Chapter 25: Carbohydrates

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

Plants: photosynthesis

$$6\ CO_2 + 6\ H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6\ O_2$$

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

Biopolymers:	Monomer units:
carbohydrates (Chapter 25)	monosaccharides
peptides and proteins (Chapter 27)	amino acids
nucleic acids (Chapter 28)	nucleotides

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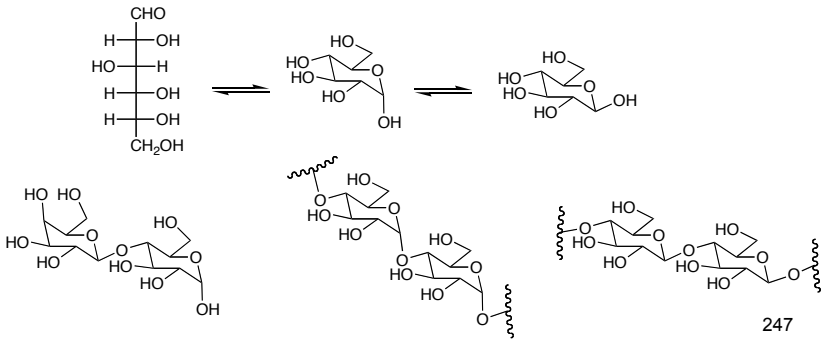
25.1: Classification of Carbohydrates.

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



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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

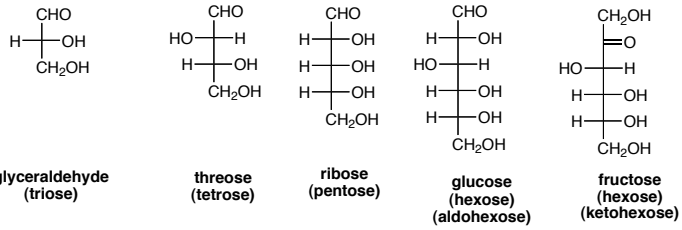
five carbons: pentose

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)

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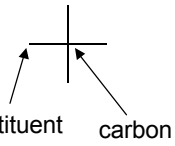
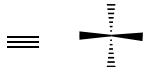
25.2: Fischer Projections and the D-L Notation. Representation of a three-dimensional molecule as a flat structure. Tetrahedral carbon represented by two crossed lines:

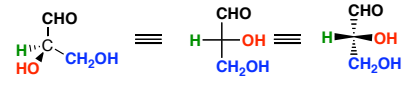
horizontal line is coming out of the plane of the page (toward you)



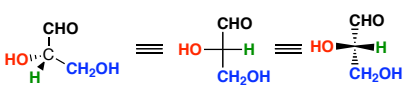
vertical line is going back behind the plane of the paper (away from you)



(*R*)-(+)-glyceraldehyde



(*S*)-(-)-glyceraldehyde



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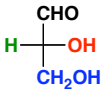
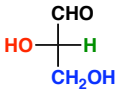
before the *R*/*S* convention, stereochemistry was related to (+)-glyceraldehyde





D-glyceraldehyde
R-(+)-glyceraldhyde
(+)-rotation = dextrorotatory = D

L-glyceraldehyde
S-(-)-glyceraldhyde
(-)-rotation = levorotatory = L

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

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.

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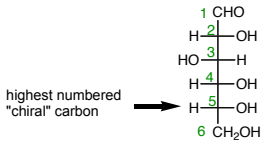
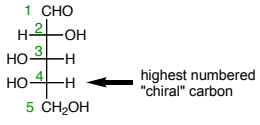
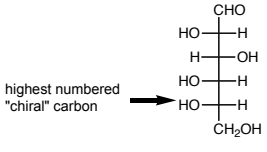
Carbohydrates are designated as D- or L- according to the stereochemistry of the highest numbered chiral carbon of the Fischer projection. If the hydroxyl group of the highest numbered chiral carbon is pointing to the right, the sugar is designated as **D** (*Dextro*: Latin for *on the right side*).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



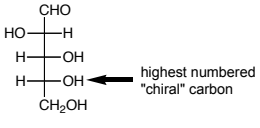
D-Glucose



L-Arabinose



L- glucose



D-Arabinose

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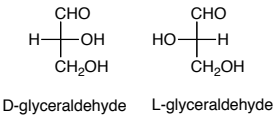
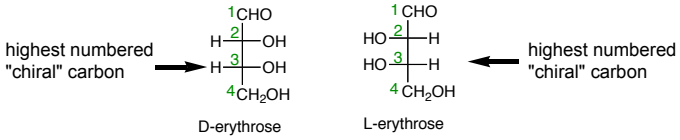
25.3: The Aldotetroses. Glyceraldehyde is the simplest carbohydrate (C_3, aldotriose, 2,3-dihydroxypropanal). The next carbohydrate are aldotetroses (C_4, 2,3,4-trihydroxybutanal).

