Sugars and Polysaccharides

March 24, 2015

Sugars and Polysaccharides

- **Carbohydrates** or **Saccharides** are the most abundant class of biological molecules.
- General formula $(C{\bullet}H_2O)_n$ where $n \geq 3$.
- **Monosaccharides** are basic building blocks.
- **Oligosaccharides**: a few covalently linked monosaccharides.
- **Polysaccharides**: many covalently linked monosaccharides.

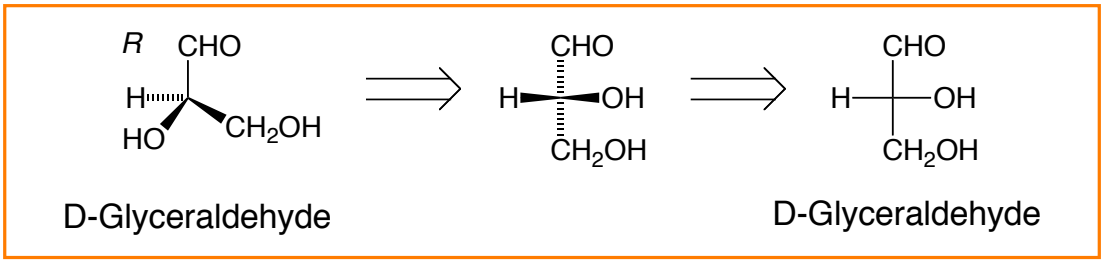
Major Carbohydrate Classes

- Monosaccharides
  - Single polyhydroxy aldehyde or ketone units
- Oligosaccharides
  - Short chains of monosaccharides, <20
  - Most abundant are the disaccharides
  - Most oligosaccharides of 3 or more units are joined to nonsugar molecules
- Polysaccharides
  - Contain more than 20 monosaccharide units
  - Many contain hundreds or thousands of monosaccharides
  - May be in linear (cellulose) or branched (glycogen) chains

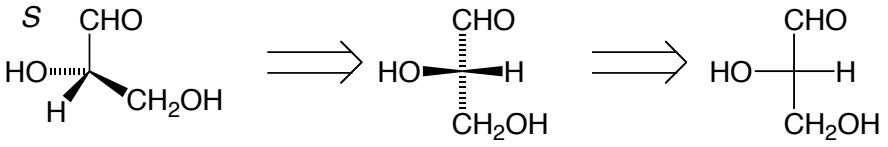
Monosaccharides

- Consist of aldehydes or ketones with one or more hydroxyl groups.
- Identified based on the nature of the carbonyl group:
  - Aldehyde -> aldose
  - Ketone -> ketose
- Further classified based on the number of carbon atoms.
  - 3 -> trioses
  - 4 -> tetroses
  - 5 -> pentoses
  - Etc…
- Often contain multiple chiral centers.
  - D sugars have the same configuration as does D-glyceraldehyde at the asymmetric center farthest from the carbonyl group. [Fischer Convention]
  - Aldoses generally have 2^{n-2} stereoisomers.

Fischer Projections and Stereochemistry



D-Glyceraldehyde D-Glyceraldehyde

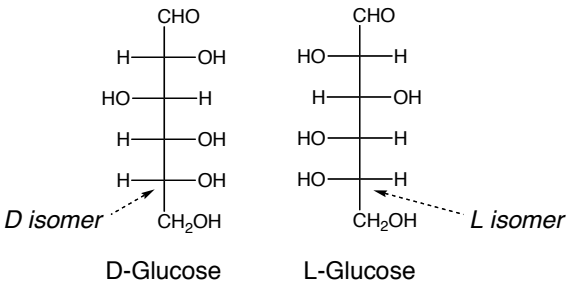


L-Glyceraldehyde L-Glyceraldehyde

Monosaccharide Stereoisomers

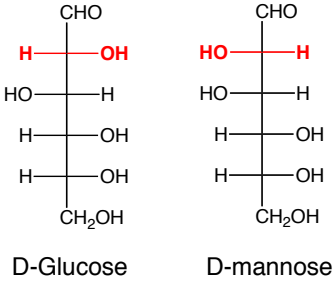
- The L sugars are the mirror images of their D isomer counterparts.

