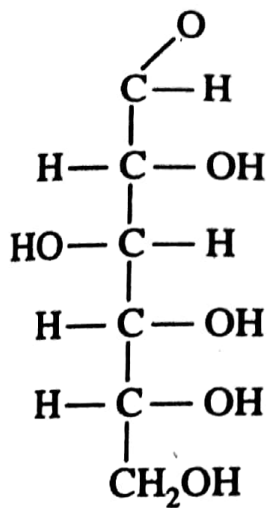


... D-Glucose would

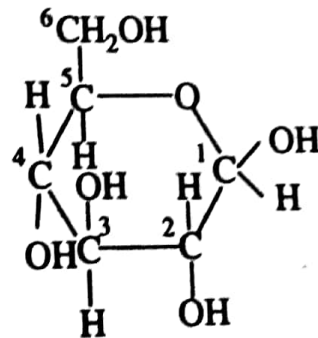
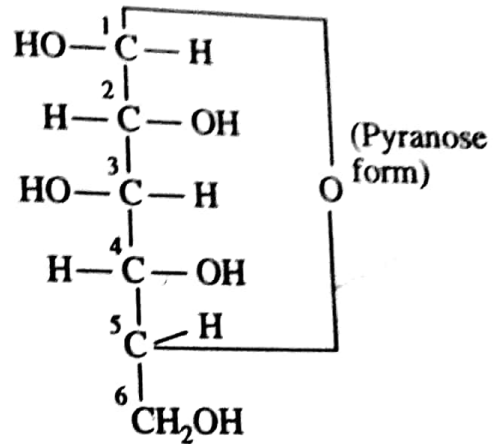
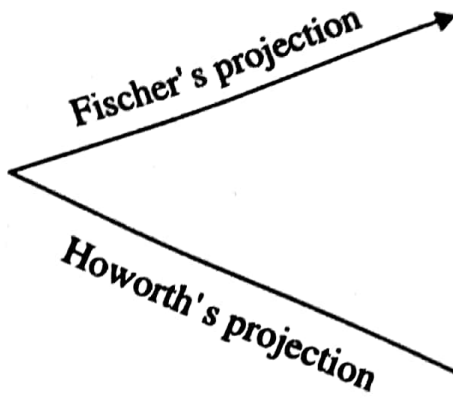
Fischer's Projection and Haworth's Projection

The formula written in the chain form with carbon atoms, along with oxygen atom forming a ring was given by *Fischer*. This formula does not show the proper arrangement of molecules in the ring form e.g., in the Fischer's formula the ring form of glucopyranose does not show that—

- (i) C₆ and its attached groups are trans i.e., they are alternately up and down with respect to hydroxyl groups on carbons 1, 2, and 4.
- (ii) It does not show the proximity of carbon 1 and 5. Both these things are clear in *Haworth's* projection.



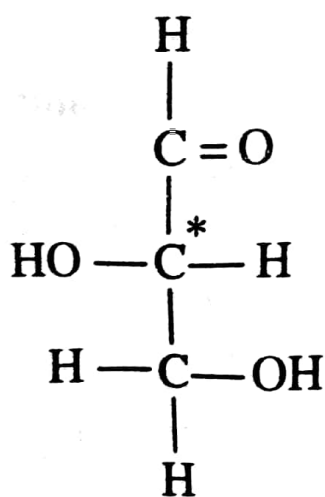
D-Glucose



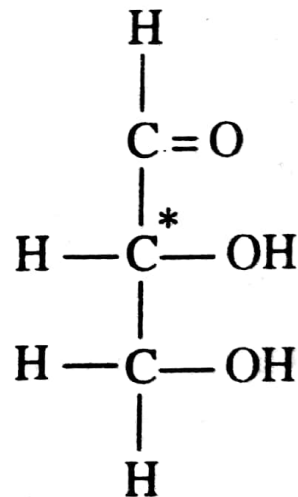
β -D-glucose, (Pyranose) or Glucopyranose

Properties of monosaccharides

Physical. Monosaccharides are sweet tasting colourless solids. They are soluble in water, sparingly soluble in alcohol and insoluble in ether. They contain asymmetric carbon atom and hence exist in different isomeric forms. For example, glyceraldehyde may exist in two forms.