aldotriose

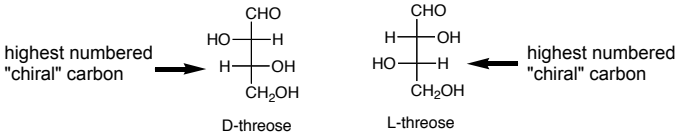


D-glyceraldehyde L-glyceraldehyde

aldotetroses

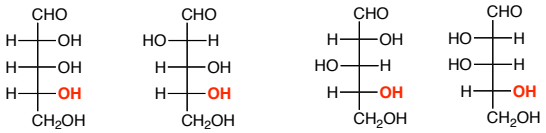


D-erythrose L-erythrose



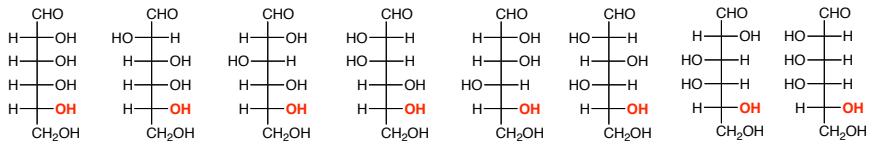
D-threose L-threose

25.4: Aldopentoses and Aldohexoses.
Aldopentoses: C_5, three chiral carbons, eight stereoisomers



D-ribose D-arabinose D-xylose D-lyxose

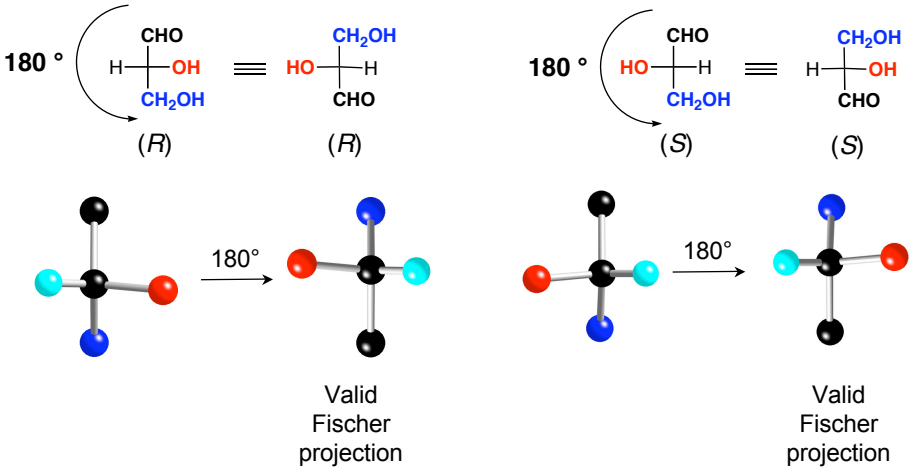
Aldohexoses: C_6, four chiral carbons, sixteen stereoisomers



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 rotate by 180° (in the plane of the page) only!



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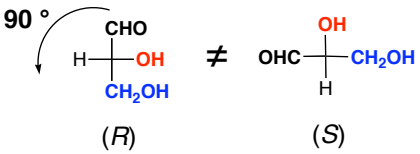
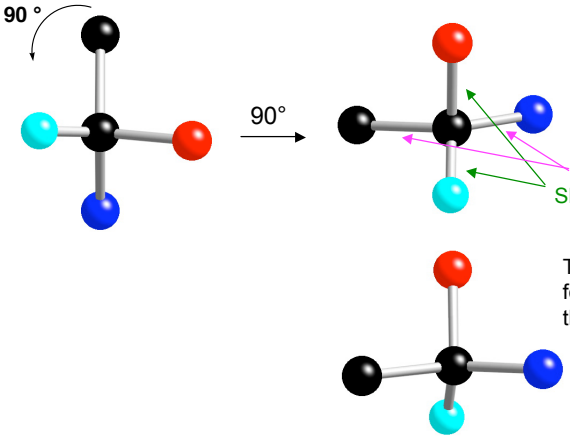
a 90° rotation inverts the stereochemistry and is illegal!





