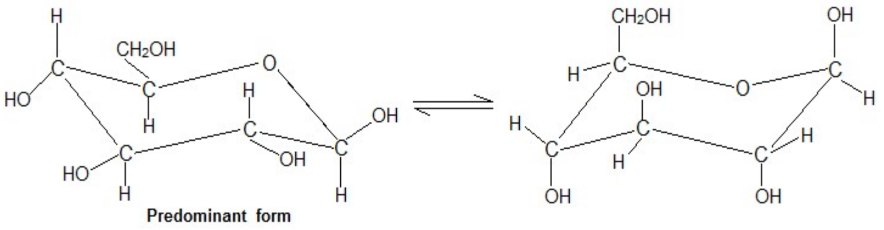


Figure (1.9): The two alternative chair conformations of β-D-glucopyranose. In the conformation on the left, which predominates, the relatively bulky OH and CH_2OH substituents all occupy equatorial positions, whereas in that on the right they occupy the more crowded axial positions.

The majority, about 64% of D-glucose exist in β form because when the molecule is in chair conformation, all the bulky hydroxyl groups will be placed in equatorial position which have lesser steric hindrance between the bulky groups. Thus, β-D-glucose is more stable than α-D-glucose that occupied typically 35% of D-glucose molecules, whereas the remaining 1% is in the open-chain form.

Monosaccharides as reducing agents:

A reducing sugar is any sugar that either has an aldehyde group or is capable of forming one in solution through isomerism. The aldehyde functional group allows the sugar to act as a reducing agent, for example in the Tollens' test or Benedict's reagent.

Reducing sugars can be oxidized by relatively mild oxidizing agents such as cupric ion (Cu^{2+}) (Fig. 1-10). The carbonyl carbon (aldehyde group) is oxidized to a carboxylic acid, at the same time; cupric ion (Cu^{2+}) is reduced to cuprous ion (Cu^{1+}).

Reducing sugar: A carbohydrate that reacts with a mild oxidizing agent under basic conditions to give an aldonic acid; the carbohydrate reduces the oxidizing agent.

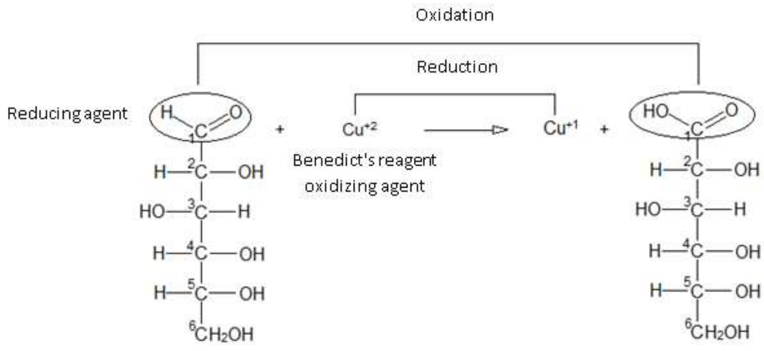


Figure (1.10): Oxidation process by reducing sugar.

In fact, a sugar is classified as a reducing sugar only if it has an open-chain form with an aldehyde group or a free hemiacetal group. Monosaccharides which contain an aldehyde group are known as aldoses, and those with a ketone group are known as ketoses. The aldehyde can be oxidized via a redox reaction in which another compound is reduced. Thus, a reducing sugar is one that reduces certain chemicals. Sugars with ketone groups in their open chain form are capable of isomerizing via a series of tautomeric shifts to produce an aldehyde group in solution. Therefore, ketone-bearing sugars like fructose are considered reducing sugars but it is the isomer containing an aldehyde group which is reducing since ketones cannot be oxidized without decomposition of the sugar. This type of isomerization is catalyzed by the base present in solutions which test for the presence of aldehydes. Under the basic conditions of the oxidation process, Carbon 1 (a CH_2OH group) of a ketose is not oxidized directly. Instead, a 2-ketose exists in equilibrium with an aldose by way of an enediol intermediate (Fig. 1.11).

