UNIT 2 CARBOHYDRATES

Structure

2.1 INTRODUCTION

In Unit 1, we described the structure of a typical cell, and the function of its various organelles. Besides this, we also outlined the average chemical composition of a cell. You will recall that the dry weight of a cell mainly comprises of proteins, lipids, nucleic acids and carbohydrates. These are all important biomolecules required to sustain a living organism. In Unit 2 you will be introduced to carbohydrates. These important molecules, in addition to being part of the structure of a cell, also provide energy for its functioning. We shall classify carbohydrates into various types and describe their chemical structures. You shall also briefly learn about the stereochemistry of sugars, and the biological role carbohydrates play. In Unit 3 you will study another important biomolecule, namely lipids. These molecules form part of the structure of membranes, store energy for the cell, and perform other functions also.

Objectives

After studying this unit, you should be able to,

- define monosaccharides, oligosaccharides and polysaccharides,
- identify a monosaccharide as an aldose or a ketose,
- describe stereochemistry and anomeric forms of sugars,
- draw the straight chain (Fischer projection) and ring structure (Haworth formula) of sugars,
- describe the chemical nature/properties of carbohydrates and their biological roles,
- describe storage and structural polysaccharides, and
- describe some complex polysaccharides and their biological significance.

2.2 CLASSIFICATION

Before we describe the classification of carbohydrates, let us first know more about the general nature and functions of these biomolecules. Carbohydrates are the most abundant of all forms of biomolecules. They comprise of polyhydroxy aldehydes, polyhydroxy ketones, and their derivatives which can be hydrolysed to yield polyhydroxy aldehydes and polyhydroxy ketones. Carbohydrates include saccharides or sugars, glycogen, starches, cellulose, dextrins, etc. In addition to these, carbohydrates are also found in combination with other molecules, in the form of glycosaminoglycans, lipopolysaccharides, glycoproteins and glycolipids. Carbohydrates, together with fats and proteins, constitute three major components of our food.

Carbohydrates generally serve as a source of energy for the living organism. In plants, these molecules (e.g., cellulose) are also components of the supporting tissue (such as the wood in trees). Certain carbohydrates like ribose in nucleic acids, galactose in cerebrosides, lactose in milk and cell surface carbohydrates are responsible for highly specialised functions. Monosaccharides, which are the simplest of sugars, serve as building blocks for the more complex sugars, and are the immediate source of energy for the cells. Large amount of energy is stored in more complex carbohydrates, like starch in plants and glycogen in animals. This energy is utilised by breaking these molecules into simpler molecules within the living system. While plants synthesise carbohydrates by photosynthesis, animals cannot do so and must get their carbohydrate supply from plants, which serve their energy requirements. Carbohydrates along with fatty acids are the most important metabolic fuels in the cells of animals.

Mono-one
Oligo-few
Poly-many

Let us now study the classification of carbohydrates. These biomolecules can be classified into monosaccharides, oligosaccharides and polysaccharides, according to the size of the molecule. Monosaccharides are carbohydrates that cannot be broken into smaller units upon hydrolysis, e.g., glucose. Oligosaccharides upon hydrolysis yield between 2-6 monosaccharide units and, depending upon the number of monosaccharide units so obtained, are known as disaccharides, trisaccharides, etc. Polysaccharides produce a large number of monosaccharide units (more than six) upon hydrolysis. They may contain as many as 3000 monosaccharide units.

-ose is the characteristic suffix used to denote a sugar.

Monosaccharides, which are also known as simple sugars, are further classified by the number of carbon atoms in the molecule, i.e., a three carbon monosaccharide is known as a triose, and four, five and six carbon monosaccharides as tetroses, pentoses, hexoses and so on. Depending upon the nature of the carbonyl function, a monosaccharide is further classified as an aldose (containing an aldehyde functional group) or a ketose (containing a ketone functional group). For example, ribose is an aldopentose (a 5-carbon sugar molecule containing an aldehyde group), glucose is an aldohexose (a 6-carbon sugar with an aldehyde group) and fructose is a ketohexose (a 6-carbon sugar with a ketone group).

We shall now describe monosaccharides in detail.

2.3 MONOSACCHARIDES

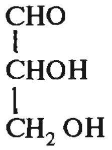
Most disaccharides are reducing sugars, sucrose (common table sugar) being an exception as it is a nonreducing sugar.

As outlined above, monosaccharides usually contain a 3-6 carbon atom chain with an aldehyde or a ketone group. These simple sugars are white crystalline solids. They are highly soluble in water, due to the presence of polar hydroxyl groups. This implies that these sugars will have low solubility in nonpolar solvents. Most nosaccharides have a sweet taste. All monosaccharides whether aldoses or ketoses are reducing sugars, since they reduce Fehling's or Benedict's or Tollen's reagent.

Before we describe some individual monosaccharides, let us have a look at the stereochemistry of these molecules first.

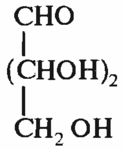
2.3.1 Stereochemistry of Monosaccharides

Study the structures of some monosaccharides which are shown below:



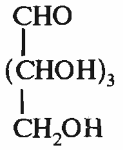
$$\begin{array}{c} CHO \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Aldotriose



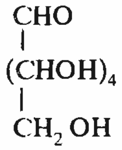
$$\begin{array}{c} CHO \\ | \\ (CHOH)_2 \\ | \\ CH_2OH \end{array}$$

Aldotetrose



$$\begin{array}{c} CHO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}$$

Aldopentose



$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

Aldohexose

You would observe that aldotriose (glyceraldehyde) has one chiral carbon atom. Therefore, it exists in two enantiomeric forms, with optical activity of opposite sign, namely, dextrorotatory and levorotatory glyceraldehydes. Higher sugars have two or more chiral carbon atoms and, therefore, have a larger number of stereoisomers.

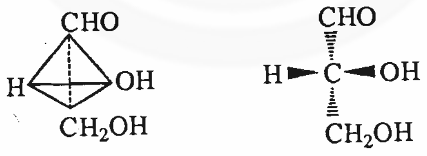
The number of stereoisomers is equal to 2^n, where *n* is the number of chiral carbon atoms. Those aldoses which are related to dextrorotatory glyceraldehyde (also called D-(+)-glyceraldehyde), i.e., those aldoses which can be synthesised from, or chemically degraded to this compound, are said to belong to the D-series of sugars. Similarly, the L-series sugars are related to the levorotatory glyceraldehyde (also called L-(–)- glyceraldehyde). You should note that the capital letters D and L, as applied to the higher sugars, do not refer to the actual sign of their optical activity. These refer only to their structural relationship to D-or L-glyceraldehyde. As you will see later, D or L notations also refer to the configuration around the chiral arbon, next to CH_2OH group, which is also the chiral carbon farthest from the aldehyde group. Since the carbon atoms of aldoses are numbered starting with the aldehyde carbon, the configuration around the chiral carbon, with the highest position number, determines whether a sugar belongs to the D or the L series.

A tetrahedral carbon, with four different atoms or group of atoms carbon. It is generally designated with an asterisk(*).