L-glyceraldehyde



D-glyceraldehyde

* Asymmetric carbon atom

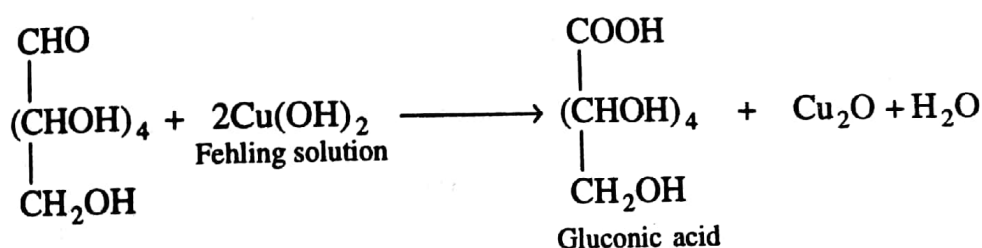
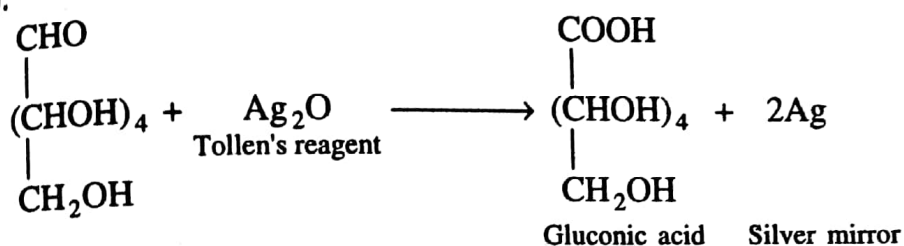
When a polarized light (light vibrating in one plane) is passed through a solution of these carbohydrates, the plane of the light is rotated to either right or left. All monosaccharides which contain a D-glyceraldehyde unit are called D-sugars. L-monosaccharides contain a L-glyceraldehyde unit in their structure.

Carbohydrates isolated from living system are a mixture of several isomers. The degree of optical rotation may change due to interconversion of isomers. Fresh solution of glucose gives an optical rotation of $+112^\circ$ which changes to $+52.7^\circ$ on standing.

Similarly, fructose gives an optical rotation of -113° which changes to -92° . This change in optical rotation is called **mutarotation**.

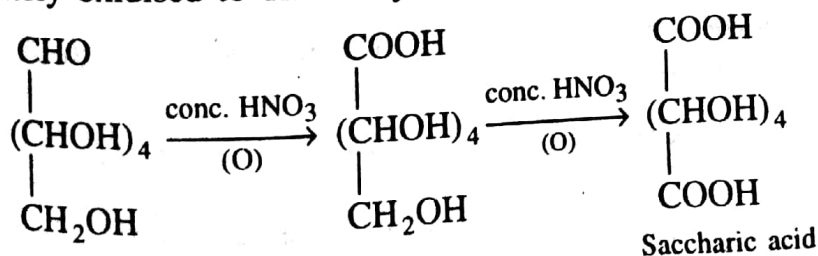
Chemical. The properties of monosaccharides are based on $-\text{CHO}$ or $=\text{CO}$ and $-\text{OH}$ groups present in them.

(a) **Oxidation.** Monosaccharides are easily oxidised by the oxidising agents. Glucose yields gluconic acid after oxidation with mild reagents such as Tollen's reagent (ammoniacal Ag_2O) or Fehling solution (alkaline CuSO_4).



The reduction of Tollen's reagent yields silver as polishing on the surface of the tube whereas with Fehling solution red precipitate is obtained. Similarly potassium ferricyanide can be reduced to ferrocyanide. These reactions are used in the estimation of glucose and other sugars containing free carbonyl groups. Such sugars are called **reducing sugars**.

When strong oxidizing agents like conc. HNO_3 are used, gluconic acid is ultimately oxidised to dicarboxylic saccharic acid.



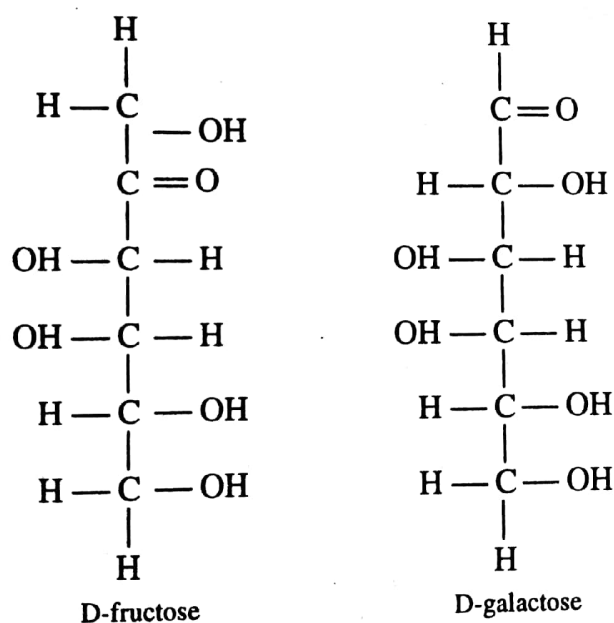
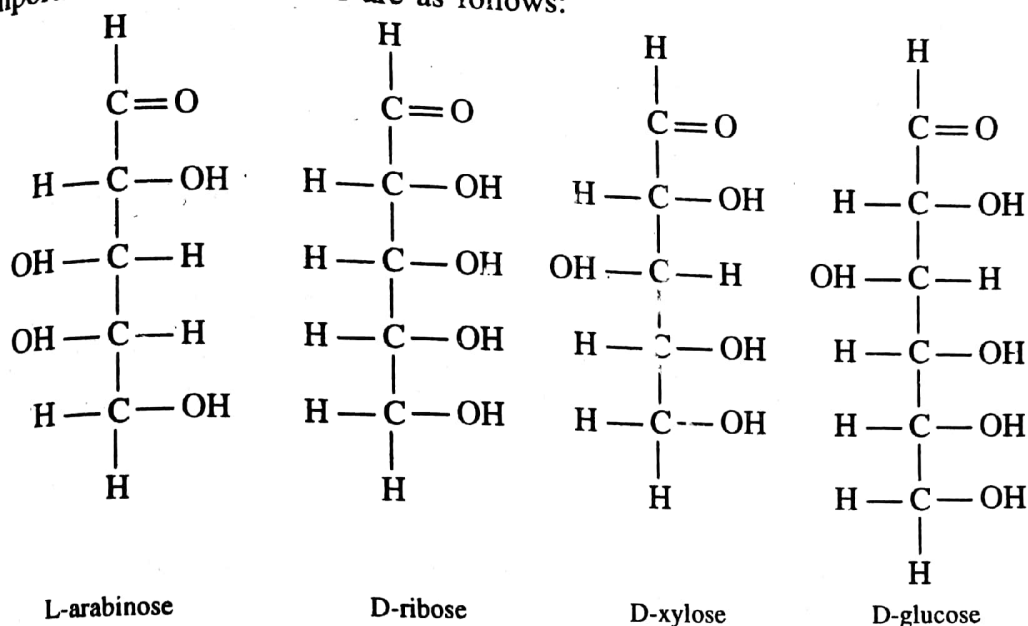
In the animal body, slow oxidation of glucose may yield glucuronic acid. In glucuronic acid, aldehyde group is intact and the primary alcohol group on carbon 6 is oxidised to a carboxylic group.

