

Correct

Incorrect

Types of functional groups

Monosaccharides can be classified into aldoses and ketoses.

Aldoses are monosaccharides with an aldehyde group.

Ketoses are monosaccharides containing a ketone group.

For example, the monosaccharide *glucose* is an *aldohexose*; that is, it has six-carbon (-hexose) and an aldehyde group (aldo-). Similarly *fructose* is a *ketohexose*; that is, it has six-carbon (-hexose) and a ketone group (keto-). Trioses are simplest monosaccharides. There are two trioses- dihydroxyacetone and glyceraldehyde. Dihydroxyacetone is a *ketose* because it contains a *keto* group, whereas glyceraldehyde is an *aldose* because it contains an *aldehyde* group.

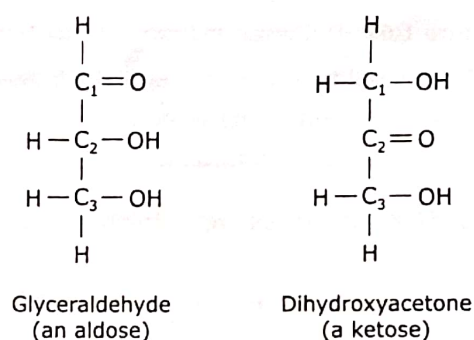


Figure 1.60 Trioses, the simplest monosaccharides.

All the monosaccharides except *dihydroxyacetone* contain one or more chiral carbon atoms. Glyceraldehyde has a central carbon (C-2) which is chiral or asymmetrical. Chiral molecules such as glyceraldehyde can exist in two configurations that are non-superimposable mirror images of each other. These two configurations are called *enantiomers*. An enantiomer is identified by its absolute configuration. Glyceraldehyde has two absolute configurations. When the hydroxyl group attached to the chiral carbon is on the left in a Fischer projection, the configuration is L; when the hydroxyl group is on the right, the configuration is D.

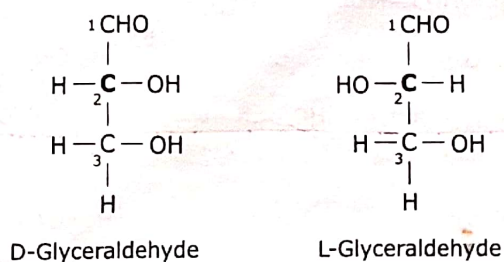


Figure 1.61 The enantiomers of glyceraldehyde. The configuration of groups around the chiral carbon 2 (shown in bold) distinguishes D-glyceraldehyde from L-glyceraldehyde. The two molecules are mirror images and cannot be superimposed on one another.

The absolute configurations of monosaccharide containing more than one chiral centers like hexose are determined by comparing the configuration at the highest-numbered chiral carbon (the chiral carbon farthest from the aldehyde or ketone group) to the configuration at the single chiral carbon of glyceraldehyde.

1.8.2 Epimers

Many common sugars are closely related, differing only by the stereochemistry at a single carbon atom. For example, D-glucose and D-mannose differ only at carbon 2. Sugars that differ only by the stereochemistry at a single carbon (other than anomeric carbon) are called *epimers*. Similarly D-glucose and D-galactose are epimers. D-mannose and D-galactose are not epimers because their configuration differ at more than one carbon.

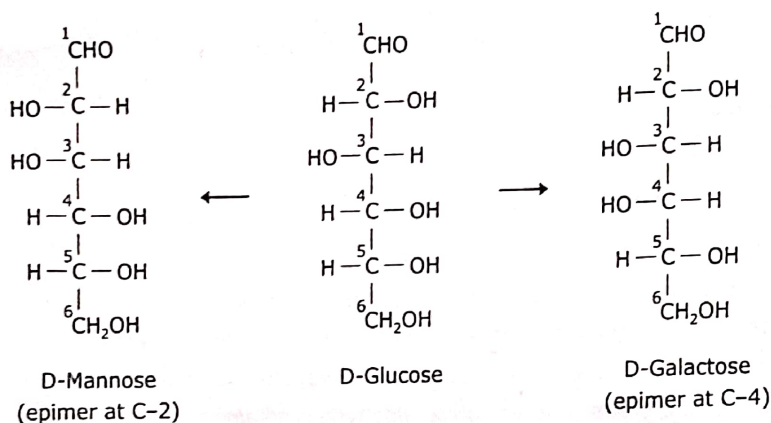


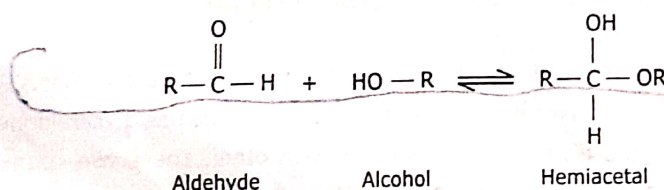
Figure 1.62 D-Glucose and two of its epimers.