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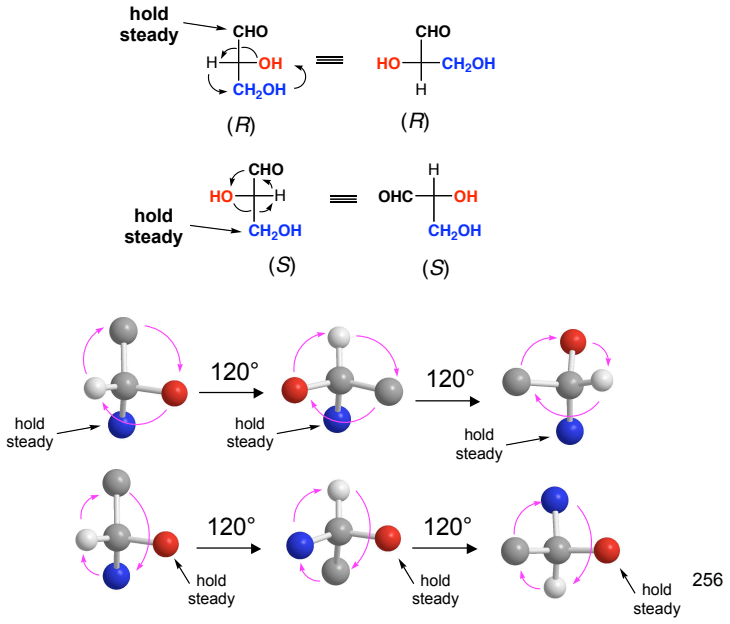
2. If one group of a Fischer projection is held steady, the other three groups can be rotated clockwise or counterclockwise.



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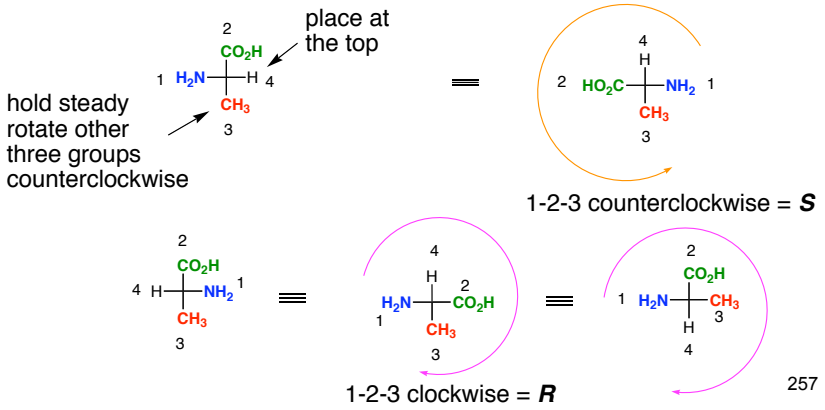
Assigning *R* and *S* Configuration to Fischer Projections

1. Assign priorities to the four substitutents 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*.



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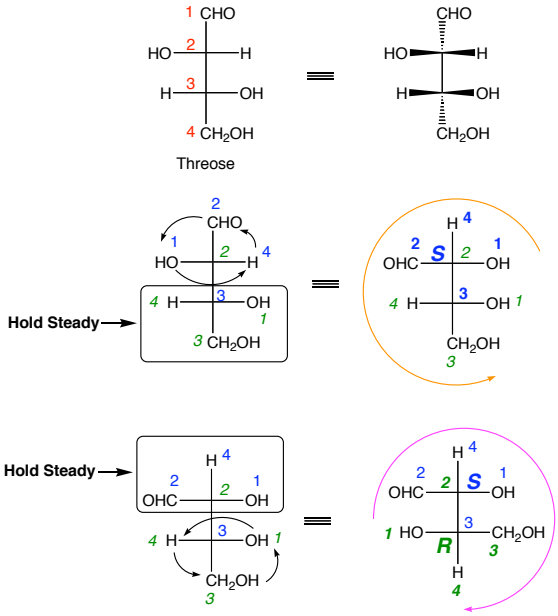
Fischer projections with more than one chiral center:



(2*S*, 3*R*)

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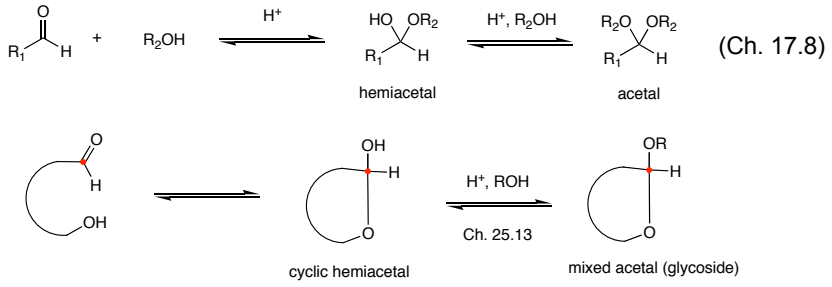
25.5: A Mnemonic for Carbohydrate Configuration. (please read)

25.6: Cyclic Forms of Carbohydrates: Furanose Forms.



