

1

CHAPTER

CARBOHYDRATES



- * Classificatio
- * Disaccharides
- * Glucose and Fructose
- * Polysaccharides

INTRODUCTION

1.1.1

Biomolecules

Living organism is made of some organs. Organs are made of some type of tissues. These tissues are made of a group of cells, but the cell is made by cellular organells. Cellular organells are formed from biomolecules. The biomolecules like proteins, nucleic acids, lipids, vitamins, hormones and carbohydrates play an important role in biochemical reactions.

Mechanism of biochemical reactions is complex

The mechanism of biochemical reactions is complex, but generally takes place at body temperature and one atmosphere pressure in dilute neutral solutions of pH value nearly equal to 7.

A living organism is made of one or more cells which are considered as the smallest units of life. Energy is necessary for the various activities in the cells. The biomolecules like glucose undergo controlled oxidation in the presence of enzymes liberating energy.

The metabolic reactions take place in human body are generally endergonic with positive free energy change ($\Delta G > 0$) and are seemed to be forbidden reactions. But these reactions will take place by coupling with certain exergonic reactions with $\Delta G < 0$.

1.1.2

Classification

Carbohydrates are mainly the compounds of C, H and O. Initially the carbohydrates were considered as the hydrates of carbon with formula, $C_x(H_2O)_y$. eg: Glucose : $C_6H_{12}O_6$ or $C_6(H_2O)_6$; Sucrose : $C_{12}H_{22}O_{11}$ or $C_{12}(H_2O)_{11}$.

But all the compounds with formula $C_x(H_2O)_y$ are not necessarily carbohydrates. eg: Formaldehyde : $HCHO$ or $C(H_2O)$; Acetic acid : CH_3COOH or $C_2(H_2O)_2$.

A few carbohydrates may not have the formula, $C_x(H_2O)_y$. eg: Rhamnose, $C_6H_{12}O_5$.

Acetylation of salicylic acid gives aspirin

Most of the carbohydrates are sweet to taste hence these are also called saccharides. Carbohydrates are now defined as optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis. Based on the hydrolysis products of carbohydrates, these are classified into 3 types.

Monosaccharides : These are single unit carbohydrates and cannot be broken into lower sugars during hydrolysis. About 20 monosaccharides occur in nature. Glucose and fructose are the most important members of this class.

Monosaccharides are again of two types. The optically active polyhydroxy aldehydes are called aldoses and optically active polyhydroxy ketones are called ketoses. Based on the number of carbon atoms, carbohydrates are called trioses, tetroses, pentoses, hexoses, etc., when the number of carbon atoms present is 3, 4, 5, 6, etc. This classification is given in Table 1.1.

Table 1.1 Examples of aldoses and ketoses

Number of carbon atoms	Aldoses	No. of chiral carbon	Number of optical isomers	Ketoses	No. of chiral carbon	No. of optical isomers
3	Aldotriose	1	2	-	-	-
4	Aldotetrose	2	4	Ketotetrose	1	2
5	Aldopentose	3	8	Ketopentose	2	4
6	Aldohexose	4	16	Ketohexose	3	8

Mono-, di- and oligosaccharides are all water soluble and are called sugars

Disaccharides and oligosaccharides : Disaccharides on hydrolysis give two monosaccharides of same or different kind.

eg : Sucrose, maltose, lactose, etc.

Oligosaccharides on hydrolysis give three to ten monosaccharides. Disaccharides may also be treated as oligo saccharides.

eg : Raffinose $\xrightarrow{\text{hydrolysis}}$ fructose + glucose + galactose

Gentianose $\xrightarrow{\text{hydrolysis}}$ fructose + glucose + glucose

Polysaccharides : Polysaccharides on hydrolysis give a large number of same or different monosaccharides, generally more than ten. The general formula is $(C_6H_{10}O_5)_n$.

eg : Starch, cellulose, glycogen, dextrin, etc.

Depending on the solubility in water, carbohydrates can be classified into two types. Natural mono, di and oligosaccharides are crystalline solids, soluble in water, sweet to taste and are called sugars. Polysaccharides are colourless amorphous solids and generally insoluble in cold water, and are tasteless. These are generally called non-sugars.

Basing on the reducing nature of carbohydrates, these are again classified into reducing sugars and non-reducing sugars. Carbohydrates which reduce Tollen's reagent and Fehling's solution are called reducing sugars. They form silver mirror with Tollen's reagent and give red precipitate with Fehling's solution.

All monosaccharides and disaccharides except sucrose are reducing sugars. Saccharides which cannot reduce Fehling's solution and Tollen's reagent are called non-reducing sugars. In disaccharides, if the reducing groups of monosaccharides are bonded, these are non-reducing sugars. eg : Sucrose.

Sugars can be classified into D- and L- forms basing on their configuration. The enantiomer which rotates the monochromatic light to right is written as (+) or 'd' and the other which rotates the monochromatic light to the left is written as (-) or 'l'.

Based on the configuration sugars are 2 types, D- and L-

Sugars with same configuration of D-glyceraldehyde at chiral carbon are called D-sugars

Natural glucose is in D-form

The direction of the rotation of monochromatic light can be denoted by (+) and (−), but cannot indicate the arrangement of −OH and −H around chiral carbon atom.

Rosanoff proposed a system to designate the stereo chemistry of carbohydrates by considering the simplest sugar, glyceraldehyde as standard. The sugars having the same configuration as D-glyceraldehyde at the least priority chiral carbon adjacent to primary alcoholic group (−CH₂OH) are called D-sugars and having the configuration as L-glyceraldehyde are called L-sugars.

Practically D-sugars may be D-(+) or D-(−) and L-sugars may be L-(+) L-(−). The symbol (+) or 'd' is used for dextro and (−) or 'l' is used for laevo rotatory compound. It is observed that natural glucose, ribose and fructose are in D-form. Some of the D-sugars are given in Fig 1.1.