1.8.3 Cyclic forms

Monosaccharides having 5 or 6 carbons in the chain gives cyclic structure in aqueous solution via internal hemiacetal or hemiketal formation.

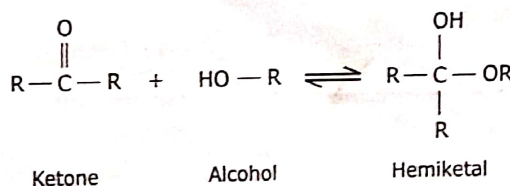
Hemiacetal

In general, an aldehyde can react with an alcohol to form a *hemiacetal*.



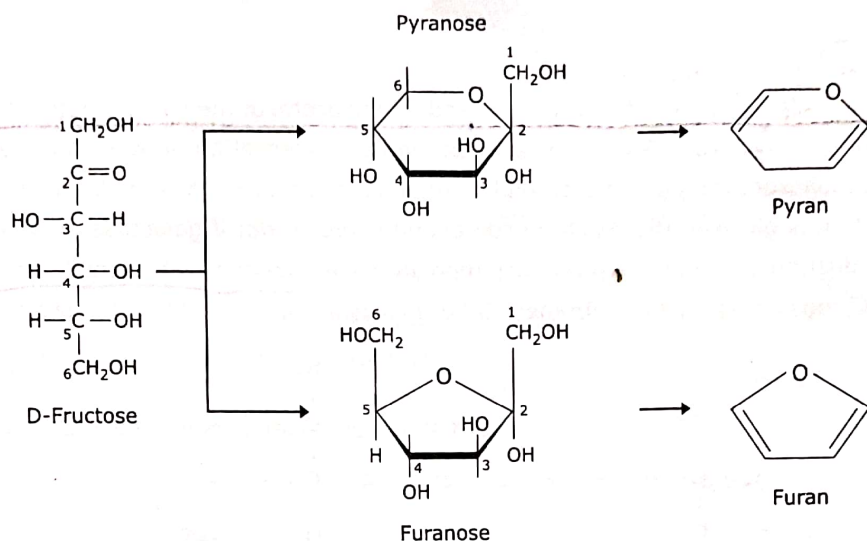
Hemiketal

A ketone can react with an alcohol to form a *hemiketal*.



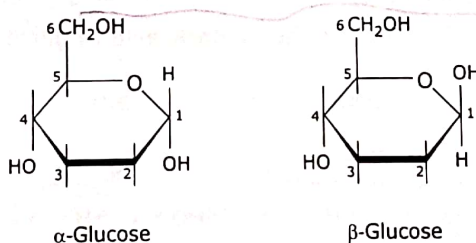
For an aldohexose such as glucose, the C-1 aldehyde group in the open-chain form of glucose reacts with the C-5 hydroxyl group to form an intramolecular *hemiacetal*. The resulting cyclic hemiacetal, a six-membered ring, is called *pyranose* because of its similarity to **pyran**.

Similarly, the C-2 keto group in the open-chain form of a ketohexose, such as fructose, can form an intramolecular *hemiketal* by reacting with either the C-6 hydroxyl group to form a six-membered cyclic hemiketal or the C-5 hydroxyl group to form a five-membered cyclic hemiketal. The five-membered ring is called a *furanose* because of its similarity to **furan**. Thus, fructose forms both pyranose and furanose rings.



Aldopentoses such as ribose can form furanose or pyranose rings. For the five carbon sugar ribose, the pyranose form arises when the carbonyl group reacts with the terminal hydroxyl group. The carbon 5 is incorporated into the ring. If cyclization occurs between the hydroxyl group on carbon 4 and the carbonyl group then the furanose ring forms. This places the carbon 5 outside the ring.

Cyclic structure exists in two different configurational forms. If the hydroxyl on the anomeric carbon is below the plane of the ring, it is said to be in the α -position; if above the plane of the ring, it is in the β -position. These two diastereoisomers are called **anomers** and the hemiacetal or hemiketal carbon is known as *anomeric carbon*.



In glucose, the C-1 carbon atom is called the *anomeric carbon atom*, and the α and β forms are called *anomers* (as shown in the figure). An equilibrium mixture of glucose contains approximately 37% α -form and 63% β -form and less than 1% of the open chain form. The two anomers have different physical and chemical properties. For example α -D-glucose has a specific rotation of $+112^\circ$ whereas the β -D-glucose form has a specific rotation of $+19^\circ$. When either of these pure substances is dissolved in water, the specific optical rotation of the solution slowly changes until it reaches an equilibrium value of specific rotation of $+52.7^\circ$. In aqueous solution the interconversion of α - and β -forms via the open chain structure, to give an equilibrium mixture is known as **mutarotation**.