Enantiomers

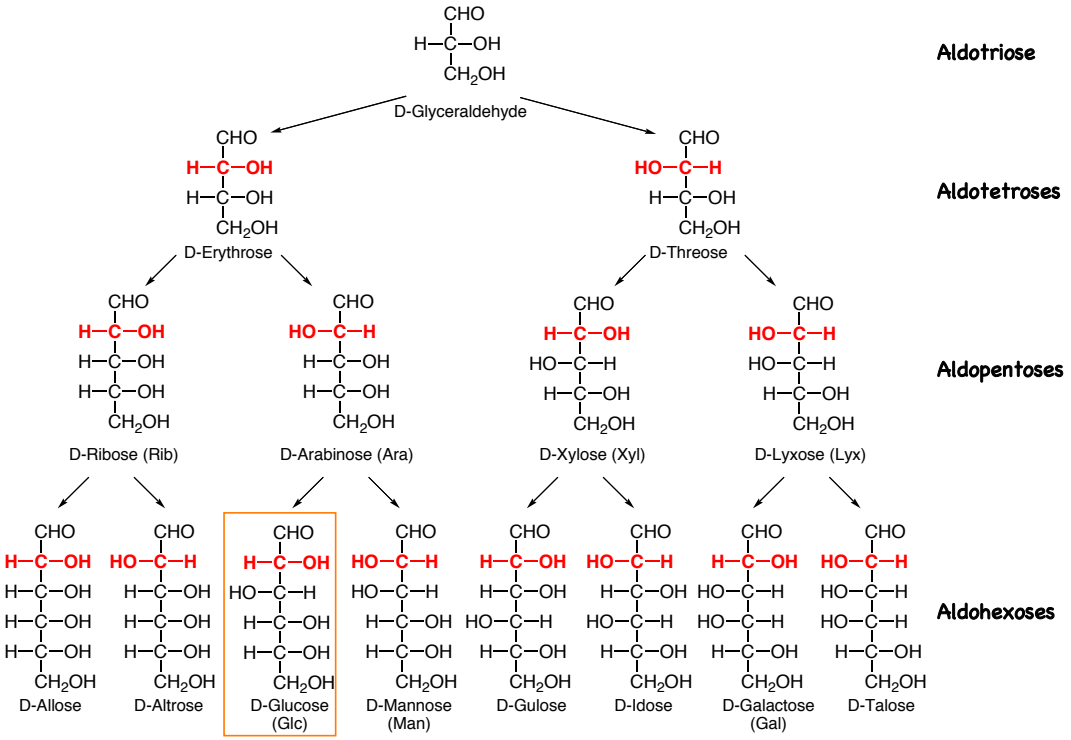


- Epimers are stereoisomers that differ only in their configuration at one chiral carbon atom.