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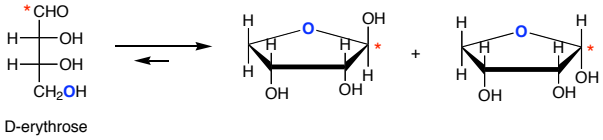
In the case of carbohydrates, cyclization to the hemiacetal creates a new chiral center.



Converting Fischer Projections to Haworth formulas

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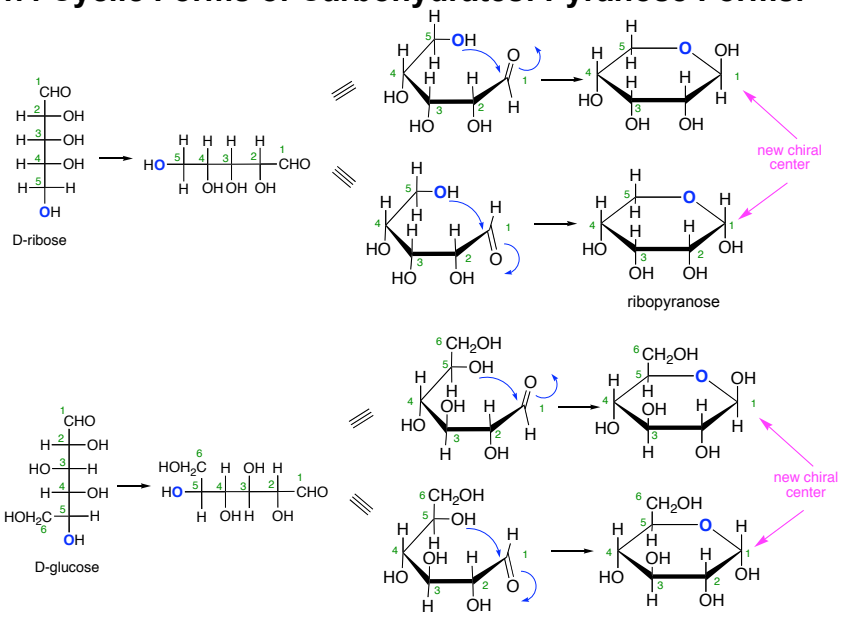
25.7: Cyclic Forms of Carbohydrates: Pyranose Forms.



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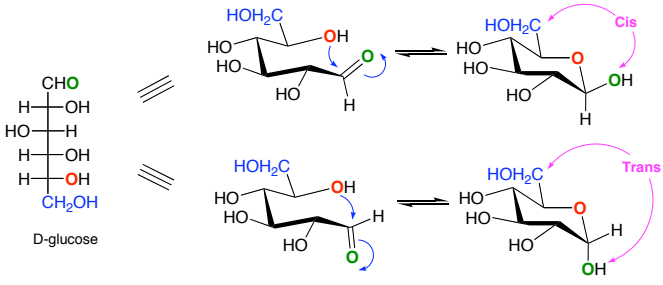
25.8: Mutarotation and the Anomeric Effect. The hemiacetal or hemiketal carbon of the cyclic form of carbohydrates is the *anomeric carbon*. Carbohydrate isomers that differ only in the stereochemistry of the anomeric carbon are called *anomers*.

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.



β-D-Glucopyranose (64%) (β-anomer: C1-OH and CH_2OH are cis)

α-D-Glucopyranose (36%) (α-anomer: C1-OH and CH_2OH are trans)

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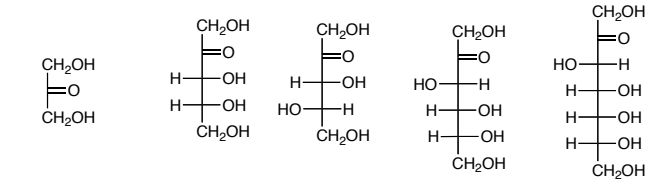
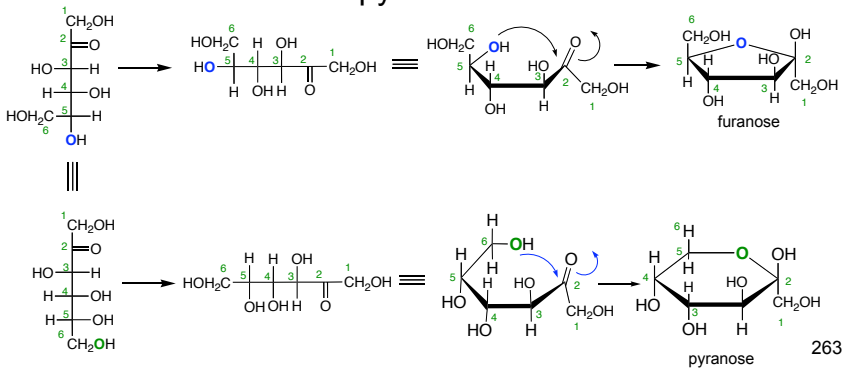
25.9: Ketoses. Ketoses are less common than aldoses



