

4. Functional Isomerism

Functional isomers have the same molecular formula but differ in their functional groups. For example, glucose and fructose have same molecular formula $C_6H_{12}O_6$, but glucose contains aldehyde as functional group and fructose keto group (Fig. 1.5). Hence, glucose and fructose are functional isomers. This type of functional isomers is also called as *aldose-ketose isomerism* because aldose is an isomer of ketose and vice versa.

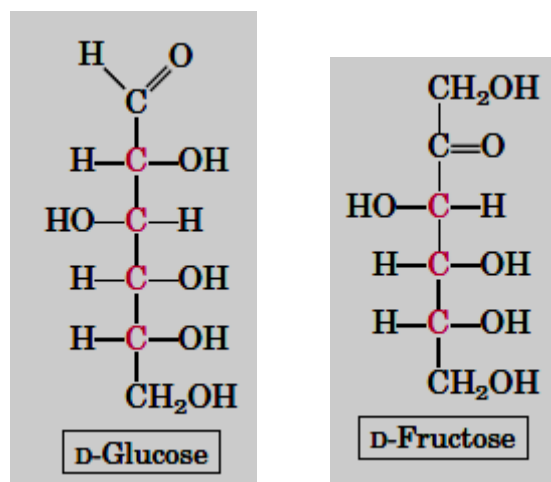


Figure 1.5 Aldose-ketose isomerism

5. Ring Structures

In solution, the functional aldehyde group of glucose combines with hydroxyl group of 5th carbon atom. As a result a 6 numbered heterocyclic pyranose ring structure containing 5 carbons and one oxygen is formed (Fig. 1.6). The linkage between aldehyde group and alcohol is called 'hemiacetal' linkage. Similarly, a 5 numbered furanose ring structure form fructose when keto group combines with hydroxyl group on 5 carbon atom. The linkage between keto and alcohol group is called 'hemiketal' linkage (Fig. 1.7). Both hemiacetal and hemiketal are intramolecular linkages.