Epimers

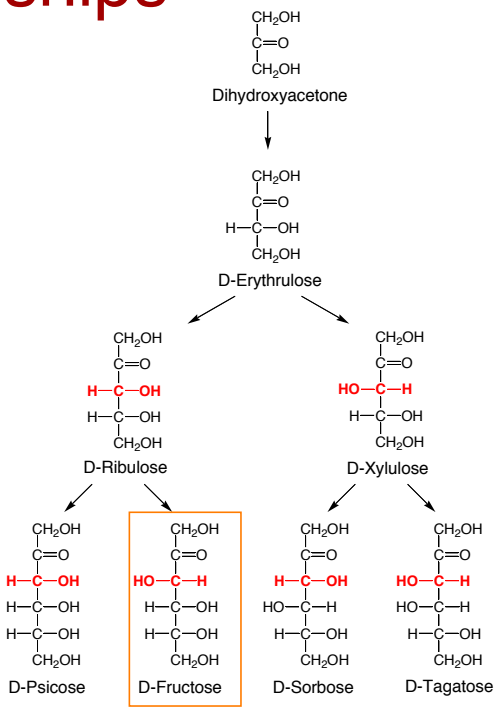


Aldoses: Stereochemical Relationships



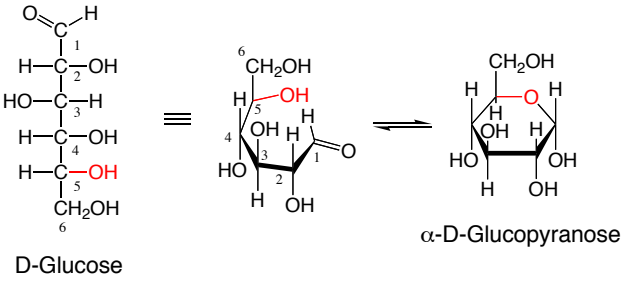
Ketoses: Stereochemical Relationships

- Ketoses have one less chiral center than their aldose counterparts.
- Ketoses have 2^{n-3} stereoisomers (n = number of carbon atoms).
- Ketoses with the carbonyl at the C2 position are most prevalent.
- Nomenclature: insert *-ul-* before the *-ose* ending in the name of the corresponding aldose.



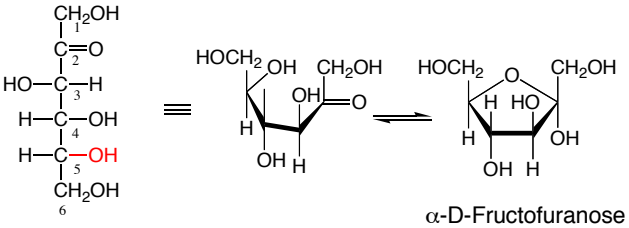
Configurations and Conformations

- Aldehydes and ketones can react with alcohols to form hemiacetals and hemiketals respectively.
- Aldehydes/ketones of monosaccharides can react with hydroxyl groups intramolecularly to form cyclic hemiacetals/hemiketals.
- Haworth projection formulas.



D-Glucose

α-D-Glucopyranose

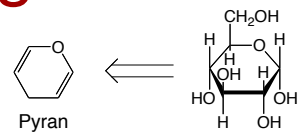


D-Fructose

α-D-Fructofuranose

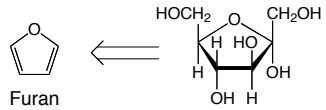
Cyclic Sugars

- 6-membered rings: pyranoses.
- 5-membered rings: furanoses.
- Anomers differ in configuration at the hemiacetal or hemiketal carbon.
- This carbon is called the anomeric carbon.
- Anomers: α and β isomers.



Pyran

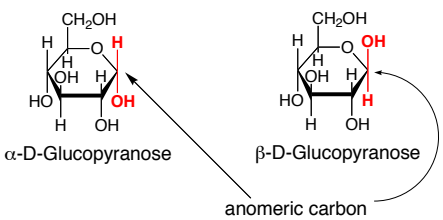
α-D-Glucopyranose



Furan

α-D-Fructoruranose

Anomers



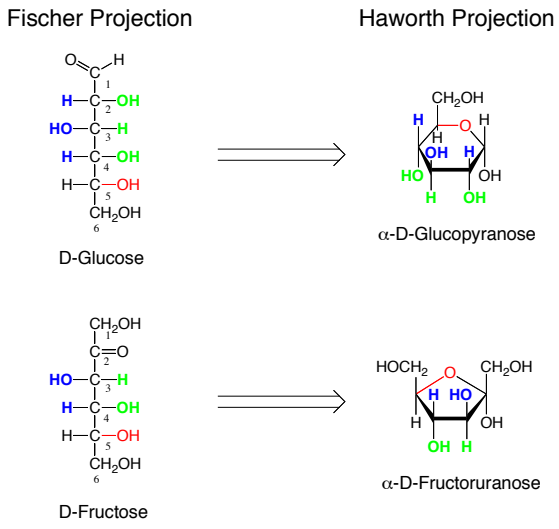
α-D-Glucopyranose

β-D-Glucopyranose

anomeric carbon

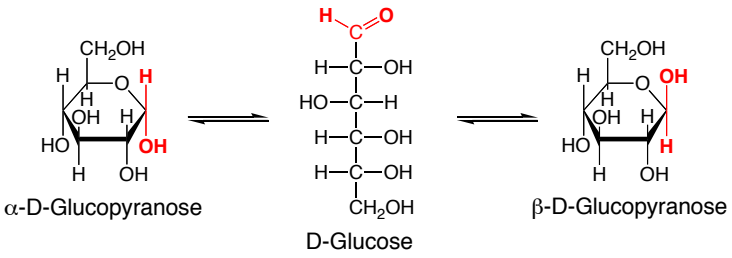
Fischer -> Haworth

- Haworth projections used to represent cyclic saccharide structures.
- Substituents extend either above or below the ring.
  - Substituents on the left in a Fischer projection are drawn above the ring.
  - Substituents on the right in a Fischer projection are drawn below the ring.
  - **Exception:** the carbon whose hydroxyl group forms the hemiacetal/hemiketal.
  - *Remember α- and β-configurations.*



