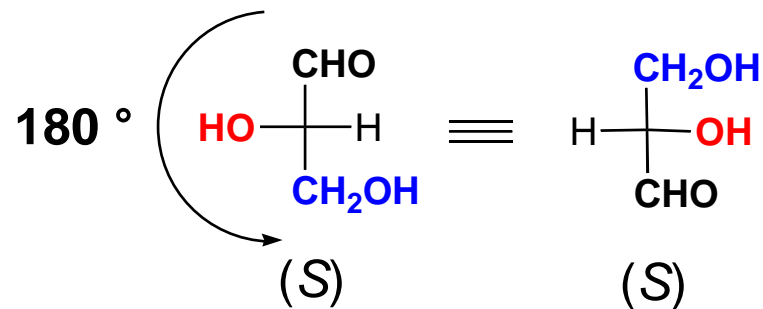
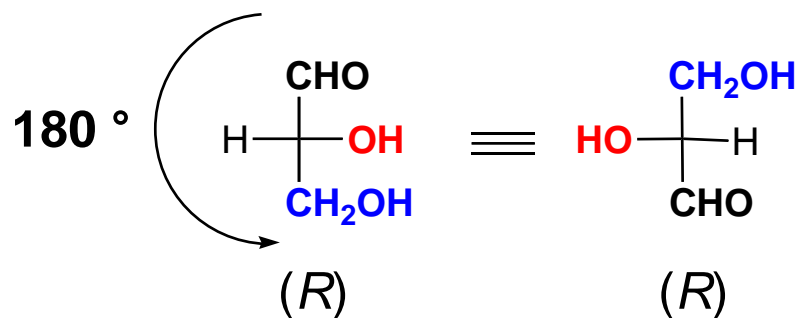
D-galactose



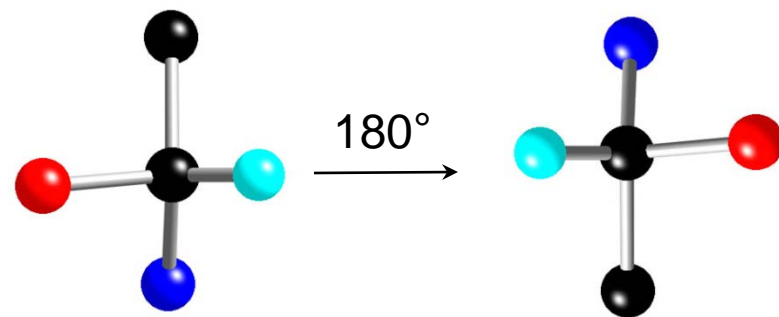
D-talose

Manipulation of Fischer Projections

1. Fischer projections can be rotated by 180° (in the plane of the page) only!



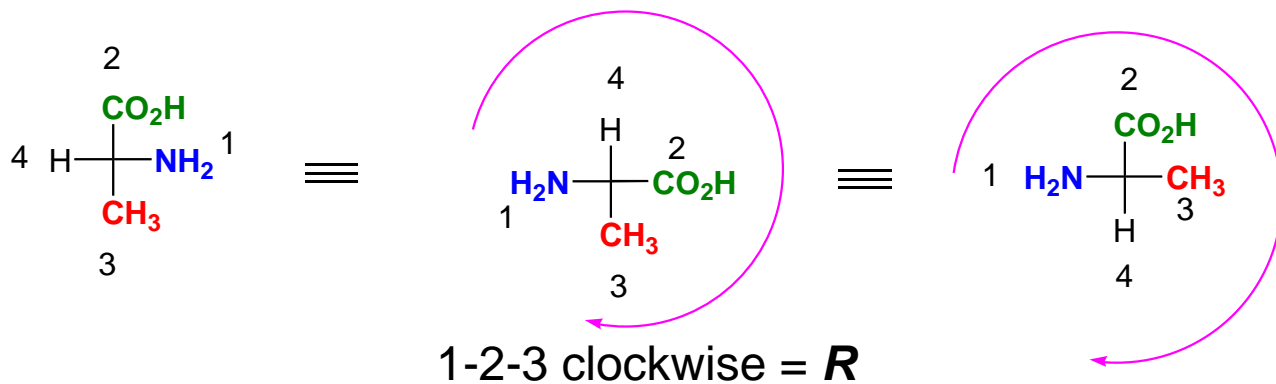
Valid
Fischer
projection



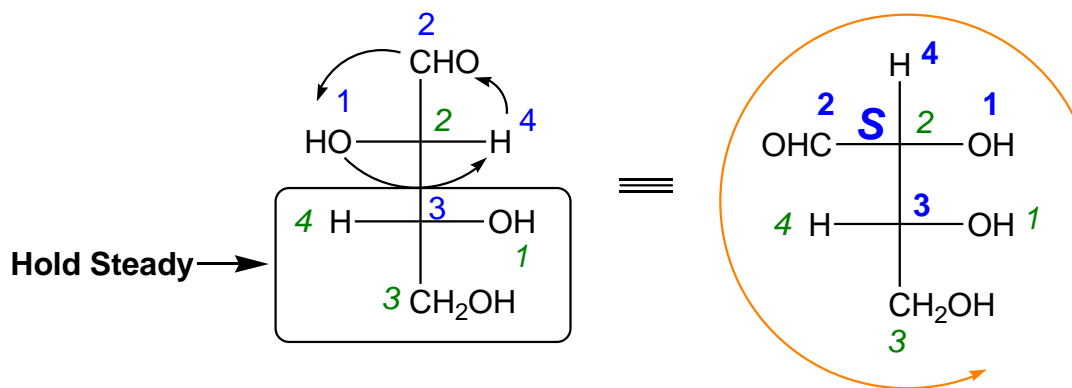
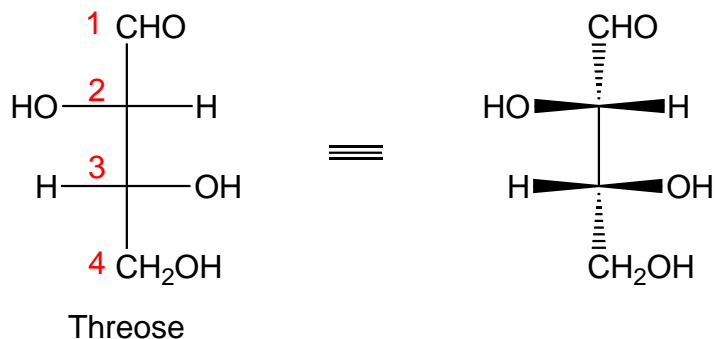
Valid
Fischer
projection

Assigning *R* and *S* Configuration to Fischer Projections

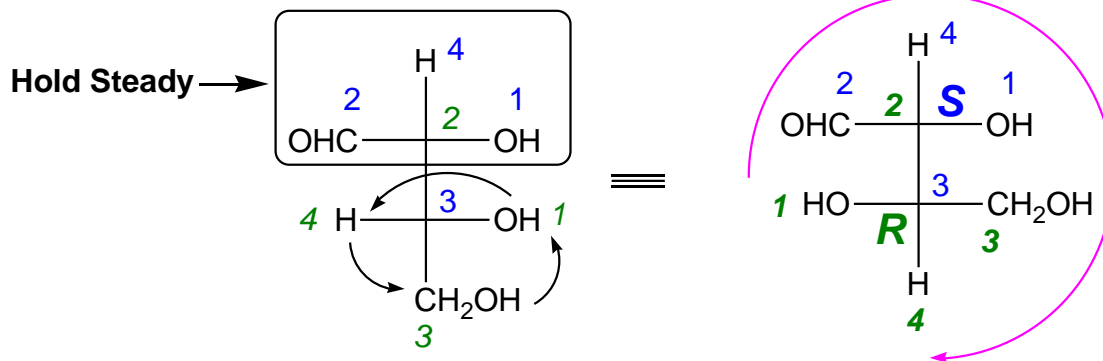
1. Assign priorities to the four substituents according to the Cahn-Ingold-Prelog rules
2. Perform the two allowed manipulations of the Fischer projection to place the lowest priority group at the top or bottom.
3. If the priority of the other groups 1→2→3 is clockwise then assign the carbon as *R*, if priority of the other groups 1→2→3 is counterclockwise then assign the center as *S*.



