

Carbohydrates

Typical formula: $C_x(H_2O)_y$, eg glucose: $C_6H_{12}O_6$.

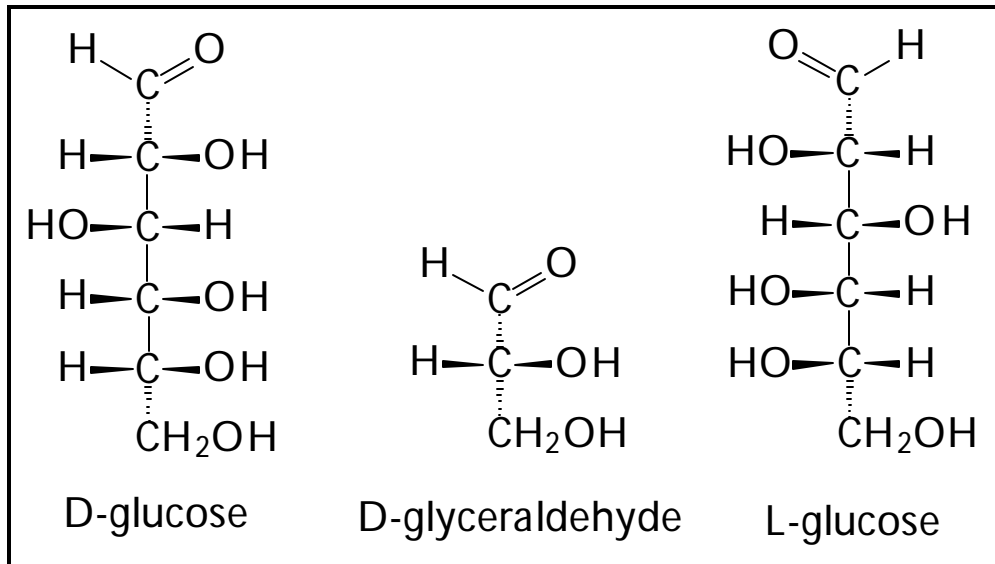
Structure —

Simplest carbohydrates are monosaccharides; one sugar unit. Monosaccharides can combine to form di-, tri-, polysaccharides. These more complex carbohydrates can be hydrolyzed to give their constituent monosaccharides.

Monosaccharides are usually, at least partly, polyhydroxy aldehydes or ketones.

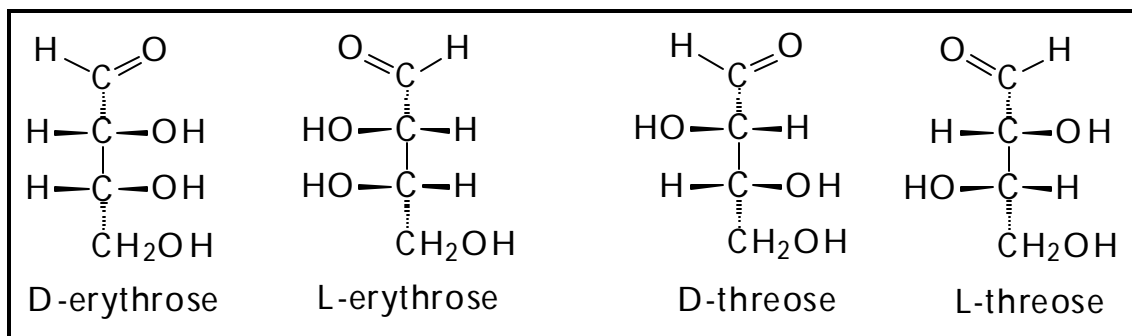
Saccharides that are at least partly polyhydroxy aldehydes or ketones are *reducing sugars*.

D-glucose is a monosaccharide and is the most abundant organic compound in free and combined form.



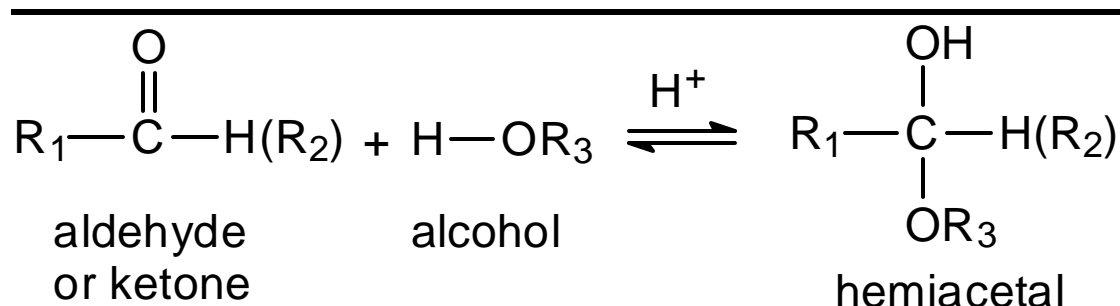
The chiral center that determines D- or L- is the one furthest from the carbonyl. Most naturally occurring sugars are in the D- family.