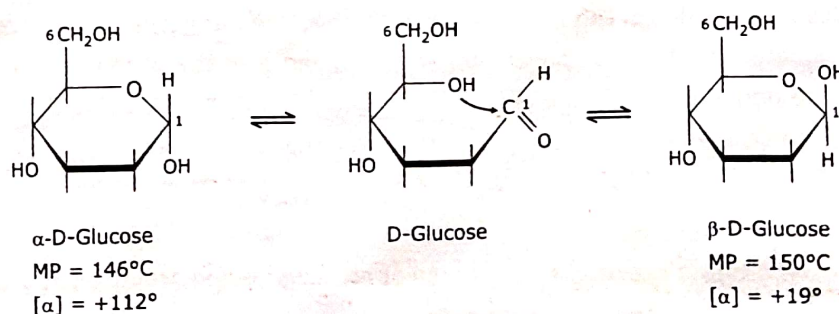


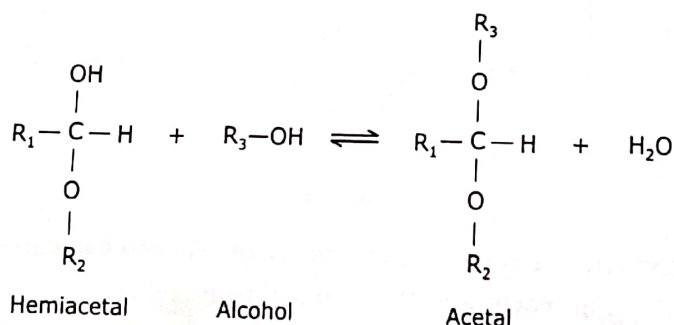
Figure 1.63 The α and β cyclic isomers of D-glucose can interconvert, with the open-chain structure as the intermediate.

The same nomenclature applies to the furanose ring form of fructose, except that α and β refer to the hydroxyl groups attached to C-2, the anomeric carbon atom.

1.8.4 Derivatives of monosaccharide

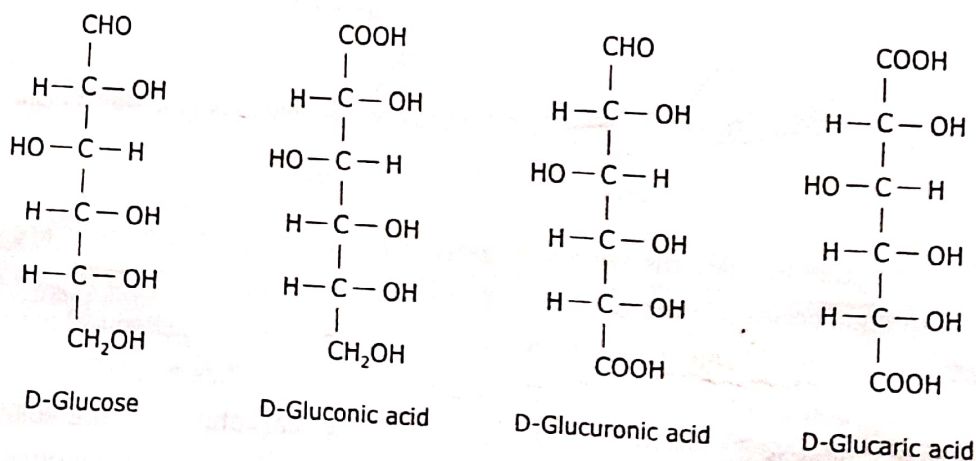
Glycosides

When hemiacetals react with alcohols, it forms acetals and if hemiacetal of the sugar reacts with an alcohol to form an acetal, it is known as a *glycoside*. Glycosides are formed by condensation between the hydroxyl group of the anomeric carbon of a monosaccharide, and a second compound that may or may not be another monosaccharide. If the hemiacetal portion is glucose, the resulting compound is *glucoside*; if galactose, a *galactoside*; and so on. Glycosides are widely distributed in nature. A very common glycoside is *ouabain* which inhibits the action of enzymes that pump Na^+ and K^+ ions across cell membranes. Other glycosides include antibiotics such as streptomycin.



Sugar acids

The aldehyde group in aldoses can be oxidized to produce a class of monosaccharides called **aldonic acids** (if glucose, it is gluconic acid). One important aldonic acid is *L-ascorbic acid* or *vitamin C*. Aldoses can undergo selective oxidation also. If terminal -OH group oxidizes, it produces uronic acid (if glucose, it is glucuronic acid). If both the aldehyde group and the terminal -OH oxidizes then **aldaric acid** (if glucose, it is glucaric acid) is produced.



Sugar alcohols

Carbonyl groups in aldoses and ketoses can be reduced to the hydroxyl group to form *sugar alcohols* or *alditols*. Sugar alcohols are designated by the addition of *-itol* with the name of the parent sugar. The reduction of the carbonyl group of glucose and xylose produce polyhydroxy alcohols.