Fischer projections with more than one chiral center:



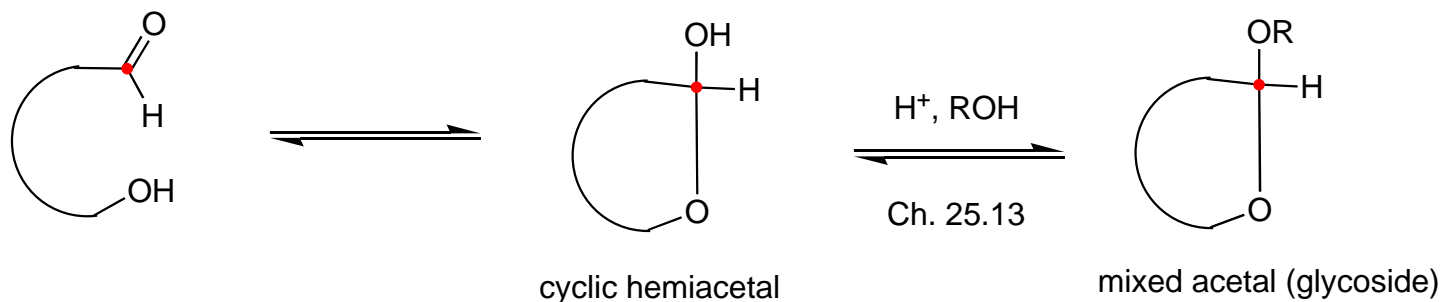
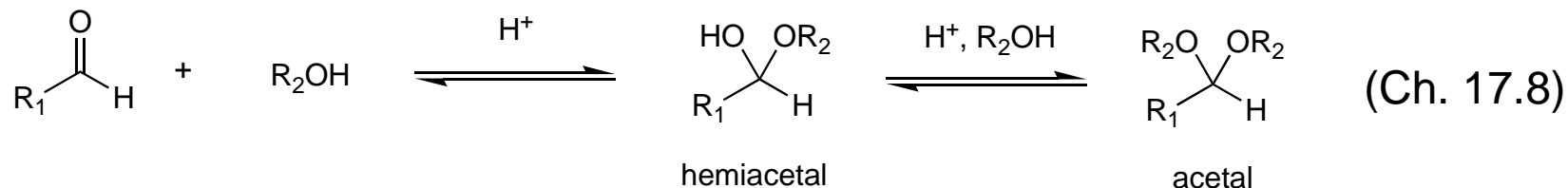
$(2S, 3R)$



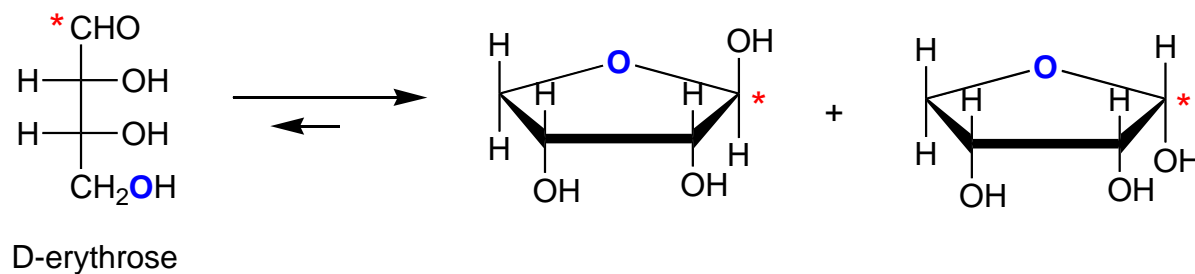
25.5: A Mnemonic for Carbohydrate Configuration.

(please read)

25.6: Cyclic Forms of Carbohydrates: Furanose Forms.

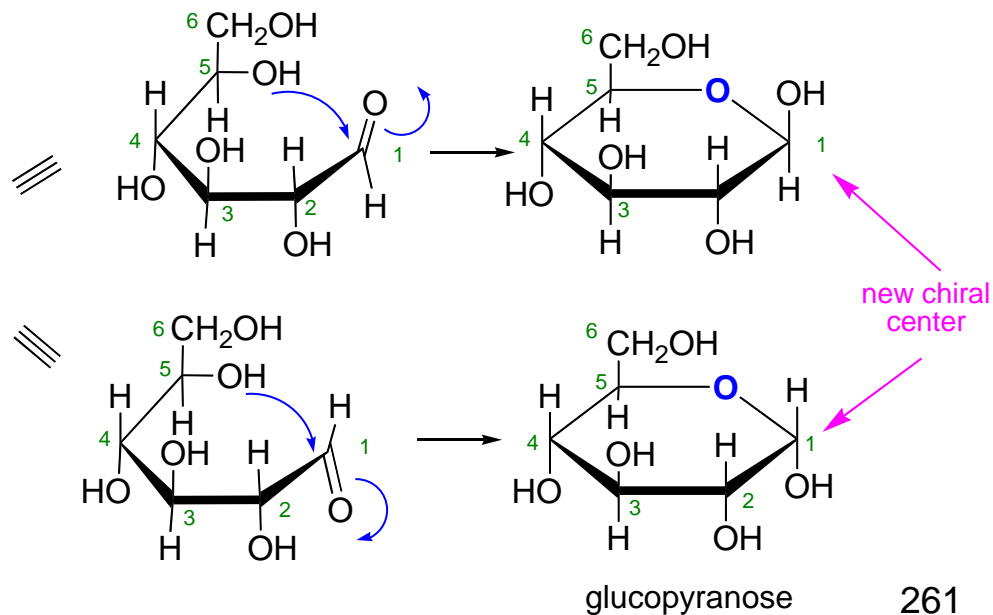
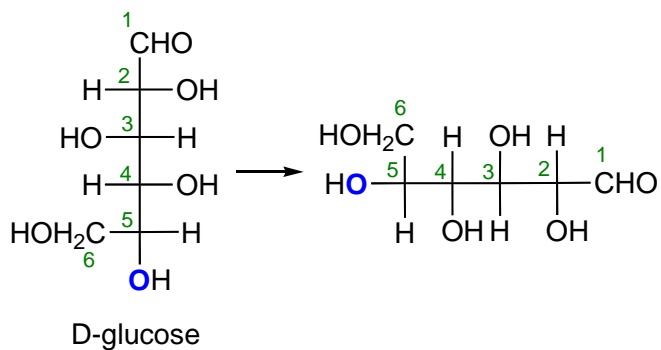
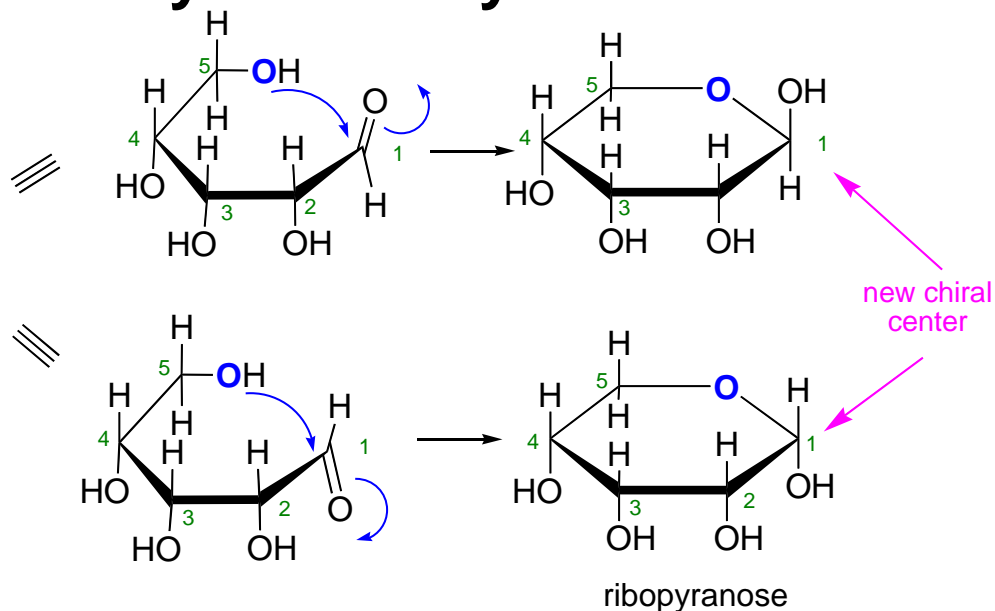
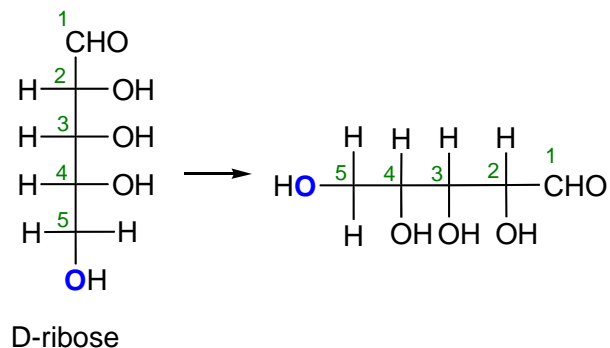


In the case of carbohydrates, cyclization to the hemiacetal creates a new chiral center.