The family name for sugars has the suffix -ose. Monosaccharides can be characterized as to how many carbons they have: triose, tetrose, pentose, hexose. They can also be characterized as to whether they are aldehydes, *aldose*, or ketones, *ketose*. By combination erythrose and threose (below) are aldotetroses.



Aldohexoses have 4 chiral centers. Meso forms are impossible, so there are $2^4 = 16$ stereoisomeric aldohexoses: 8 D,L-pairs, of which the glucoses are one.

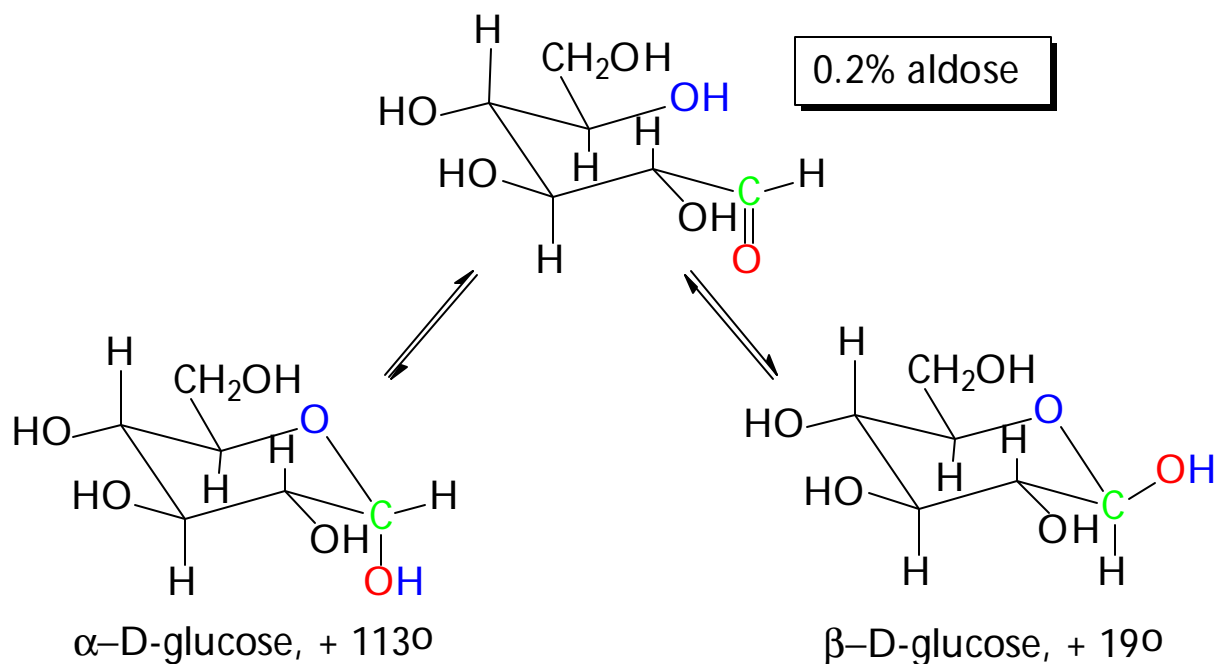
Aldehydes and some ketones react with alcohols to form hemiacetals –



R_1 , R_2 , and R_3 are different R groups;
the subscripts do not indicate how many groups.

Aldoses and ketoses may form internal hemiacetals (the carbonyl reacts with an -OH in the same molecule), resulting in a ring. If the ring is 5-membered, it is called a furanose; if it is 6-membered, it is called a pyranose. [Note that when the ring is formed, the former carbonyl carbon becomes tetrahedral and a chiral center.]

Glucose forms two pyranoses when dissolved in water; they differ from each other in configuration around the former carbonyl carbon.

