Chapter 23: 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 23)	monosaccharides
peptides and proteins (Chapter 25)	amino acids
nucleic acids (Chapter 26)	nucleotides
Synthetic Polymers (Chapter 27)	various

23.1: Classification of Carbohydrates.

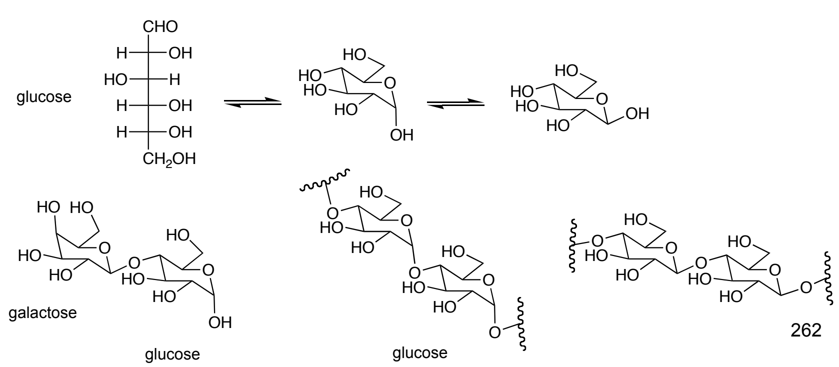
I. Number of carbohydrate units

monosaccharides: one carbohydrate unit (simple carbohydrates)

disaccharides: two carbohydrate units (complex carbohydrates)

trisaccharides: three carbohydrate units

polysaccharides (*oligosaccharides*): many carbohydrate units



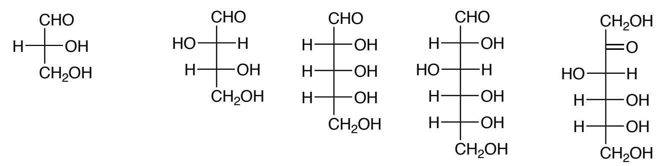
II. Position of carbonyl group

the carbonyl at C1 is an aldehyde: *aldose*
the carbonyl at any other carbon is a ketone: *ketose*

III. Number of carbons

three carbons: *triose*	six carbons: *hexose*
four carbons: *tetrose*	seven carbons: *heptose*
five carbons: *pentose*	etc.

IV. Cyclic form (Chapter 23.6 and 23.7)



glyceraldehyde (triose) **threose (tetrose)** **ribose (pentose)** **glucose (hexose) (aldohexose)** **fructose (hexose) (ketohexose)**

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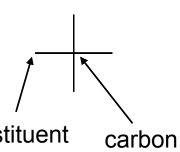
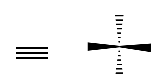
23.2: Fischer Projections and the D, L Notation.

Representation of a three-dimensional molecule as a flat structure (Ch. 7.7). Tetrahedral carbon represented by two crossed lines:

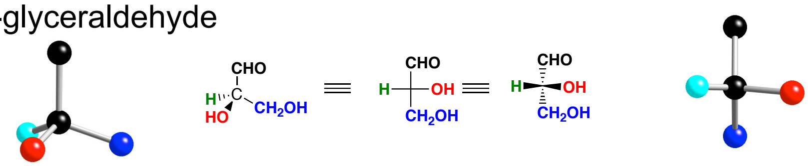
horizontal line is coming out of the plane of the page (toward you)



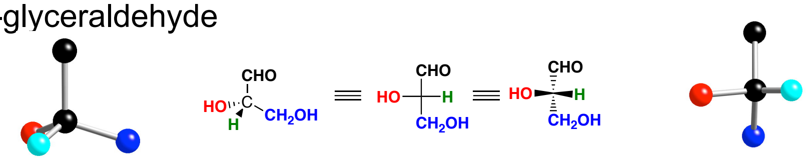
vertical line is going back behind the plane of the paper (away from you)



(*R*)-(+)-glyceraldehyde



(*S*)-(-)-glyceraldehyde



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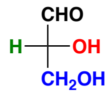
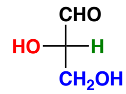
before the *R*/*S* convention, stereochemistry was related to (+)-glyceraldehyde





D-glyceraldehyde
R-(+)-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.

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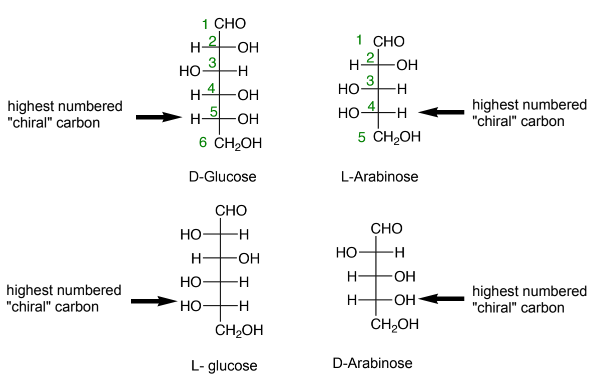
Carbohydrates are designated as D- or L- according to the stereochemistry of the highest numbered chiral carbon of the Fischer projection. If the hydroxyl group of the highest numbered chiral carbon is pointing to the right, the carbohydrate is designated as **D** (*<u>Dextro</u>*: Latin for *on the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