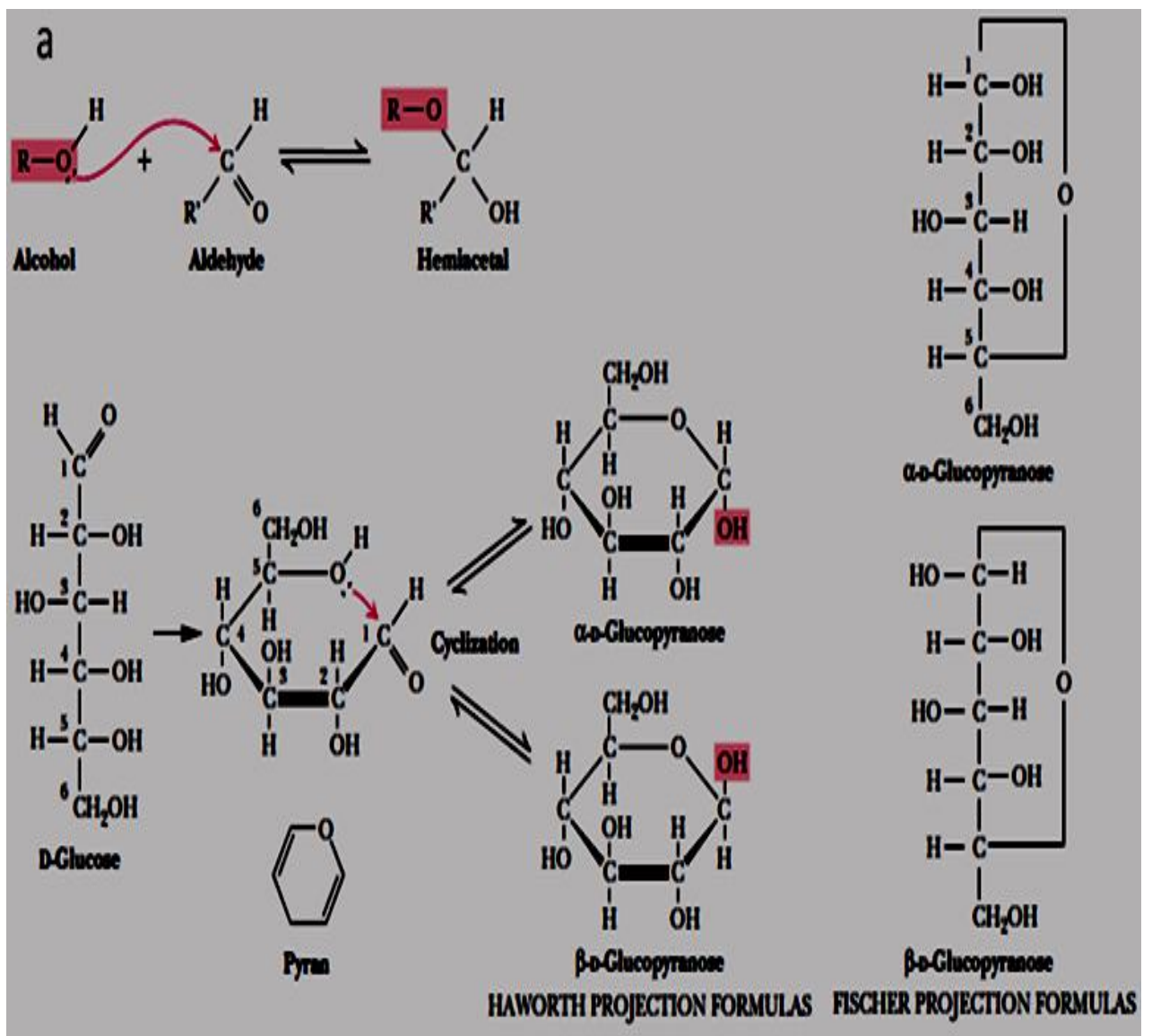


Figure 1.6 Glucose ring structure formation

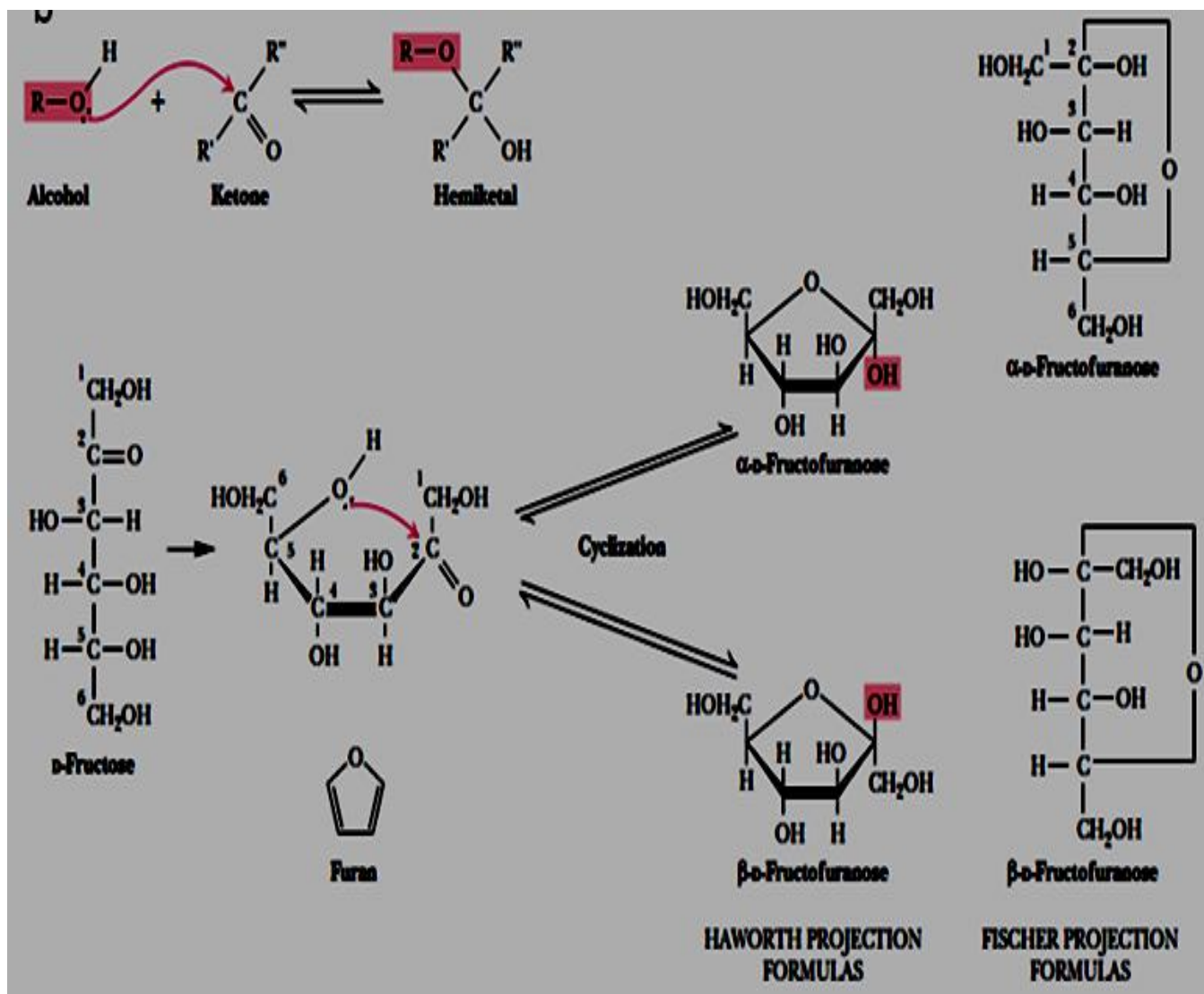


Figure 1.7 Formation of fructose ring structure

6. Anomers

Those monosaccharides that differ in configuration of OH group on carbonyl carbon or anomeric carbon are called anomers. Formation of ring structure of glucose generates anomers of glucose, which are designated as α and β forms. These two forms of glucose differ in the configuration of OH on carbonyl carbon or 1st carbon atom. In the α -form the hydroxyl group on anomeric carbon (1st carbon) atom points to the right whereas in the β -form to the left (Fig. 1.6 and Fig. 1.7).

7. Mutarotation

Monosaccharides containing asymmetric carbon atom rotate plane polarized light. When optical rotation for α -D-glucose is measured it will be 112° and on standing the rotation decreased slowly and attains a constant value $+52.5^\circ$. Likewise when optical rotation for β -D-glucose is measured the rotation changed from initial $+19^\circ$ to $+52.5$. the change in optical rotation for α and β forms of glucose are shown in (Fig. 1.8). The changed in optical rotation when either form of glucose is allowed to stand in solution is called mutarotation. It is due to conversion of cyclic form of glucose to straight chain form.

