

Paper No. 01

Paper Title: Food Chemistry

Module-04: Food carbohydrates: Monosaccharides and Oligosaccharides

Monosaccharides

The simplest form of carbohydrates is the monosaccharide. Monosaccharides are either aldoses or ketoses. Aldoses such as glucose consists of a carbon backbone and a carbonyl group (C=O) located at the end of the chain. Ketoses such as fructose consists of a carbon backbone with a carbonyl group located at any other carbon in the chain. The remaining carbon atoms are bound to hydroxyl groups (-OH).

Monosaccharide classifications based on the number of carbons

Number of Carbons	Category Name	Examples
4	Tetrose	Erythrose, Threose
5	Pentose	Arabinose, Ribose, Ribulose, Xylose, Xylulose, Lyxose
6	Hexose	Allose, Altrose, Fructose, Galactose, Glucose, Gulose, Idose, Mannose, Sorbose, Talose, Tagatose
7	Heptose	Sedoheptulose, Mannoheptulose

Monosaccharides

Three common sugars glucose, galactose and fructose share the same molecular formula: $C_6H_{12}O_6$. Because of their six carbon atoms, each is a hexose. Although all three share the same molecular formula, the arrangement of atoms differs in each case. Substances such as these three, which have identical molecular formulas but different structural formulas, are known as structural isomers.

Glucose

"Blood sugar" is the immediate source of energy for cellular respiration. Glucose, which is also referred to as dextrose, is a moderately sweet sugar found in vegetables and fruit. When glucose is fermented by the enzyme zymase, in yeast, it results in the formation of carbon dioxide and ethyl alcohol. It is the basic structure to which all carbohydrates are reduced to in the end, for transport via the bloodstream and use by the cells of the body.

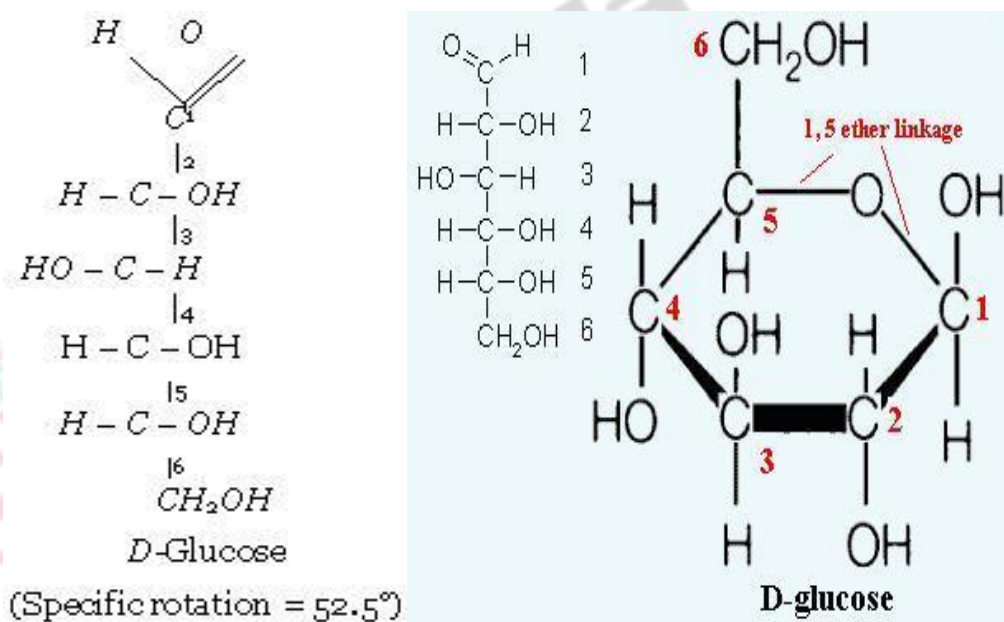
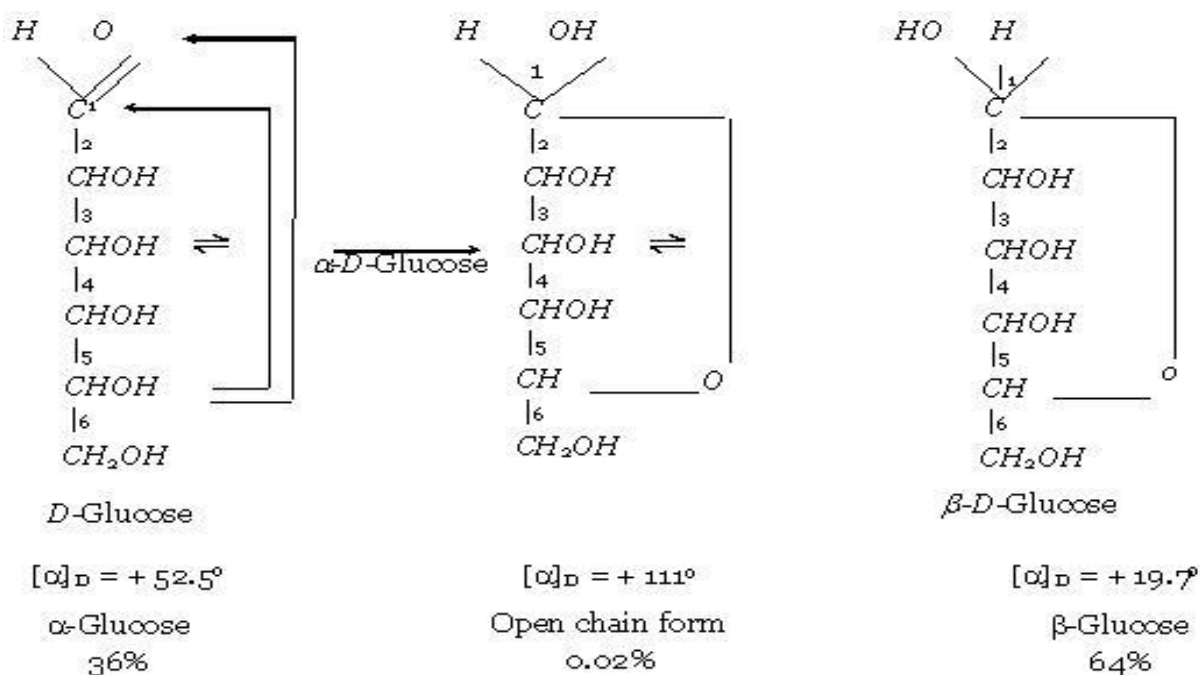