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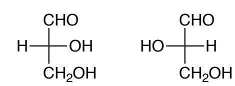
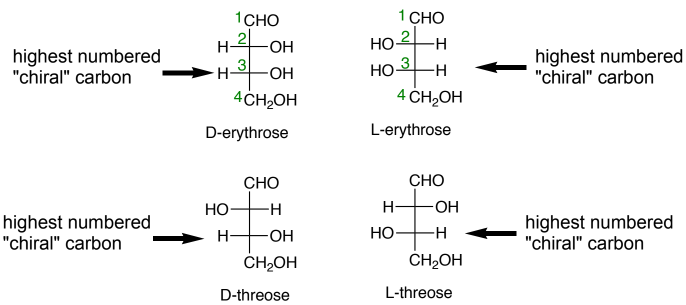
23.3: The Aldotetroses. Glyceraldehyde is the simplest carbohydrate (C_3, aldotriose, 2,3-dihydroxypropanal). The next carbohydrate are aldotetroses (C_4, 2,3,4-trihydroxybutanal).

aldotriose

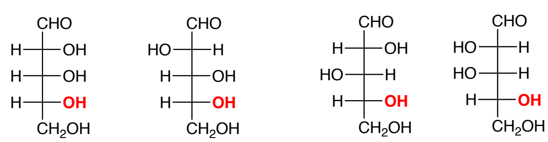


D-glyceraldehyde L-glyceraldehyde

aldotetroses

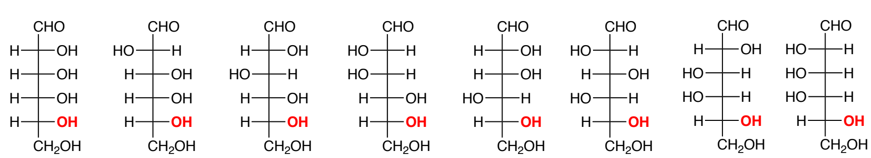


23.4: Aldopentoses and Aldohexoses.
Aldopentoses: C_5, three chiral carbons, eight stereoisomers



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

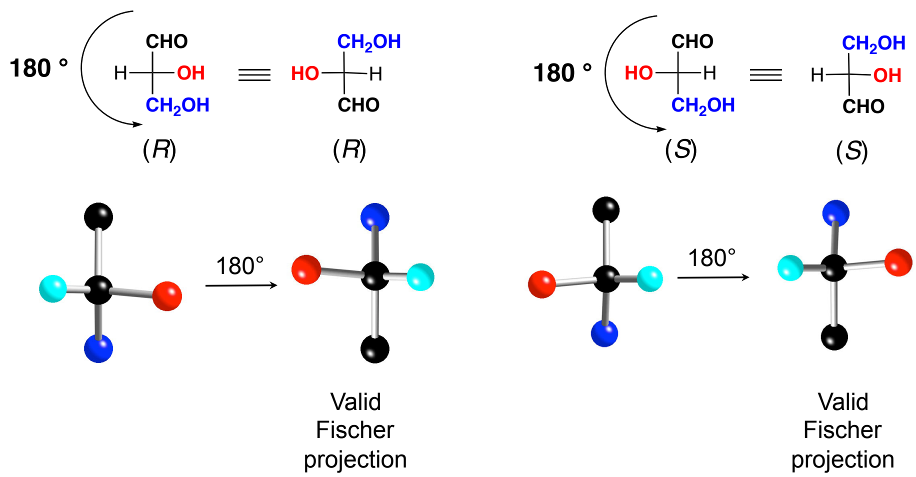
Aldohexoses: C_6, four chiral carbons, sixteen stereoisomers



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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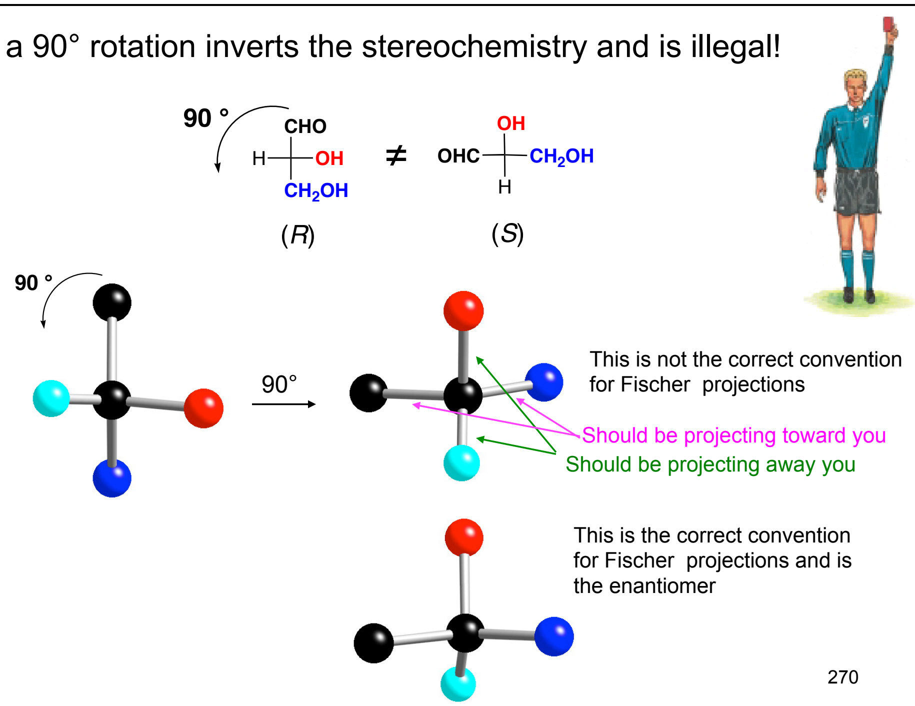
a 90° rotation inverts the stereochemistry and is illegal!