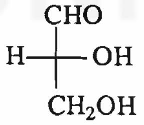
Enantiomers are stereoisomers that are non-superimposable mirror images of each other.

Stereoisomers that are not mirror images of each other are called diastereomers.

Emil Fischer, who described assignment of configuration around all chiral carbon atoms of glucose and some other sugars, proposed a method (convention) for representing configuration of carbohydrates, called **Fischer's projection** formula. This is explained below for D-glyceraldehyde.



D-Glyceraldehyde : For arriving at the projection formula, the tetrahedron containing the chiral carbon at its center (not shown in the drawing on extreme left) is held with CHO on the top, CH_2OH at the bottom and the line joining them (i.e. the edge of the tetrahedron) is below the plane of the paper. H and OH point towards the viewer.

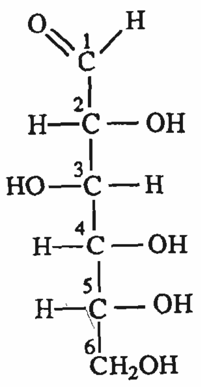


Fischer's projection formula is a two-dimensional projection(on paper) of the molecule when it is held as explained in the accompanying drawing. Thus horizontal lines represent bonds above the plane of paper, and vertical lines represent bonds below the plane of paper.

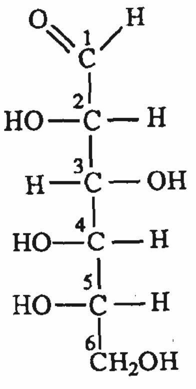
Fischer's projection formulae are specially helpful for representing the configurations of higher sugars having several chiral carbon atoms. In each case, it is a two-dimensional projection of the molecule, when the latter is held with CHO on the top, CH_2OH at the bottom, all the carbon-carbon bonds below the plane of the paper, and H & OH on all chiral carbon atoms pointing towards the viewer.

Inter-relationship of various D-aldoses is shown in Fig. 2.1, using the Fischer's projection formulae. The L-aldoses are simply mirror images of their

D-counterparts, as is shown below for D- and L-glucoses. The L-sugars are much less abundant than the D-sugars in nature.



D-Glucose



L-Glucose

D- and L-sugars are referred to as enantiomers. As can be seen there are several pairs of isomeric aldoses which differ from each other at only one of the several chiral carbon atoms, e.g. glucose and mannose (differing at C – 2 only) and glucose and galactose (differing at C-4). Such isomers are referred to as **epimers**. Note that mannose and galactose are not epimers of each other.

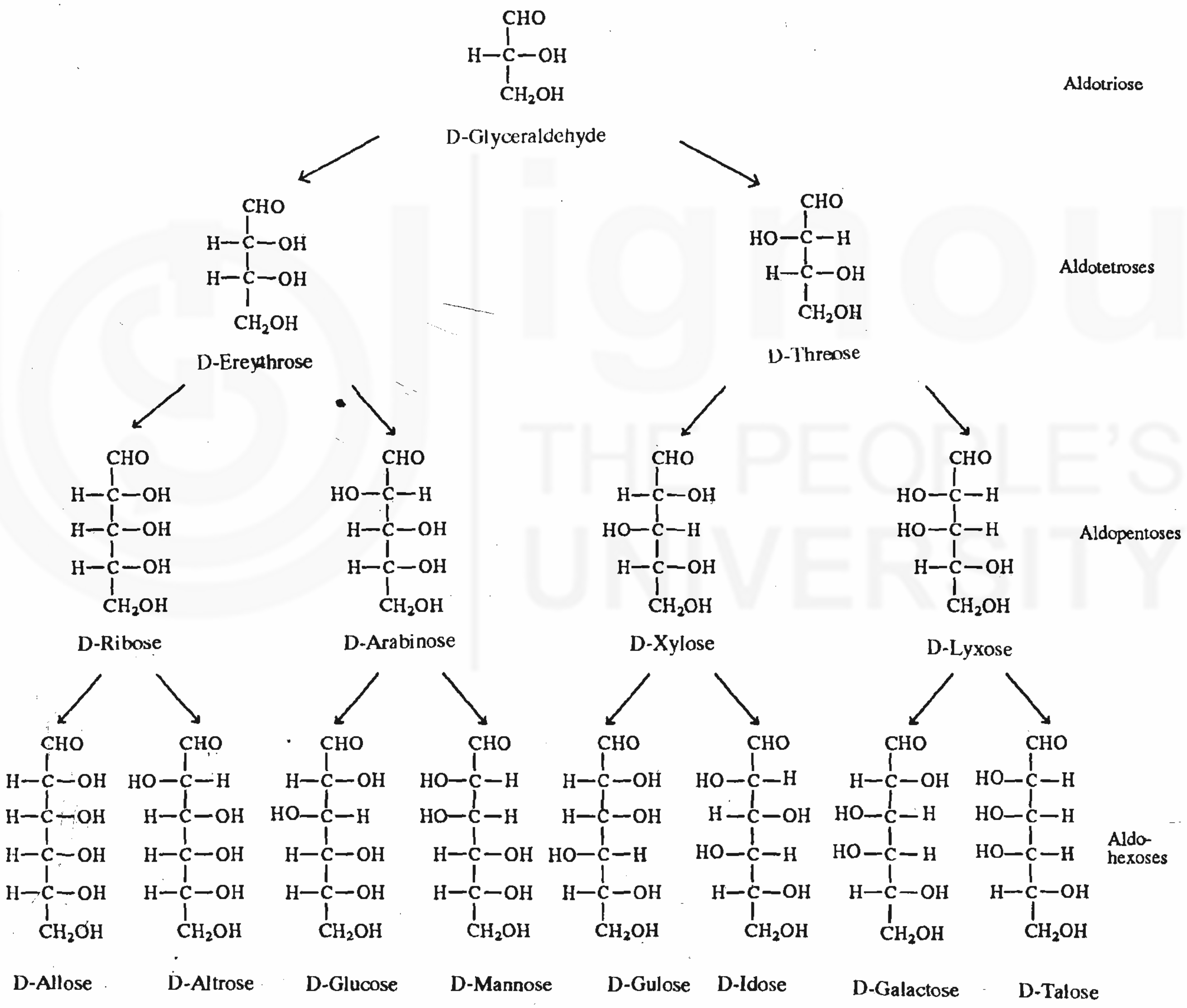


Fig. 2.1: Stereochemical relationship among the D-aldoses with 3 to 6 carbon atoms

In a similar manner, ketoses may be related to dihydroxy acetone (ketotriose). In this case also, the capital letters D and L are used to denote the configuration around the chiral carbon farthest from the keto group, i.e., the one with the highest position number since the numbering starts from the end nearer to the keto group. Inter-relationship of various keto sugars is shown in Fig. 2.2. You would observe that for the same chain length, the ketoses have one chiral carbon less than the aldoses. For example, an aldohexose has four chiral carbons and a ketohexose has only three. Therefore, the number of stereoisomers of ketoses will be half of those of the corresponding aldoses.