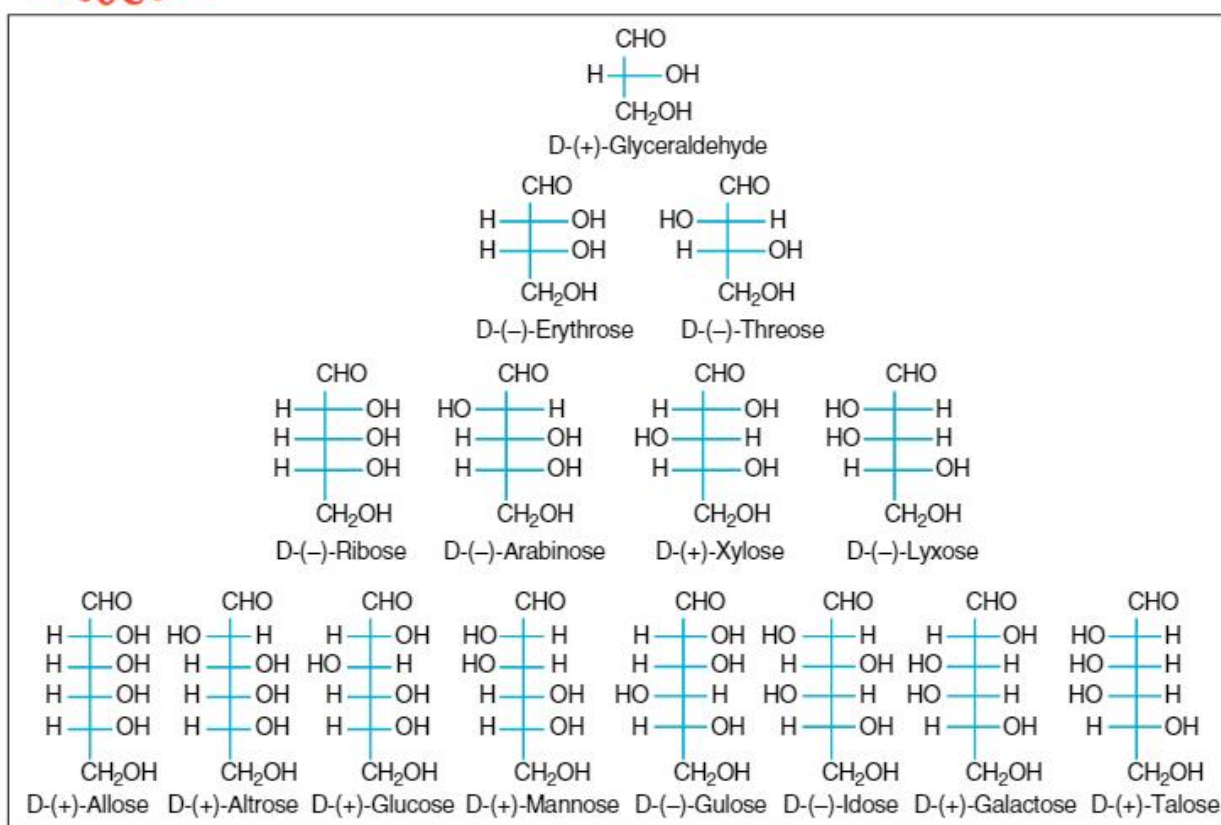


Fig 1.1 Important sugars with D-configuration



P.1.1 Biochemical reactions with $\Delta G > 0$ are forbidden reactions. How do they take place spontaneously?

Solution The metabolic reactions with $\Delta G > 0$ are coupled with some other reactions of $\Delta G < 0$, such that the net free energy change is negative. Hence some biological reactions with $\Delta G > 0$ are also spontaneous.



P.1.2 Can all the trioses are optically active ?

Solution No. The aldotriose, glyceraldehyde is optically active due to presence of an asymmetric carbon. But ketotriose is optically inactive due to absence of asymmetric carbon.

GLUCOSE AND FRUCTOSE

1.2.1

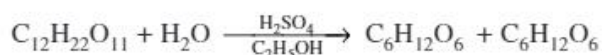
Glucose

Glucose is dextrorotatory and is called dextrose

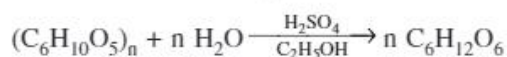
Glucose is called grape sugar because grapes contain nearly 20% glucose. It is also present in fruits and honey. It occurs in free form and in combined form as starch, cellulose and sucrose. It is probably the most abundant organic compound on earth.

Glucose occurs as dextrorotatory compound in nature, so it is called dextrose. Human blood contains a normal range of 65–110mg glucose per 100ml. It is also called blood sugar.

In the laboratory, glucose is prepared by the acid hydrolysis of sucrose in the presence of alcohol. Glucose and fructose are formed in equal amounts. Glucose being less soluble in ethyl alcohol than fructose, crystallises out.



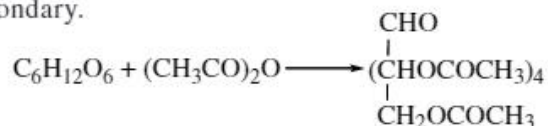
Glucose is prepared on a large scale by acid hydrolysis of starch or cellulose in alcohol at 120°C under a pressure of 2–3 atm.



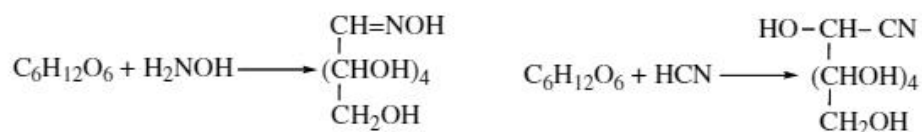
Structure of glucose

Glucose forms pentaacetate with acetic anhydride, suggesting five –OH groups

- The molecular formula of glucose was found to be $\text{C}_6\text{H}_{12}\text{O}_6$.
- Glucose forms glucose pentaacetate with acetic anhydride, which exists as a stable compound. It indicates the presence of five –OH groups in glucose molecule and the five hydroxyl groups should be attached to different carbon atoms. Out of these five –OH groups, one was found to be primary and the remaining four are secondary.



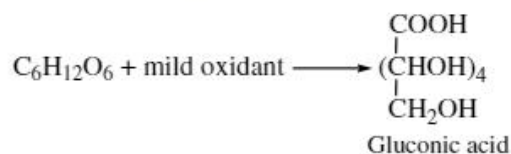
- Glucose forms glucose oxime with NH_2OH and glucose cyanohydrin with HCN .



These reactions indicate that glucose has one carbonyl group.

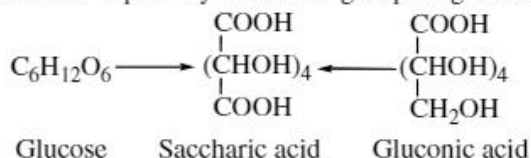
Glucose reduces Tollen's reagent and Fehling's solution

- Glucose gets oxidised to six carbon monocarboxylic acid (gluconic acid) on reaction with mild oxidising agent like bromine water or an alkaline solution of iodine. Glucose reduces Tollen's reagent to metallic silver and also Fehling's solution to reddish brown cuprous oxide. All these are mild oxidising agents. These reactions indicate that the carbonyl group present in glucose is an aldehydic group.