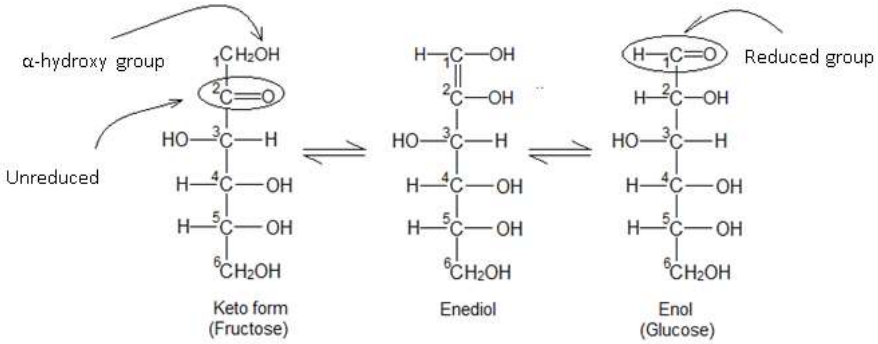


Figure (1.11): Equilibrium between ketose and aldose by way of an enediol intermediate.

Disaccharides and Oligiosaccharides:

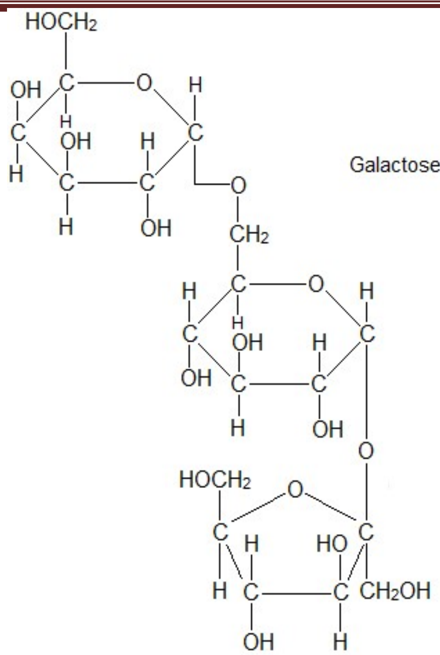
Most carbohydrates in nature contain more than one monosaccharide unit. Those that contain two units are called disaccharides; those that contain three units are called trisaccharides, and so forth. We use the general term oligosaccharide to describe carbohydrates that contain from three to ten monosaccharide units, which can be hydrolyzed by enzymes or acid to give the constituent monosaccharide units. Carbohydrates containing larger numbers of monosaccharide units are called polysaccharides.

Disaccharide: A carbohydrate containing two monosaccharide units joined by a glycosidic bond.

Figure (1.12) represents the chemical structure of Raffinose, which is a trisaccharide composed of galactose, glucose and fructose. Raffinose can be found in peas, beans, cabbage, brussels sprouts, broccoli, asparagus, other vegetables and whole grains.

Oligosaccharide: A carbohydrate containing from three to ten monosaccharide units, each joined to the next by a glycosidic bond.

Polysaccharide: A carbohydrate containing a large number of monosaccharide units, each joined to the next by one or more glycosidic bonds.



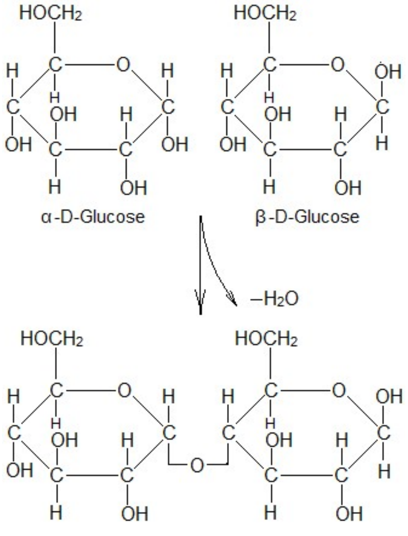
Raffinose
Galactose α(1-6) glucose α(1-2) fructose

Figure (1.12): Chemical structure of Raffinose.

In a disaccharide, two monosaccharide units are joined by a glycosidic linkage between the anomeric carbon of one unit and an OH group of the other unit. Three important disaccharides are sucrose, lactose, and maltose.

Maltose:

Maltose derives its name from its presence in malt, the juice from sprouted barley and other cereal grains. It consists of two units of D-glucopyranose joined by a glycosidic bond between carbon 1 (the anomeric carbon) of one unit and carbon 4 of the other unit. Because the oxygen atom on the anomeric carbon of the first glucopyranose unit is alpha, the bond joining the two units is an α-1,4-glycosidic bond.