The D and L configurational notation has been retained in sugar chemistry. For other organic compounds, it has been replaced by a more convenient and unambiguous R (rectus) and S (sinister) notation. In the latter system, it becomes necessary to give configurational notation for each chiral carbon atom. It can be shown that D- and L-glyceraldehydes are R- and S-glyceraldehydes, respectively. As mentioned above, the capital letters D and L do not provide any information about the direction of optical activity. Wherever necessary, the latter is shown by (+) and (–) which stand for the dextrorotation and levorotation, respectively, e.g. D-(+)-glucose and D-(–)-fructose.

The difference in the arrangement of atoms between the D and L isomers is small and appears to be unimportant to us. However, to our body and its cells, it is quite critical. This minor difference is recognised by the cells, which often use only one of the isomers. For example, yeast can ferment D-glucose to produce alcohol, but it cannot ferment L-glucose.

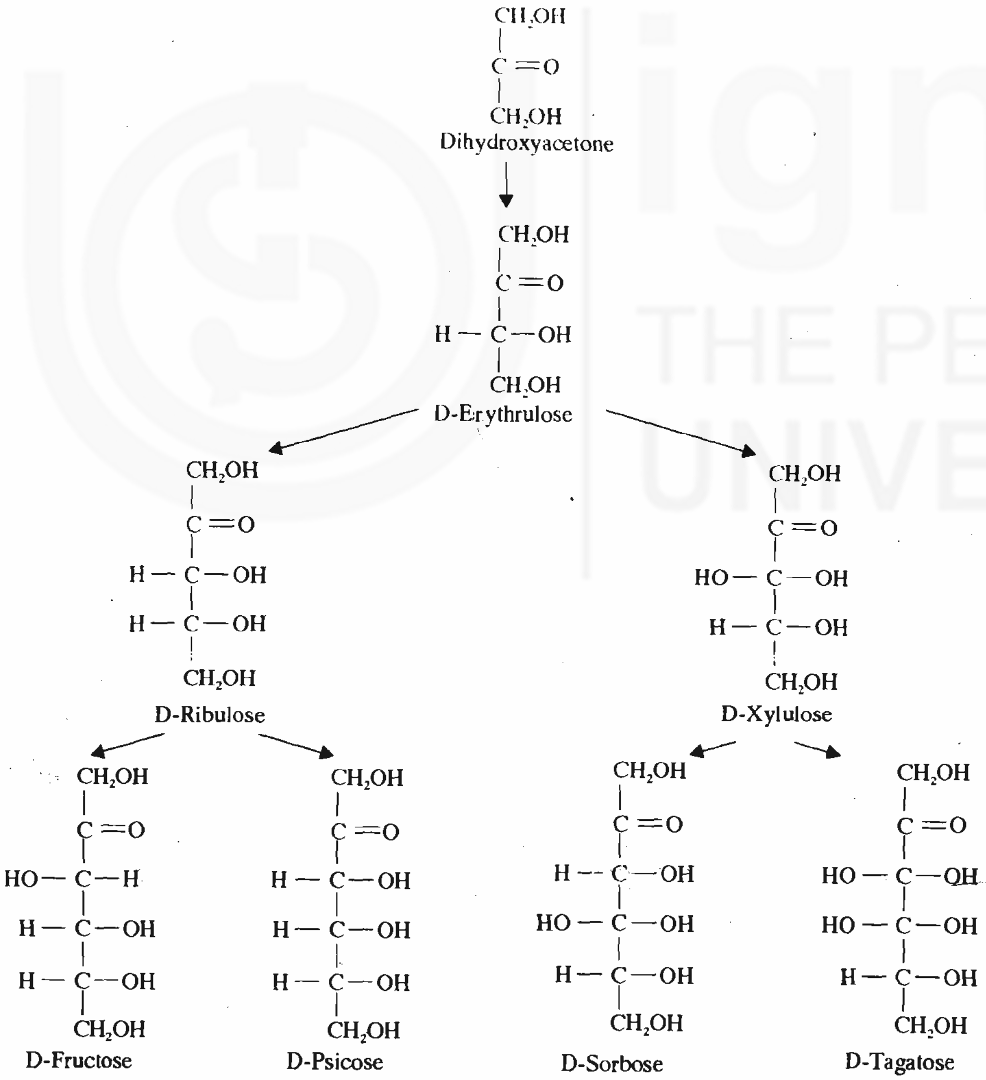


Fig. 2.2: Stereochemical relationship among the D-ketoses with three to six carbon atoms

Let us now describe glucose first, as it is a common aldohexose.

2.3.2 Glucose (Dextrose): An Aldohexose

Glucose, also known as blood sugar and grape sugar, is the most common hexose and is found in fruit juices, grape juice in particular, in the saps of plants, in the blood and tissue of animals. As already mentioned, it is the immediate source of energy for all metabolic reactions in the animals. Adult human body contains about 1 teaspoon (5-6 grams) of glucose in the blood, which supplies energy needs of the body for around fifteen minutes. Glucose in the blood is continuously replaced from glycogen stored in the liver.

D-glucose is a part of many oligo/polysaccharides. Because of its presence in a large number of living cells, its chemistry is very important. A study of glucose can help in learning about other monosaccharides as well. Elemental analysis and molecular weight determination indicates that glucose has a molecular formula of $C_6H_{12}O_6$. Further, its chemical behaviour supports a six carbon, pentahydroxy aldehyde structure. These chemical reactions, supporting an aldohexose structure, are summarised in Fig. 2.3.