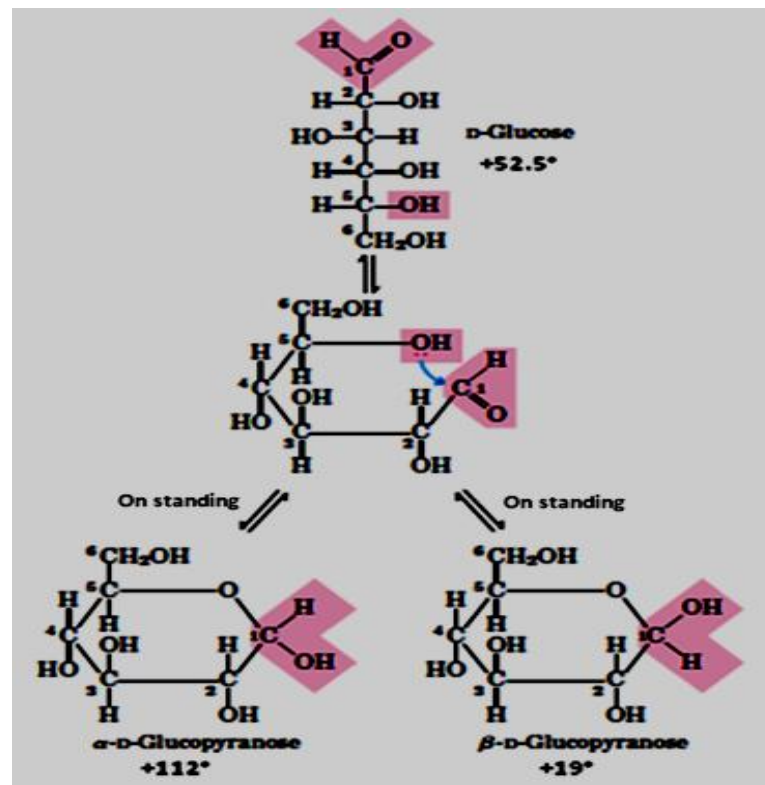


Figure 1.8 Mutarotation of glucose

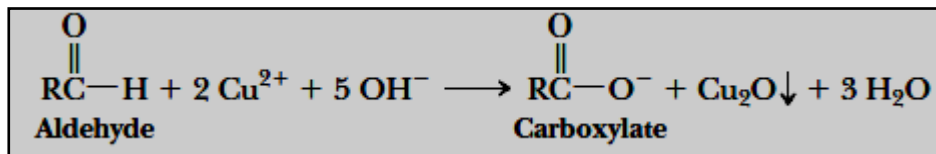
Importance of monosaccharides in the metabolic point of view are glucose, fructose, galactose, ribose, erythrose and glyceraldehydes. Glucose is found in several fruit juice blood of humans and in honey. Galactose is referred as dextrose. All monosaccharides containing free aldehyde or keto group reduce ions like Cu^{2+} under alkaline conditions.

Biologically Important Sugar (Glucose) Derivatives

Sugar derivatives of biological importance are sugar acids, sugar alcohol, deoxy sugars, sugar phosphates, amino sugars and glycosides.

1. Sugar acids

Sugars with free anomeric carbon atoms are reasonably good reducing agents and will reduce hydrogen by certain metals (Cu^{2+} and Ag^+) and other oxidizing agents. Such reactions convert the sugar to a sugar acid. For example, addition of alkaline CuSO_4 (called *Fehling's solution*) to an aldose sugar produces a red cuprous oxide (Cu_2O) precipitate:



and converts the aldose to an aldonic acid, such as gluconic acid (Fig. 1.8).