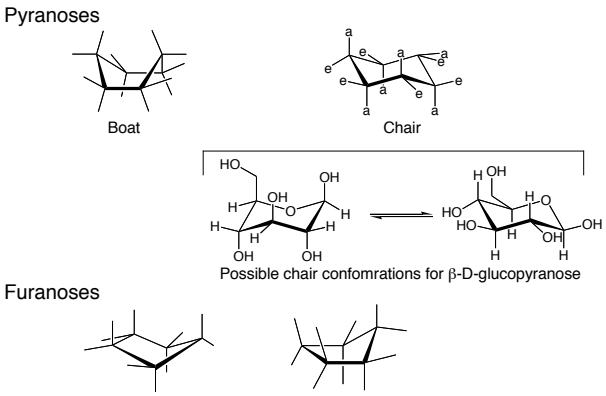
Anomers and Interconversion

- Anomers are defined based on the relative position of the OH group on the anomeric carbon.
  - α - OH on the opposite side of the ring from the CH_2OH.
  - β - OH on the same side of the ring from the CH_2OH.
- Monosaccharide anomers in solution interconvert readily.
- Interconvesion proceeds via the linear form.

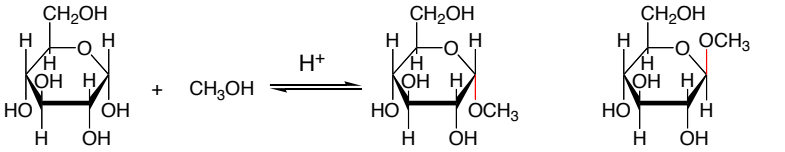


Conformational Variability

- Pyranoses can assume boat and chair conformations.
- Ring conformation effects chemical reactivity.
  - Equatorial OH groups esterify more readily than axial OH groups.
- Furanose rings have similar conformational variability.
- Substituents influence conformational preferences.



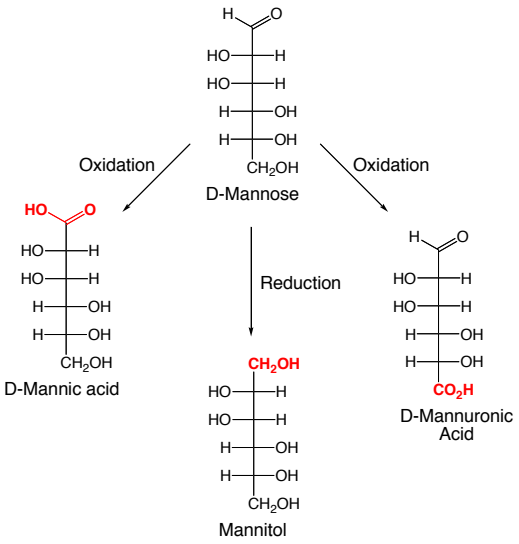
Glycosidic Bonds



- Glycosidic bonds are formed by the condensation of the anomeric OH and another OH group (or in the case of nucleosides, N).
- Formation of glycosidic bonds is acid catalyzed.
- Glycosidic bonds link sugar monomers in di- and polysaccharides.