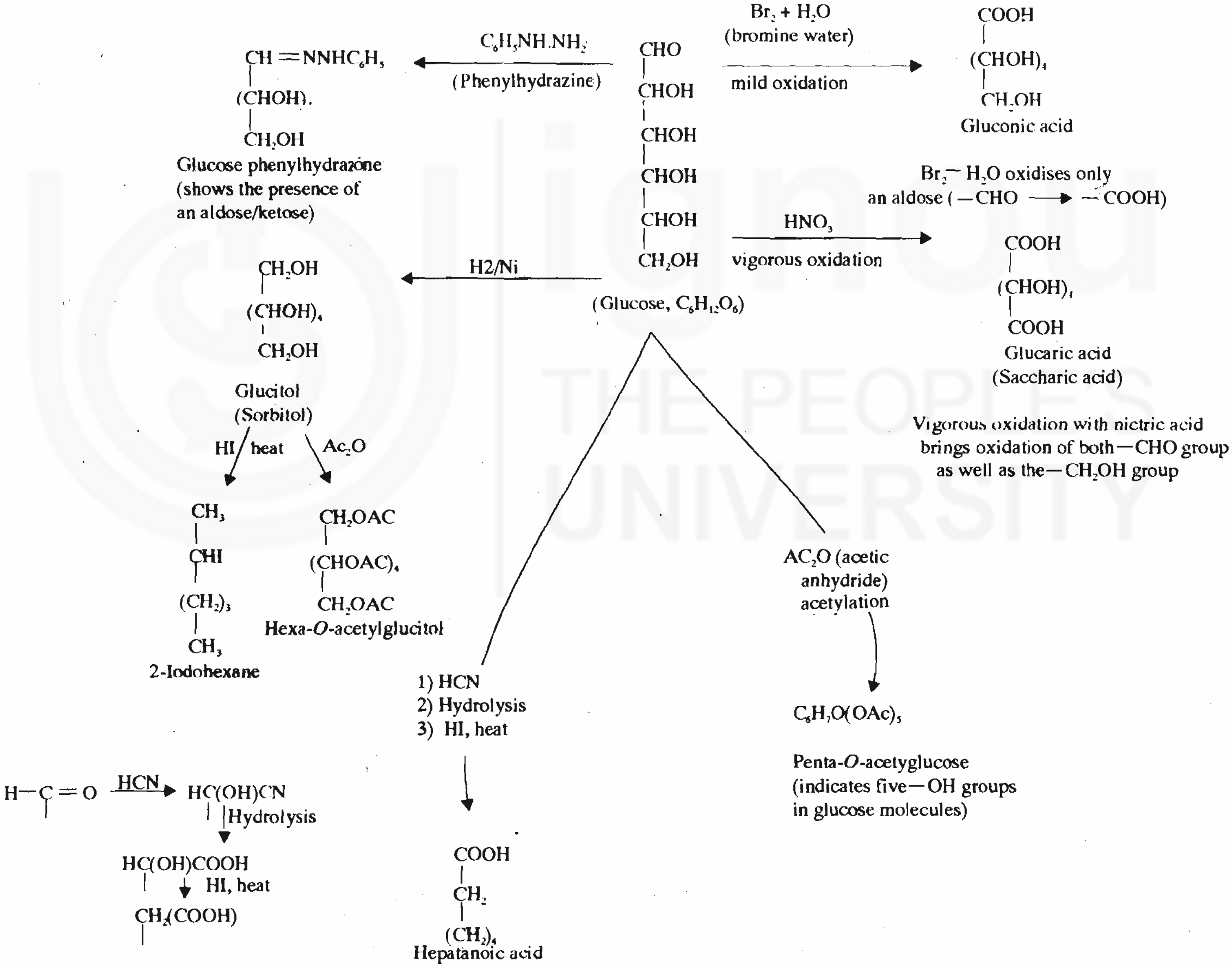


Fig. 2.3: Some chemical reactions of glucose

The open chain structure of glucose, which we have described so far, does not explain many of its properties. So let us study other possible structures of glucose. But before that attempt the following SAQs.

SAQ 1

Tick [√] mark the following statements as true or false

a) All aldose sugars are derived from glyceraldehyde. [True/False]

b) D-Ribose is an aldose. [True/False]

c) Monosaccharides are insoluble in water. [True/False]

d) Polysaccharides upon hydrolysis yield 2-6 monosaccharide units. [True/False]

SAQ 2

Fill in the blanks with appropriate words

a) D-Glucose is an epimer of ....

b) .... sugars are less abundant than .... sugars.

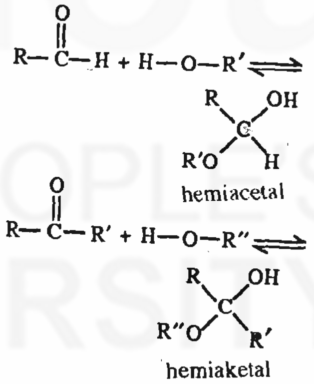
c) Ketoses have less number of .... than aldoses.

d) ....is a part of many oligo/polysaccharides.

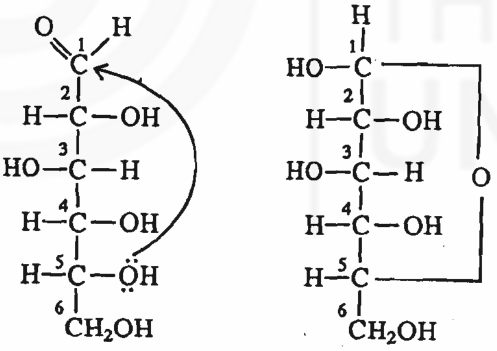
2.3.3 Ring Structures of Monosaccharides

In an aqueous solution, glucose actually exists in three forms, which are in equilibrium and are readily converted into one another. The straight chain makes up only 0.02% of these molecules. The rest of the molecules are the other two ring forms that result from an internal (intramolecular) hemiacetal formation. Since monosaccharides (aldoses and ketoses) contain both carbonyl as well as an alcoholic function within the same molecule, the two groups combine intramolecularly to give a cyclic hemiacetal/hemiketal. In glucose, the hemiacetal will be formed between the aldehyde group on C-1 and the alcohol group on C-5.

A general reaction of a carbonyl group (aldehyde or ketone) with an alcohol, is to form a hemiacetal or a hemiketal.

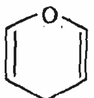


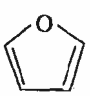
The hemiacetal/hemiketal is in equilibrium with the aldehyde/ketone.



In addition to the Fischer projection formula for sugars, the configuration of the substituents at each carbon atom can also be conveniently represented by **Haworth projection formula**. In fact, these formulas are often used to simplify the drawing of sugar ring structures, discussed above. According to this convention, a sugar with a 6-membered ring is a pyranose and a sugar with a 5-membered ring a furanose. The ring structure in the two cases is similar to pyran and furan, respectively.

In Haworth projections, the ring formed by the sugar molecule (after internal hemiacetal/hemiketal formation) is shown in a manner as if we are looking at it from the side, instead of looking down at the ring from above. The side nearer to us is shown by thickened lines and the groups attached to each carbon atom are then shown as above or below the plane of the ring. The cyclic forms of glucose and fructose, as represented by Haworth projections, are known as glucopyranose and fructofuranose, respectively (Fig. 2.4).


Pyran


Furan

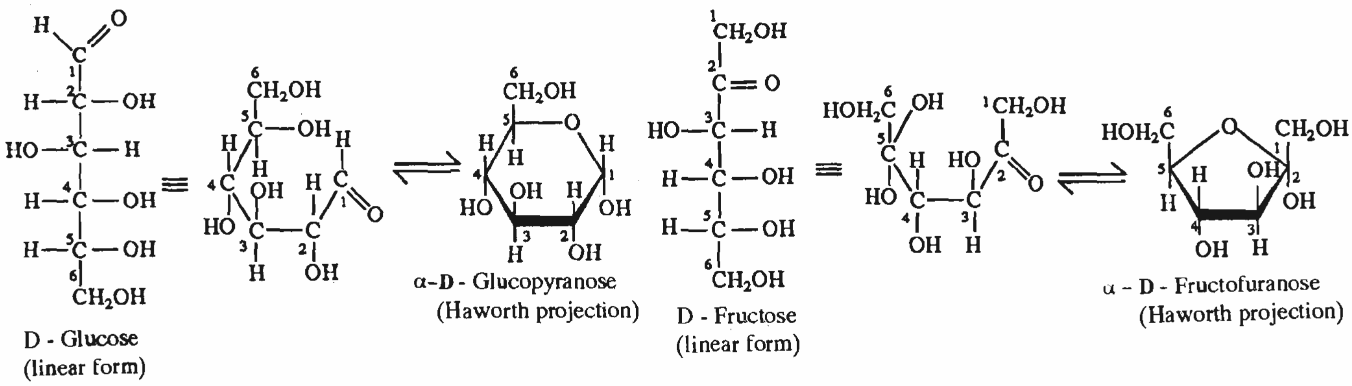
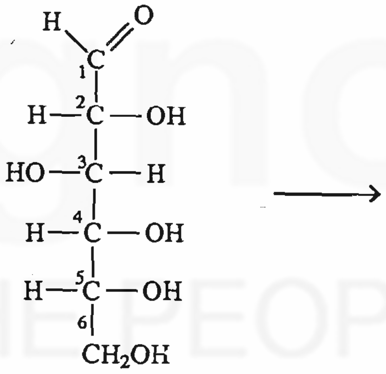