Fructofuranose and Fructopyranose



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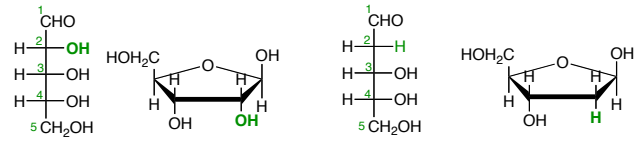
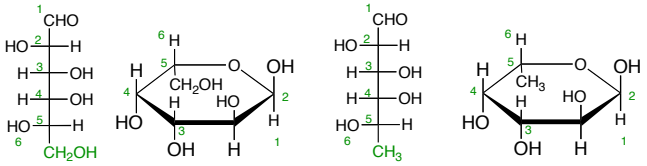
25.10: Deoxy Sugars. Carbohydrates that are missing a hydroxy group.



D-ribose

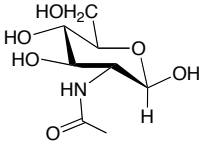
2-Deoxy-D-ribose



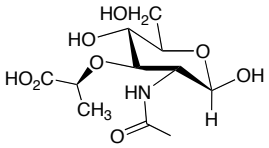
L-Galactose

6-Deoxy-L-Galactose
(fucose)

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



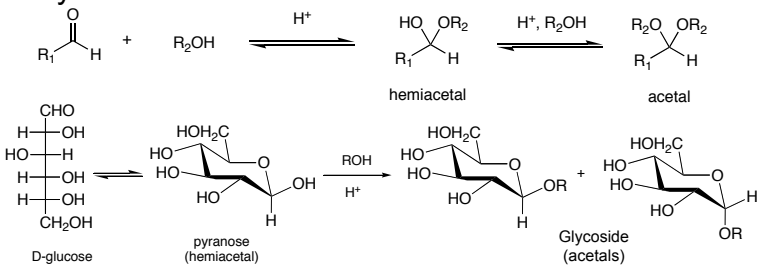
N-acetyl-D-glucosamine
(GlcNAc or NAG)



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

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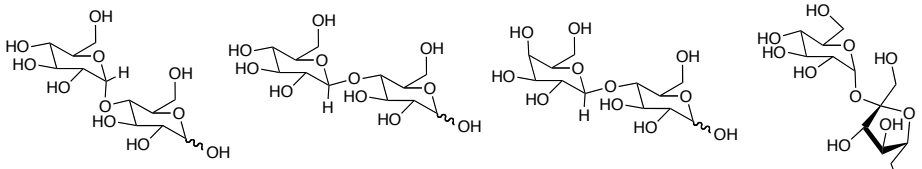
25.14: Disaccharides. A glycoside in which ROH is another carbohydrate unit (complex carbohydrate).



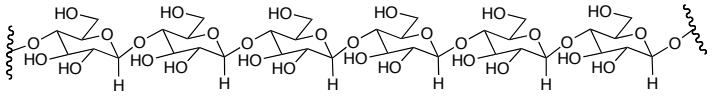
maltose (1,4'-α-glycoside)

cellobiose (1,4'-β-glycoside)

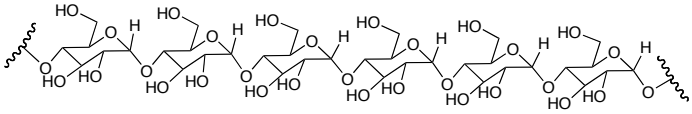
Lactose (1,4'-β-glycoside)