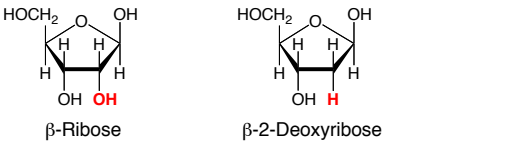
Oxidation and Reduction

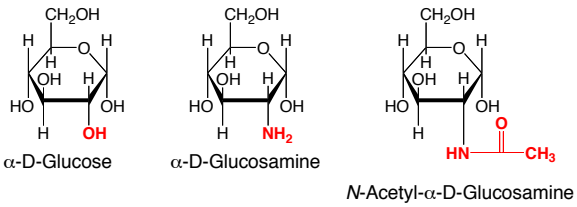
- Aldehydes of aldoses can be oxidized to carboxylic acids under mild conditions (resulting in aldonic acids).
- Saccharides bearing anomeric carbons that are not involved in glycosidic bonds are called reducing sugars.
- Oxidation of the terminal primary alcohol to the carboxylic acid results in uronic acids.
- Both aldoses and ketoses can be reduced to their alcohols resulting in sugar alcohols.



Sugar Derivatives

- In deoxy sugars, an -OH group has been replaced with and H.
- In amino sugars, one or more OH groups have been replaced with amino groups or acetylated amino groups.
- Amino sugars are common components in polysaccharides.





Intro to Polysaccharides

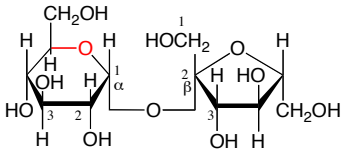
- Most carbohydrates in nature are polysaccharides.
- Have four characteristics:
  - Identity of monosaccharide units
  - Length of chains
  - Types of bonds linking units
  - Degree of branching in chains

Polysaccharides

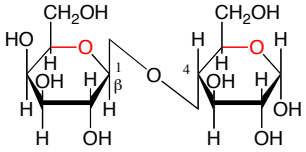
- Polysaccharides (glycans): monosaccharides linked together by glycosidic bonds.
- Homopolysaccharides are composed of one type of monosaccharide.
- Heteropolysaccharides are composed of more than one type of monosaccharide. Their composition is usually repetitive.
- Polysaccharides are not limited to linear construction. They can be branched.
- Exoglycosidases and endoglycosidases: enzymes that cleave glycosidic bonds.

Disaccharides

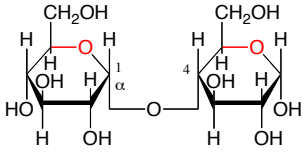
- **Disaccharides** are two monosaccharides joined by an *O*-glycosidic bond.
- The reaction generally involves the anomeric carbon.
- They end with a free anomeric carbon is the reducing end.
- Few tri- or higher oligosaccharides.



Sucrose



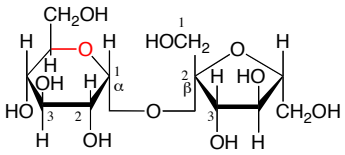
Lactose



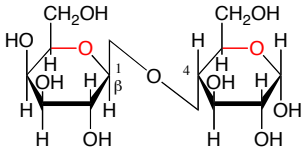
Maltose

Naming of Disaccharides

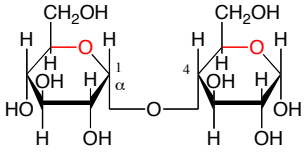
- Anomeric configuration of left monosaccharide is given first.
- Nonreducing residue is named, including furanosyl or pyranosyl.
- The two carbons in the glycosidic bond are identified: (1→ 4), (1->6) etc.
- The second residue is named.
  - Sucrose : O-α-D-glucopyranosyl-(1->2)-β-D-fructofuranoside [note -ide ending].
  - Lactose : O-β-D-galactopyranosyl-(1->4)-D-glucopyranose.



Sucrose



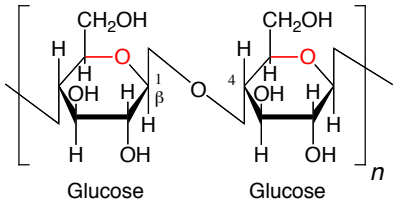
Lactose



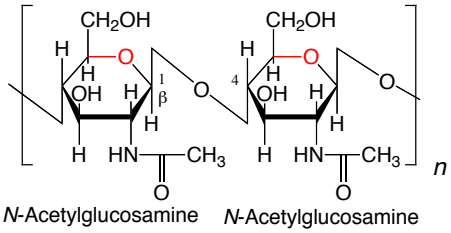
Maltose

Polysaccharides

- **Structural Polysaccharides: Cellulose and Chitin.**
- Cellulose is the primary component of plant cell walls.
- Linear polymer of D-glucose.
- Linkages, β(1->4).
- Up to 15,000 saccharide units.
- Extensive interstrand hydrogen bonding.
- Accounts for almost half the carbon in the biosphere.