Fig.2.4: Rings forms of glucose and fructose

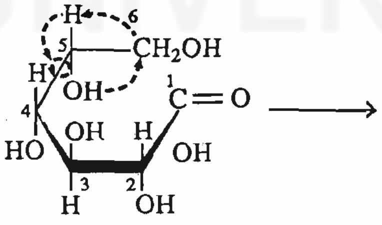
Anomeric forms of sugars

The carbonyl carbon of a monosaccharide, which has no chirality, becomes asymmetric following cyclisation and the resultant diastereoisomers are known as **anomers**, i.e., the α-anomer and the β-anomer. The hemiacetal (C-1) or hemiketal (C-2) carbon in these ring forms is called the anomeric carbon. The two anomeric ring forms depend on the placement of the hydrogen and hydroxyl group on the anomeric carbon. If the — OH group is below the plane of the ring, it is *cis* or the α form and if it is above the plane of the ring it is *trans* or the β form. The process of ring formation, as shown for glucose below indicates why the hemiacetal

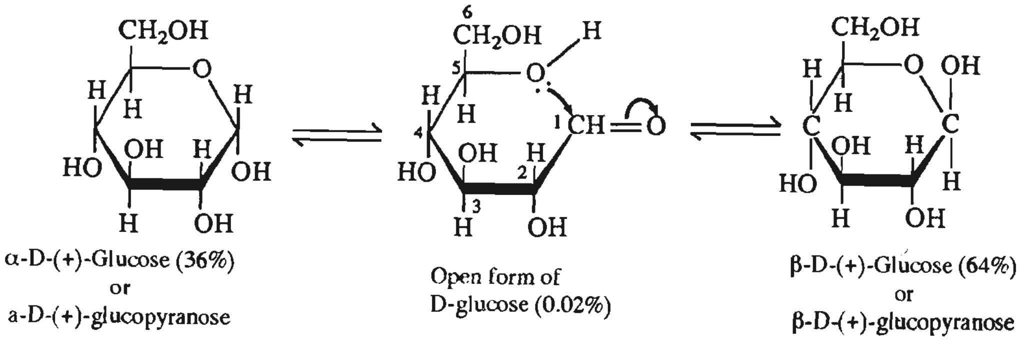


D-Glucose

A model of the above coils as sown:



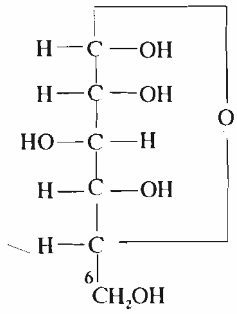
The direction of the arrows indicates how the group attached to C-4 is pivoted



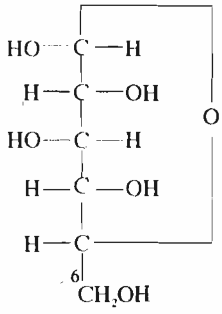
Scheme depicting the formation of the hemiacetal forms of D-glucose

can exist in two anomeric forms. A simple rotation of the bond between C-4 and C-5 in a counterclockwise manner brings the C-5 hydroxyl into a position for reaction with the carbonyl group. Thus, the –OH group will now occupy the position originally occupied by the hydrogen at C-5. Since C-1 becomes an asymmetric carbon in the hemiacetal, two diastereomeric molecules are possible. The α-anomer has the anomeric hydroxyl group below the plane of the ring. In the β-anomer, the hemiacetal hydroxyl group is above the plane of the ring. The structures of the two anomers of D-glucose in Fischer and Haworth projections are shown below:

Fischer projection formulas

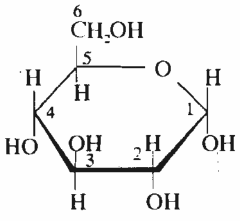


α-D-glucose

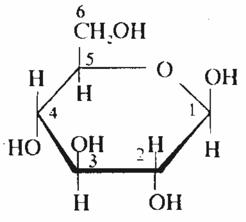


β-D-glucose

Haworth formulas



α-D-glucose



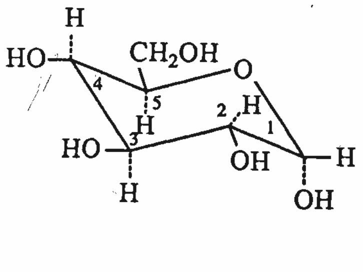
β-D-glucose

You may ask as to what difference the position of just one hydroxyl group on the ring could possibly make. Well, it is this very small difference which determines whether a cell can utilise a molecule in the metabolic process of a living organism. For example, the position of hydroxyl group on C-1 of glucose units in starch (polysaccharide made up of α-glucopyranose units) and cellulose (polysaccharide made up of β-glucopyranose units) is responsible for large differences in their properties. For example, starch is digested by humans but cellulose is not digestible.

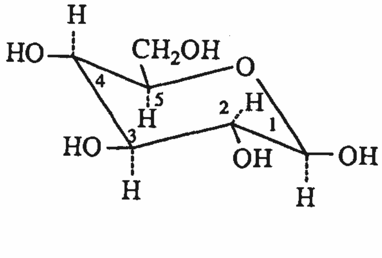
The α and β anomers of D-glucose possess different properties. α-D-Glucose melts at 419K and has a specific rotation of +112.2°. β-D-Glucose melts at 423K and has a specific rotation of +18.7°. If either α-D-glucose or β-D-glucose is dissolved in water, the specific rotation changes slowly until it reaches an equilibrium value of +52.7°. This gradual change in specific rotation from +112.2° or 18.7° to +52.7°, is called as **mutarotation** and results from an interconversion of and β-glucose to an equilibrium mixture containing 36% α-anomer and 64% β-anomer. The two forms undergo interconversion through the open form of glucose (0.02%).

Another important aspect of the structure of monosaccharides is in relation to their conformation. The C–O–C bnght C bond angle in the hemiacetal ring is 111° and is similar to that of the C–C–C ring angle (109°) of the cyclohexane ring. The pyranose ring of glucose, rather than forming a true planar ring, is puckered in a manner similar to the cyclohexane ring which exists in the chair and boat forms. The chair conformation of glucose minimises the ring strain and it is this ring form that is preferred:

Conformation is a particular orientation of the atoms in a molecule, differing from other possible orientations by rotation around single bonds.