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



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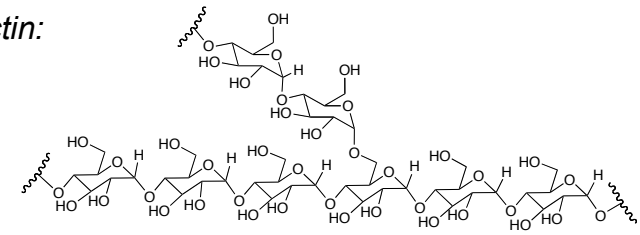
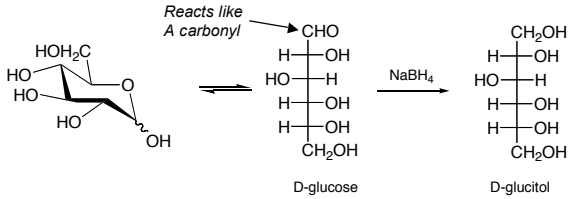
Amylopectin:



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*)



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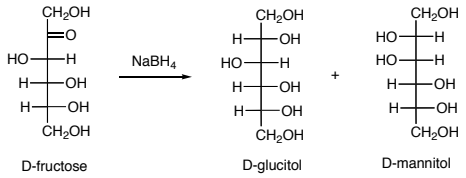
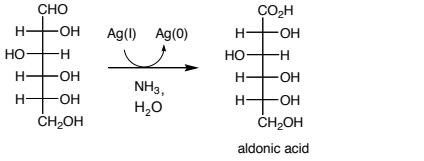
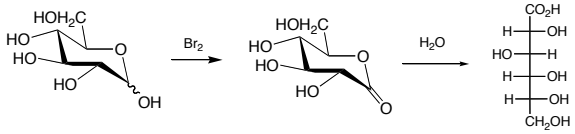
Reduction of ketoses



25.17: Oxidation of Monosaccharides. C1 of aldoses can be selectively oxidized to the carboxylic acid (*aldonic acids*) with Br_2 or Ag(I) (Tollen's test).





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

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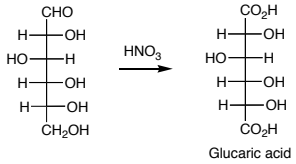
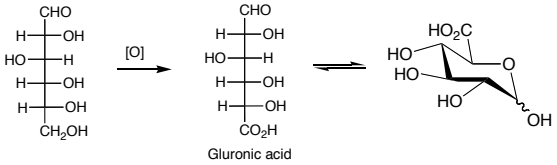
Oxidation of aldoses to *aldaric acids* with HNO_3.



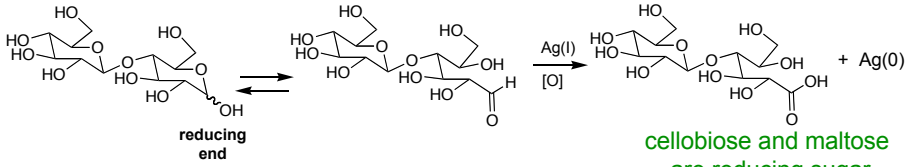
Glucaric acid

Uronic Acid: Carbohydrate in which only the terminal -CH_2OH is oxidized to a carboxylic acid.

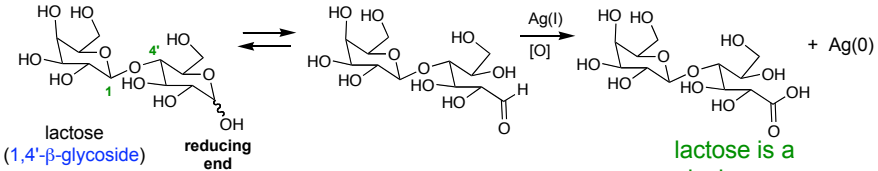


Gluronic acid

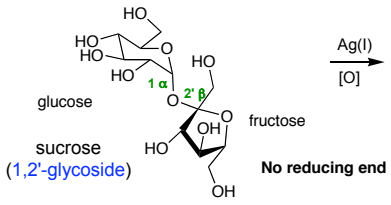
Reducing sugars: carbohydrates that can be oxidized to aldonic acids.



cellobiose and maltose are reducing sugar



lactose is a reducing sugar



sucrose is not a reducing sugar

25.19: Cyanohydrin Formation and Chain Extension.