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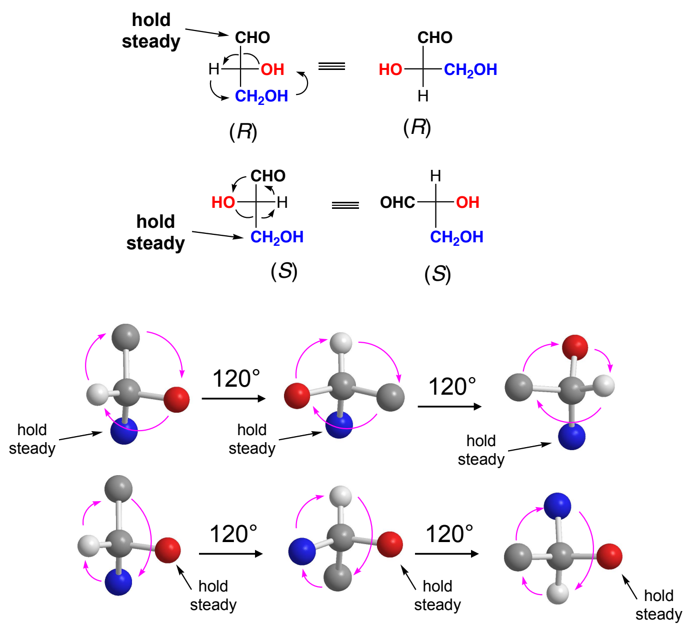
2. If one group of a Fischer projection is held steady, the other three groups can be rotated clockwise or counterclockwise.



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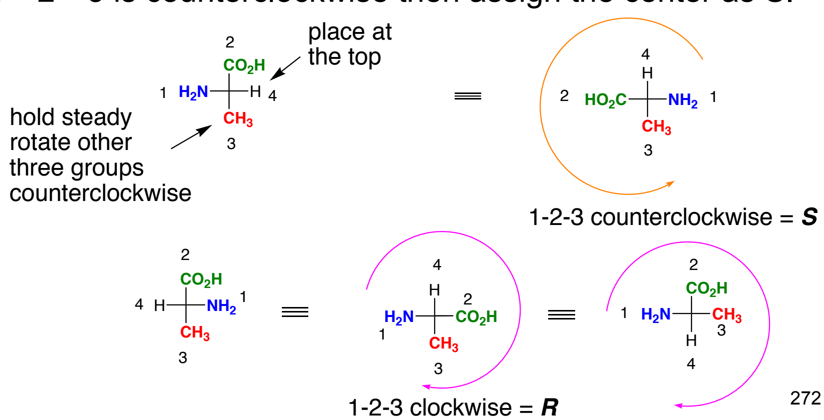
Assigning *R* and *S* Configuration to Fischer Projections

1. Assign priorities to the four 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 the priority of the other groups 1→2→3 is counterclockwise then assign the center as *S*.



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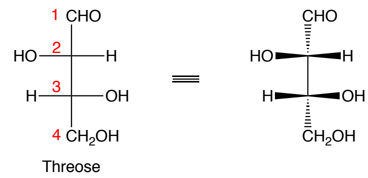
Fischer projections with more than one chiral center:



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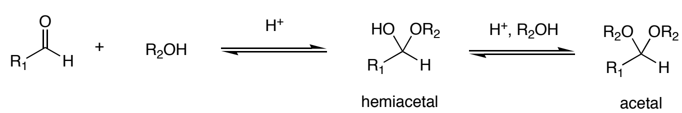
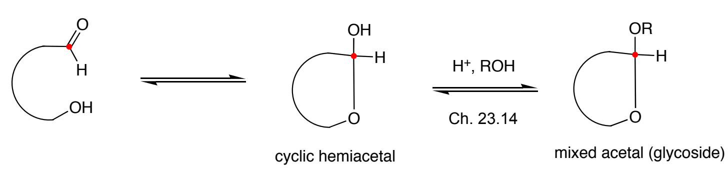
23.5: A Mnemonic for Carbohydrate Configuration.
(please read)

25.6: Cyclic Forms of Carbohydrates: Furanose Forms.