Structure of monosaccharides

Naturally occurring sugars exist in two structural forms ; either straight chain or ring. About 1 to 10% of the total sugars occur as straight chain whereas the remaining bulk in the form of closed ring. The property which lead to the confirmation of straight chain structure in glucose was, its conversion to polyhydroxy heptylic acid via cyanohydrin. Since, during this reaction HCN was added to terminal carbon which was then hydrolysed to a $-COOH$ group; the carbonyl group of glucose must occupy a terminal position and hence it would be an aldehyde. The acetylation properties of glucose have proved it to be a pentahydroxy molecule. The correct position of asymmetric carbon in a glucose molecule was determined by **Emil Fisher**

(BC-5)

in 1896. These methods were used for the determination of structure of other monosaccharides also. The structural formula (linear chain) of some important monosaccharides are as follows:

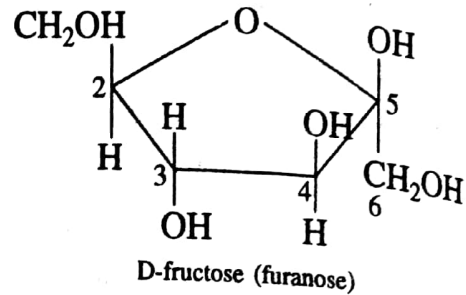
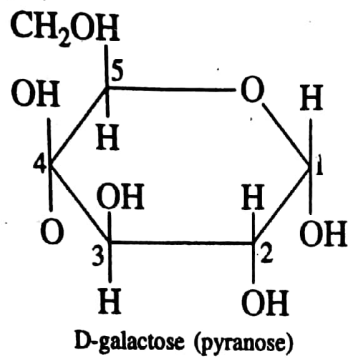


After the advent of x-ray crystallography technique, it was shown that all these sugars indeed do have structures assigned to them by Emil Fisher and other earlier workers.

In many reactions, the aldehyde sugars do not behave as aldehydes but as hemiacetals. This may happen, for example, if the carbon 1 of glucose approaches near carbon 5 and the aldehyde and hydroxy groups react to form a hemiacetal. In fructose, hemiacetal can be formed by reacting carbon 2 and 5. Two types of hexose rings may be formed in this way; a 5 membered ring with one oxygen atom in the ring or a six membered ring with one oxygen atom. Five membered cyclic compound is furan while 6

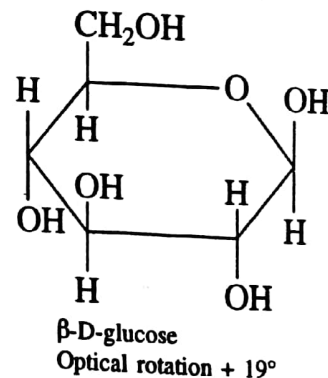
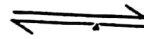
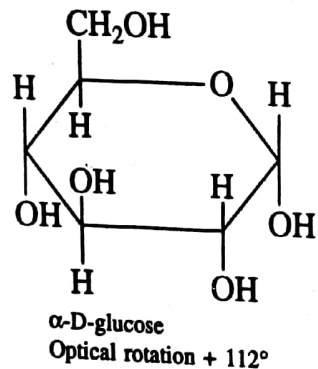
(BC-5)

membered is pyrane and hence the corresponding structures are furanose and pyranose rings. Furanose and pyranose rings of hexose sugars are as follows:



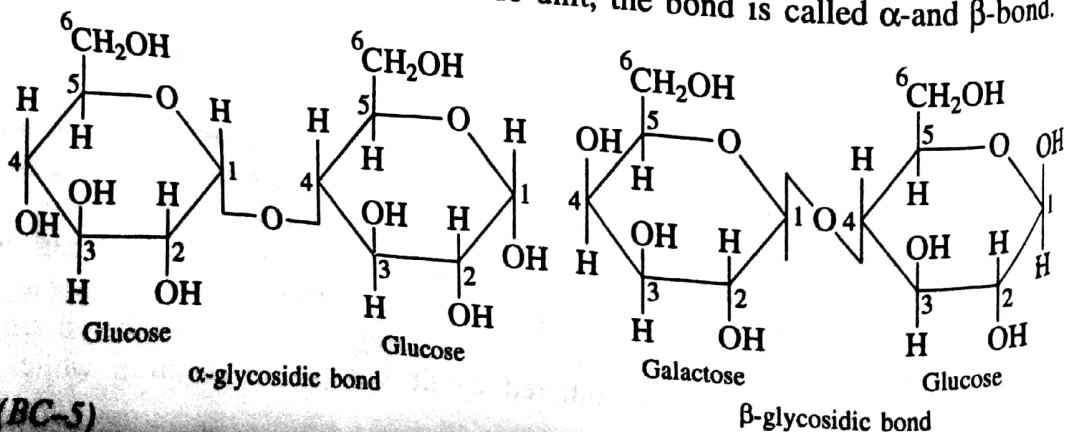
Most of the hexose sugars occur in pyranose form. Fructose, however, occurs in furanose form in the disaccharide, sucrose. Pentoses occur in furanose form.

During the formation of ring, a new asymmetric carbon is created which contains four different substitutes. Therefore, two different anomeric forms, the α - and β -forms, in these sugars are possible. These anomers differ in their physical constants (Chapter 2).



Oligosaccharides

Oligosaccharides are composed of few monosaccharide units. During union of monosaccharide units water molecule is eliminated and the units are linked through an oxygen bridge. It is a **glycosidic linkage**. Depending upon the steric configuration at carbon 1, which is involved in the formation of glycosidic linkage of monosaccharide unit, the bond is called α - and β -bond.



(BC-5)

In the modern system of nomenclature, the oligosaccharides are named according to the constituent monosaccharide units and the position of glycosidic bond (Table 2).

Table 2. Systematic name of some important oligosaccharides zymogen

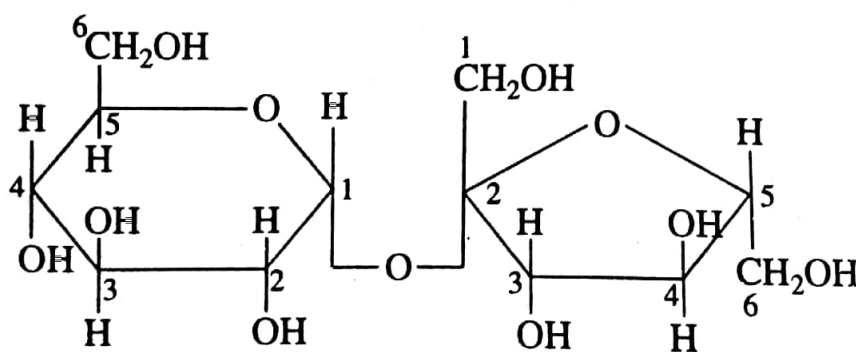
Common name	Systematic name
Sucrose	4- α -glucopyranoside - β -fructofuranoside
Lactose	4- β -galactosyl-glucose
Maltose	4- α -D-glucopyranosyl-D-glucopyranose
Cellobiose	4- β -glucopyranosyl-glucose
Gentiobiose	6- β -glucosyl-glucose
Raffinose	α -D-galactosyl- (1 \rightarrow 6) α -D-glucosyl, (1 \rightarrow 2) β -D-fructofuranoside
Stachyose	α -D-galactopyranosyl (1 \rightarrow 6) - α -D-galactopyranosyl (1 \rightarrow 6) - α -D-glucopyranosyl (1 \rightarrow 2) β -D-fructofuranose

The arrow shows the direction of glycosidic bond.

The natural source of oligosaccharides are green plants. Most of them are obtained as colourless solids. They are crystalline substances and readily soluble in water. Structure and properties of some important oligosaccharides are described in the following paragraphs.

Sucrose

It is formed by the union of one α -D-glucose and one β -D-fructose unit with the elimination of one water molecule. The glycosidic bond involves carbon 1 of pyranose ring of glucose and carbon 2 of fructose furanose ring. It is easily hydrolysed to glucose and fructose units when warmed with dilute mineral acids. It is dextrorotatory (+66.5°) but the mixture of glucose and fructose produced after hydrolysis is laevorotatory because angle of laevorotation by fructose is more than that of dextrorotation by glucose.