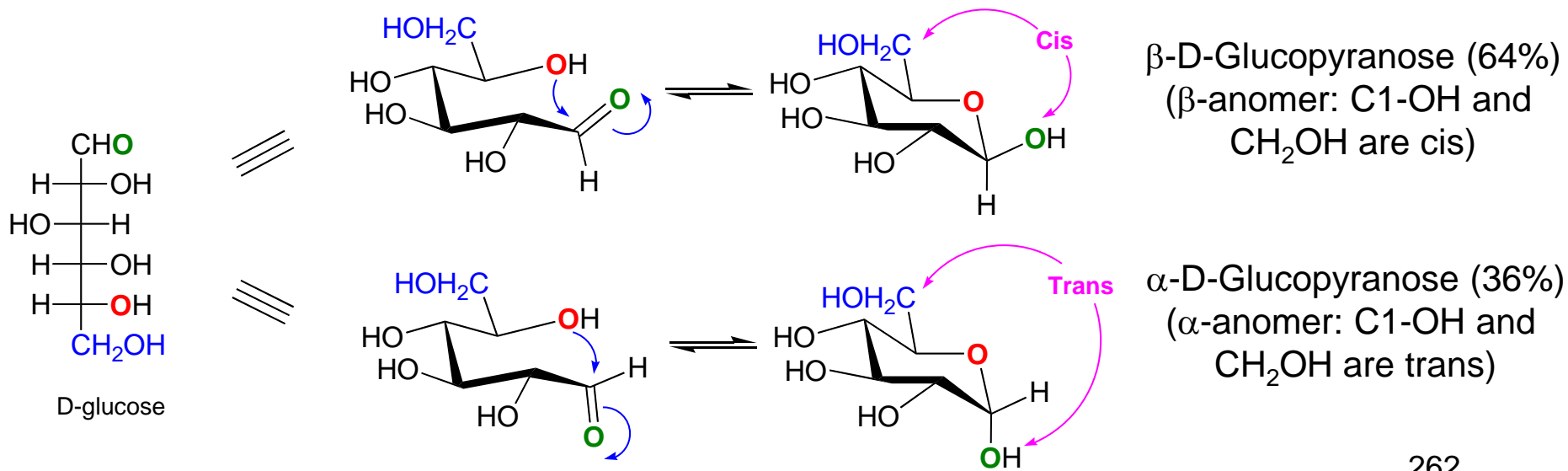
Converting Fischer Projections to Haworth formulas

25.7: Cyclic Forms of Carbohydrates: Pyranose Forms.

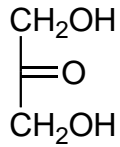


25.8: Mutarotation and the Anomeric Effect. The hemiacetal or hemiketal carbon of the cyclic form of carbohydrates is the *anomeric carbon*. Carbohydrate isomers that differ only in the stereochemistry of the anomeric carbon are called *anomers*.

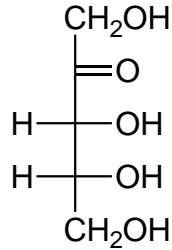
Mutarotation: The α - and β -anomers are in equilibrium, and interconvert through the open form. The pure anomers can be isolated by crystallization. When the pure anomers are dissolved in water they undergo mutarotation, the process by which they return to an equilibrium mixture of the anomer.



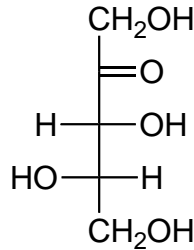
25.9: Ketoses. Ketoses are less common than aldoses



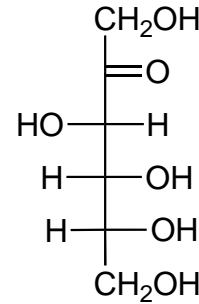
dihydroxyacetone



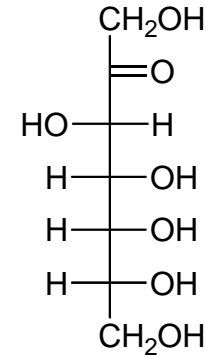
D-ribulose



Dxylulose

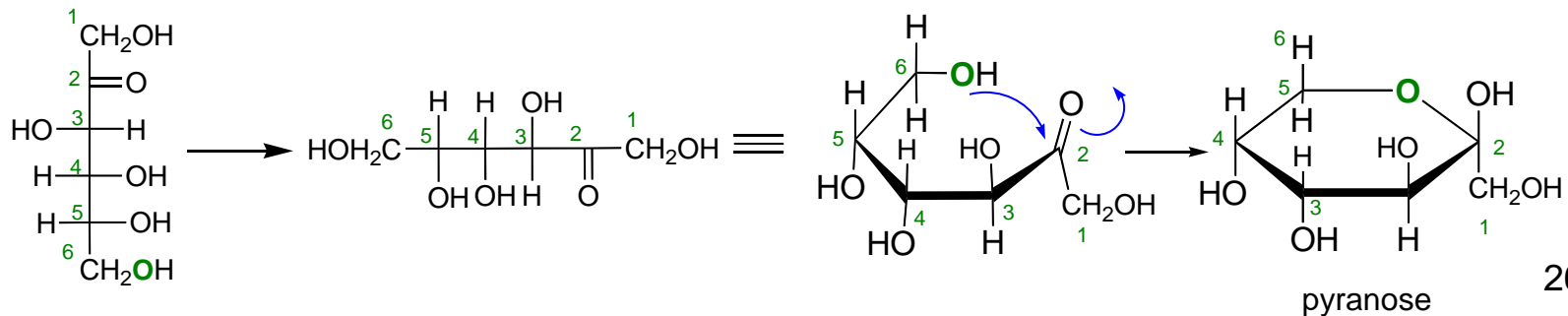
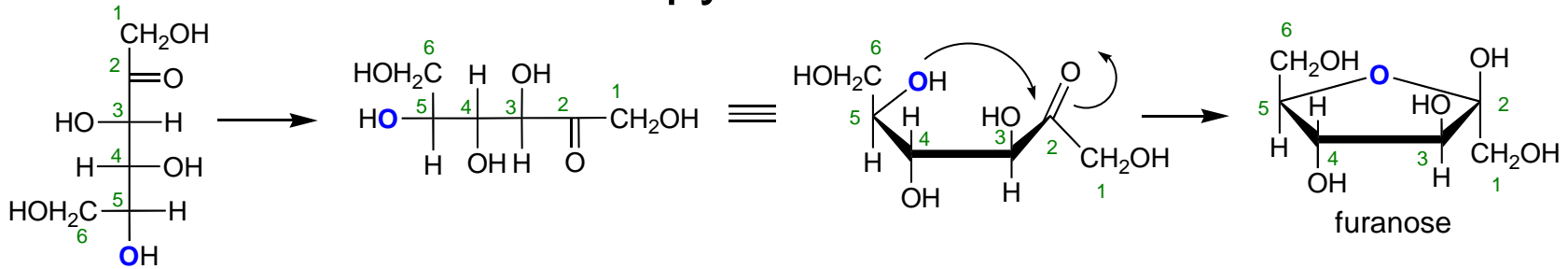


D-fructose

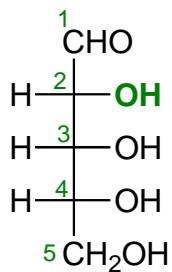


D-sedohepuloase

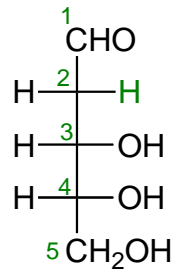
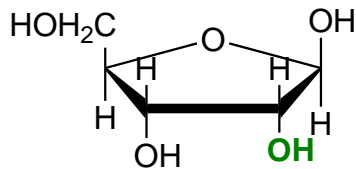
Fructofuranose and Fructopyranose



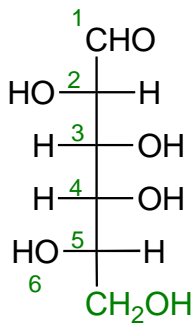
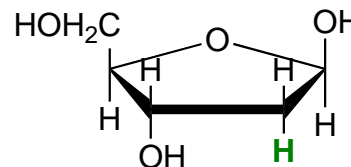
25.10: Deoxy Sugars. Carbohydrates that are missing a hydroxy group.