(Ch. 17.8)



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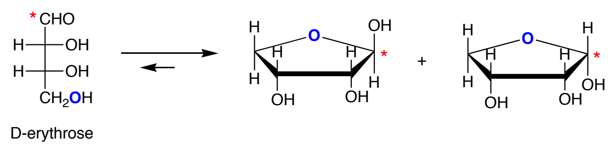
Cyclization of carbohydrates to the hemiacetal creates a new chiral center. The hemiacetal or hemiketal carbon of the cyclic form of carbohydrates is the *anomeric carbon*. Carbohydrate isomers that differ only in the stereochemistry of the anomeric carbon are called *anomers* and designated as α and β.



Converting Fischer Projections to Haworth formulas

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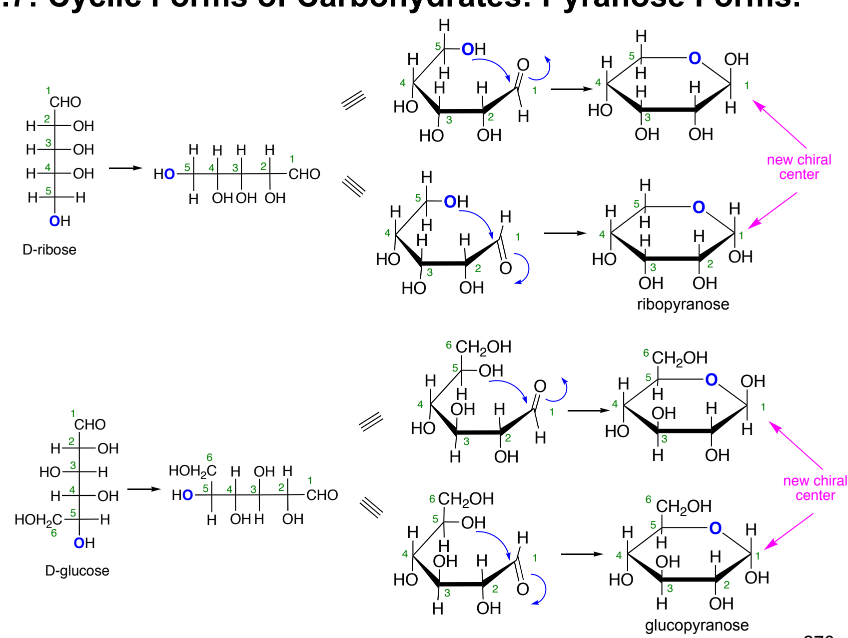
23.7: Cyclic Forms of Carbohydrates: Pyranose Forms.



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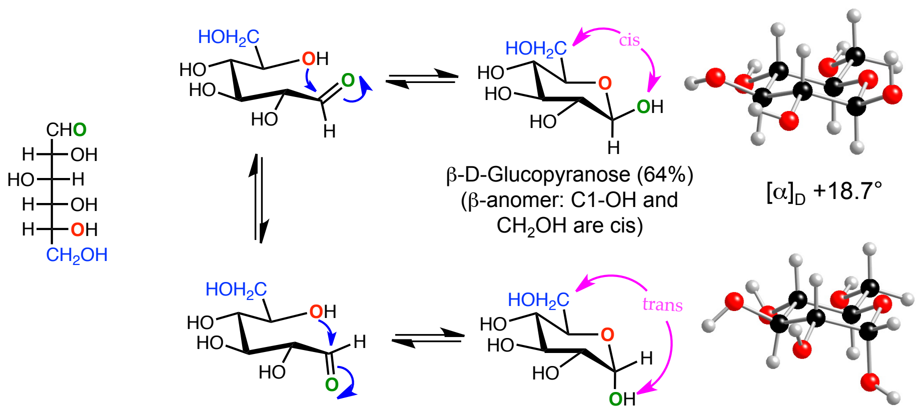
Note: the pyranose forms of carbohydrates adopt chair conformations.

23.8: 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)

$[\alpha]_D$ +18.7°

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

$[\alpha]_D$ +112.2°

acid-catalyzed mechanism: p. 959

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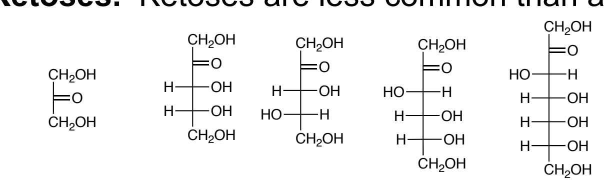
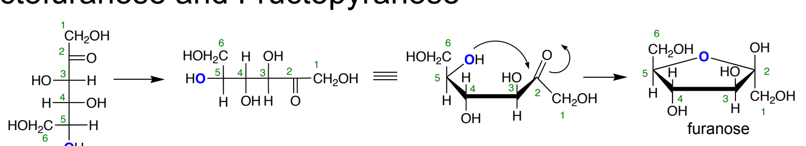
23.9: Carbohydrate Conformation: The Anomeric Effect
(please read)