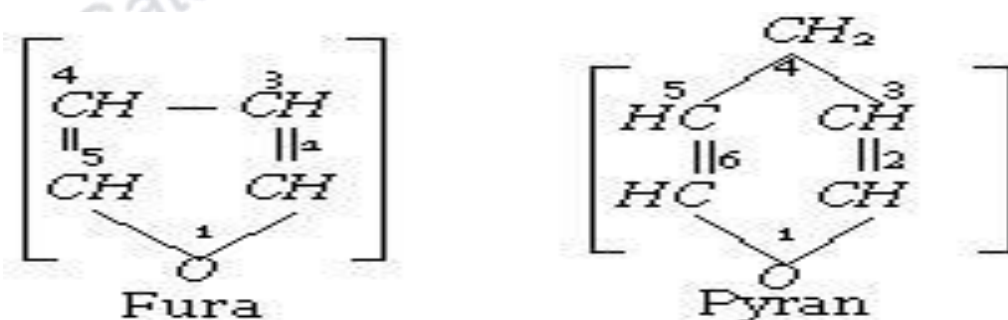
Figure: structure of glucose

Ordinary glucose is α -glucose, with a fresh aqueous solution has specific rotation, $[\alpha]_D + 111^\circ$. On keeping the solution for some time; α -glucose slowly changes into an equilibrium mixture of α -glucose (36%) and β -glucose (64%) and the mixture has specific rotation $+ 52.5^\circ$. Similarly a fresh aqueous solution of β -glucose having specific rotation, $[\alpha]_D + 19.7^\circ$, on keeping (standing) gradually changes into the same equilibrium mixture (having, specific rotation $+52.7^\circ$). So an aqueous solution of glucose shows a physical property, known

as **mutarotation**, i.e., a change in the value of specific rotation (muta=change; rotation = specific rotation) is called **mutarotation**.