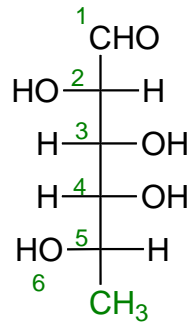
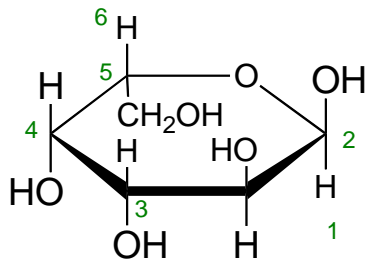
D-ribose



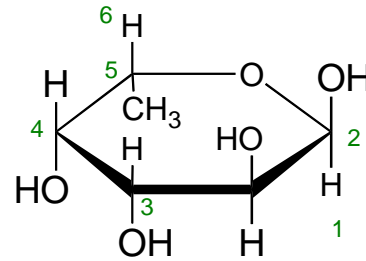
2-Deoxy-D-ribose



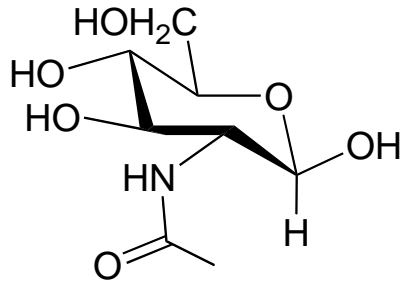
L-Galactose



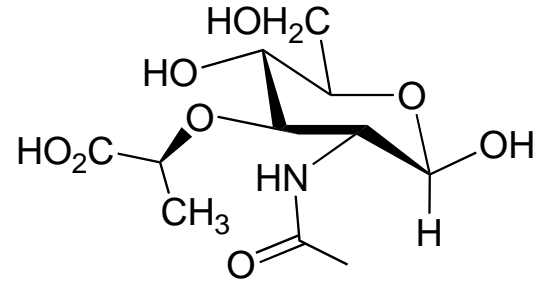
6-Deoxy-L-Galactose
(fucose)



25.11: Amino Sugars. Carbohydrates in which a hydroxyl group is replaced with an $-NH_2$ or $-NHAc$ group



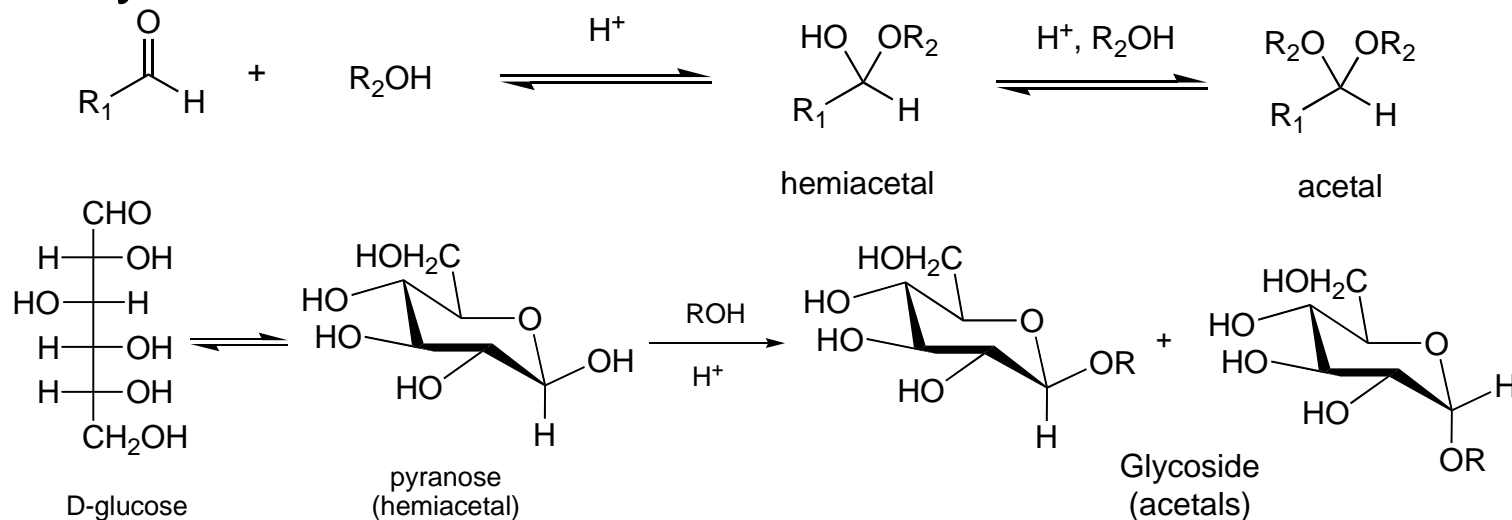
N-acetyl-D-glucosamine
(GlcNAc or NAG)



N-Acetylmuramic acid
(MurNAc)

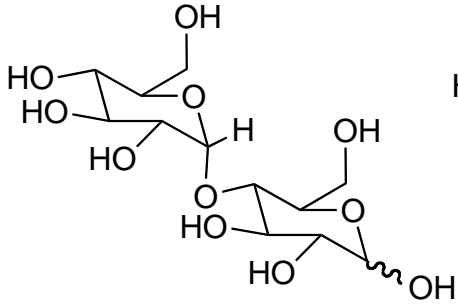
25.12: Branched-Chain Sugars. (Please read)

25.13: Glycosides. Acetals and ketals of the cyclic form of carbohydrates.

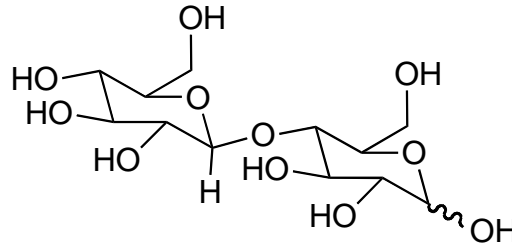


Note that only the anomeric hydroxyl group is replaced by ROH

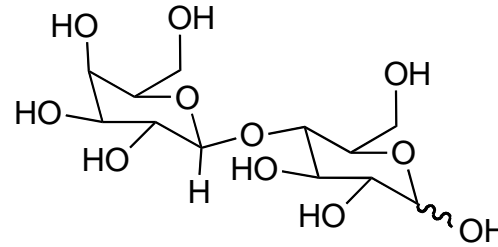
25.14: Disaccharides. A glycoside in which ROH is another carbohydrate unit (complex carbohydrate).



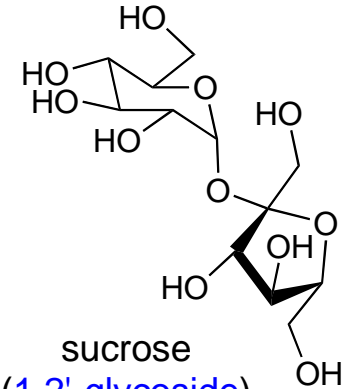
maltose
(1,4'- α -glycoside)



cellobiose
(1,4'- β -glycoside)

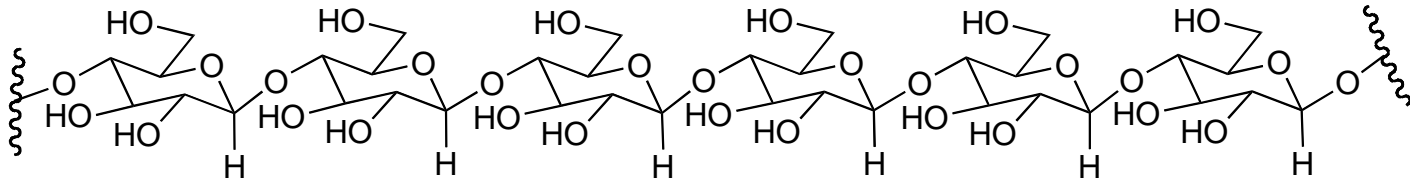


Lactose
(1,4'- β -glycoside)

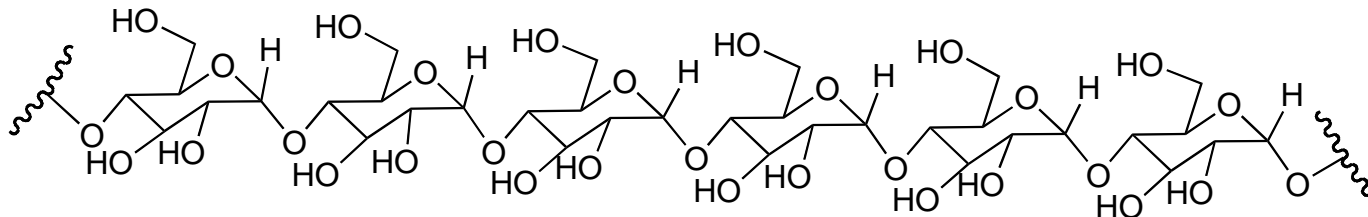


sucrose
(1,2'-glycoside)

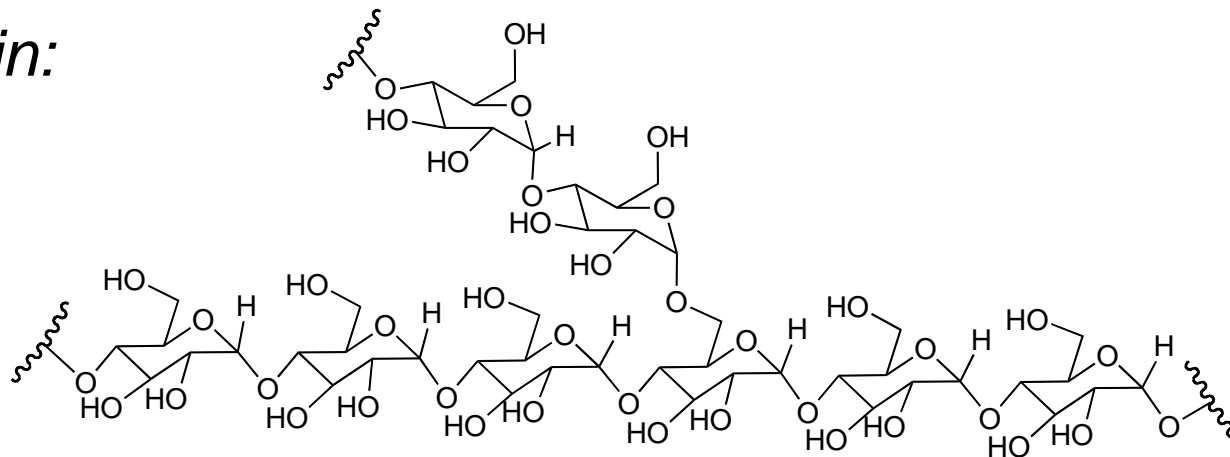
25.15: Polysaccharides. *Cellulose:* glucose polymer made up of 1,4'- β -glycoside linkages