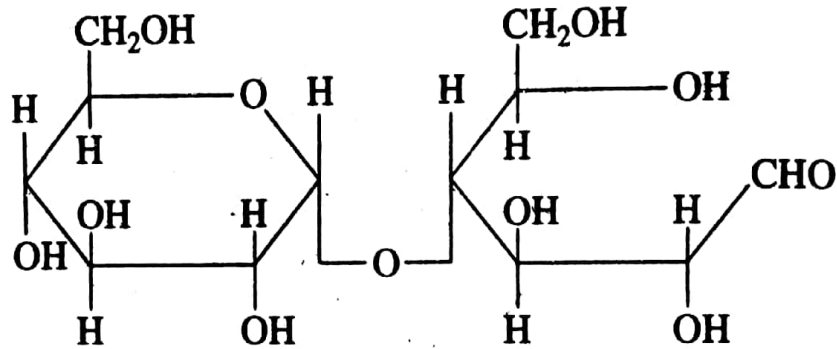


Sucrose (α -glucopyranoside β -fructofuranoside)

This change in optical rotation of sucrose due to hydrolysis is sometimes called **inversion**. Sucrose is a major metabolic product of green plants but does not occur in higher animals.

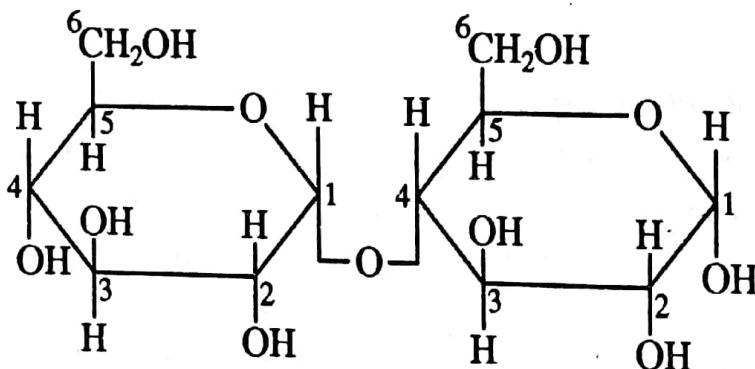
Maltose

Maltose is composed of two units of D-glucose joined together through their 1 and 4 carbon atoms. One of the units normally exists as open chain with free aldehyde group. Hence this disaccharide is a reducing sugar.

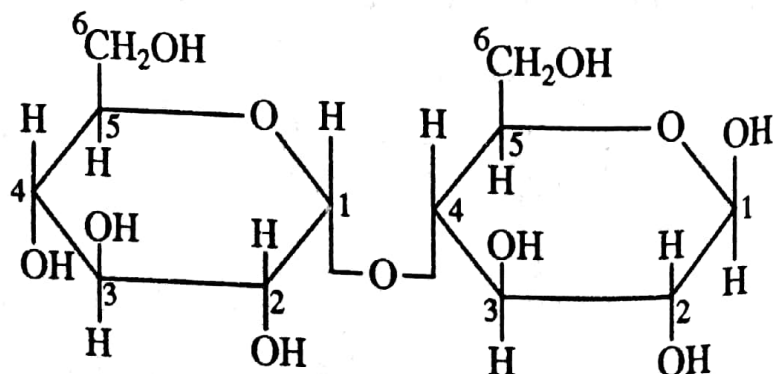


Maltose

The second unit may close also to form a ring through its carbon 1 and 5 giving rise to two forms of maltose; α -maltose or β -maltose. Maltose occurs in plants as a degradation product of the storage polysaccharide starch. The enzyme amylase, which is responsible for this hydrolytic degradation, is abundant in germinating seeds. Commercial corn syrup, which is prepared by hydrolysing corn starch, is a rich source of maltose. Free maltose has been detected in leaves.



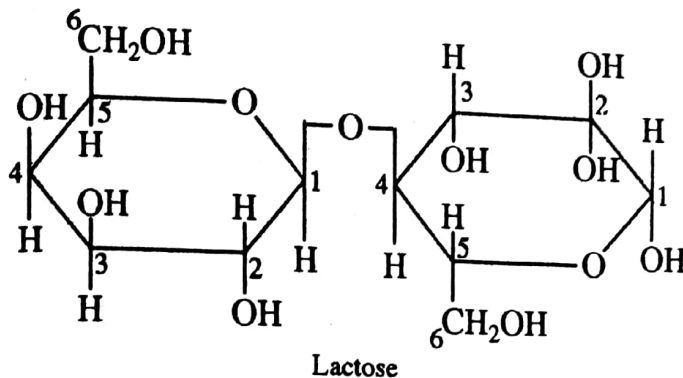
α -maltose



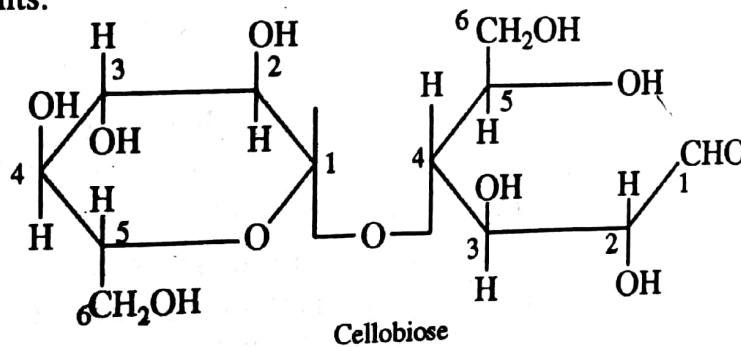
β -maltose

Lactose

Lactose is made up of glucose and galactose units joined together through carbon 1 of galactose and carbon 4 of glucose. It is also a reducing sugar because open chain configurations also exist. Lactose occurs naturally in the milk of mammals up to 5%. It has been detected in the flowers of some plants (*Forsythia sapotacea* etc.) also. Hydrolysis of this sugar yields galactose and glucose.