α-D - (+) -Glucopyranose

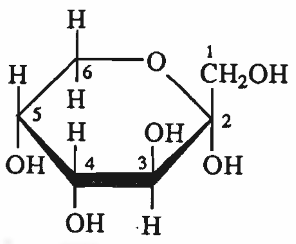


β-D - (+) -Glucopyranose

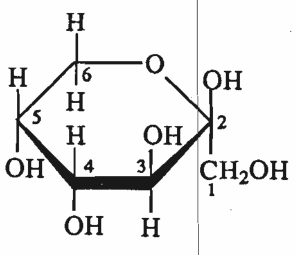
You might have observed that although Haworth projections are easy to draw, they do not correctly represent the true shape of a sugar ring. But for easy and simple representation of a sugar ring, we shall continue to use them in this unit. The knowledge you gained about D & L isomers as well as α and β anomers will make it easier to understand about other carbohydrates. Now let us describe briefly some other important monosaccharides.

2.3.4 Fructose and Other Monosaccharides

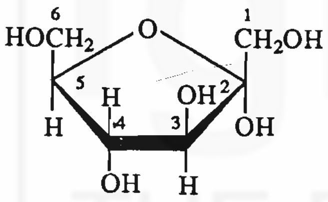
Fructose, also called levulose or fruit sugar (mol. formula $C_6H_{12}O_6$), is found in many fruit juices and in honey. It is a ketohexose and the sweetest sugar known, much sweeter than sucrose, which is the common table sugar or cane sugar. It is also a component of sucrose and is produced by hydrolysis of the polysaccharide inulin. Fructose molecules also form internal hemiketals and exist in 5-member furanose ring structures (Fig.2.4). Although its structure can be represented as a fructopyranose as well as a fructofuranose, it is the furanose form that is usually present in solution:



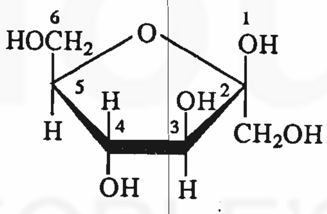
α-D-Fructopyranose



β-D-Fructopyranose

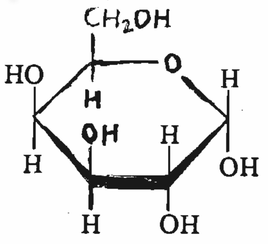


α – D – Fructofuranose

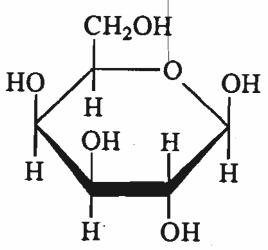


β – D – Fructofuranose

Galactose (mol. formula $C_6H_{12}O_6$) does not occur as a free monosaccharide. This aldohexose can be formed by hydrolysis of larger carbohydrates. It is a component of milk sugar, lactose.



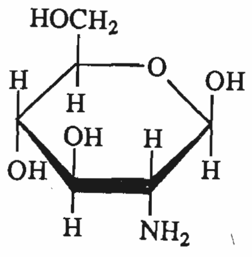
α – Galactose or α – Glactopyranose



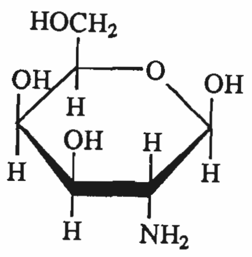
β – Galactose or β – Glactopyranose

Sugars in which an -OH group is replaced by hydrogen, are known as deoxysugars. The carbon at which this replacement occurs is denoted by the number of that carbon in the deoxysugar.

Glycolipids, which are components of the brain and nervous system, also contain galactose. D-galactose as well as D-glucose exist in nature as their 2-amino derivatives and are commonly referred to as **amino sugars**. β-D-mm Glucosamine is a component of chitin, which is the major component of the exoskeleton of insects and crustaceans. D-Galactosamine is an important component of cartilage.



2-Deoxy-2-amino-β -glucopyranose
(β-D-Glucosamine)

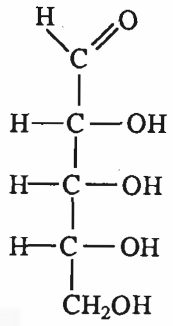


2-Deoxy-2-amino-β-D-galactopyranose
(β-D-Galactosamine)

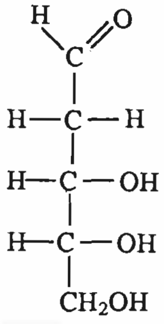
Among the pentose sugars, that play a major role in human metabolism, are **D-ribose** and **deoxyribose**. D-Ribose which exists as a furanose is a component of RNA while 2-deoxyribose is a component of DNA.

Fischer projections

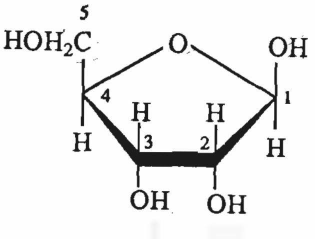
Haworth projections



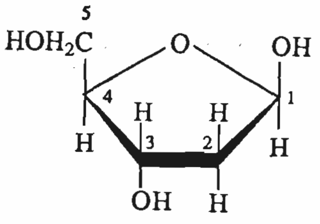
D – Ribose



2 – Deoxy – D – ribose



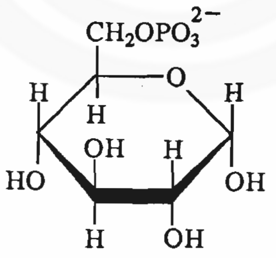
β - D - Ribose
(β-D – Ribofuranose)



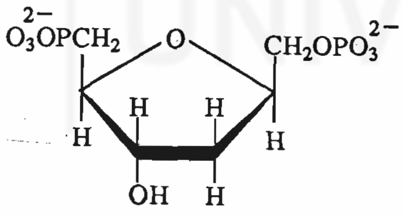
2– Deoxy – β – D – ribose

Both the α and β forms of ribose exist in solution, however, it is the β form that is found in nucleic acids and other metabolically active compounds.

Some metabolically active forms of sugars are present as phosphate esters of the primary alcohol group. For example, **glucose-6-phosphate** and **fructose diphosphate** are some important sugar phosphates.



α–D–Glucose -6-phosphate (G6P)



Fructose 1, 6-diphosphate (FDP)

SAQ 3

Tick mark [√] the following statements as true or false.

a) A fresh solution of glucose has a specific rotation of 52.7°. [True/False]

b) Fructose is present mostly as a furanose. [True/False]

c) Ribose is a ketopentose [True/False]

d) The common form of glucose, as represented by Haworth projection, is known as glucopyranose. [True/False]

SAQ 4

What do the notations D & L refer to in sugars. Draw the Fischer projections for D and L glucose.

....

....

....