Amylose: glucose polymer made up of 1,4'- α -glycoside linkages

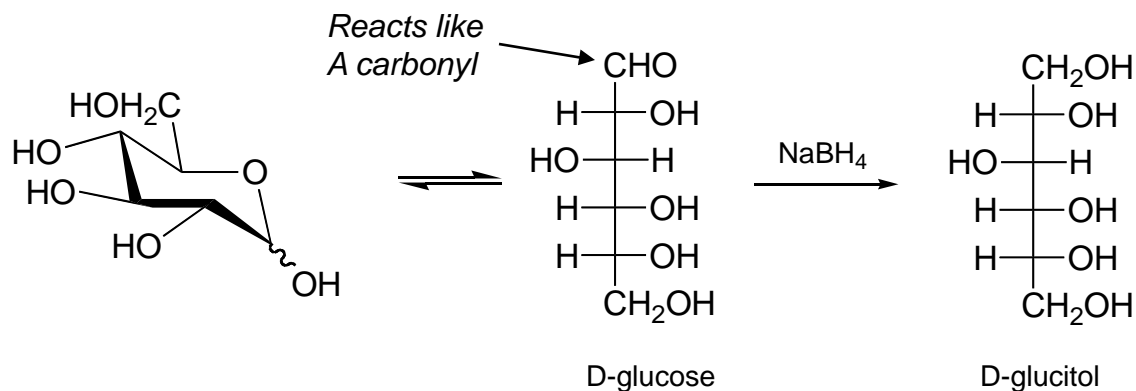


Amylopectin:

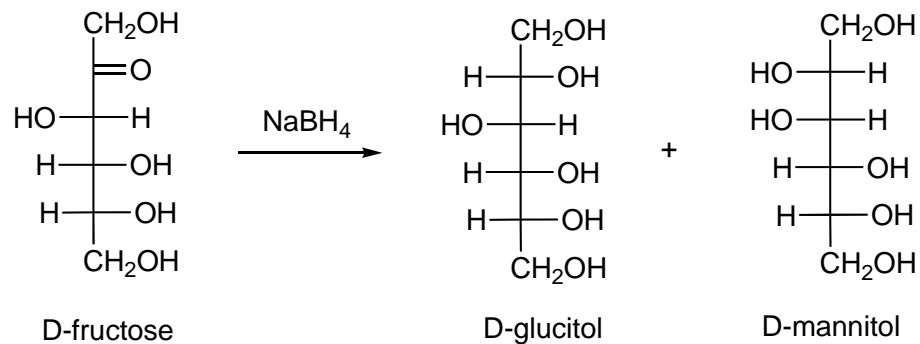


25.16: Reactions of Carbohydrates. Glycoside formation is related to acetal formation.

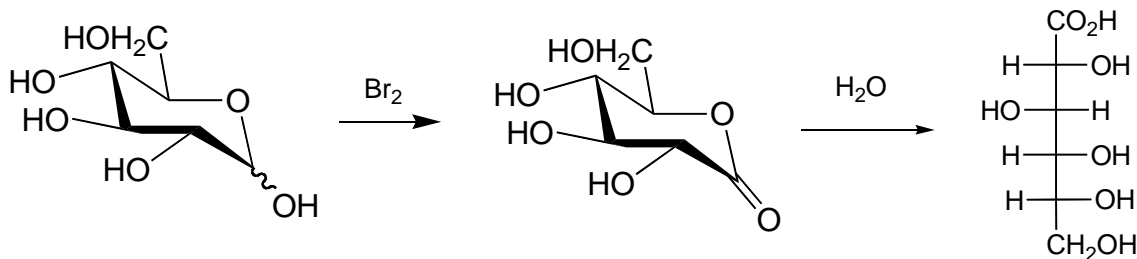
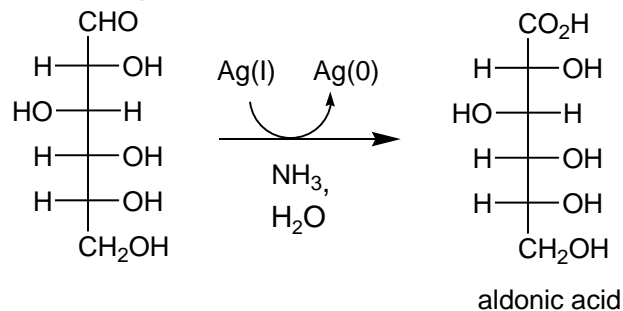
25.17: Reduction of Monosaccharides. C1 of aldoses are reduced with sodium borohydride to the 1° alcohol (*alditols*)



Reduction of ketoses

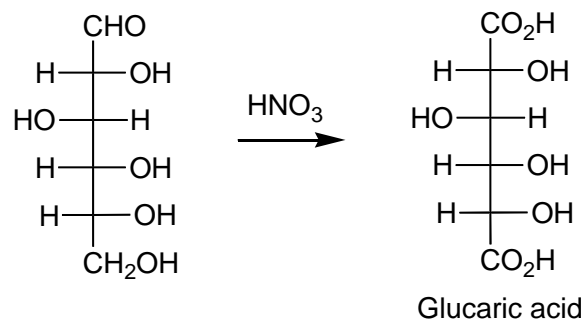


25.17: Oxidation of Monosaccharides. C1 of aldoses can be selectively oxidized to the carboxylic acid (*aldonic acids*) with Br₂ or Ag(I) (Tollen's test).

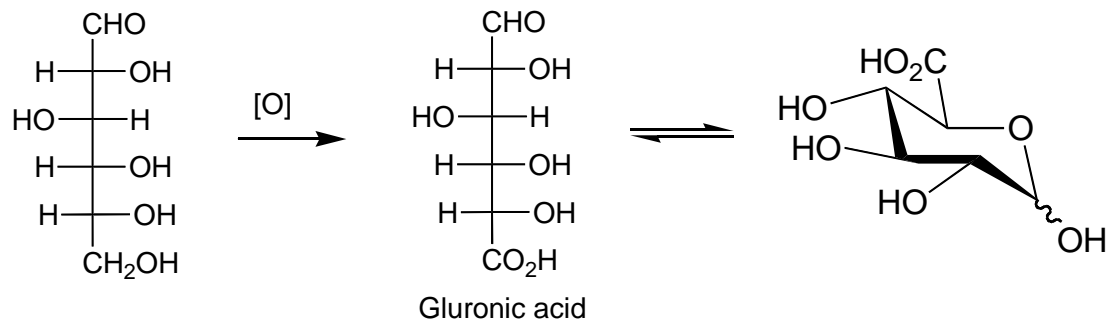


Reducing sugars: carbohydrates that can be oxidized to aldonic acids.