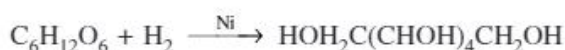


Glucose on mild oxidation gives gluconic acid and on strong oxidation gives saccharic acid

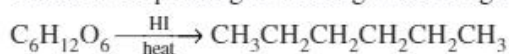
5. On oxidation with strong oxidising agents like nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic group in glucose.



6. Glucose is reduced to sorbitol, a hexahydric alcohol, with hydrogen in presence of nickel.



7. Glucose on prolonged heating with HI gives n-hexane.



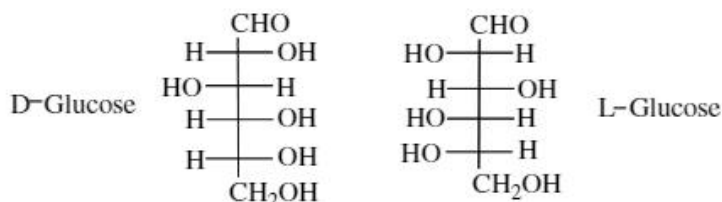
The above two reactions suggest that the six carbon atoms in glucose are linked in an unbranched linear chain.

8. When glucose is treated with dilute sodium hydroxide solution, it undergoes reversible isomerisation resulting in the formation of a mixture of D-glucose, D-fructose and D-mannose. This reaction is known as Lobry de Bruyn van Ekenstein's rearrangement.



It is because of this isomerisation that D-fructose reduces Tollen's reagent and Fehling's solution, though fructose does not contain any aldehydic group.

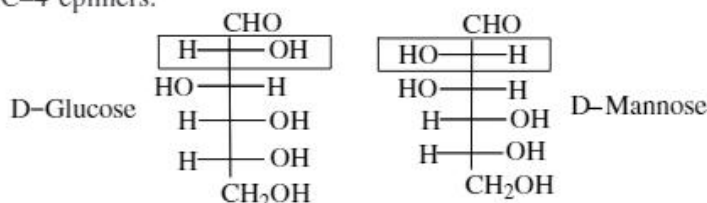
9. Glucose when heated with excess of phenyl hydrazine, a dihydrazone known as glucosazone is formed. On the basis of these experimental observations, glucose was given the open chain structure by Baeyer.



D-glucose and D-mannose are diastereomers, called epimers

Glucose is (2R, 3S, 4R, 5R)-2, 3, 4, 5, 6-pentahydroxyhexanal.

D-glucose and D-mannose are diastereomers. They differ in the configuration only at C-2 carbon and are known as epimers. Similarly, D-glucose and D-galactose are C-4 epimers.



Cyclic structure of glucose : The open chain formula of glucose accounts for most of the reactions satisfactorily but fails to explain the following reactions.

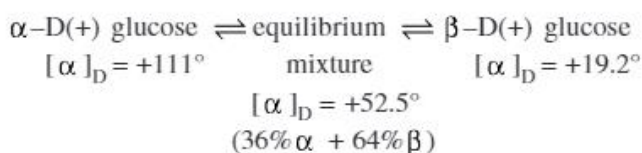
- (a) Glucose does not react with Schiff's reagent, NaHSO_3 and NH_3 , even though it contains an aldehydic group.

- (b) Glucose pentaacetate does not react with hydroxylamine, indicating the absence of free aldehydic group.
- (c) Glucose forms two isomeric methyl glucosides (α - and β -) on heating with methyl alcohol in the presence of dry HCl gas.
- (d) Glucose exists in two stereo isomeric forms : α - and β - forms. These two forms differ from each other in the stereo chemistry at C-1. The aqueous solution of glucose shows mutarotation.

Glucose crystallised from concentrated solution at 30°C gives α -D(+) glucose with melting point 146°C and $[\alpha]_D = +111^\circ$. When pure crystals of α -D(+) glucose are dissolved in water, the specific rotation gradually decreases from +111° to +52.5°.

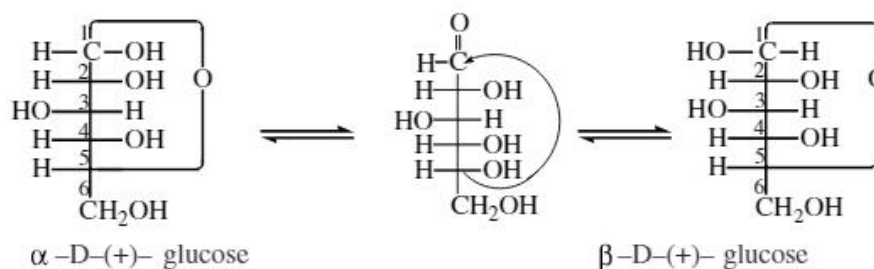
Glucose crystallised from hot saturated aqueous solution above 98°C gives β -D(+) glucose with melting point 150°C and $[\alpha]_D = +19.2^\circ$. When pure crystals of β -D(+) glucose are dissolved in water, the specific rotation gradually increases from +19.2° to +52.5°.

The change in optical rotation is made fast by the addition of traces of acid or base. The spontaneous change of specific rotation of an optically active compound in solution with time, to an equilibrium level, is called mutarotation.

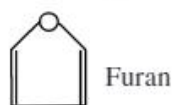
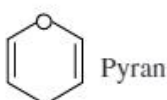


This mutarotation cannot be explained by open chain structure of glucose, but can be explained by cyclic structure.

Generally alcoholic groups undergo rapid and reversible addition to aldehyde group to form hemiacetals. The alcoholic group bonded to C-5 of glucose reacts intramolecularly with -CHO forming a 6-membered hemiacetal ring. The asymmetric carbon now at C-1 gives two optical isomers. They are not mirror images of each other and hence they are diastereomers. They differ in the configuration only at C-1 and are called anomers. The two cyclic forms exist in equilibrium with Fischer chain structure as shown below.



Glucose forms a six membered ring pyranose containing 5 carbon atoms and one oxygen atom like pyran. The five membered ring formed like furan is called furanose. Glucose is present in pyranose form only as shown in Fig 1.2.