Kiliani-Fischer Synthesis- chain lengthening of monosaccharides

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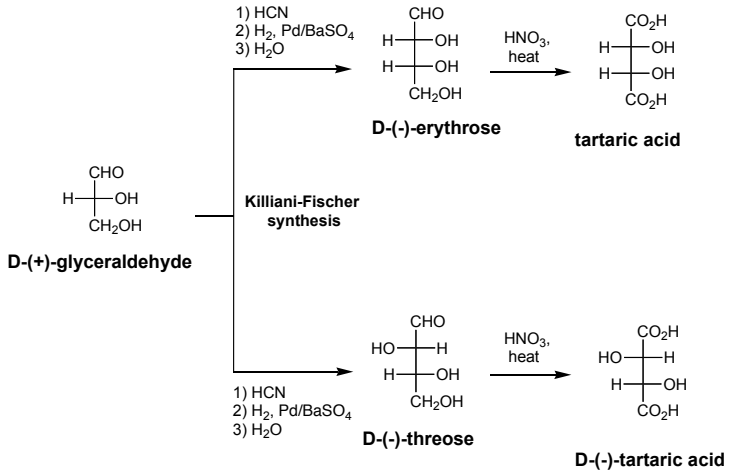
Determination of carbohydrate stereochemistry



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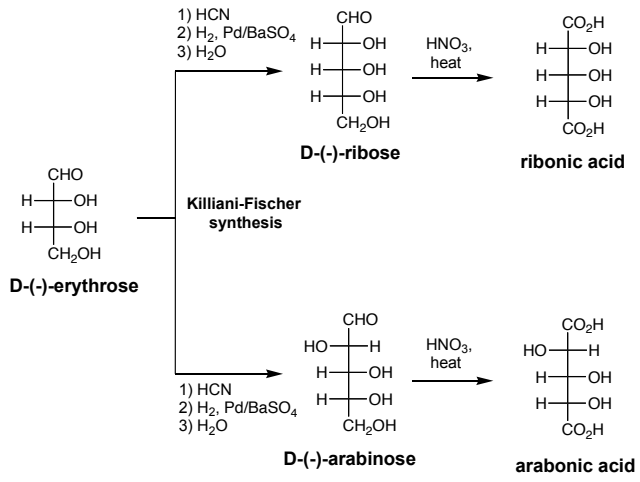
1) HCN
2) H2, Pd/BaSO4
3) H2O
D-(-)-ribose
HNO3, heat
ribonic acid
D-(-)-erythrose
Killiani-Fischer synthesis
1) HCN
2) H2, Pd/BaSO4
3) H2O
D-(-)-arabinose
HNO3, heat
arabonic acid

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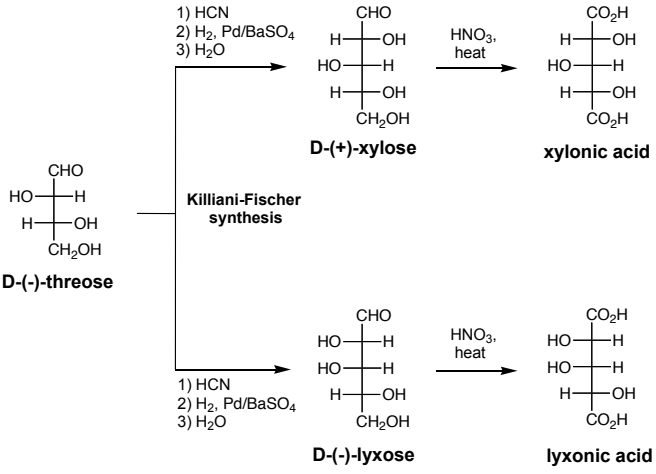
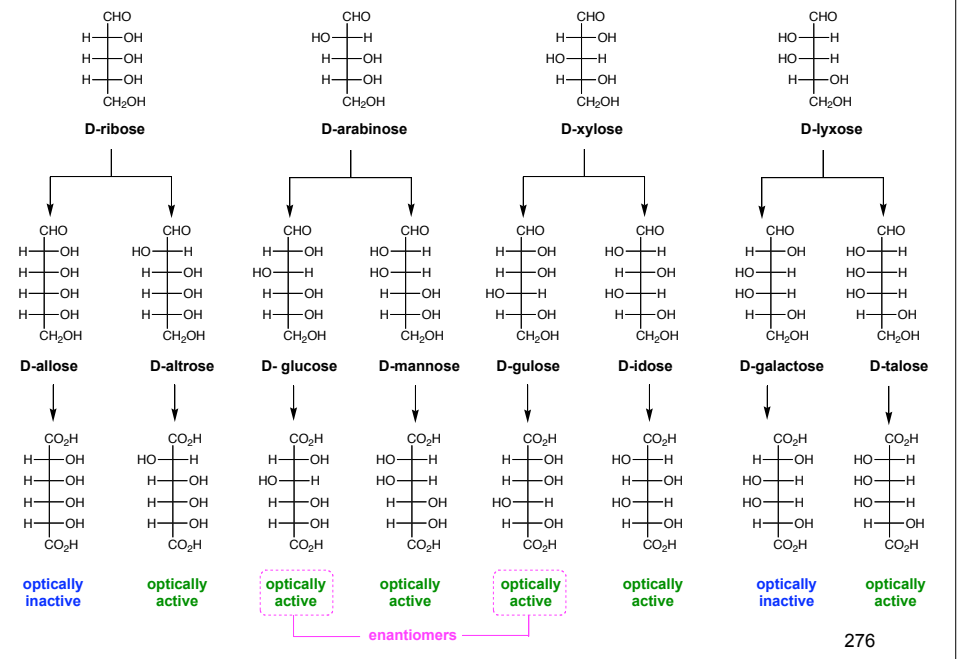