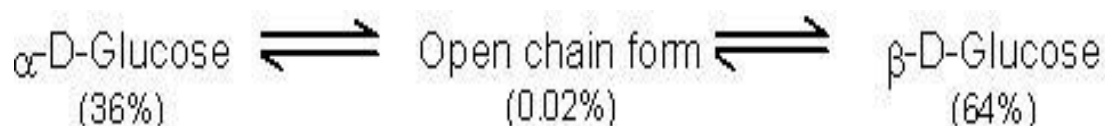


Fischer and Tollen's proposed that the ring or the internal hemiacetal is formed between C^1 and C^4 . It means the ring is **Furan type** or 5-membered ring; this is called **Furanose structure**. However according to Haworth and Hirst the ring is formed between C^1 and C^5 . It means the ring is **Pyran type** or 6-membered ring, this is called **Pyranose structure**.

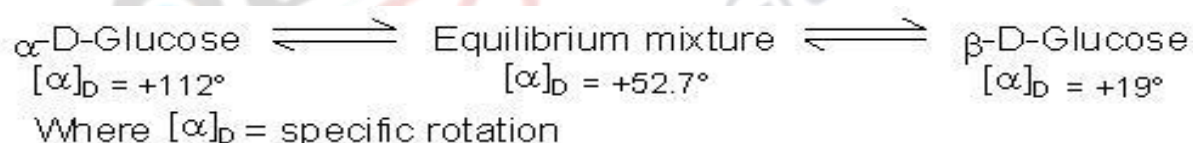


Mutarotation

The two stereoisomeric forms of glucose, i.e., α -D-glucose and β -D-glucose exist in separate crystalline forms and thus have different melting points and specific rotations. For example α -D-glucose has a m.p. of 419 K with a specific rotation of $+112^\circ$ while β -D-glucose has a m.p. of 424 K and has a specific rotation of $+19^\circ$. However, when either of these two forms is dissolved in water and allowed to stand, it gets converted into an equilibrium mixture of α - and β -forms through a small amount of the open chain form.



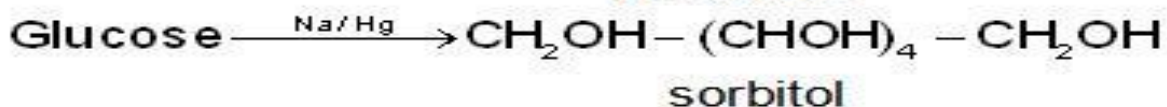
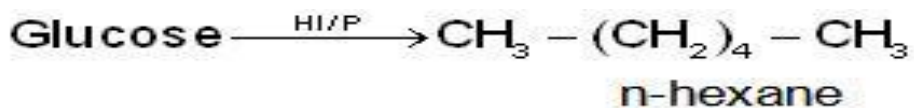
As a result of this equilibrium, the specific rotation of a freshly prepared solution of α -D-glucose gradually decreases from of $+112^\circ$ to $+52.7^\circ$ and that of β -D-glucose gradually increases from $+19^\circ$ to $+52.7^\circ$.



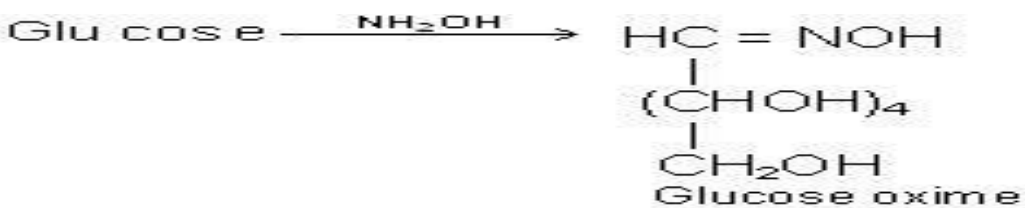
This change in specific rotation of an optically active compound in solution with time, to an equilibrium value, is called mutarotation. During mutarotation, the ring opens and then recloses either in the inverted position or in the original position giving a mixture of α - and β -forms. All reducing carbohydrates, i.e., monosaccharides and disaccharides (maltose, lactose etc.) undergo mutarotation in aqueous solution.