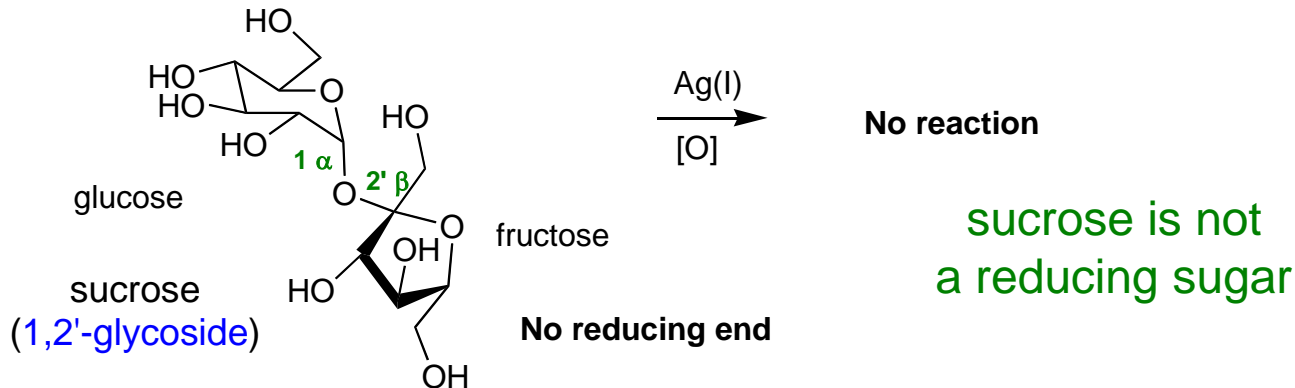
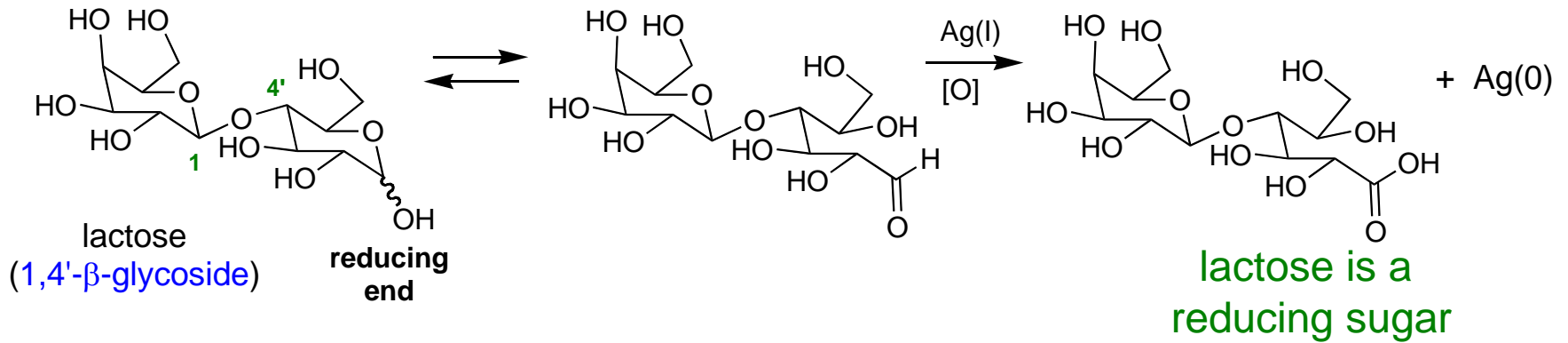
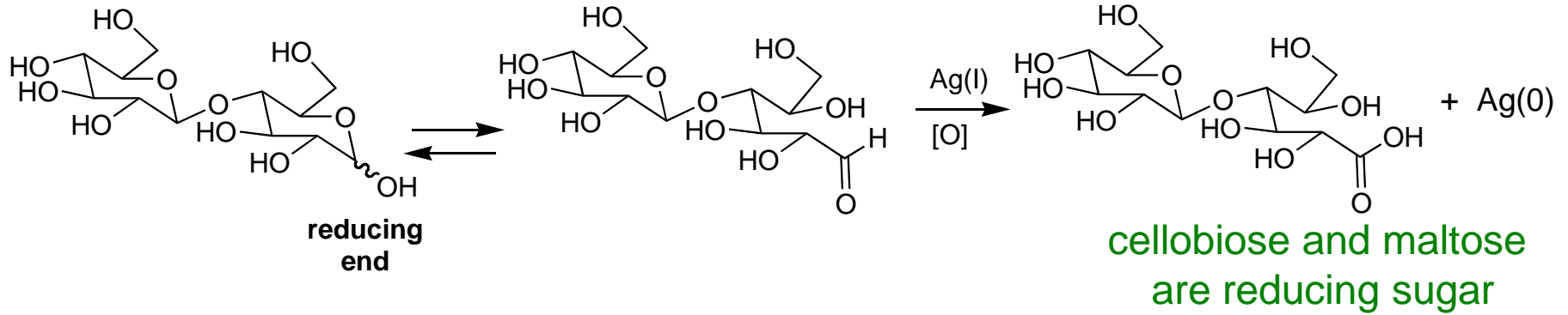
Oxidation of aldoses to *aldaric acids* with HNO_3 .



Uronic Acid: Carbohydrate in which only the terminal $-\text{CH}_2\text{OH}$ is oxidized to a carboxylic acid.



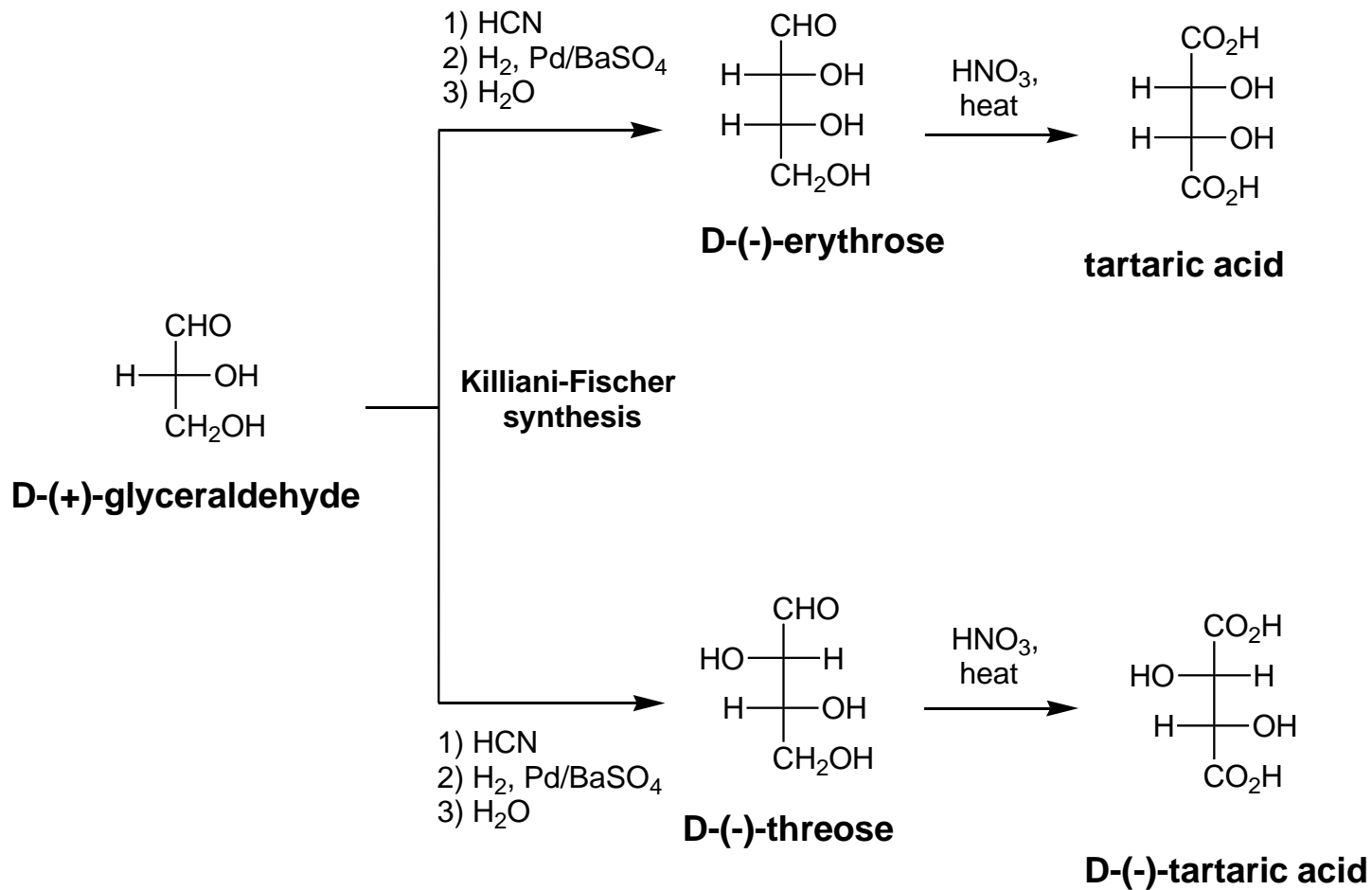
Reducing sugars: carbohydrates that can be oxidized to aldonic acids.