1) HCN
2) H2, Pd/BaSO4
3) H2O
D-(+)-xylose
HNO3, heat
xylonic acid
D-(-)-threose
Killiani-Fischer synthesis
1) HCN
2) H2, Pd/BaSO4
3) H2O
D-(-)-lyxose
HNO3, heat
lyxonic acid

275



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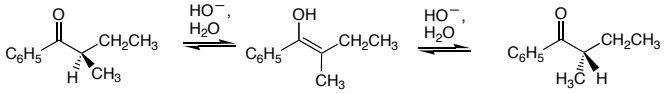
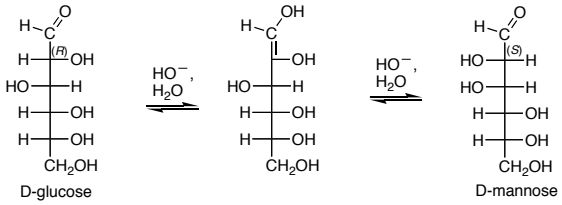
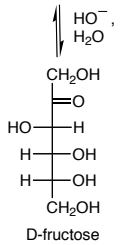
25.20: Epimerization, Isomerization and Retro-Aldol Cleavage.



From Ch 18.10





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

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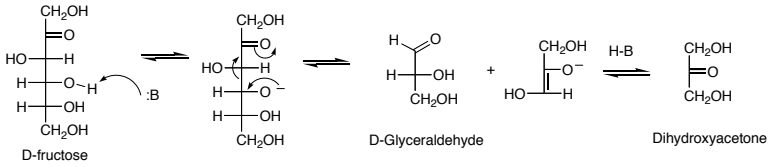
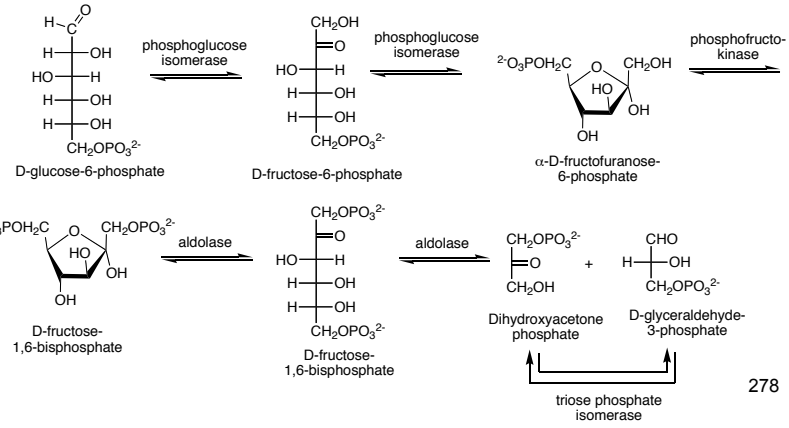
Retro-aldol reaction of carbohydrates



Glycolysis



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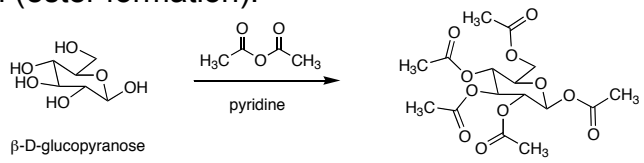
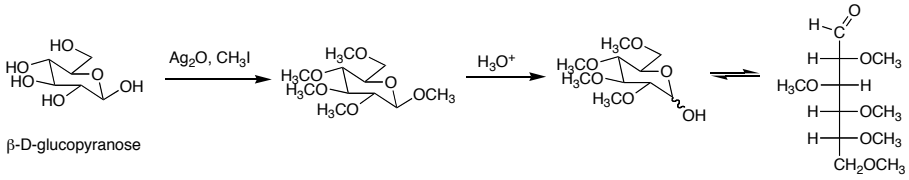
25.21: Acylation and Alkylation of Hydroxyl Groups

Acylation (ester formation):



Alkylation (ether formation):



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

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