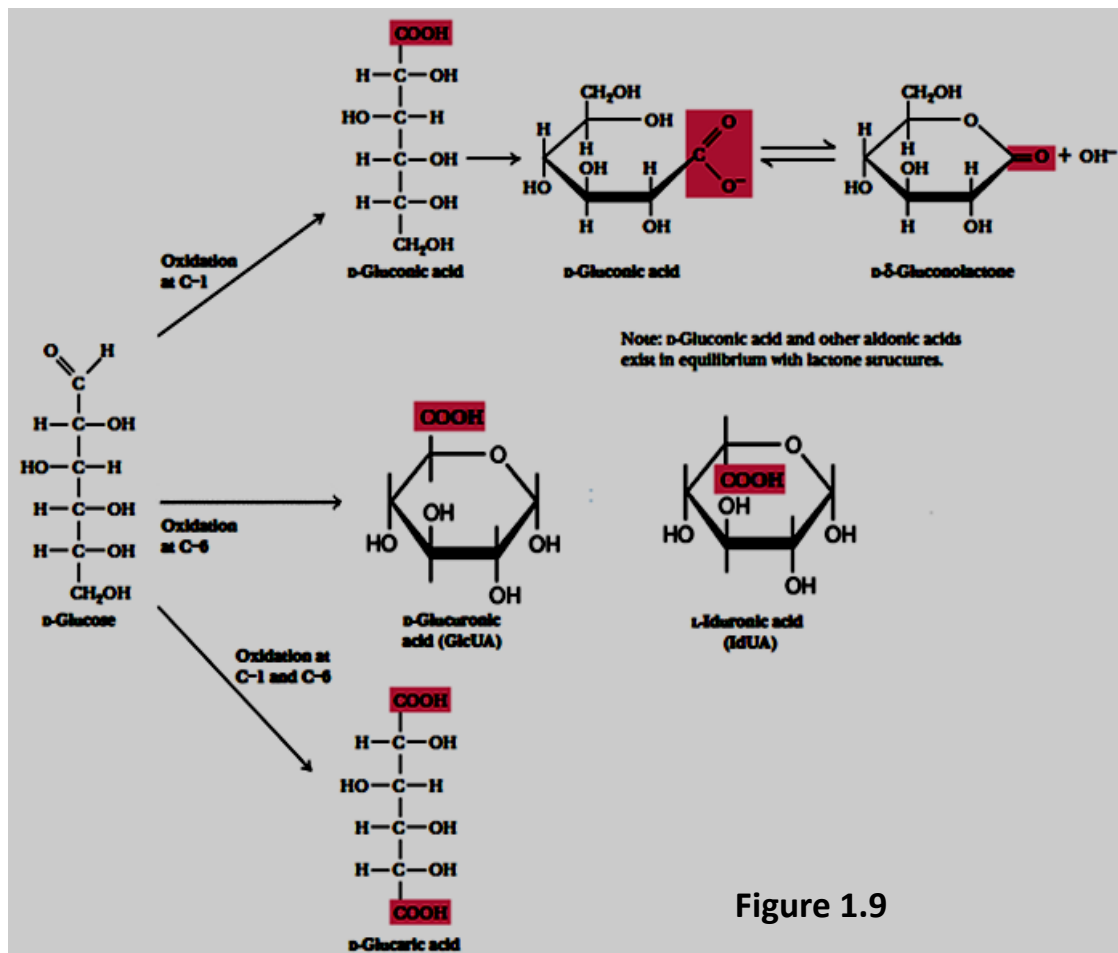


Figure 1.9

Formation of a precipitate of red Cu_2O constitutes a positive test for an aldehyde. Carbohydrates that can reduce oxidizing agents in this way are referred to as reducing sugars. By quantifying the amount of oxidizing agent reduced by a sugar solution, one can accurately determine the concentration of the sugar. *Diabetes mellitus* is a condition that causes high levels of glucose in urine and blood, and frequent analysis of reducing sugars in diabetic patients is an important part of the diagnosis and treatment of this disease. Over-the-counter kits for the easy and rapid determination of reducing sugars have made this procedure a simple one for diabetics. Monosaccharides can be oxidized enzymatically at C-6, yielding uronic acids, such as D-glucuronic and L-iduronic acids (Fig. 1.8). L-Iduronic acid is similar to D-glucuronic acid, except for having an opposite configuration at C-5. Oxidation at both C-1 and C-6 produces aldaric acids, such as D-glucaric acid.

2. Sugar alcohols

another class of sugar derivative, can be prepared by the mild reduction of the carbonyl groups of aldoses and ketoses. Sugar alcohols, or **alditols**, are designated by the addition of *-itol* to the name of the parent sugar. The alditols are linear molecules that cannot cyclize in the manner of aldoses. Other sugar alcohols are glycerol and inositol. The alcohols formed from glucose, galactose and fructose are sorbitol, galactitol and sorbitol respectively. Sorbitol buildup in the eyes of diabetics is implicated in cataract formation. Glycerol and myo -inositol, a cyclic alcohol, are components of lipids. There are nine different stereoisomers of inositol. The one shown in Figure 1.9 was first isolated from heart muscle and thus has the prefix myo- for muscle.

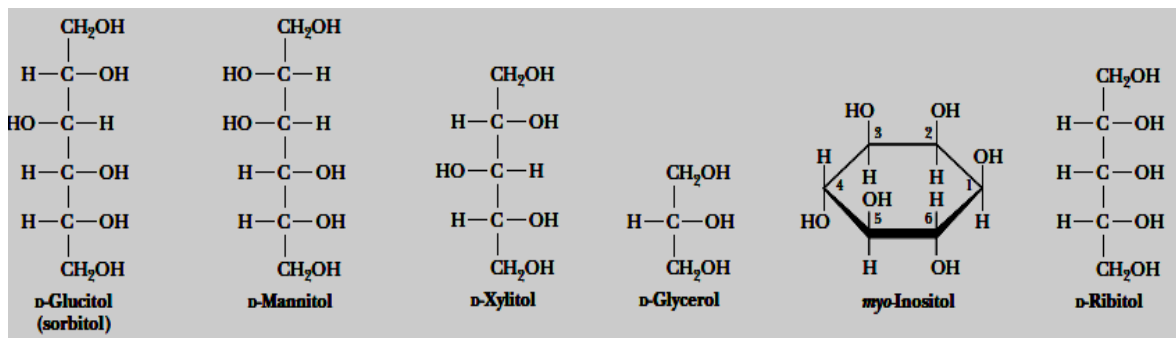


FIGURE 1.10 Structures of some sugar alcohols

3. Sugar phosphates: Breakdown of sugar in animals involves formation of sugar phosphates. Glucose-6-phosphate is an example for sugar phosphate.