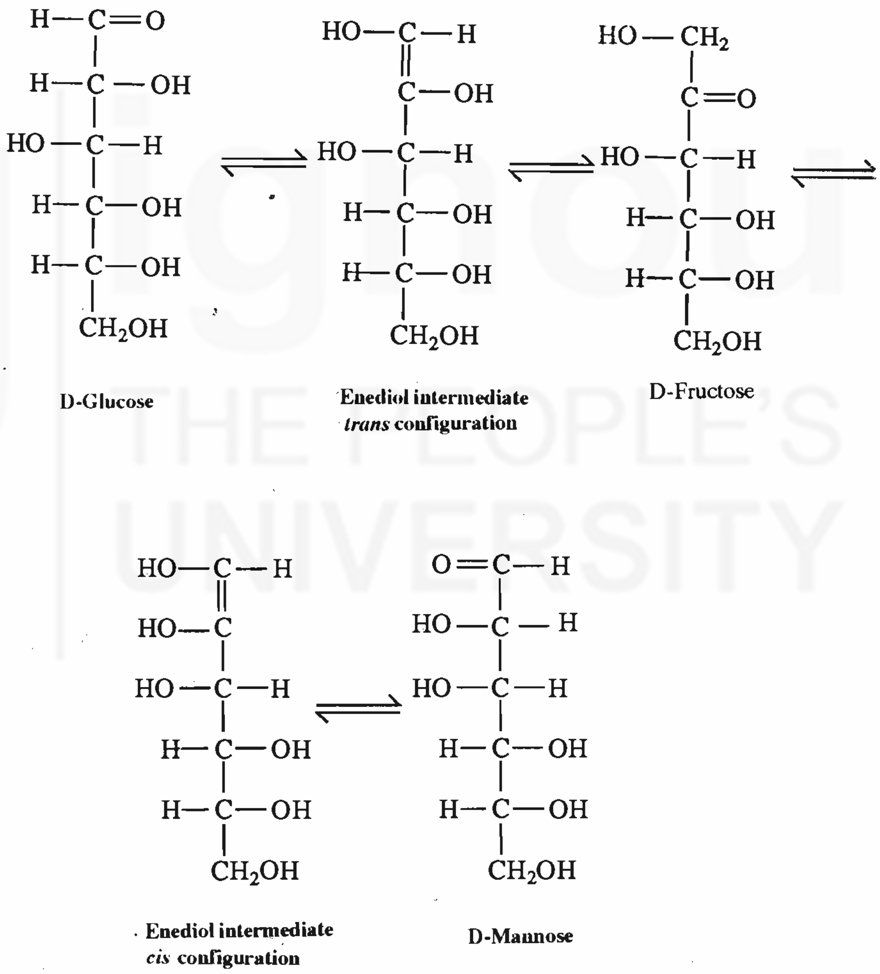
....

We shall now study some reactions of monosaccharides.

2.3.5 Reactions of Monosaccharides

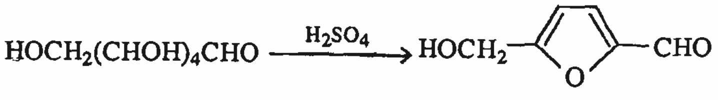
Presence of a large number of functional groups in sugar molecules gives rise to diverse chemical reactions. Some of these were outlined in Fig.2.3 for glucose. We shall now describe some general reactions of monosaccharides in this subsection.

Monosaccharides, when treated with dilute alkali for several hours, undergo isomerisation. For example, D-glucose undergoes isomerisation to D-fructose and D-mannose:

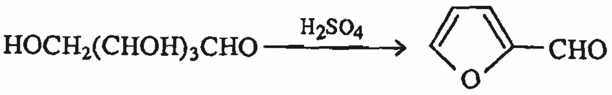


Isomerisation of D-glucose in dilute alkali

Monosaccharides are generally more stable to dilute mineral acids. However, aldose sugars, e.g., glucose when heated in strong mineral acids, undergo dehydration to form hydroxymethyl furfural. Pentose sugars, under the same conditions yield furfural:



Hydroxymethyl furfural

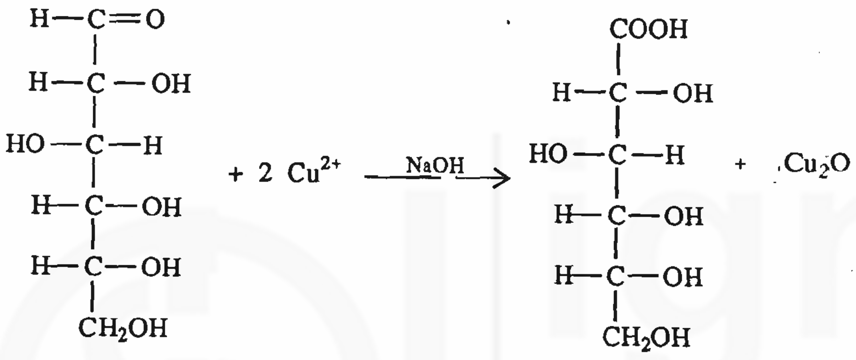


Furfural

This reaction forms the basis for a qualitative test (Molisch test) for sugars, as furfural and its derivatives, can react with α-naphthol to form a coloured product.

Sugars that contain a free aldehyde or ketone group, reduce solutions of mild oxidising agents such as, Cu^{2+} (Benedict's solution, Fehling's solution) or Ag^+ (Tollens' solution). Benedict's solution, which is an alkaline solution of $CuSO_4$, is widely used for the detection of reducing sugars. It forms the basis of clinical detection of glucose in urine samples, when glucose, if present, reduces Cu^{2+} ions to Cu^+ ions, and a brick red precipitate of cuprous oxide is formed:

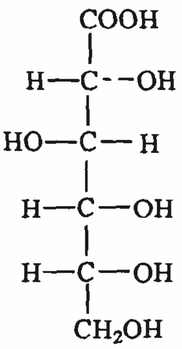
Molisch test - An alcoholic solution of α-naphthol is mixed with the carbohydrate solution in a test tube and cold concentrated H_2SO_4 is poured along the sides, a red-violet ring is formed where the two solutions meet.



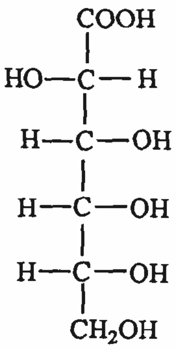
D-Glucose **D-Gluconic acid**

In general, mild oxidising agents and some enzymes, convert sugars to monocarboxylic acids, called **aldonic acids**. For example, D-gluconic acid, D-galactonic acid and D-mannonic acids are products of mild oxidation of glucose, galactose and mannose, respectively.

You will recollect from Fig.2.3 that bromine water also oxidises the aldehyde function to the carboxylic function. However, it does not oxidise a ketose and therefore, is used to differentiate an aldose from a ketose.

