

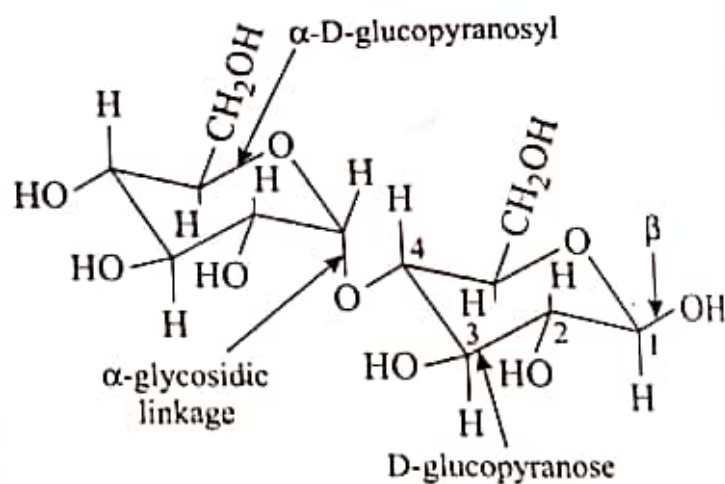
13. DISACCHARIDES : LINKAGE BETWEEN TWO MONOSACCHARIDES

The anomeric carbon of a monosaccharide can react with the hydroxyl group of an alcohol to give an acetal called a *glycoside*. If the hydroxyl group is part of another sugar molecule, then the glycoside is a *disaccharide*. Thus disaccharides are compounds with two monosaccharide (same or different) units linked together by an acetal linkage. This acetal linkage is known as glycosidic linkage.

In principle, the anomeric carbon can react with *any* of the hydroxyl groups of another sugar to form a disaccharide. In naturally occurring disaccharides, however, there are three principal glycosidic bonding arrangements.

1. A 1, 4-link. The anomeric carbon (C-1) of one monosaccharide is bonded to the oxygen atom on (C-4) of the other. Examples are lactose, maltose and cellobiose.
2. A 1, 6-link. The anomeric carbon (C-1) of one monosaccharide is bonded to the oxygen atom on (C-6) of the second sugar. Examples are melibiose, gentibiose.
3. A 1, 1-link. The anomeric carbon (C-1) of the first sugar is bonded to the oxygen atom of the anomeric carbon of the second sugar. Example is sucrose.

The structure of disaccharides are drawn as below. The structure of the sugar, whose anomeric hydroxyl group is involved in glycosidic linkage is drawn on the left side and the other sugar, which is behaving as alcohol for glycosidic linkage formation, is drawn on the right hand side. The name of the disaccharide is derived by adding the suffix 'osyl' to the name of the sugar whose anomeric hydroxyl is involved in glycosidic linkage (*i.e.*, sugar of left hand) and then adding the name of the other sugar. A prefix *O*- is added before the name of the sugar to indicate its *O*-glycosidic nature. The number of carbon atoms involved in glycosidic bond are also indicated. Thus the structure of β -maltose, will be drawn as above will have the name 4-*O*-(α -D-glucopyranosyl)- β -D-glucopyranose.

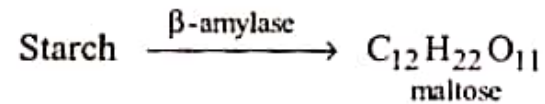


This name tells that a β -D-glucopyranose ring (the right hand ring) is substituted in its 4-position by an oxygen attached to a (β -D-glucopyranosyl) ring drawn on the left. The name in parantheses says that the substituent is an α -glucose, and the -syl ending indicates that the ring is in the form of a glycoside. Notice that the left ring with -syl ending exists as an acetal and cannot mutarotate, while the right ring with the -ose ending is a hemiacetal and can mutarotate.

Since α -anomeric hydroxyl group is involved in glycosidic linkage formation, it is called an α -glycoside.

1. Maltose

Maltose is the major product of the hydrolysis of starch by β -amylase (an enzyme).



The name *maltose* or *malt sugar* stems from the formation of this disaccharides by enzymic hydrolysis of the starch found in malt.