Reactions of glucose

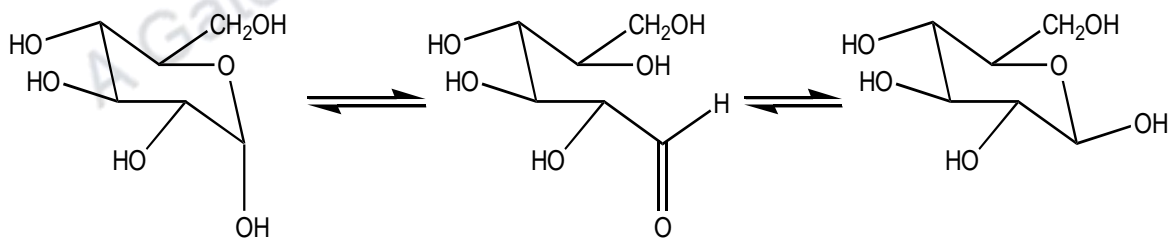
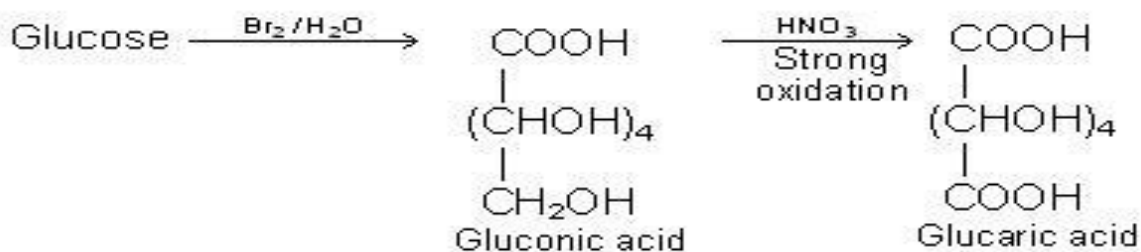
1. With HI/P: It undergoes reduction to form n-hexane while with sodium amalgam it forms sorbitol.



2. With Hydroxylamine (NH₂OH)



3. Oxidation: Glucose on oxidation with Br₂ gives gluconic acid which on further oxidation with HNO₃ gives glucaric acid



α -D-glucose

open-chain form

β -D-glucose

m.p. 146°C, $\alpha = +112^\circ$

m.p. 150°C, $\alpha = +19^\circ$

When α -D-(+)-glucose is dissolved in water, the specific rotation of the sample decreases from a value of $+112^\circ$ to a value of $+53^\circ$. The specific rotation of 112° corresponds to α -D-(+)-glucose. The specific rotation of $+53^\circ$ corresponds to an equilibrium mixture of α -D-(+)-glucose and β -D-(+)-glucose. A change in the optical rotation of freshly prepared solutions of sugars is called mutarotation. The forms of glucose involved in mutarotation are the open chain form and two cyclic forms, which are in equilibrium. The 2 cyclic forms are diastereomers, which have different physical properties (different m.p. and specific rotations). They are referred to as anomers since they differ only in the configuration at the hemiacetal carbon. If either cyclic compound is dissolved in water, the specific rotation changes to $+53^\circ$. The specific rotation decreases from $+112^\circ$ to $+53^\circ$ when α -D-(+)-glucose is dissolved in water and increases from $+19^\circ$ to $+53^\circ$ when β -D-(+)-glucose is dissolved in water. The mutarotation of glucose is acid-catalyzed and proceeds rapidly at a pH of 7.

Galactose

Galactose is not normally found in nature, but is mostly hydrolyzed from the disaccharide lactose, which is found in milk, as part of a disaccharide made by glycosidic linkage to a glucose molecule.