Spontaneous change of specific rotation in solution with time is called mutarotation

Diastereomers of glucose differ in configuration at C-1 are called anomers

Haworth structure of glucose is called glucopyranose

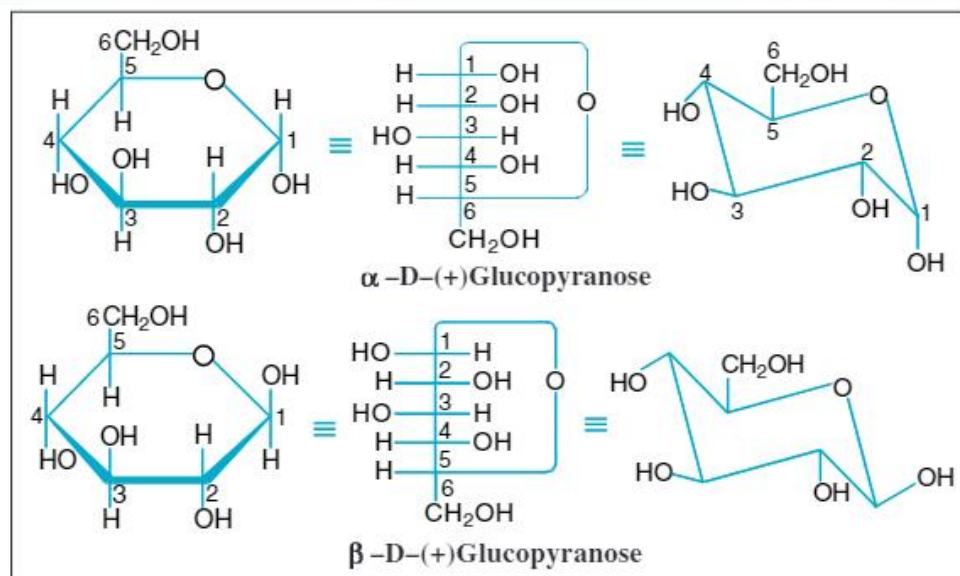
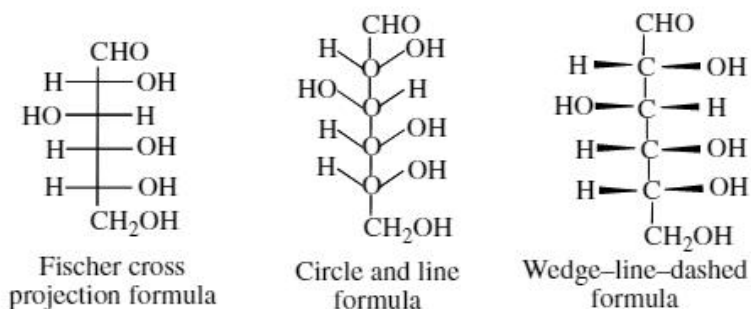


Fig 1.2 The α- and β- forms of Glucopyranoses

The Haworth horizontal structure of glucopyranose is identical to the Fischer vertical projection structure. The groups present on the right side in Fischer formula are written below the plane of the ring and those on the left side are written above the plane.

The cyclic structure of glucose explains the presence of α- and β- forms, mutarotation. It explains the inability of glucose to form aldehyde ammonia and bisulphite compound. In the presence of other carbonyl reagents, the ring is opened and free aldehyde group is produced, which can react with those reagents.

Glucose is also represented by different models as shown below :



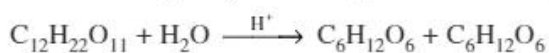
1.2.2

Fructose

Fructose is laevorotatory and is sweetest of all sugars

Fructose is a ketohexose. It is called fruit sugar since it is more abundant in ripe fruits. The naturally occurring fructose is laevorotatory, so it is called laevulose. It is present in honey and cane sugar along with glucose in combined form. It is the sweetest of all the sugars. Inulin on acidic hydrolysis gives only fructose. Fructose belongs to D-series and is laevorotatory. Hence it is written as D-(-)-fructose.

Sucrose on hydrolysis in the presence of acid gives glucose and fructose.

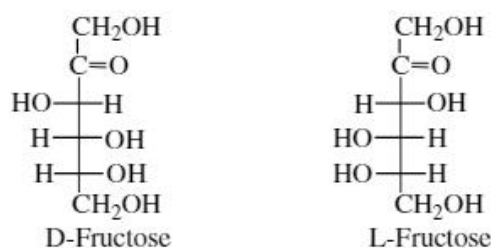


Structure of fructose

1. The molecular formula of fructose was found to be $C_6H_{12}O_6$.
2. Fructose contains five hydroxyl groups, out of which two are primary and three are secondary.
3. Fructose contains a carbonyl group and it was found to be ketonic from its oxidation products with a strong oxidising agent.
4. Fructose was found to contain ketonic functional group at second carbon atom and all the six carbon atoms are in unbranched chain as in the case of glucose.
5. Since fructose and glucose form identical osazones when heated with excess of phenyl hydrazine, it was found that both glucose and fructose have the same configuration at C-3; C-4 and C-5.
6. Like glucose, fructose also shows mutarotation.
7. Though fructose does not contain an aldehydic group, it behaves as a reducing sugar due to Lobry de Bruyn van Ekenstein rearrangement.
8. Unlike glucose, fructose has cyclic furanose structure.
9. The α - and β - forms of fructose are anomers at C-2.

Fructose has no aldehyde group, but is a reducing sugar

The open chain structure of fructose is shown below.



The α - and β - forms of fructose are anomers at C-2

The Fischer and Haworth structures of α -D-fructose and β -D-fructose are shown in Fig 1.3.

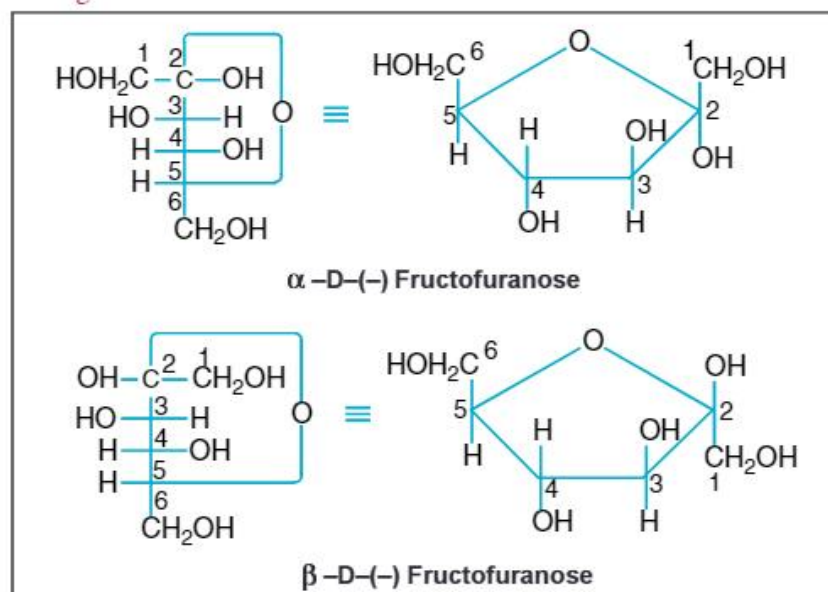


Fig 1.3 Cyclic structures of fructose



P.1.3 Though fructose is a keto hexose, it is a reducing sugar. Why?