Maltose
Glucose α(1-4) glucose

Maltose has been recorded occasionally in plants. It is usually obtained as a product of the enzyme hydrolysis of starch during germination or malting process. It is used as a sweetener and as a substrate for fermentation. Maltose is a reducing sugar; the hemiacetal group on the right unit of D-glucopyranose is in equilibrium with the free aldehyde and can be oxidized to a carboxylic acid (Fig. 1.13).

***Note: If two monosaccharides are linked through their anomeric centers the disaccharide formed is a non-reducing disaccharide. If one monosaccharide is linked by one of its other hydroxyl groups, then the anomeric center is unsubstituted and a reducing disaccharide occurs*.**

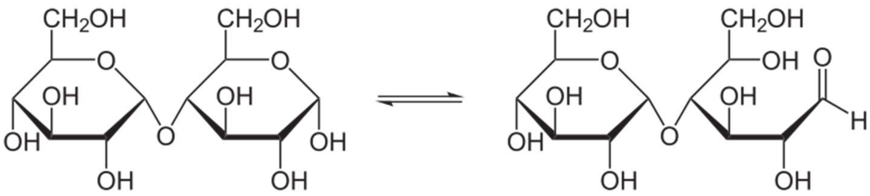
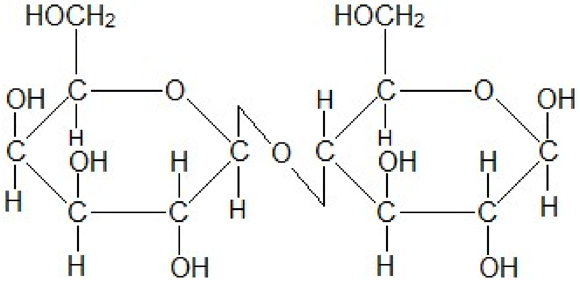


Figure (1.13): Equilibrium between cyclic and open-chain form in one ring of maltose.

Lactose:

Lactose is the principal sugar present in milk. It accounts for 5 to 8% of human milk and 4 to 6% of cow's milk. It is digested by the enzyme Lactase. Pure lactose is found in whey, the watery byproduct of cheese production.

Lactose consists of D-galactopyranose bonded by a β-1,4-glycosidic bond to carbon 4 of D-glucopyranose. It is a reducing sugar, because the cyclic hemiacetal of the D-glucopyranose unit is in equilibrium with its open-chain form and can be oxidized to a carboxyl group.

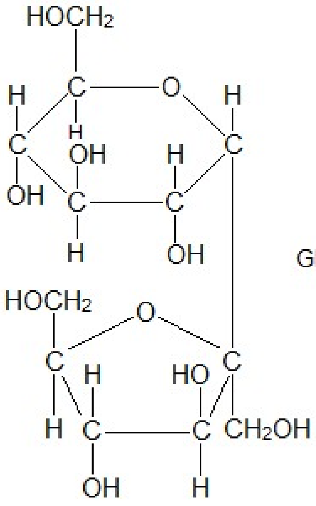


Lactose
Galactose β(1-4) glucose

Sucrose:

Sucrose (table sugar, 10^8 tons of sucrose are produced annually for consumption) is the most abundant disaccharide in the biological world. It is found in fruits, nectar, sugar cane, and sugar beets; maple syrup contains about 65% sucrose, with glucose and fructose present as well. Caramel is the solid residue formed from heating sucrose. A flavoring agent called invert sugar is produced by the hydrolysis of sucrose under acidic conditions, which breaks it apart into glucose and fructose; invert sugar is sweeter than sucrose because of the fructose. Some of the sugar found in honey is formed in this fashion; invert sugar is also produced in jams and jellies prepared from acid-containing fruits.

In sucrose, carbon 1 of α-D-glucopyranose bonds to carbon 2 of D-fructofuranose by an α-1,2-glycosidic bond. Because the anomeric carbons of both the glucopyranose and fructofuranose units are involved in formation of the glycosidic bond, neither monosaccharide unit is in equilibrium with its open-chain form. Thus sucrose is a non-reducing sugar.



Sucrose
Glucose α(1-2)β -fructose

Polysaccharides:

Polysaccharides consist of large numbers of monosaccharide units bonded together by glycosidic bonds. The polysaccharides found in nature either serve a structural function (structural polysaccharides) or play a role as a stored form of energy (storage polysaccharides). They are not reducing sugars, since the anomeric carbons are connected through glycosidic linkages. Three important polysaccharides, all made up of glucose units, are starch, glycogen, and cellulose.