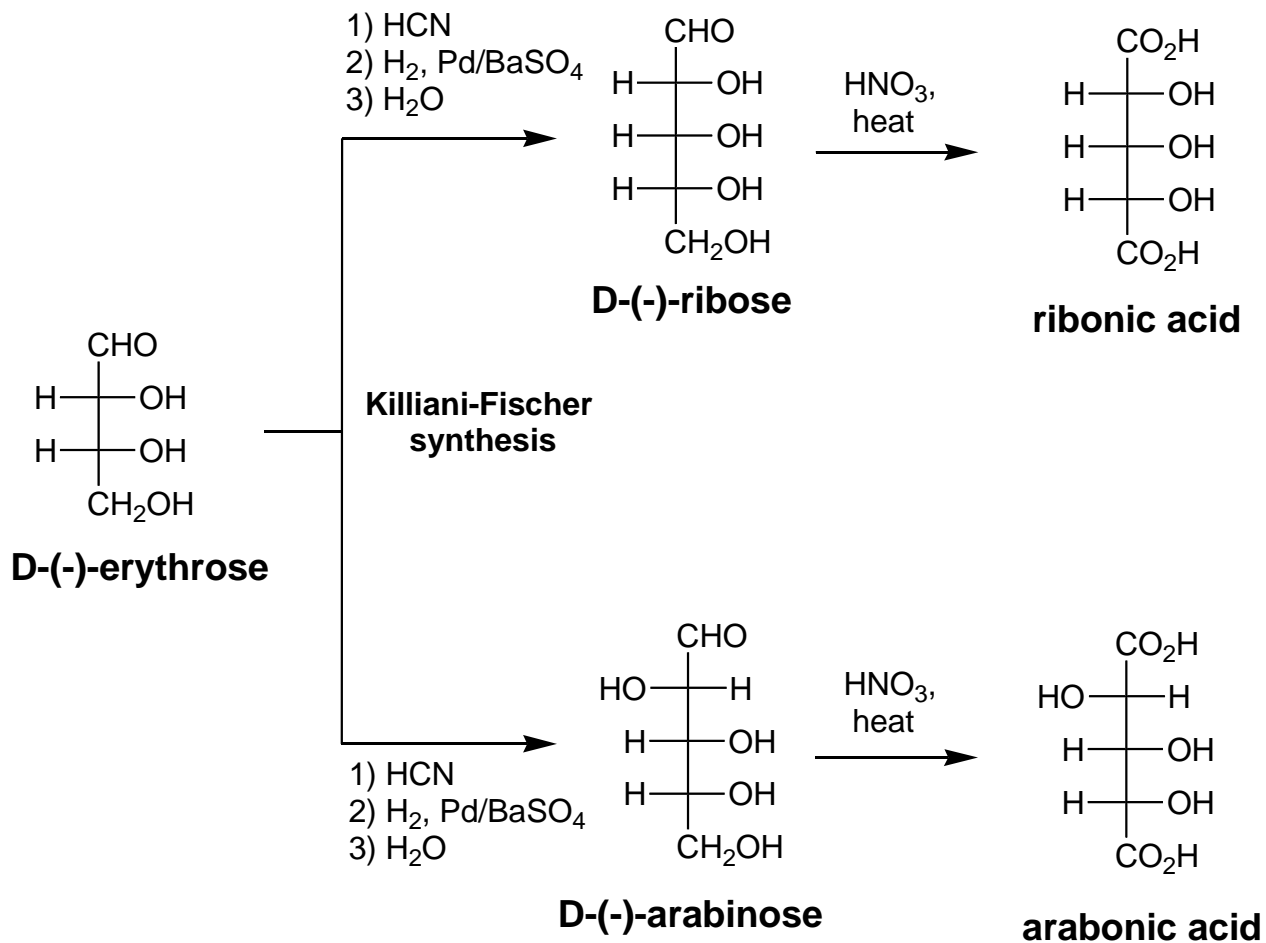


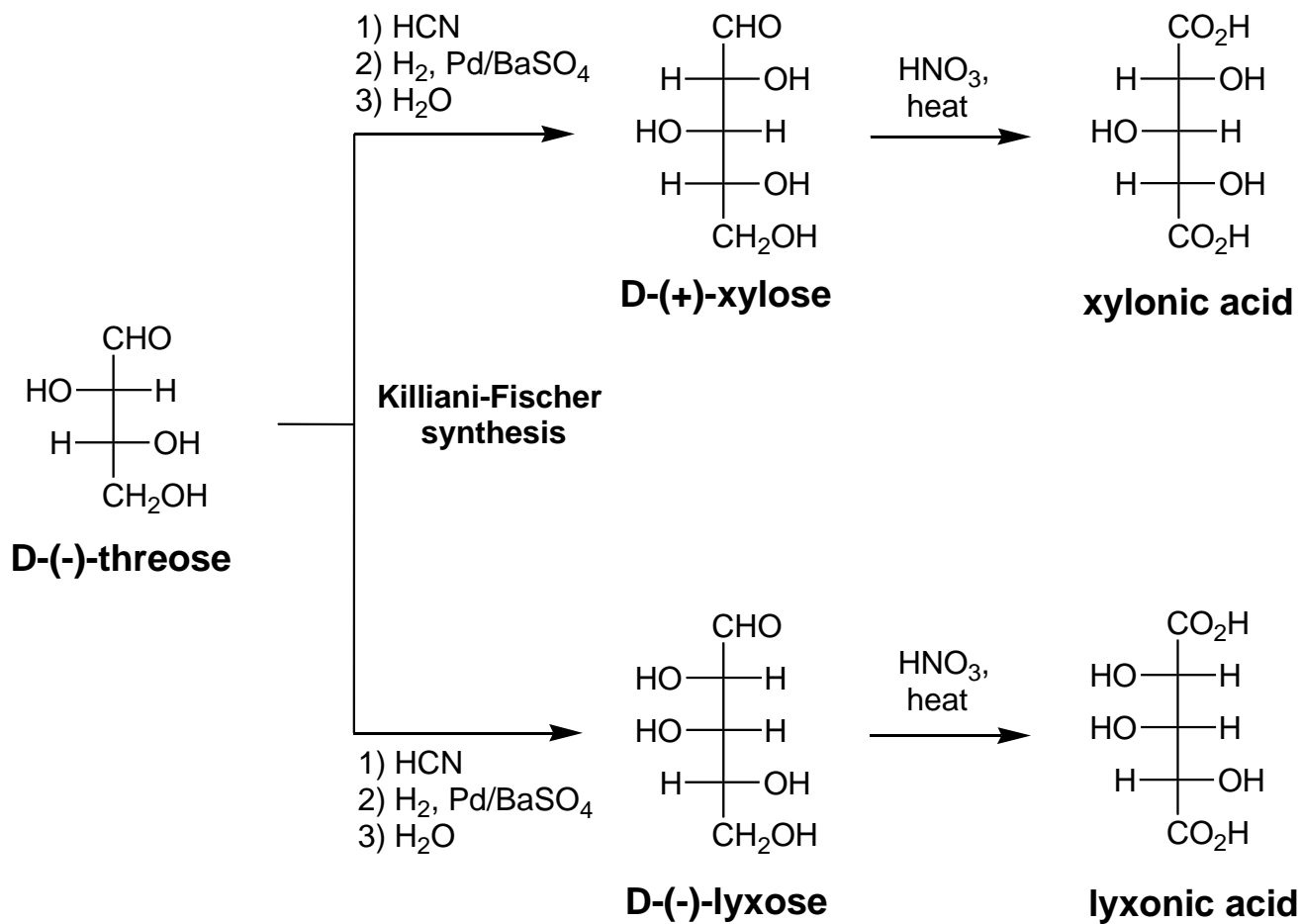
25.19: Cyanohydrin Formation and Chain Extension.

Kiliani-Fischer Synthesis- chain lengthening of monosaccharides

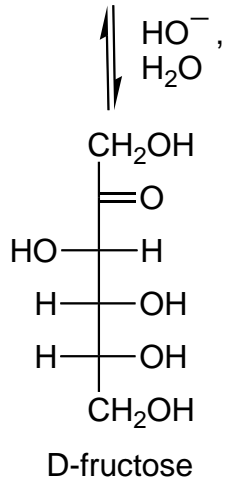
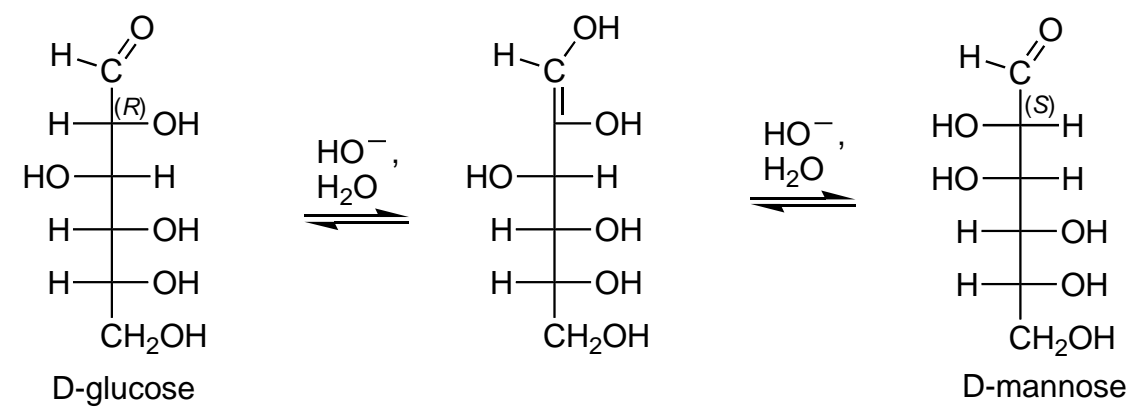
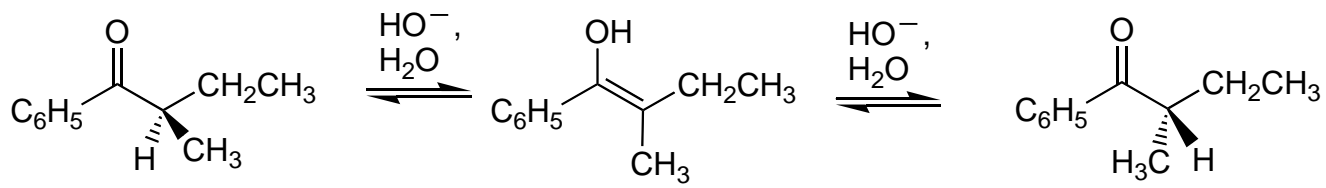
Determination of carbohydrate stereochemistry