Solution

In aqueous basic solution like Fehling's solution or Tollen's reagent, fructose undergoes Lobry de Bruyn van Ekenstein rearrangement and forms a mixture of D-glucose, D-mannose and D-fructose. Hence it acts as reducing sugar.



P.1.4 A disaccharide 'X' on hydrolysis gives two C_4 -epimeric monosaccharides 'Y' and 'Z'. Then what is disaccharide 'X'?

Solution

Glucose and galactose are C_4 -epimers.

Compound X is Lactose. It undergoes hydrolysis to give glucose (Y) and galactose (Z).



P.1.5 Both glucose and fructose on reaction with excess of phenylhydrazine form the same osazone. In this reaction, how many moles of phenyl hydrazine react with one mole of glucose or fructose? Why?

Solution

One mole of glucose or fructose reacts with three moles of phenylhydrazine. In the reaction with phenyl hydrazine, glucose or fructose undergoes condensation first and then osazone is formed, through oxidation and condensation.



P.1.6 Why sucrose is called invert sugar?

Solution

Natural sucrose is dextrorotatory with $[\alpha]_D = +66.5^\circ$.

When it is hydrolysed forms D-glucose with $[\alpha]_D = +52.5^\circ$ and D-fructose with $[\alpha]_D = -92.4^\circ$. Then the resultant mixture becomes leavo rotatory. So it is called invert sugar.



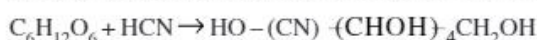
P.1.7 How is the presence of one carbonyl group in glucose supported ?

Solution

Glucose on treating with hydroxylamine forms glucose oxime



Glucose on treating with hydrogen cyanide forms glucose cyanohydrine



These two reactions indicate the presence of one carboxyl group in glucose



P.1.8 Which is more stable among α -D-glucose and β -D-glucose? Why?

Solution

β -D-glucose is more stable.

In α -D-glucose -OH group at C-1 is in axial position while in β -D-glucose, -OH group at C-1 is equatorial. In both, groups at other carbon atoms are in equatorial positions.

DI AND TRI SACCHARIDES

1.3.1

Disaccharides

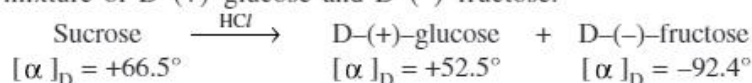
Monosaccharide units are joined by glycosidic linkages in polysaccharides

A disaccharide on hydrolysis gives two monosaccharides. Similarly a tri-saccharide on hydrolysis gives three monosaccharides. Oligosaccharides on hydrolysis give 3 to 10 monosaccharide molecules of same or different kind.

In oligo and polysaccharides, monosaccharide units are linked through oxygen atom. This linkage is called glycosidic linkage. For example, in sucrose C-1 of α -D-glucose and C-2 of β -D-fructose are linked through glycosidic linkage.

Sucrose : Molecular formula of sucrose is $C_{12}H_{22}O_{11}$. Sucrose is present in all photosynthetic plants. It is mainly present in sugar cane, beet root, etc. It is a disaccharide consisting glucose and fructose. Naturally available sucrose is a dextro-rotatory substance but does not show mutarotation. It is a colourless and odourless crystalline substance, which is highly soluble in water.

Inversion of cane sugar : The acid hydrolysis of sucrose produces equimolar mixture of D-(+)-glucose and D-(-)-fructose.



Process of hydrolysis of sucrose to give equimolar mixture of glucose and fructose is called inversion

Sucrose in an aqueous solution is dextrorotatory with $[\alpha]_D = +66.5^\circ$. The net specific rotation of equimolar mixture of D-glucose and D-fructose is $\frac{+52.5 - 92.4}{2} = -20^\circ$. The laevorotation of fructose (-92.4°) is more than dextrorotation of glucose ($+52.5^\circ$). Hence its aqueous solution is laevorotatory and sign changes from 'd' ($+66.5$) to 'l' (-20°). This process is called inversion of cane sugar and the product is named as invert sugar.

In sucrose, glucose is present in pyranose form and fructose is present in furanose form with α, β -glycosidic linkage. So sucrose is known as α -D-glucopyranose and β -D-fructofuranose. The Haworth structure of sucrose is given in Fig 1.4.

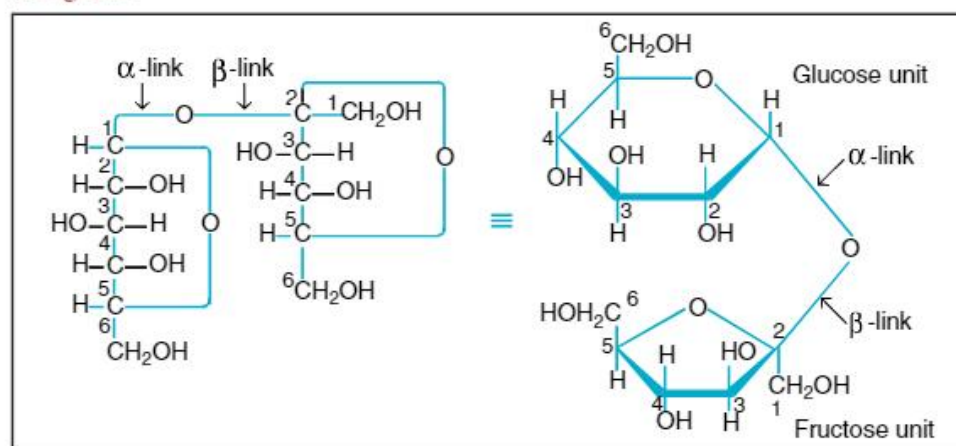


Fig 1.4 Structure of sucrose

A glycosidic linkage is formed between C-1 of α -glucose and C-2 of β -fructose. Sucrose is a non-reducing sugar, because hemiacetal hydroxyl groups of both glucose and fructose are not free. They are involved in the formation of glycosidic linkage.

Lactose is milk sugar and has 1,4- β linkage

Lactose : Lactose is called milk sugar because it is mainly present in milk. Its molecular formula is $C_{12}H_{22}O_{11}$. Lactose is a disaccharide of β -D-glucose and β -D-galactose. The two units are linked by β -glycosidic linkage with C-1 of galactose and C-4 of glucose molecule. The enzyme emulsin catalyses hydrolysis of β -glycosidic linkage. It is a reducing sugar, because it has one hemiacetal hydroxyl group in glucose unit. The structure of lactose is given in Fig 1.5.