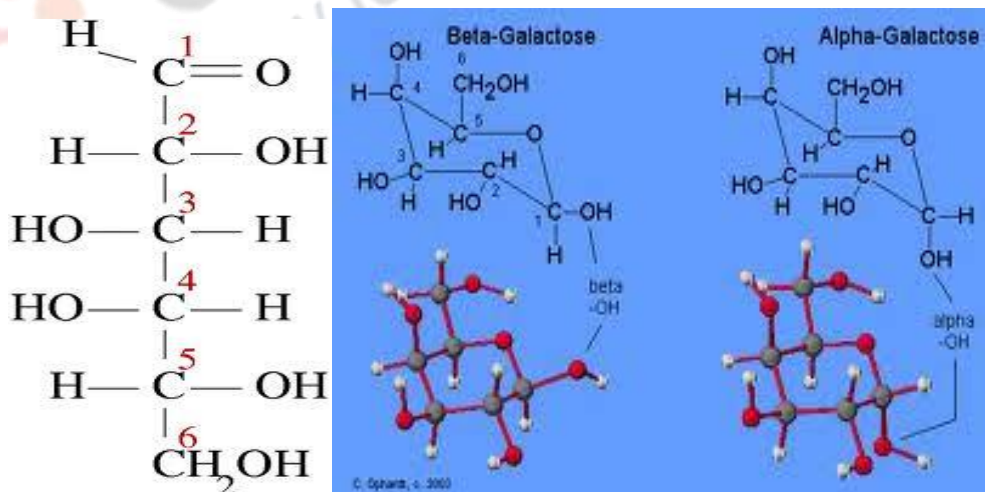


Figure: structure of galactose

Galactose is natural and is a basic component of many things, being found in milk, tomatoes and many fruits and vegetables. There is only one product range in the world that uses galactose as a basic food and drink ingredient, and that is a brand new range of energy drinks. Galactose has uniquely different properties compared to other sugars. These properties make it easier to lose and maintain weight; they are useful in warding off adult-onset diabetes; they give much steadier energy through time, and they provide the basis for products for athletes which allow them to perform better and longer.

Fructose

Fructose's chemical name is levulose. Fructose is also called the fruit sugar. Fructose is found in fruits, honey, and the sole sugar in bull and human semen. It is the sweetest sugar. It is used for preventing sandiness in ice cream. The compound's formula is $C_6H_{12}O_6$. It is shaped in orthorhombic, bispheroidal prisms.

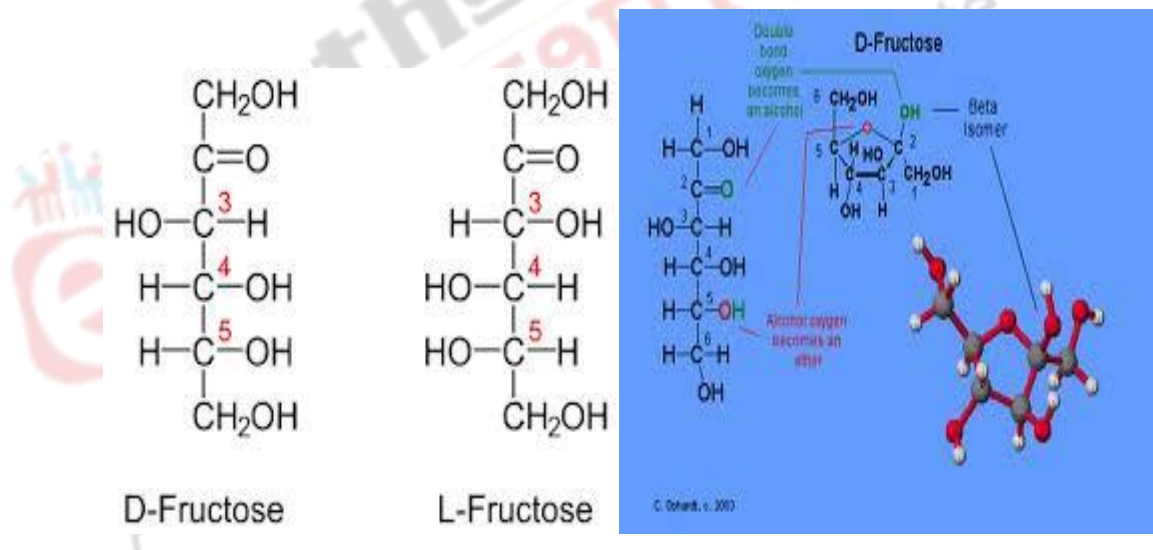


Figure: structure of fructose

Fructose taken in large quantities is associated with gastrointestinal distress, and is also associated with increases in the fat content of blood following meals rich in this. A large quantity of fat in the blood is thought to be a major risk factor for heart disease.