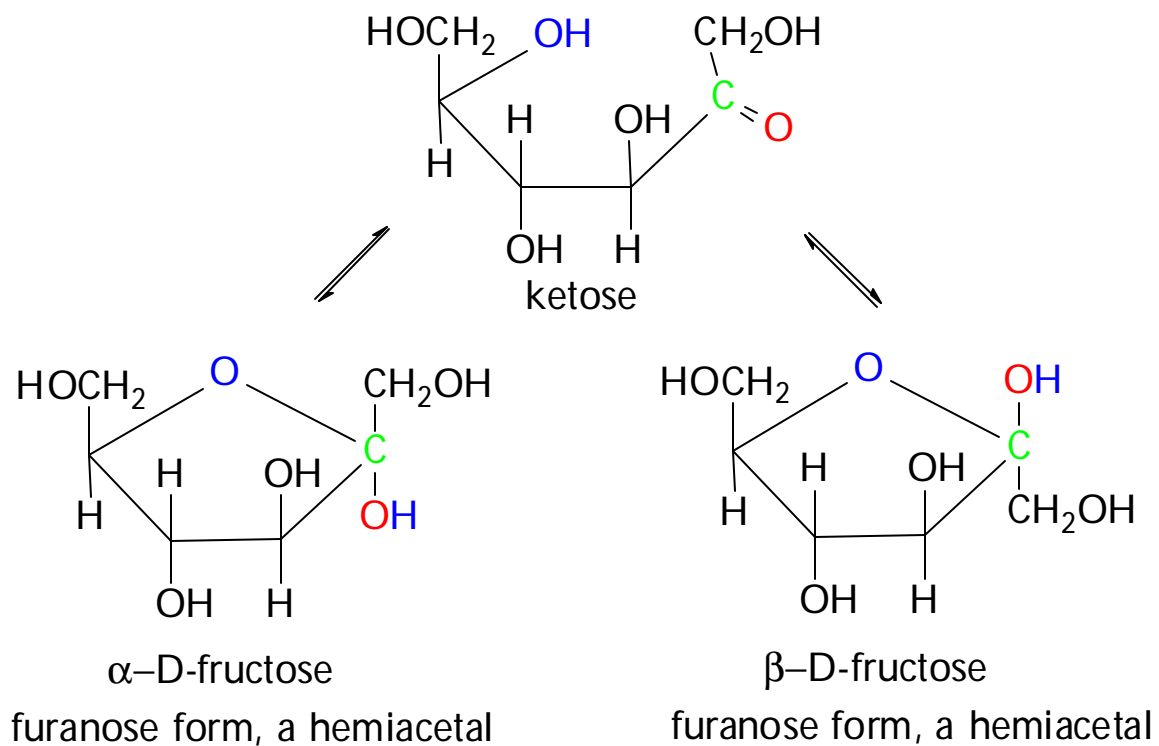


99.8% pyranose

mixture: + 52.5°

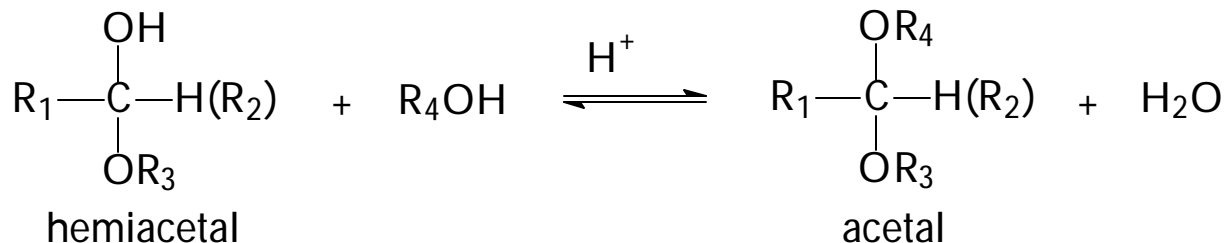
Based on the specific rotation of the mixture (assuming no contribution from the aldose form) this means the D-glucose is 64% in β form and 36% in α form.

Fructose, a ketohexose, forms furanose hemiacetals.