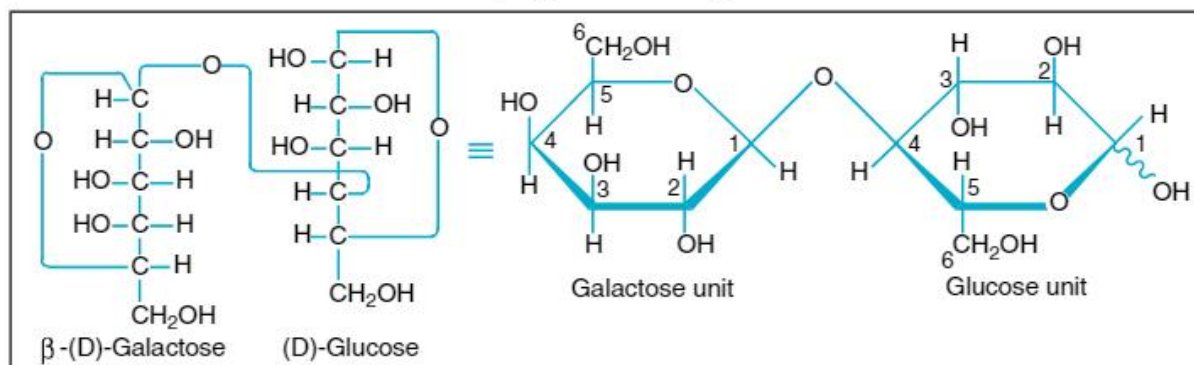
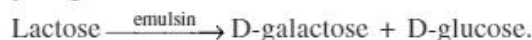


Fig 1.5 Structure of lactose

$$\begin{array}{ccccc} (\text{C}_6\text{H}_{10}\text{O}_5)_n + \text{H}_2\text{O} & \xrightarrow{\text{diastase}} & \text{C}_{12}\text{H}_{22}\text{O}_{11} & \xrightarrow{\text{maltase}} & \text{C}_6\text{H}_{12}\text{O}_6 \\ \text{starch} & & \text{maltose} & & \text{glucose} \end{array}$$

Diagram illustrating the mutarotation of D-glucose. The left side shows the cyclic forms: α -D-Glucose (left) and D-Glucose (middle). The right side shows the open-chain form of D-glucose (right).

Fig 1.6 Structure of maltose

Solution



Solution



Solution



Solution



Solution

In sucrose, hemiacetal hydroxyl groups of glucose and fructose are involved in the glycosidic linkage. Hence sucrose is a non-reducing sugar. In lactose, hemiacetal hydroxy groups of galactose involved in the glycosidic linkage but of glucose not involved in glycosidic linkage. Hence lactose is a reducing sugar.



P.1.14 There are three disaccharides A, B and C. The hydrolysis products of 'A' are functional isomers and of 'B' are epimers. But the hydrolysis products of 'C' are neither epimers nor functional isomers. Then what are A, B and C?

Solution Disaccharide 'A' is sucrose. It gives glucose and fructose upon hydrolysis. Disaccharide 'B' is Lactose. It gives glucose and galactose upon hydrolysis. 'C' is maltose. Maltose gives two glucose molecules upon hydrolysis.



P.1.15 What differences can be observed in the glycosidic links of maltose and lactose ?

Solution Both in maltose and lactose, the glycosidic linkage is present between C₁ of one glucose molecule to C₄ of another glucose molecule.

However, glucose has α - configuration in maltose structure and it has β - configuration in lactose structure.

1.3.2

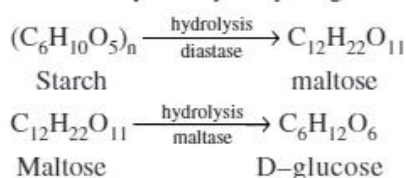
Polysaccharides

Polysaccharides act as structural materials for higher plants and reserve food for plants as well as animals. Polysaccharides are also called glycans, consisting of large number of monosaccharide units joined through glycosidic linkages. The general formula of polysaccharides is $(C_6H_{10}O_5)_n$.

eg : Starch, cellulose, dextrin, glycogen, etc.

Starch : Starch is a polysaccharide of α -D-glucose. It is also called amylum with formula $(C_6H_{10}O_5)_n$. It is widely present in vegetable kingdom. It is present in leaves, stems, fruits, roots and seeds also. Its important sources are wheat, maize, rice, potatoes, barley, sorghum, nuts, etc. It is the major food material and easily hydrolyses with enzyme, amylase present in saliva to give glucose.

Starch is a white amorphous substance with no taste and smell. It is almost insoluble in cold water but soluble relatively more in boiling water. Starch solution gives a blue colour iodine, which disappears on heating and reappears on cooling. Starch on complete hydrolysis gives D-glucose units.



Starch cannot reduce Tollen's reagent or Fehling's solution. It does not form osazone, because, the hemiacetal hydroxyl groups at C-1 of all glucose units are involved in glycosidic linkages.

Starch is mixture of two polysaccharides, amylose and amylopectin. The exact chemical nature of starch varies from source to source. Natural starch contains 15-20% amylose and 80-85% amylopectin.

Amylose is a linear polymer of α -D-glucose. It is water soluble and gives blue colour with iodine solution. Chemically amylose is a long unbranched chain with 200-1000 α -D-(+) glucose units joined by α -glycosidic linkage between C₁ of one glucose and C₄ of the next glucose.

Its molecular mass may be from 10,000 – 50,000u. The structure of amylose is given in Fig 1.7.

Natural starch contains amylose and amylopectin

Amylose is a linear polymer of α -D-glucose

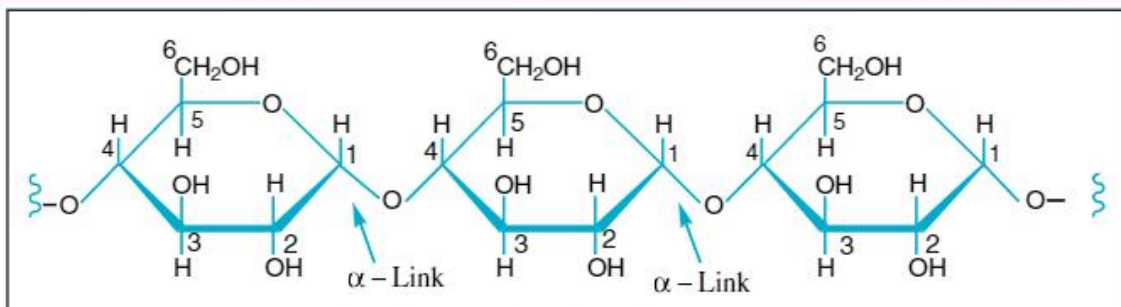


Fig 1.7 Structure of amylose

Amylopectin is a branched chain polymer of α -D-glucose. Amylopectin is water insoluble and does not give blue colour with iodine solution. It indicates that starch turns iodine solution to blue due to the presence of amylose only. Amylopectin contains 25 - 30 D-glucose units in each chain.