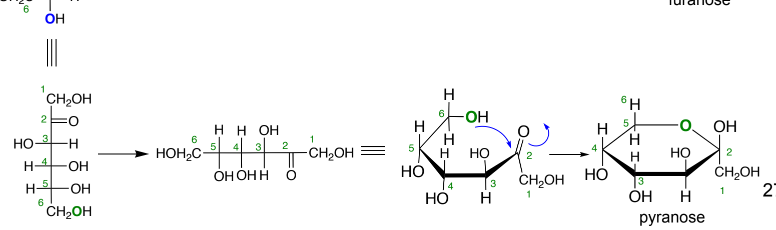
23.10: Ketoses. Ketoses are less common than aldoses



dihydroxyacetone | D-ribulose | Dxylulose | D-fructose | D-sedohepuloase

Fructofuranose and Fructopyranose





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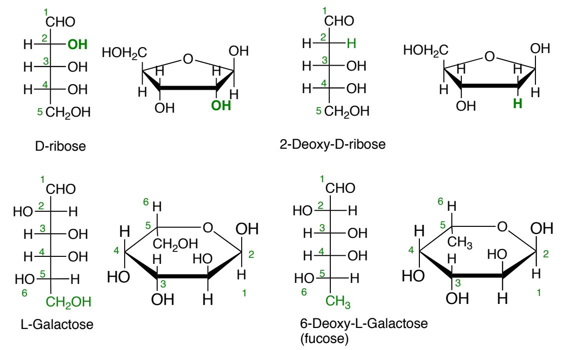
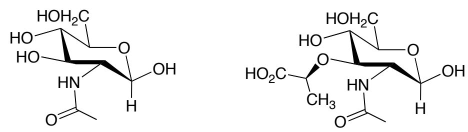
25.11: Deoxy Sugars. Carbohydrates that are missing a hydroxy group.



23.12: 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)

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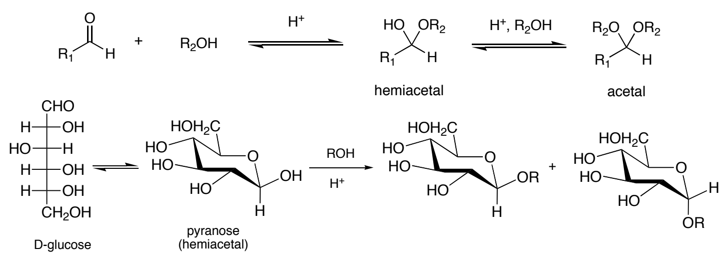
23.13: Branched-Chain Carbohydrates. (Please read)

23.14: Glycosides: The Fischer Glycosylation. Acetals and ketals of the cyclic form of carbohydrates.



acid-catalyzed mechanism: Mechanism 23.2, p. 967

Note that only the anomeric hydroxyl group is replaced by ROH

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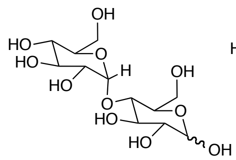
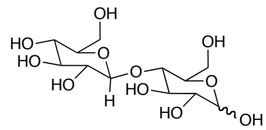
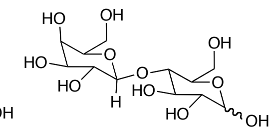
23.15: Disaccharides. A glycoside in which ROH is another carbohydrate unit (complex carbohydrate).



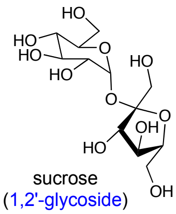
maltose
(1,4'-α-glycoside)



cellobiose
(1,4'-β-glycoside)

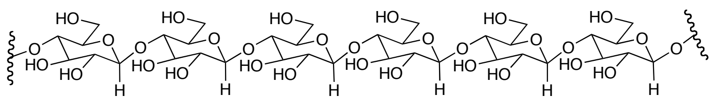


Lactose
(1,4'-β-glycoside)

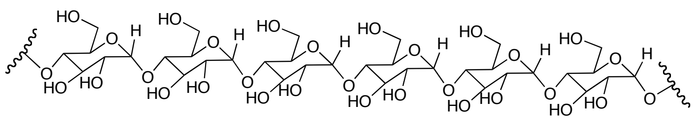


sucrose
(1,2'-glycoside)

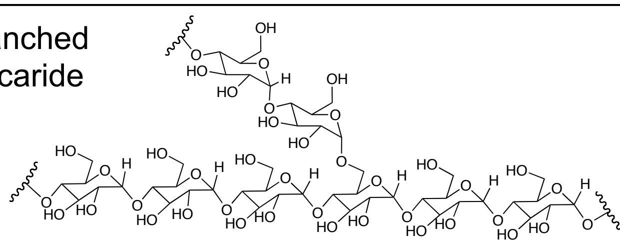
23.16: Polysaccharides. *Cellulose*: glucose polymer made up of 1,4’-β-glycoside linkages



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

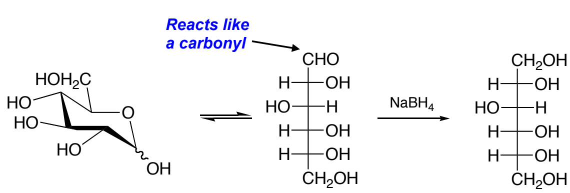


Amylopectin: Branched amylose polysaccaride



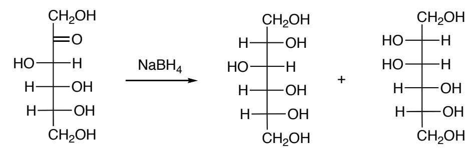
23.17: Application of Familiar Reactions to Monosaccharides. (Table 23.2, p. 974)

<u>*Reduction of Monosaccharides.*</u> C1 of aldoses are reduced with sodium borohydride to the 1° alcohol (*alditols*).