**Cellobiose**

Cellobiose is composed of glucose units (1-4 linkage). It may also exist in reducing form with a free aldehydic group. Alternatively the ring may close to form α - or β -cellobiose. Cellobiose is present only in trace amounts in nature. The cellulases present in micro-organisms and growing seedlings are able to hydrolyse plant cellulose to cellobiose. Its further hydrolysis yields D-glucose units.

**Trisaccharides and tetrasaccharides**

Tri and tetrasaccharides are usually present in plants in small amounts. Raffinose (a trisaccharide) is found in sugarbeet and cotton seed meal and in some fungi. It is composed of galactose (pyranose), glucose (pyranose) and fructose (furanose) units. Another trisaccharide, gentianose occurs in rhizomes of several gentian species. It is made up of glucose (pyranose), glucose (pyranose) and fructose (furanose) units.

Stachyose is a tetrasaccharide occurring in several species including *Stachys tubifera*. The composing units are two galactose (pyranose), one glucose (pyranose) and one fructose (pyranose) in a stachyose molecule.

Polysaccharides

Polysaccharides are composed of several monosaccharide units joined together by glycosidic bonds. The most frequent monosaccharide unit in polysaccharides is D-glucose, although; D-fructose, D-galactose and other hexoses also occur. The constituent monosaccharides may be either similar (homopolysaccharides) or different (heteropolysaccharides). Starch, cellulose and glycogen are examples of homopolysaccharides while hyaluronic acid, pectins and chitins are heteropolysaccharides.

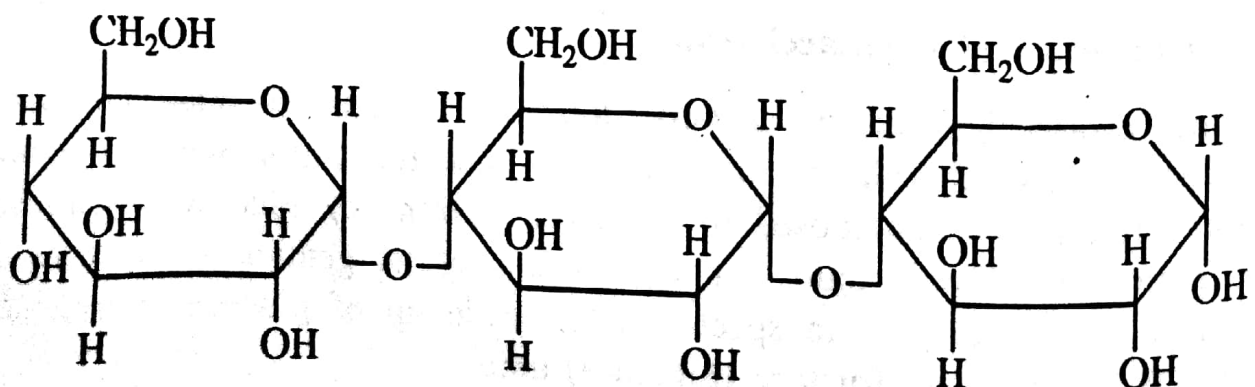
Polysaccharides are tasteless and colourless amorphous powders which are little soluble in water, although some may form colloidal solutions. They are easily hydrolysed to their monosaccharide units. Some important polysaccharides are described in the following paragraphs.

Starch

Starch is a high m.w. polysaccharide made up of two components, amylose and amylopectin. The amylose is an unbranched chain of 300 to 1000 α -D-glucose units with 1-4 glycosidic bonds. The amylopectin is also made up of α -D-glucose units but is branched like a tree. The main chain has 1-4 linkage with 1-6 linkage at branching points.

The ratio of amylose to amylopectin in starch is different for different tissues. The starch from normal maize seed contains about 20% amylose and 80% amylopectin. Waxy maize, a recently developed variety of maize, contains almost 100% amylopectin.

Starch is the storage carbohydrate of plants. It occurs as grains of $1\ \mu$ (e.g. rice) to $100\ \mu$ (e.g. potato) size in the chloroplasts or amyloplasts. The grains contain about 20% water, 10% of which is chemically bound to starch. The shape of the grains may be oval, spherical, lens shaped or irregular. The starch in the grains is contained in the form of layers. Potato starch grains are covered with thin layers of cellulose.