The C_1 of one glucose and C_4 of other glucose linked through α -glycosidic linkage to form chains. But the branchings are due to glycosidic linkage between C_1 of a glucose in one chain and C_6 of a glucose in the adjacent chain. These linkages are as shown in Fig 1.8.

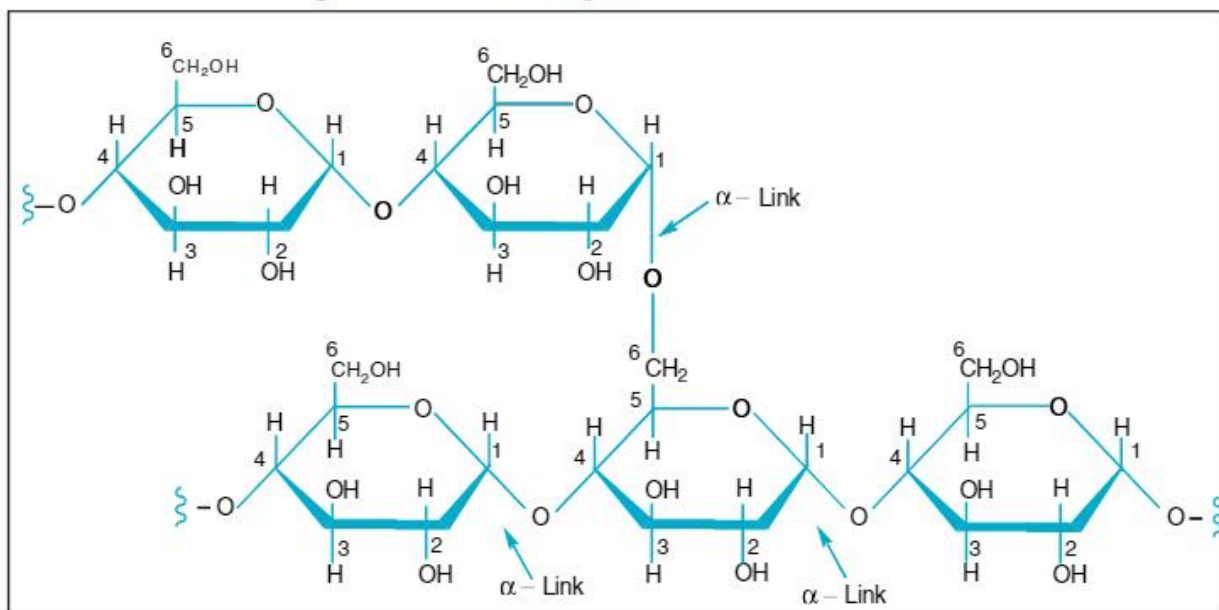


Fig 1.8 Structure of amylopectin

Cellulose is a polysaccharide of β -D-glucose

Cellulose : Cellulose is a polysaccharide of β -D-glucose. Cellulose is the principal structural component of vegetable matter. Higher percentage of cellulose is present in the natural plant polymer, cotton. Cotton contains 90% of cellulose. Wood contains 40-50% cellulose.

The molecular formula of cellulose is $(C_6H_{10}O_5)_n$. Photosynthesis in the plants is responsible for the formation of cellulose. Cellulose is a colourless amorphous solid. It is insoluble in cold water. Cellulose contains a large number of D-glucose units joined by β (1, 4)- glycosidic linkages. Cellulose is mainly linear chain polymer

and the individual strands will be connected through a number of hydrogen bonds. So it becomes rigid and acts as cell wall material. But in amylose of starch, hydrogen bonds are not formed, so it contains soft helical structure.

Cellulose is a non-reducing sugar

Cellulose does not reduce Tollen's reagent and Fehling's solution because no free hemiacetal hydroxyl group is present in it. It does not form osazone.

The molecular mass of cellulose is nearly 50,000 – 5,00,000u. It contains 300 to 2500 D-glucose units. The structure of cellulose is given in Fig 1.9.

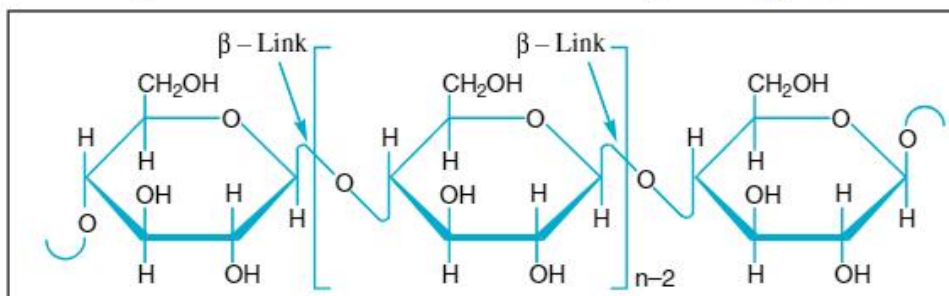


Fig 1.9 Structure of cellulose

Cellulose cannot be digested by human beings

Cellulotic bacteria is present in the stomach of ruminant animals like cattle and sheep. It breaks down the cellulose using the enzyme cellulase to get digested and to convert finally into glucose. Cellulase enzyme is not present in the intestine of human beings. Hence, human beings cannot digest cellulose.

Different glycoside linkages in respective carbohydrates are summarised in Table 1.2.

Table 1.2 Different carbohydrates and glycoside linkages

S.No.	Carbohydrate	Glycosidic linkage
1	Sucrose	$C_1\alpha - C_2\beta$ –Glycosidic linkage
2	Lactose	$C_1\beta - C_4\beta$ –Glycosidic linkage
3	Maltose	$C_1\alpha - C_4\alpha$ –Glycosidic linkage
4	Cellobiose	$C_1\beta - C_4\beta$ –Glycosidic linkage
5	Amylose	$C_1\alpha - C_4\alpha$ –Glycosidic linkage
6	Amylopectin	$C_1\alpha - C_4\alpha$ –Glycosidic linkage
		$C_1\alpha - C_6\alpha$ –Glycosidic linkage
7	Cellulose	$C_1\beta - C_4\beta$ –Glycosidic linkage
8	Glycogen	$C_1\alpha - C_6\alpha$ –Glycosidic linkage
9	Starch	$C_1\beta - C_4\beta$ –Glycosidic linkage
		$C_1\alpha - C_6\alpha$ –Glycosidic linkage

Glycogen is animal starch

Glycogen : The carbohydrates are stored in animal body as glycogen. Glycogen is also called animal starch because its structure is similar to amylopectin and is rather more highly branched. It is present in liver, muscles and brain. When the body needs glucose, enzymes breakdown glycogen to glucose. Glycogen is also found in yeast and fungi.