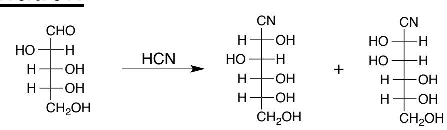
D-glucose D-glucitol

Reduction of ketoses



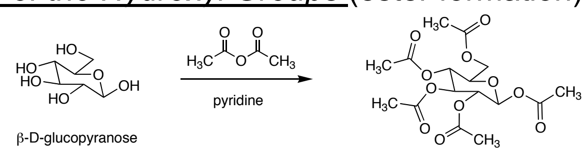
D-fructose D-glucitol D-mannitol

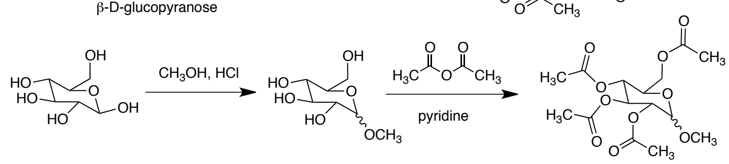
Cyanohydrin formation



D-arabinose

Acylation of the Hydroxyl Groups (ester formation):





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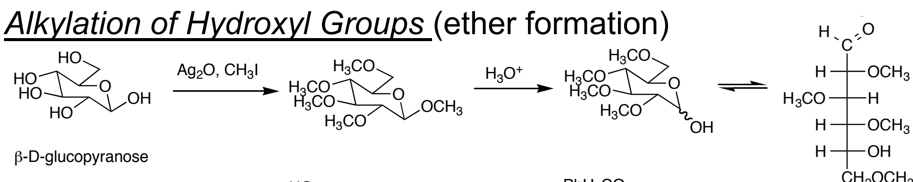
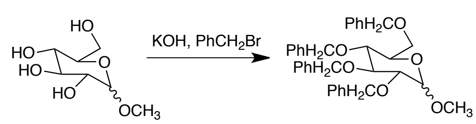
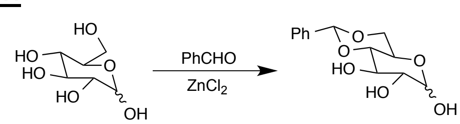
Alkylation of Hydroxyl Groups (ether formation)

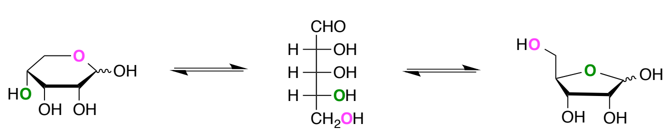




Acetal formation



Furanose – pyranose isomerization



D-ribopyranose **D-ribose** **D-ribofuranose**

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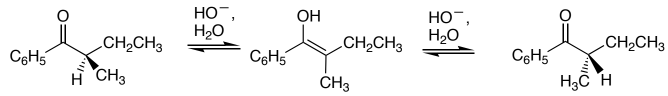
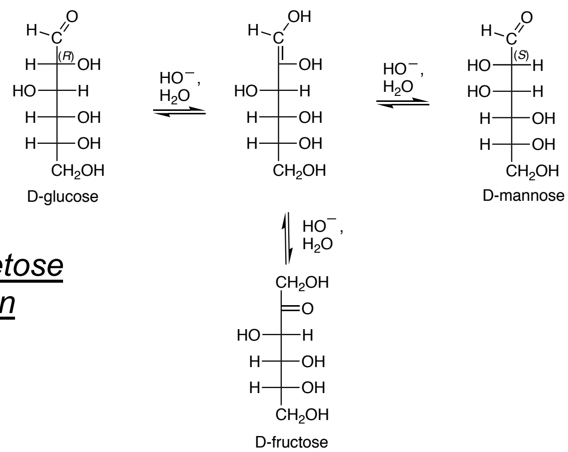
Enolization and Epimerization



from
Ch 20.2



Aldose to ketose isomerization

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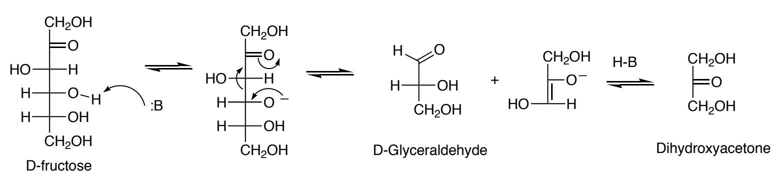
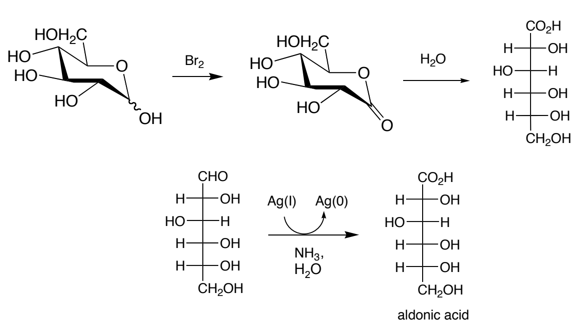
Retro-aldol reaction of carbohydrates



23.18: 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).