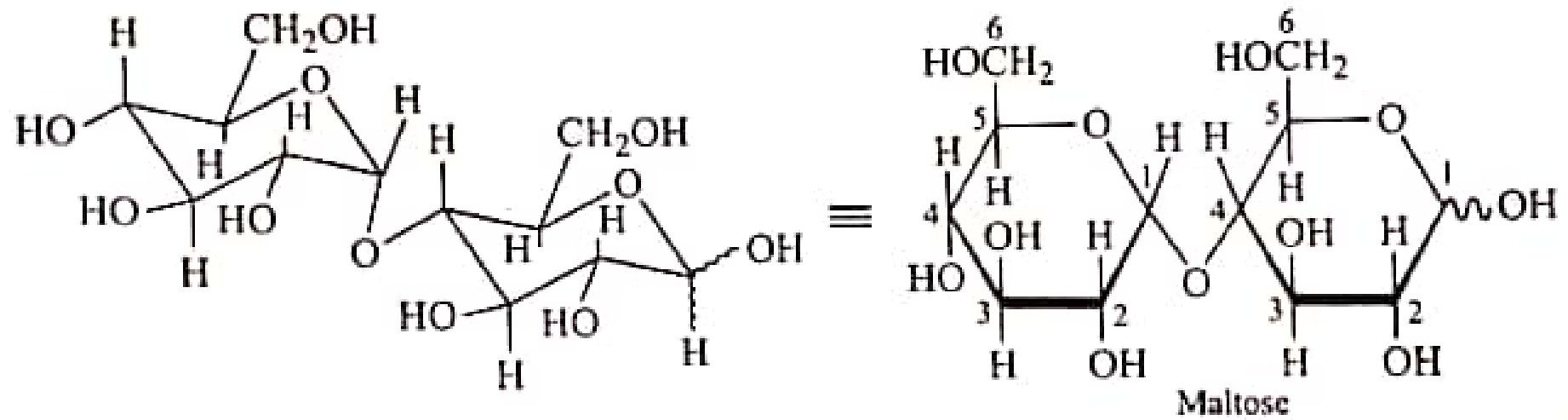
Structure of Maltose

1. The molecular formula of maltose is $\text{C}_{12}\text{H}_{22}\text{O}_{11}$.
2. One mole of maltose gives two moles of glucose on acid hydrolysis. Thus maltose is disaccharide of glucose.
3. Maltose is a reducing sugar; it gives positive test with Fehling's and Tollens solutions. Maltose also reacts with phenylhydrazine to form a monophenylosazone.
4. Maltose exists in two anomeric forms : α -maltose; $[\alpha] = +168^\circ$ and β -maltose; $[\alpha] = +112^\circ$

The anomers of maltose undergo mutarotation to yield an equilibrium mixture, $[\alpha] = +136^\circ$.

5. Maltose on oxidation with bromine water gives monobasic acid, maltobionic acid.

Facts 3, 4 and 5 indicate that one of the glucose residues of maltose is present in a hemiacetal (reducing unit) form; the other, therefore, must be present as a glucoside (acetal unit).



2. Lactose

Lactose is a naturally occurring disaccharide found in the milk of mammals including cows and humans. Lactose is hydrolysed by enzyme β -galactosidase (lactase). Some humans synthesise a β -galactosidase, others do not. This enzyme is present in the digestive fluids of normal infants to hydrolyse their mothers milk. Once the child stops drinking milk, production of this enzyme gradually stops. Consumption of milk or milk products can cause digestive discomfort in people who lack the β -galactosidase enzyme.

Structure of Lactose

1. The molecular formula of lactose is $C_{12}H_{22}O_{11}$.
2. One mole of lactose gives one mole of glucose and one mole of galactose on acid hydrolysis. Thus lactose is a disaccharide of glucose and galactose.
3. Lactose is a reducing sugar; it gives positive test with Fehling's and Tollens solutions. Lactose also reacts with phenylhydrazine to form a monophenylosazone.
4. Lactose exists in two anomeric forms; α -lactose and β -lactose.

3. Sucrose

The most common disaccharide is sucrose. Sucrose is obtained from sugar-cane and sugar-beets. Sucrose is also known as cane sugar or table sugar.

Structure of Sucrose

1. The molecular formula of sucrose is $C_{12}H_{22}O_{11}$.
2. On hydrolysis, one mole of sucrose gives one mole of glucose and one mole of fructose. Sucrose has a specific rotation of $+65.5^\circ$. When it is hydrolysed, the resulting equimolar mixture of glucose and fructose has a specific rotation of -22.0° . Because of the change in the sign of the rotation when sucrose is hydrolysed, a 1:1 mixture of glucose and fructose is called **invert sugar**. The enzyme that catalyses the hydrolysis of sucrose is called invertase. The most common form of invert sugar is honey, a supersaturated mixture of glucose and fructose hydrolysed from sucrose by the invertase enzyme of honeybees.
3. Sucrose gives negative test with Fehling's and Tollens solutions. It does not form an osazone and does not undergo mutarotation. Sucrose does not undergo oxidation by bromine water.

These results show that in sucrose the hemiacetal/hemiketal group is absent and thus sucrose is a nonreducing sugar. Thus the two

14. POLYSACCHARIDES

Polysaccharides contain as few as ten or as many as several thousand monosaccharide units joined together into long polymer chains. Except for a single unit at the end of the chain, all the anomeric carbon atoms of a polysaccharide are involved in acetal glycosidic link. Therefore, polysaccharides give no noticeable reaction with Tollens reagent, and they do not show mutarotation. Polysaccharides that are polymer of a single monosaccharide are called homopolysaccharides. Polysaccharides those made up of more than one type of monosaccharide are called heteropolysaccharides. Homopolysaccharides are also classified on the basis of their monosaccharide units. Polysaccharide of glucose is called as **glucan** and polysaccharide of galactose is called as **galactan** and so on. Similarly if

Out of many naturally occurring polysaccharides, the two most common and important are cellulose and starch.

1. Cellulose

Cellulose is glucose polysaccharide found in most plants. This polymer is insoluble in water and has an important structural function in plants. Wood contains about 50% of cellulose and cotton fibres are essentially pure cellulose. The most important physical properties result from the very high molecular weight of cellulose (3000 glucose units) and the fact that there is no branching in the molecule (*i.e.*, cellulose is a linear polymer). The most important chemical feature of cellulose is the $1 \rightarrow 4, \beta$ -linkage used to join the glucose units. The β -glucosidic linkage is not metabolised in human beings and some animals. However, some microorganisms,

2. Starch

Starch is a polysaccharide composed of many repeating glucose units. Plants use starch as their principle food reserve, storing the carbohydrate in the form of granules in the seeds, fruits, tubers or roots. Starch from different plants differ in their chemical composition.

Starch is a mixture of two different polysaccharides : (1) amylose ($\approx 20\%$), and (2) amylopectin ($\approx 80\%$). The two components may be separated as follows :