1.3.3

Importance of carbohydrates

Starch is most valuable food constituent

Carbohydrates play an important role in life of both plant and animal kingdom. Some of them are used as food reserves of animals like glycogen. Honey is the instant source of energy. Glucose is used as food for patients and children. Glucose may be used in the preparation of jams and jellies. In the treatment of calcium deficiency, calcium glucosate is used as medicine. Vitamin C can be prepared industrially using glucose. The carbohydrate antibiotic is streptomycin. Kenamycins, neomycins and gentamycins are used against bacteria which are resistant to penicillins.

Attempts are going on to develop a vaccine against cancer. It may avoid chemotherapy for cancer treatments, which has toxic side effects.

Starch is the most valuable constituent of food like rice, potatoes, etc. It is also used in the manufacture of dextrin, adhesives and explosives. Cell walls of bacteria and plants are made up of cellulose. Cotton fibre, paper and wood contain cellulose. The explosives like gun powder, medicines, paints, lacquers are manufactured using cellulose nitrate. Cellulose acetate is used in the manufacture of rayon and plastics. D-Ribose and 2-deoxy-D-ribose are present in nucleic acids.

Glycogen is produced from glucose which is absorbed from the intestine into the blood, transported to liver, muscles, etc. and is polymerised enzymatically. Similarly when body needs glucose, the enzymes breakdown glycogen to glucose.

Carbohydrates act as biofuels to provide energy for functioning of living organisms. In human system, all the carbohydrates except cellulose can serve as source of energy.



P.1.16 Starch and cellulose possess the same molecular formula, but starch is water soluble and cellulose is water insoluble. Why?

Solution

Starch has two forms, one is a linear polymer and the other is a cross linked polymer. Both forms of starch are soluble in water.

Cellulose is a net work polymer stabilized with hydrogen bonding. So it is insoluble in water.



P.1.17 What makes amylopectin different from amylose ?

Solution

Amylopectine is a branched chain polymer of α -D-glucose, while amylose is a linear polymer. The C_1 of a glucose in one chain and the C_6 of a glucose in the adjacent chain for α -glycosidic links in amylopectin.

EXERCISE - 1.1.1

1. What are di, tri and oligo saccharides? Give examples.
2. Represent pyranose and furanose structures of carbohydrates.
3. How is the presence of five -OH groups in glucose supported ?
4. Glucose and fructose have same configurations at C-3, C-4 and C-5. Substantiate.
5. What is mutarotation? Explain.
6. Mention the hydrolysis products of lactose.
7. What is animal starch? Why is it called so?
8. What is the difference between starch and cellulose?
9. Explain Lobry de Bruyn van Ekenstein rearrangement.
10. What are anomers and epimers? Give examples.
11. Starch is soft but cellulose is hard and rigid. Explain?
12. Write the importance of carbohydrates.



1.	Most of the biochemical reactions take place in dilute neutral solutions at $\text{pH} = 7$ and one atmosphere.
2.	Glucose, fructose and mannose are examples of monosaccharides. Sucrose, lactose and maltose are important disaccharides. Cellulose and starch are important polysaccharides.
3.	Glucose is an aldohexose and fructose is a ketohexose.
4.	Glucose, fructose, mannose, lactose and maltose are reducing sugars. Sucrose, starch and cellulose are non-reducing carbohydrates.
5.	Both glucose and fructose have primary and secondary hydroxyl groups.
6.	Open structure of glucose contains five $-\text{OH}$ groups and one $-\text{CHO}$ group.
7.	Glucose and fructose have same configurations at C-3, C-4 and C-5 carbon atoms.
8.	Cyclic form of glucose is called glucopyranose and of fructose is called fructofuranose.
9.	Open structure of glucose contains five $-\text{OH}$ groups and one $-\text{CHO}$ group.
10.	Cyclic form of glucose is called glucopyranose and fructose is called glucofuranose.
11.	Sucrose is a glycoside of α -glucopyranose and β -fructofuranose.
12.	Hydrolysis of sucrose to give equimolar mixture of glucose and fructose is called inversion of sugar.
13.	Lactose is milk sugar and has 1,4- β linkage.
14.	Maltose is present in barley seeds and has 1,4- α linkage.
15.	Starch contains 10–20% amylose and 80–90% amylopectin. Starch upon complete hydrolysis gives D-glucose units.
16.	Amylose is a linear polymer of α -D glucose. Amylopectin is a branched chain polymer of α -D glucose.
17.	Cellulose is a polysaccharide of β -D-glucose. Cellulase enzyme present in intestine of ruminant animals can break down β -glycosidic linkages during digestion.
18.	Glycogen is the carbohydrate stored in animal body and is called animal starch.
19.	Carbohydrates act as biofuels to provide energy for living functions.

EXERCISE - 1.2

- How many number of stereoisomers possible for a carbohydrate with molecular formula $C_6H_{12}O_6$ which is a ketohexose. (Ans : 8)
- Write the structural differences between the three monosaccharids, D-(+)-glucose, D-(+)-mannose and D-(-)-galactose.
- Give a reaction to show that glucose molecule contains the following:
(i) five -OH groups and (ii) one -CHO group
- How is a test for ketose sugar performed? What are the observations made?
- Discuss the fundamental differences between the structures of glucose and fructose.
- How can you say that all the six carbon atoms in glucose are linearly linked?
- Write the Haworth structure of a non-reducing sugar.
- What is invert sugar?
- Write on the osazone formation from glucose and fructose. Explain.
- Fructose reduces Fehling's solution, even though it is a ketone. Justify.
- How do you explain the formation pyranose structures for glucose and fructose?
- What type of carbohydrates exhibit mutarotation?
- Write the complete name of maltose? (Ans : 4-(O)- α -D-glucopyranosyl-D-glucopyranose)
- Write the hydrolysis products and structures of sucrose, lactose and maltose.
- What are the hydrolysis products of lactose and maltose?
- Write three important properties of each amylose and amylopectin.
- Write the main structural differences, observed for starch and cellulose ?
- What is glycogen ?
- Which carbohydrates are present in nucleic acids?
- Carbohydrates are essential for life both in plants and animals. Justify.