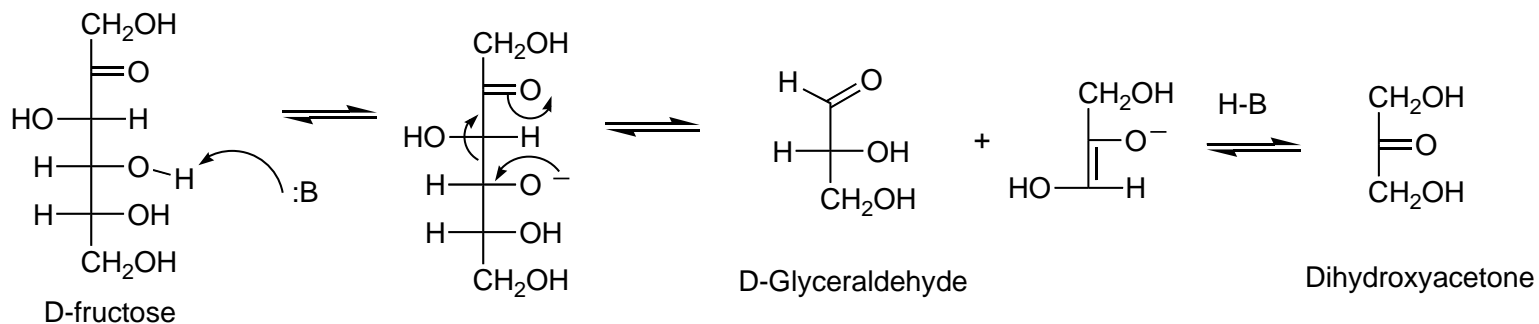


25.20: Epimerization, Isomerization and Retro-Aldol Cleavage.

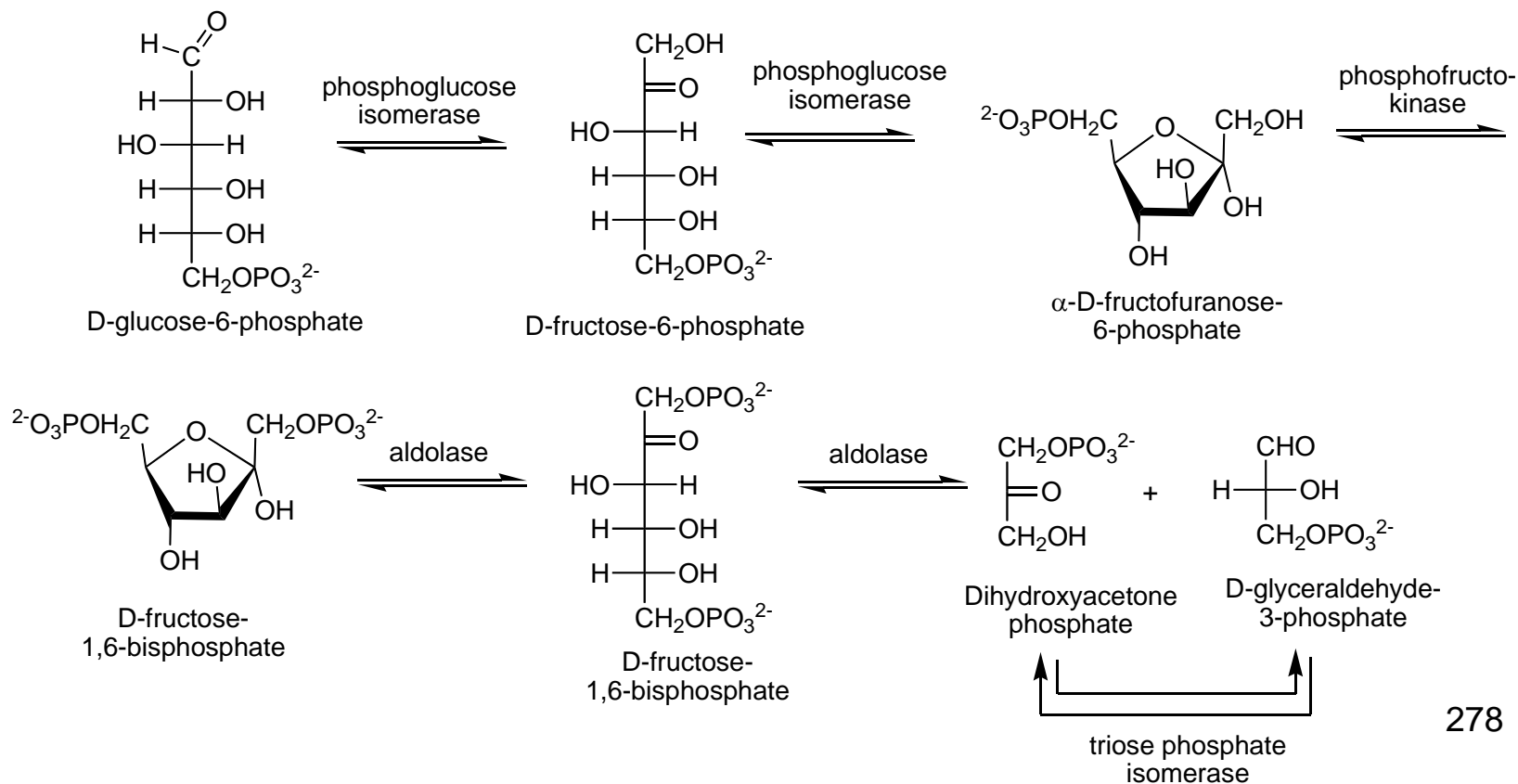


Fructose is a reducing sugar (gives a positive Tollen's test)

Retro-aldol reaction of carbohydrates

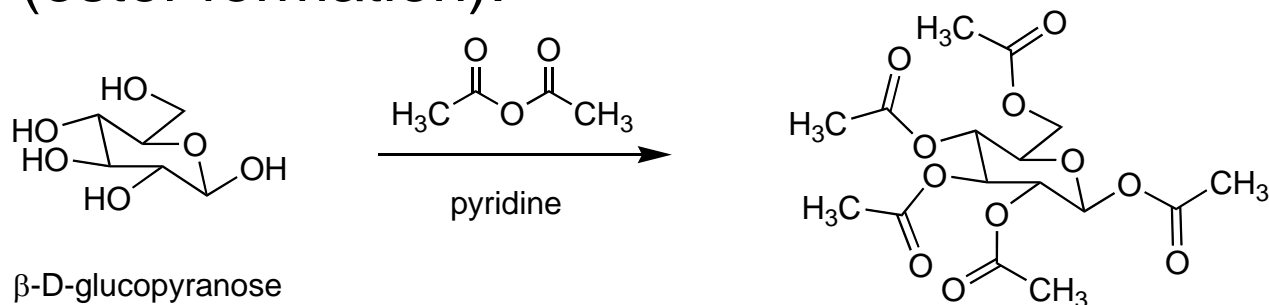


Glycolysis

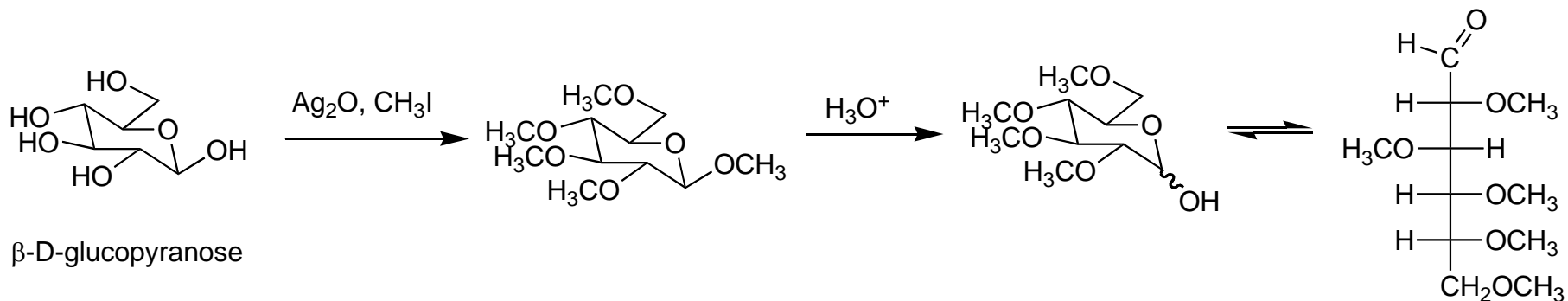


25.21: Acylation and Alkylation of Hydroxyl Groups

Acylation (ester formation):



Alkylation (ether formation):



25.22: Periodic Acid Oxidation. The vicinal diols of carbohydrate can be oxidative cleaved with HIO_4 .