4. Deoxy Sugars

The **deoxy sugars** are monosaccharides with one or more hydroxyl groups replaced by hydrogens. 2-Deoxy-D-ribose is a constituent of DNA in all living things. Deoxy sugars also occur frequently in glycoproteins and polysaccharides. L-Fucose and L-rhamnose, both 6-deoxy sugars, are components of some cell walls, and rhamnose is a component of **ouabain**, a highly toxic *cardiac glycoside* found in the bark and root of the ouabaio tree.

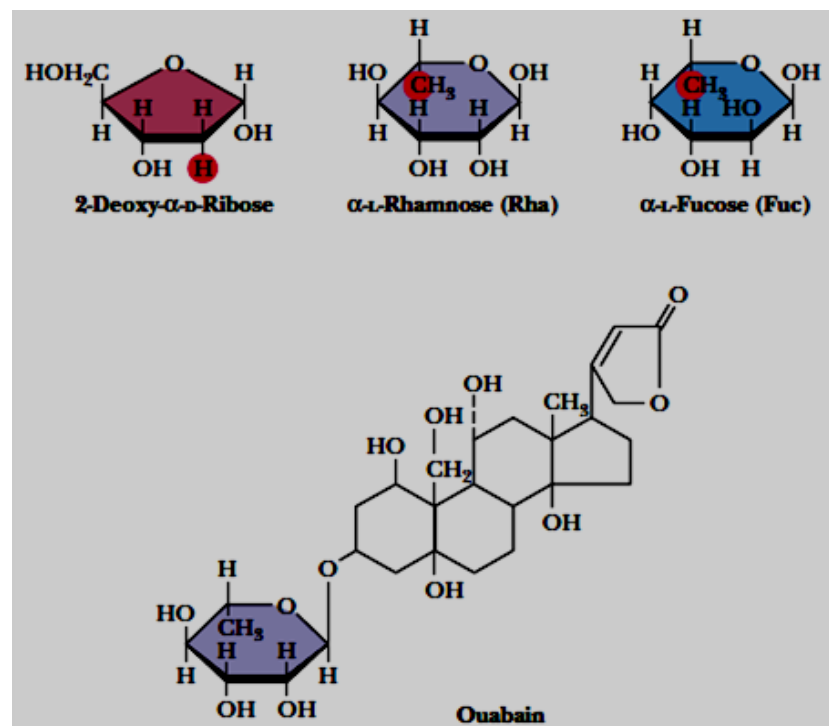


FIGURE 1.11 Several deoxy sugars and ouabain, which contains α -L-rhamnose (Rha).

5. Amino sugars

Including D-glucosamine and D-galactosamine (Fig. 1.11), contain an amino group (instead of a hydroxyl group) at the C-2 position. They are found in many oligo- and polysaccharides, including *chitin*, a polysaccharide in the exoskeletons of crustaceans and insects.

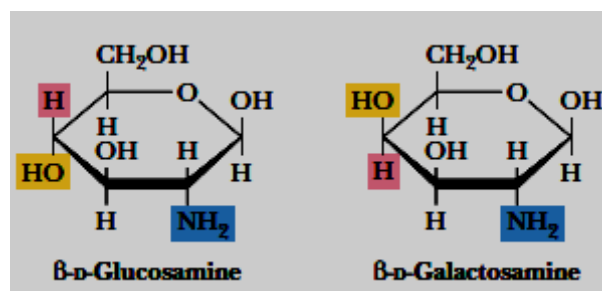


FIGURE 1.12 Structures of D-glucosamine and D-galactosamine.

6. Glycosides

Are two types:

(a) **O-glycosides.** When hydroxyl group on anomeric carbon of a sugar reacts with an alcohol (sugar) O-glycoside is formed. O-glycoside linkage is present in disaccharides and polysaccharides. So, disaccharides, oligosaccharides and polysaccharides are O-glycosides.

(b) **N-glycosides.** Are formed when hydroxyl group on anomeric carbon of sugar react with an amine. N-glycosidic linkage is presents in nucleotides, RNA and DNA. So, nucleotides, RNA and DNA are examples of N-glycosides.