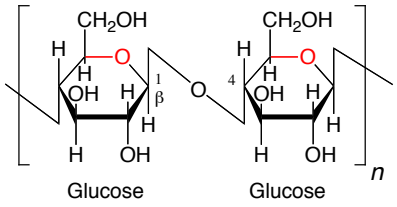
Cellulose



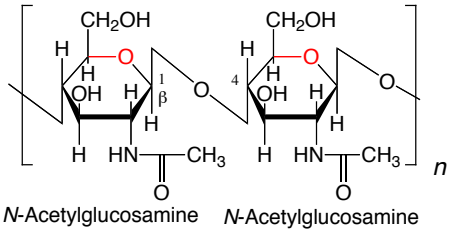
Chitin

Structural Polysaccharides

- **Structural Polysaccharides: Cellulose and Chitin.**
- Chitin is the primary component of invertebrate exoskeletons.
- Almost as abundant as cellulose.
- Linear homopolymer of *N*-acetyl-D-glucosamine.
- Linkages, β(1->4).
- Structure is similar to that of cellulose.



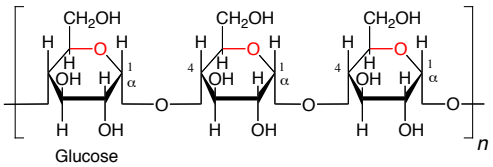
Cellulose



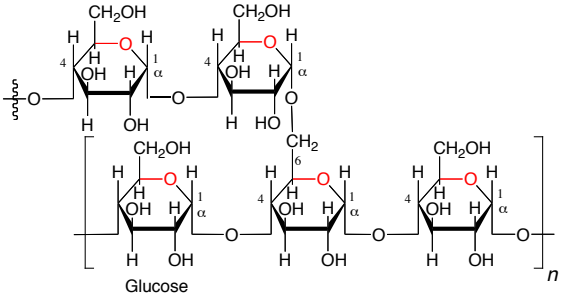
Chitin

Storage Polysaccharides

- Starch: storage in plants.
- Mixture of glycans:
  - The linear homopolymer α-amylose (1->4).
  - The branched homopolymer amylopectin (1->4) and (1->6).
  - Amylopectin molecules can be as large as 10^6 glucose residues.
- Glycogen: storage in animals.
  - Resembles amylopectin.
  - More highly branched.



α-Amylose (1->4 linkages)

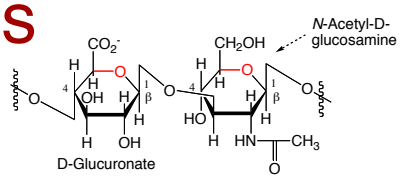


Amylopectin (1->4 linkages, 1->6 branches every 24-30 residues.)

Glycogen (1->4 linkages, 1->6 branches every 8-12 residues.)

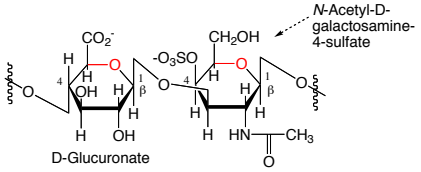
Glycosaminoglycans

- Glycosaminoglycans = mucopolysaccharides.
- Primary component of ground substance, gel-like matrix.
- Extracellular spaces contain collagen and elastin fibres embedded in ground substance.
- Linear polysaccharides consisting of alternating uronic acid and hexosamine.
- Solutions are viscous and demonstrate elasticity.



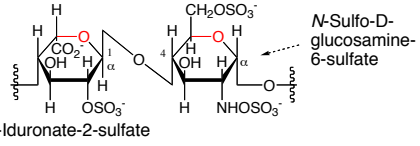
Hyaluronate (hyaluronan)

Important component of ground substance, synovial fluid and vitrious humor of the eye. (also in bacterial capsules)



Chondroitin-4-sulfate

Component of cartiledge and connective tissues



Heparin

Variably sulfated, most negaive polyelectrolyte in mammalian tissues. Inhibits blood clotting.