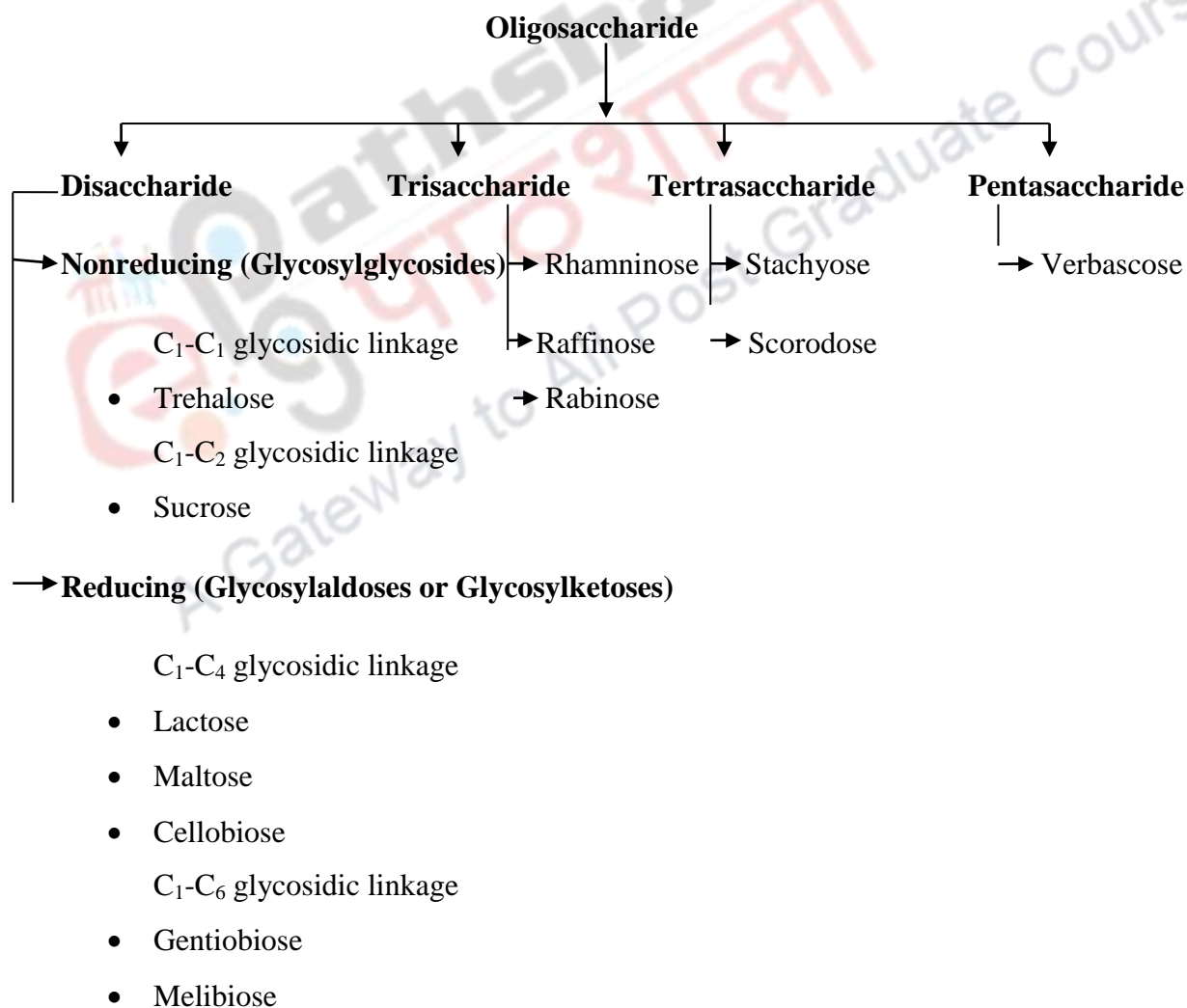
Epimers – if two monosaccharides differ from each other in their configuration around a single carbon atom. Eg. Glucose and Galactose (C-4), Glucose and Mannose (C-2).

Enantiomers – Enantiomers are stereoisomers that are mirror images of each other. Eg. D- and L-sugar.

Anomers – The α and β cyclic forms of D-glucose are known as anomers. They differ from each other in configuration only around C-1 known as anomeric carbon.

Oligosaccharides

Oligosaccharide contains 2-4 sugar units joining by glycosidic bonds. Disaccharides are the most common oligosaccharides found in the nature, which contains 2 monosaccharide units either same or different. A compound containing monosaccharide units is a trisaccharide, and so on. Oligosaccharide composed of the monosaccharide D- glucose, D- galactose, and D- fructose.



- Isomaltose

Sucrose (Saccharose)

Sucrose is also known as table, cane or beet sugar. Sucrose is non reducing sugar. It is distributed in all photosynthetic plants. Sucrose is composed of an α -D-glucopyranosyl unit and a β -D-fructofuranosyl unit linked head to head (reducing end to reducing end) rather than usual head-to-tail linkage.