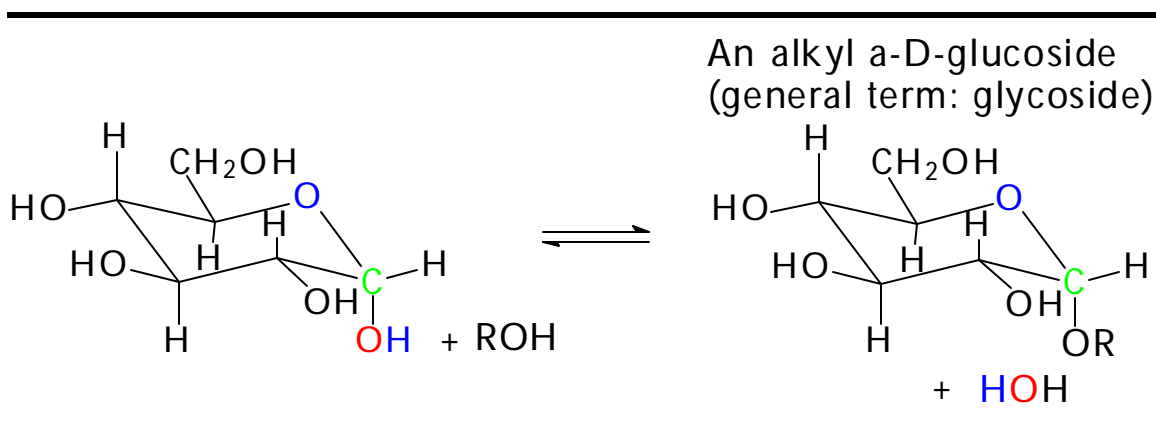


Glycosides —

Acetal formation:



Acetals are stable in neutral, basic solution.

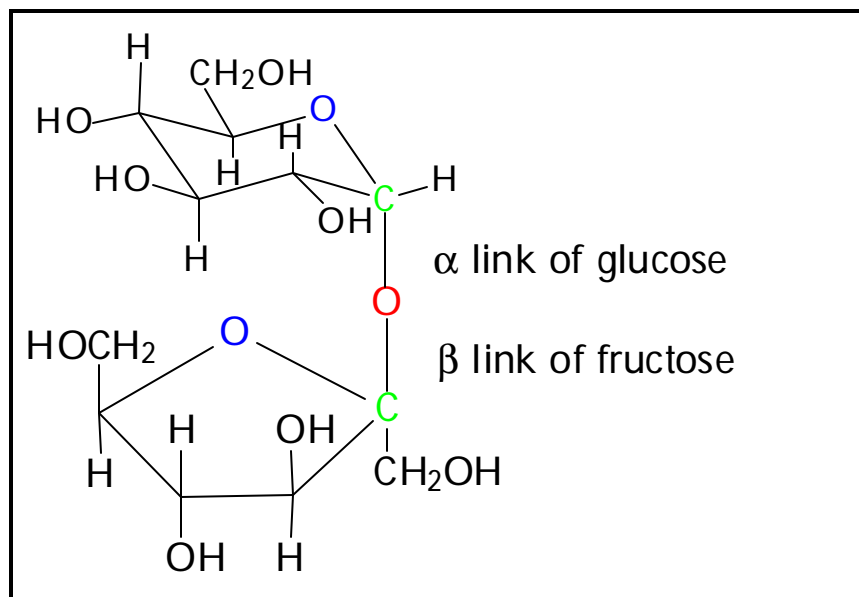


A glycoside (acetal) does not mutarotate in neutral or basic solution (unless R, itself, is a hemiacetal that can open to an aldose or ketose).