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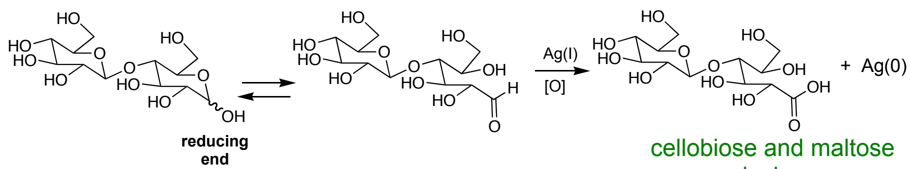
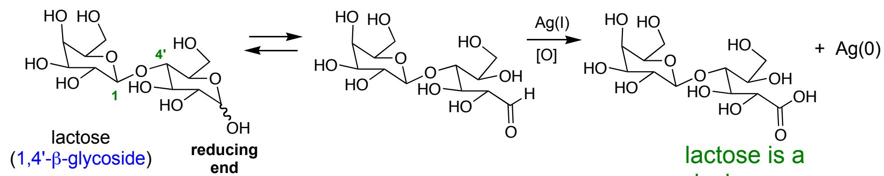
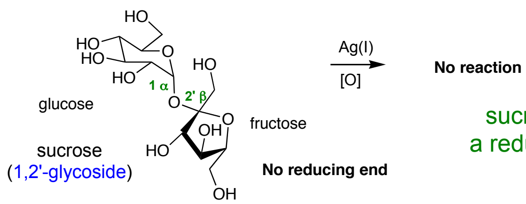
Reducing sugars: carbohydrates that can be oxidized to aldonic acids.



cellobiose and maltose are reducing sugar

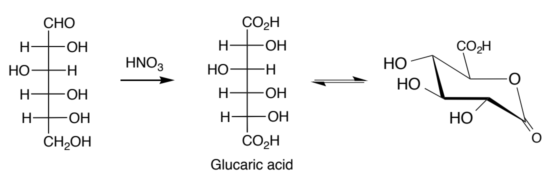


lactose is a reducing sugar

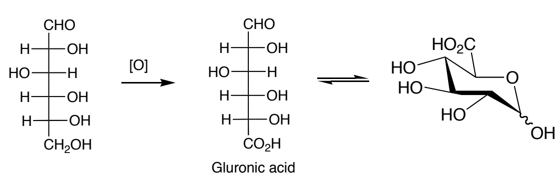


sucrose is not a reducing sugar

Oxidation of aldoses to *aldaric acids* with HNO_3.



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



<u>*Periodic Acid Oxidation*</u>. The vicinal diols of carbohydrate can be oxidative cleaved with HIO_4.

Kiliani-Fischer Synthesis: chain lengthening of monosaccharides

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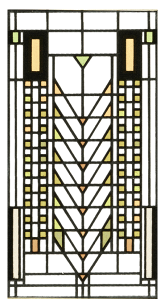
Symmetry

Monarch butterfly:
bilateral symmetry=
mirror symmetry



Mirror
symmetry

Mirror symmetry &
axis (6 fold) of symmetry

Whenever winds blow
butterflies find a new place
on the willow tree
-Basho (~1644 - 1694)

Point (center)
of symmetry

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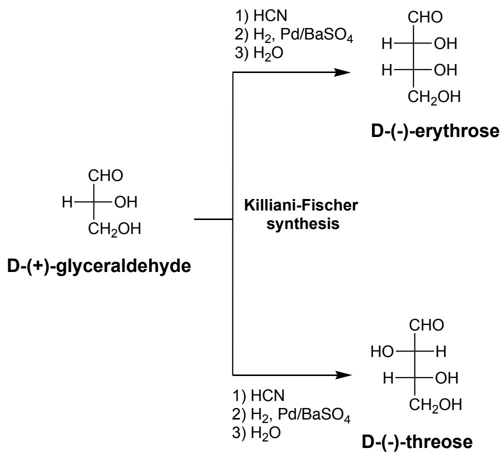
Determination of carbohydrate stereochemistry