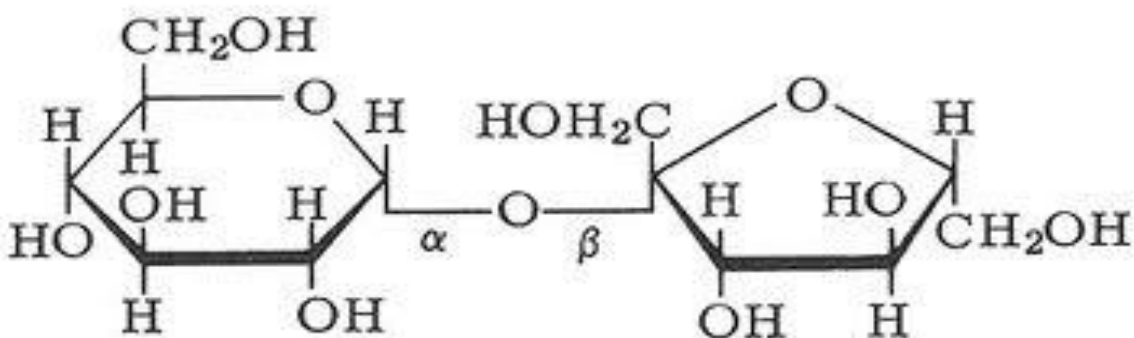
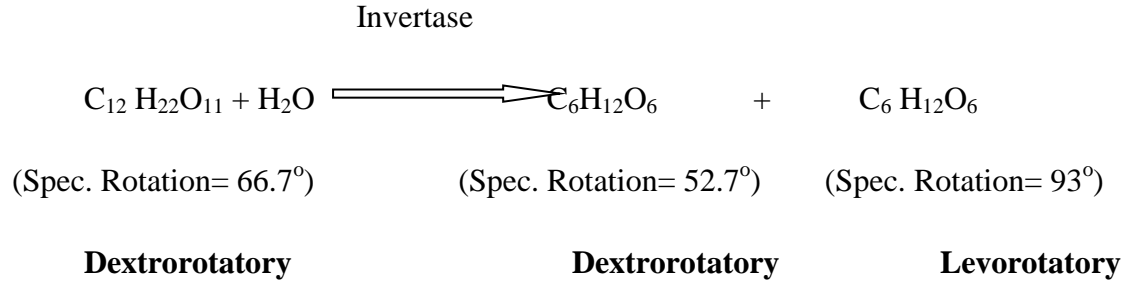


Figure: Structure of sucrose.

Sucrose is soluble in water. When sucrose is heated above its melting point (180°C), approx. 210°C , partial decomposition takes place and caramel is formed (brown colour). It is dextrorotary and a specific rotation of $+66.7^{\circ}$.

Upon hydrolysis, sucrose yields equimolar mixture of D- glucose and D- fructose, which is often called as invert sugar. The name 'invert sugar' is given to this mixture because the levorotary fructose, thus produced, changes (or inverts) the previous dextrorotary action of the sucrose. Sucrose is a dextrorotary with a specific rotation of $+66.7^{\circ}$, gives a mixture of equimolar quantities of D (+) glucose (dextrorotary; specific rotation of $+52.7^{\circ}$ and D (-) fructose (levorotary; specific rotation of -93°).

And as the levorotary of fructose is greater than the dextrorotary of glucose, the mixture so obtained is levorotary.



Mixture of glucose and fructose is levorotatory with specific rotation value of $(93-52.7) = -40.3^\circ$.

Maltose

Maltose is readily produced by hydrolysis of starch using the enzyme β - amylase. Maltose is a reducing sugar because its aldehyde group is free to react with oxidants. Maltose is produced during malting of grains, especially barley, is an excellent source of maltose. Maltose is 4- α -D- glucopyranosyl - β - D- glucopyranose. Maltose exists in 3 forms- α , β and aldehydo, but usually found in β -form.