Amylose

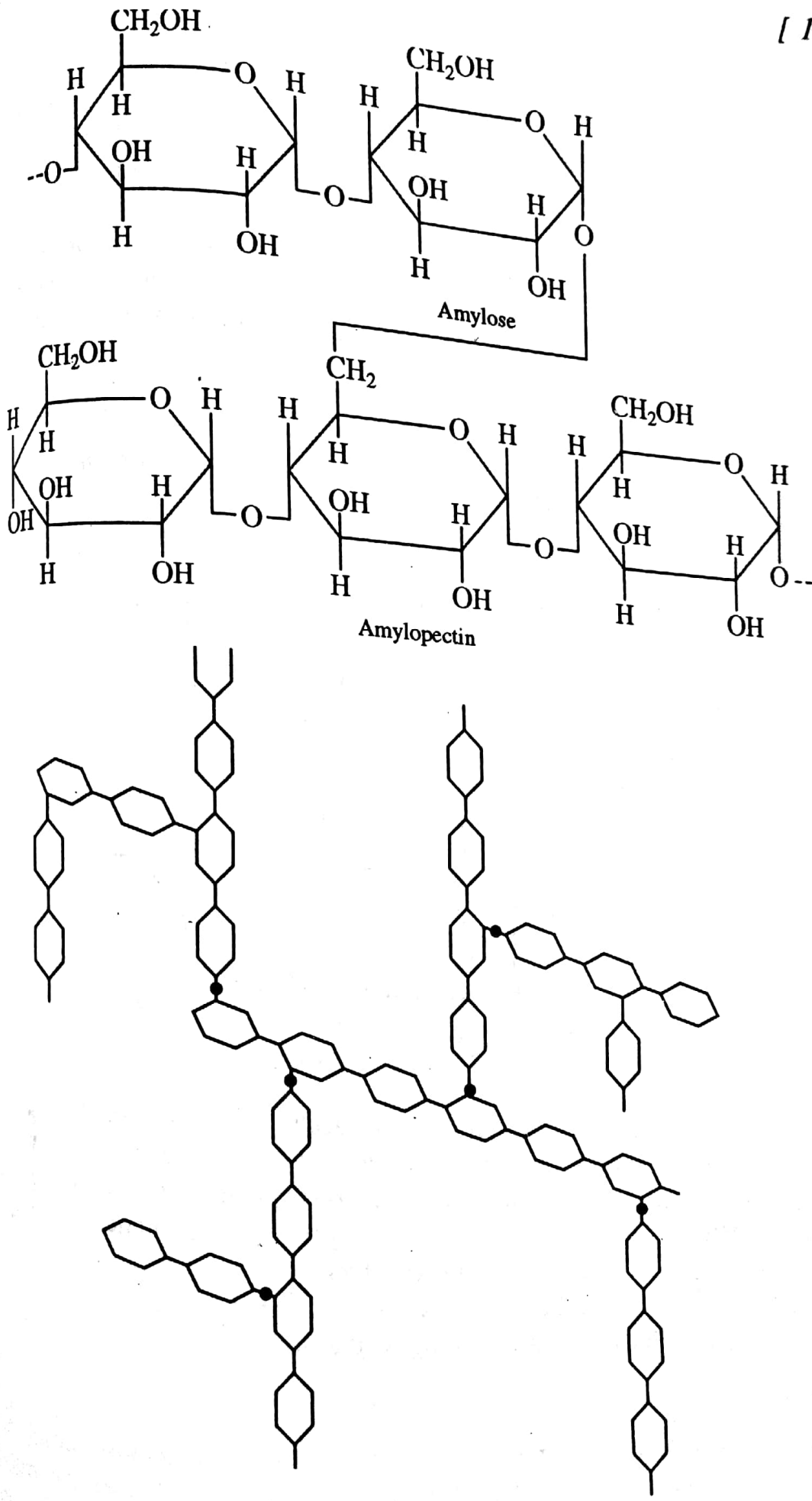


Fig. 1. Diagrammatic representation of glycogen molecule. Each hexagon represents a gluco-pyranose unit.

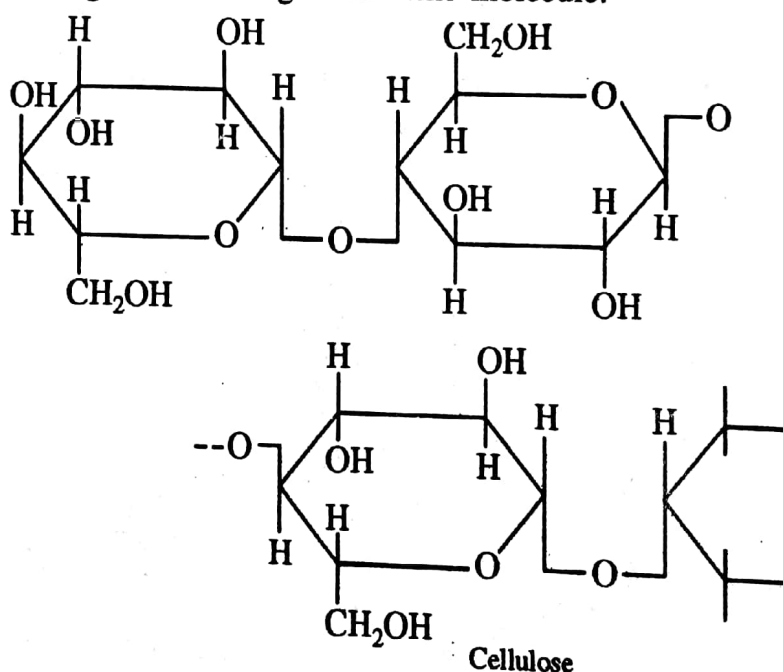
Glycogen

The storage carbohydrate of animals is glycogen. It is similar to amylopectin in its structure except that the m.w. is lower and the chains are shorter (Fig. 1). The branching is also extensive, each branch containing about 12 glucose units.