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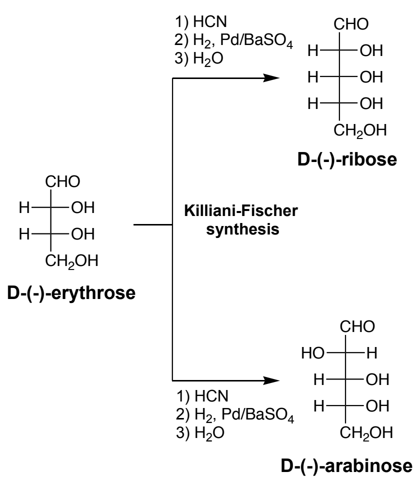
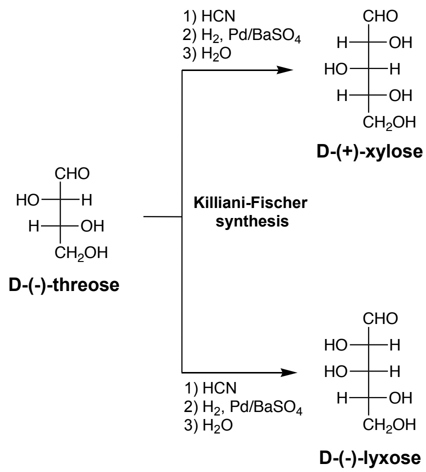


292


1) HCN
2) H_2, Pd/$BaSO_4$
3) H_2O
CHO
H OH
HO H
H OH
CH_2OH
D-(+)-xylose
CHO
HO H
H OH
CH_2OH
D-(-)-threose
Killiani-Fischer synthesis
CHO
HO H
HO H
H OH
CH_2OH
1) HCN
2) H_2, Pd/$BaSO_4$
3) H_2O
D-(-)-lyxose

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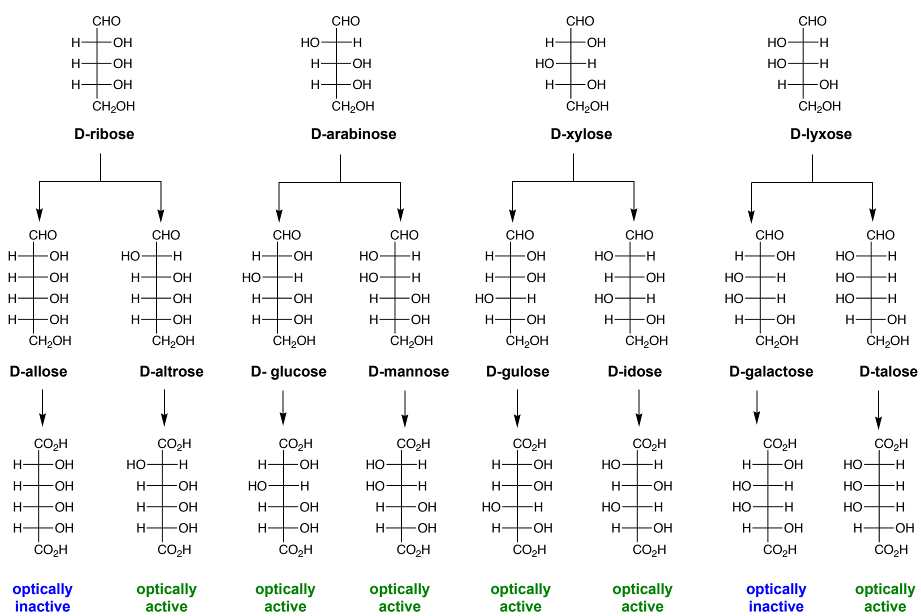
D-ribose
D-arabinose
D-xylose
D-lyxose
D-allose
D-altrose
D- glucose
D-mannose
D-gulose
D-idose
D-galactose
D-talose
optically inactive
optically active
optically active
optically active
optically active
optically active
optically inactive
optically active

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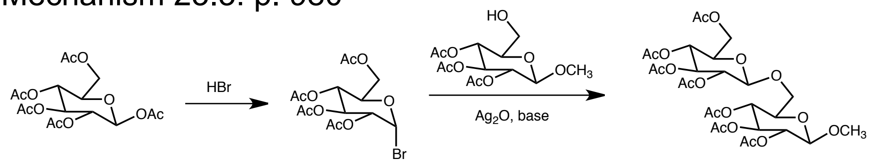
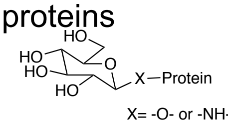
23.24: Glycosides: Synthesis of Oligosaccharides

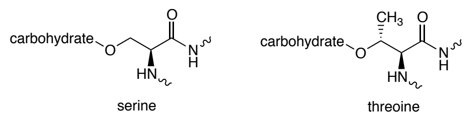
Mechanism 23.3: p. 980

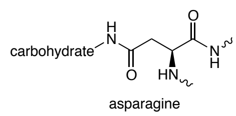


23.25: Glycobiology (please read)

Glycoproteins: glycosides of proteins







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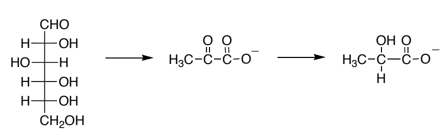
Chapter 24: Lipids. Hydrophobic (non-polar, soluble in organic solvent), typically of low molecular weight compounds of organic origin.

- fatty acids and waxes
- essential oils
- many vitamins
- hormones (non-peptide)
- components of cell membranes (non-peptide)

Share a common biosynthesis that ultimately derives their carbon source from glucose (glycolysis)

Glucose → pyruvate → lactate



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