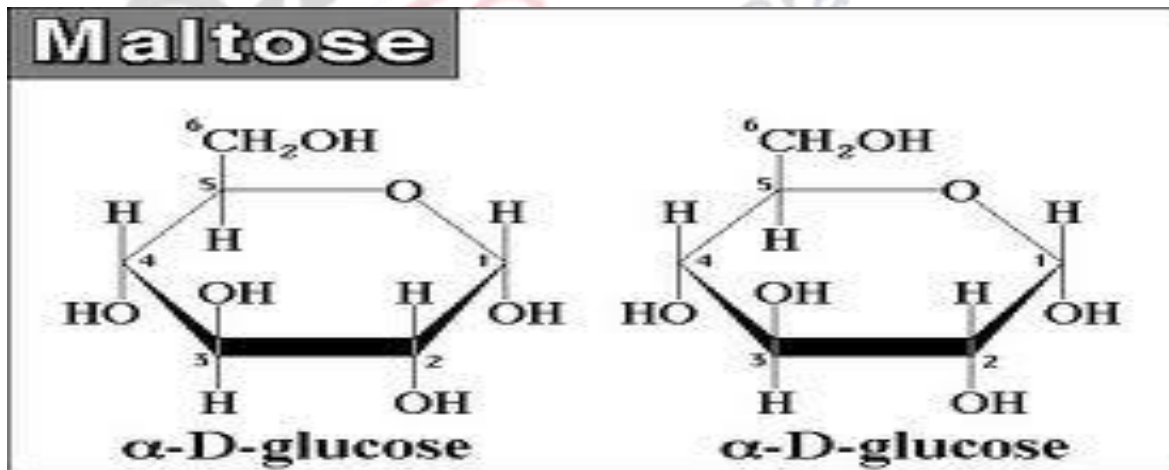


Figure: Structure of Maltose

Maltose shows mutarotation, because it is reducing diasaccharide. Melting point of maltose is $160-165^\circ\text{C}$. It is dextrorotatory sugar.

Lactose

Lactose is a disaccharide consisting of galactose and glucose, linked by a β 1-4 glycosidic bond. Its systematic name is β -O-D-galactopyranosyl (1-4) - α -D-glucopyranose (α -lactose) or β -O-D-galactopyranosyl (1-4) - β -D-glucopyranose (β -lactose).

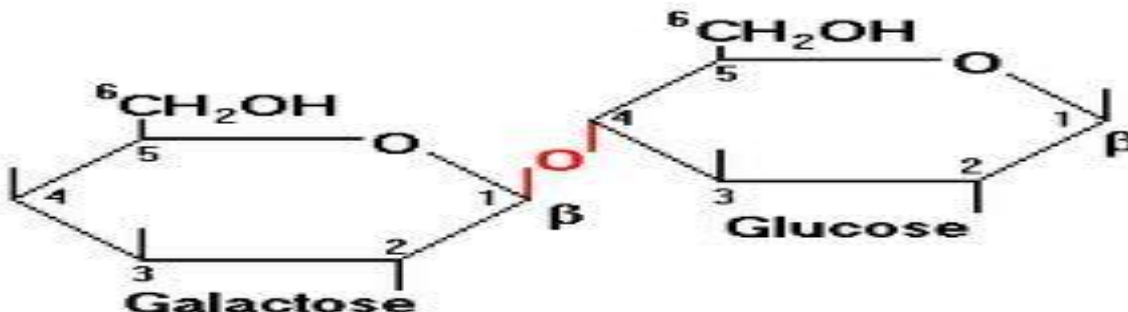


Figure: Structure of β - Lactose.

The hemiacetal group of the glucose moiety is potentially free hence, lactose is a reducing sugar. Concentration of lactose in milk varies with the mammalian source from 2.0-8.5%. Cow and goat milk contain 4.5-4.8 % and human milk about 7%. In humans, lactose constitutes 40% of the energy consumed during nursing. Lactose is less sweeter than glucose and galactose

Lactose stimulates intestinal adsorption and retention of calcium (Ca). Lactose is digested (hydrolyzed) by the enzyme lactase (β -D-galactosidase) is membrane bound enzyme located in the brush border epithelial cells of the small intestine. From the small intestine, the lactose passes into the large intestine (colon) where it undergoes anaerobic bacterial fermentation to lactic acid and other short-chain acids. Lactose is a reducing sugar, i.e. it has a free carbonyl group. Like all reducing sugars, lactose can participate in the Maillard (nonenzymatic browning) reaction, resulting in the production of (off-) flavour compounds and brown polymers.

Reference

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