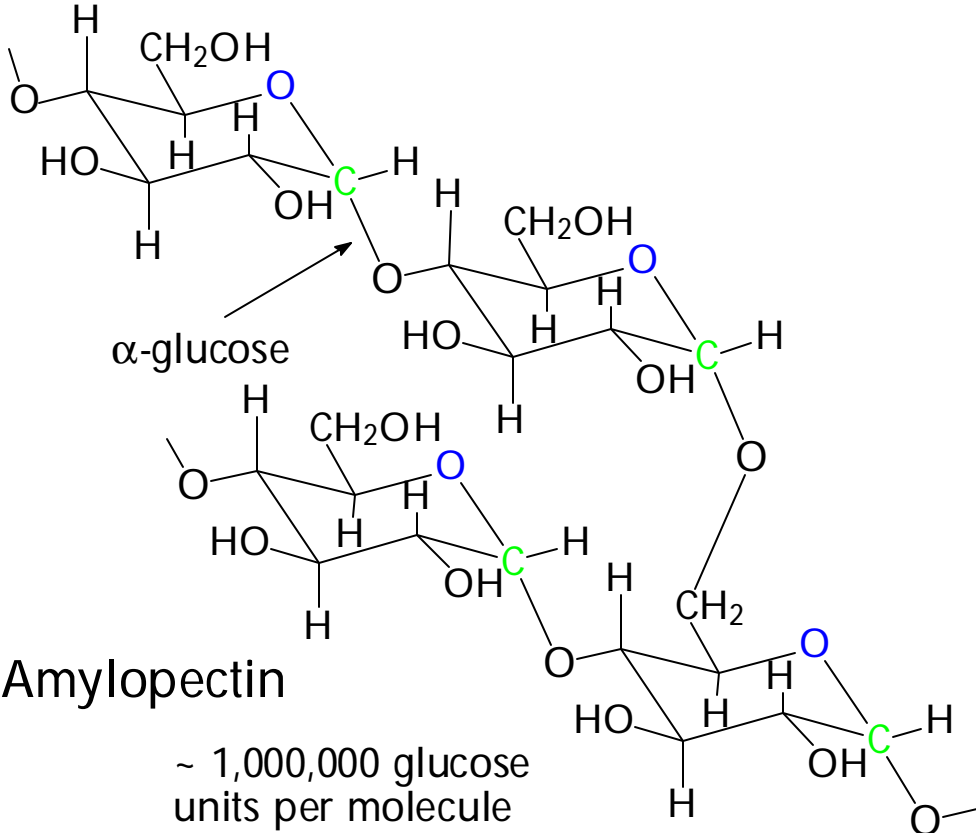
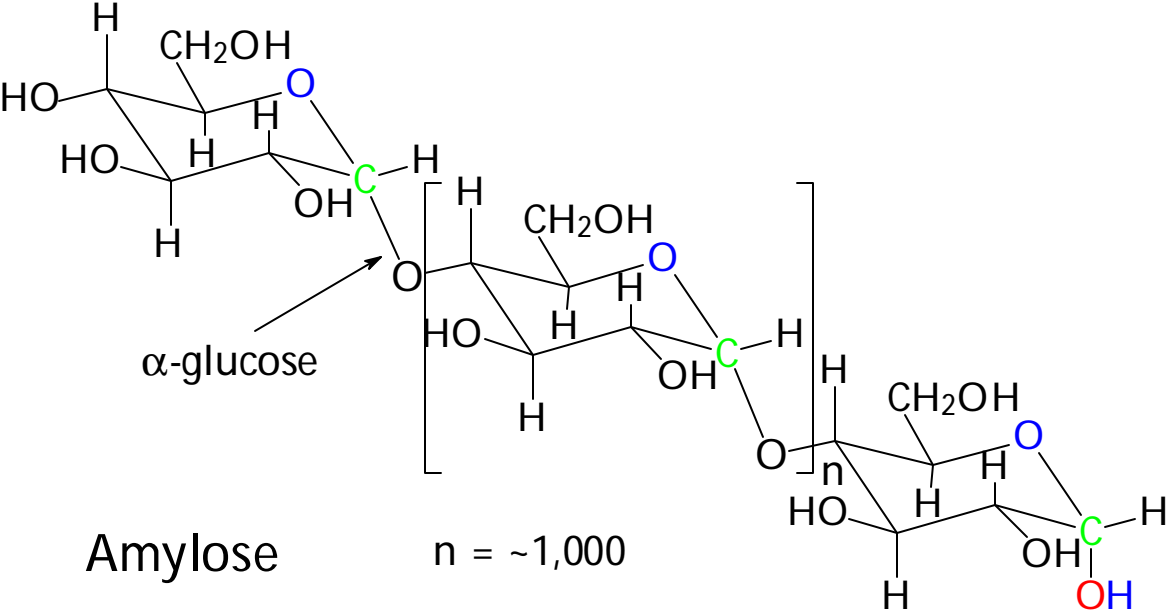
A sugar which reduces Tollen's reagent or Benedict's solution is called a reducing sugar. It is the aldehyde or α -hydroxyketone group that is oxidized. Therefore, glycosides are not reducing sugars (unless R, itself, is a hemiacetal that can open to an aldose or ketose.)

If the alcohol that reacts with the monosaccharide is itself a monosaccharide the glycoside that results is a disaccharide. Attachment of additional monosaccharide units results in tri-, tetra-, ..., polysaccharides.

Sucrose is a disaccharide: α -glucose is linked to β -fructose.



Starch: α -glucose polymers.



Cellulose: β -glucose polymer.