Glycogen is mostly found in the liver and the muscles. In the liver it is split to glucose to maintain its (glucose) proper concentration in the blood. It dissolves in water to yield opalescent solution and is easily hydrolysed to α -D-glucose.

Cellulose

Cellulose molecule is composed of 1600 to 2700 β -D-glucose units with 1-4 glycosidic linkage. It is a long thread like molecule.



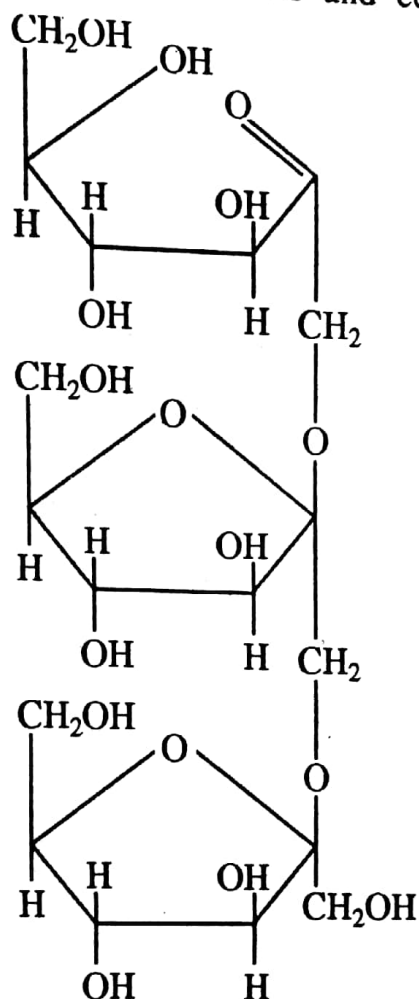
Cellulose is the major structural polysaccharide of plants. Careful acid hydrolysis of cellulose yields a series of oligo-saccharides such as cellobiose, cellotriose, cellotetrose etc. Complete hydrolysis permits recovery of about 95% of the weight of cellulose as glucose. Enzymatic hydrolysis of cellulose is brought about by cellulase which is present in some protozoans and mites. Some of the bacteria in cattle and other herbivores also secrete cellulase that enables the cattles to digest the herbal cellulose to glucose.

Inulin

Inulin is an unbranched molecule of about 30-35 D-fructose units, m.w. 5000 and the glycosidic linkage is between carbon 1 and 2 of the fructose units. Inulin is obtained commercially from Jerusalem artichoke rhizome. It is found naturally with other short chain fructans. The enzyme inulase hydrolyses inulin to fructose.

Biological Significance of Carbohydrates

Carbohydrates are involved in the structural organisation of many tissues, both in plants and animals. Cellulose, hemicelluloses (xylans and mannans) and pectic substances (galactouranans, arabans and cellulose) are common

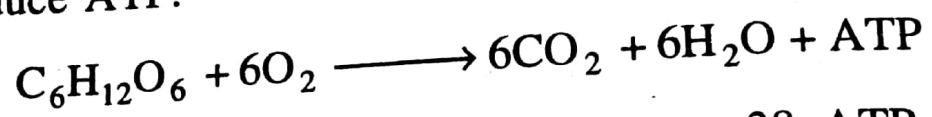


structural carbohydrates in plants. The primary cell wall in plants contains about 43% of cellulose. Lignin is also present in the cell walls of the older tissues. Chitin, hyaluronic acid and chondroitin sulphates are important structural polysaccharides of animals. They are present in the shells of lobsters, crabs and insects and in the cartilage, adult bones, heart valves and cornea.

Carbohydrates are stored as reserve products in many tissues. Normally the starch is stored in seeds, tubers and rhizomes. In some plant families, such as Compositae and Campanulaceae, the stored carbohydrate in rhizomes and tubers is inulin. Sucrose (sugar cane, beet), glucose (grapes) and fructose (fruits) are also stored. Glucose is the most common carbohydrate of human blood where it is present in a concentration of 1 g/l. In animal cells, glycogen is the storage polysaccharide.

The most important role of carbohydrates is the production of energy in the form of ATP both in plants and animals. The polysaccharides such as

starch and glycogen are converted to glucose by enzymes. The glucose is finally broken down to CO_2 and H_2O and yields NADH which is eventually oxidized to produce ATP.



In overall oxidation of 1 molecule of glucose, 38 ATP molecules are generated.

During aerobic breakdown of carbohydrates through Embden-Meyerhof pathway and Krebs's cycle, several organic compounds are produced which act as substrates for the synthesis of lipids and amino acids. The phosphogluconate oxidative pathway or pentose phosphate pathway provides pentoses ; essential components of nucleotides and nucleic acids. NADH produced during the process is used as coenzyme in several biosynthetic processes such as fatty acid and steroid synthesis.