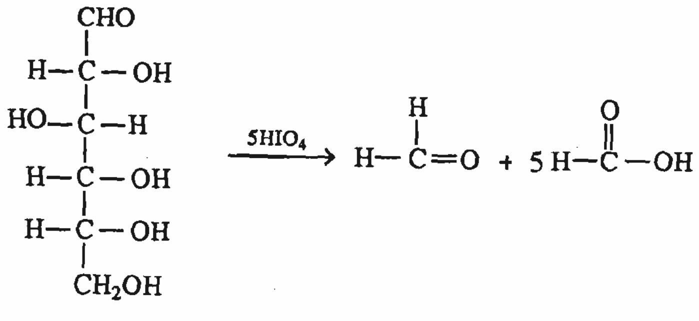


D-Galactonic acid



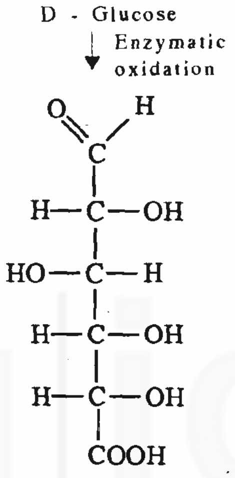
D-Mannonic acid

Carbohydrates undergo oxidative cleavage with periodic acid (HIO_4), like other compounds that contain two or more hydroxyl or keto groups on adjacent carbon atoms. This reaction, which was introduced by Malaprade in 1928, is very useful in the structure determination of carbohydrates.

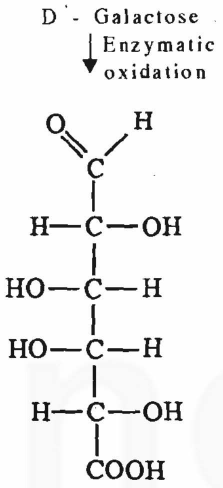


D – Glucose

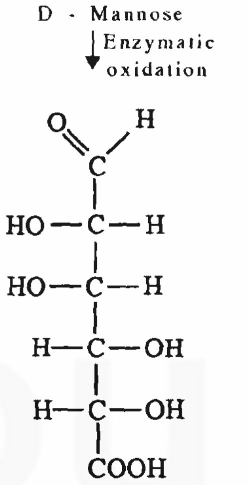
Specific oxidation of the primary alcoholic function with enzymes results in the formation of uronic acids, some of which are key components of several polysaccharides:



D-Glucuronic acid



D-Galacturonic acid



D-Mannuronic acid

Glucuronic acid is one of the principal carrier, with the help of which the metabolites of drugs and toxins are excreted from our bodies. The usually nonpolar toxins form polar complexes with it and are excreted in urine.

SAQ 5

Fill in the blanks:

a) D-Ribose, on heating with HCl gives ....

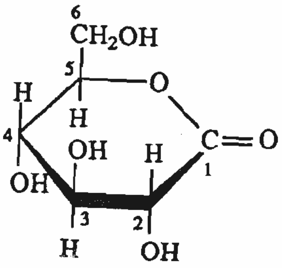
b) An alkaline solution of glucose contains .... and ....as is omerisation products.

c) Mild oxidation of glucose gives ....

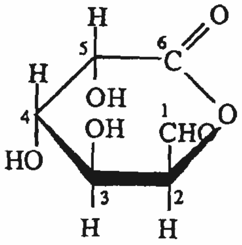
d) Enzymatic oxidation of primary alcoholic group of sugars gives ....

A lactone is an internal ester compound formed by elimination of water, from an -OH group and a -COOH group, in the same molecule.

Both aldonic acids and uronic acids undergo cyclisation to form 5 and 6 membered lactones:



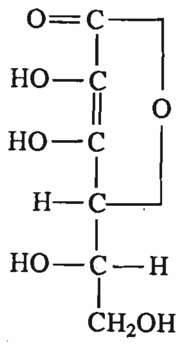
D-Glucono-δ-lactone



D-Glucurono-δ-lactone

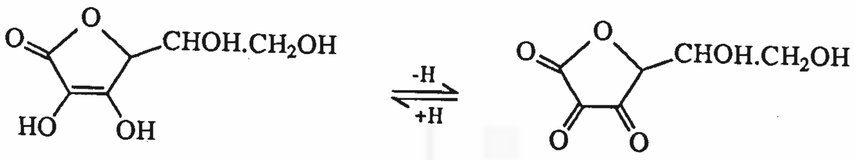
D-Glucono-δ-lactone and D-glucurono-δ-lactone are, respectively, the lactones of D-gluconic acid and D-glucuronic acid. An important naturally occuring lactone is ascorbic acid or vitamin C. It is a δ-lactone, which is synthesised by all plants and many animals.

Ascorbic acid is a carbohydrate metabolite. Human beings cannot synthesise it. They obtain it by eating foods that contain vitamin C. e.g., vegetables. On the other hand, carnivores, such as, cats can synthesise vitamin C. Prolonged dietary deficiency in vitamin C leads to scurvy.



L-Ascorbic acid

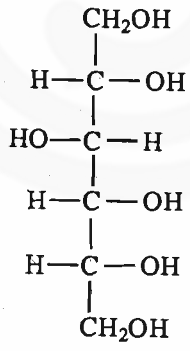
Enzyme systems in many animals modify glucose to ascorbic acid. It can easily undergo oxidation - reduction and, therefore, it participates in biological redox reactions as a cofactor.



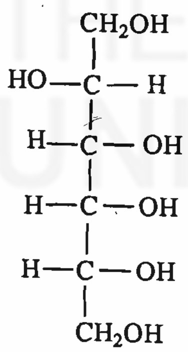
L-Ascorbic acid (reduced form)

Dehydro-L-ascorbic acid (oxidised form)

The aldehyde and ketone function of monosaccharides are reduced by sodium borohydride to the corresponding sugar alcohols. D-Sorbitol and D-mannitol are the two important naturally occurring sugar alcohols:

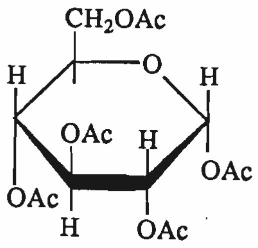


D-Sorbitol



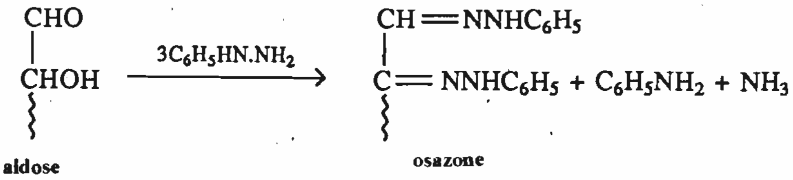
D-Mannitol

All the hydroxyl groups in sugars can be acetylated. For example, D-glucose gives a penta acetyl derivative on treatment with acetic anhydride:



Penta-*O*-acetyl-α-D-glucose (Ac = $CH_3 - \underset{\underset{O}{\|}}{C} -$)

Aldehyde group in the aldoses reacts with phenyl-hydrazine to form phenylhydrazone (Fig.2.3). However, in excess of phenylhydrazine, the reaction proceeds to yield crystalline osazones:

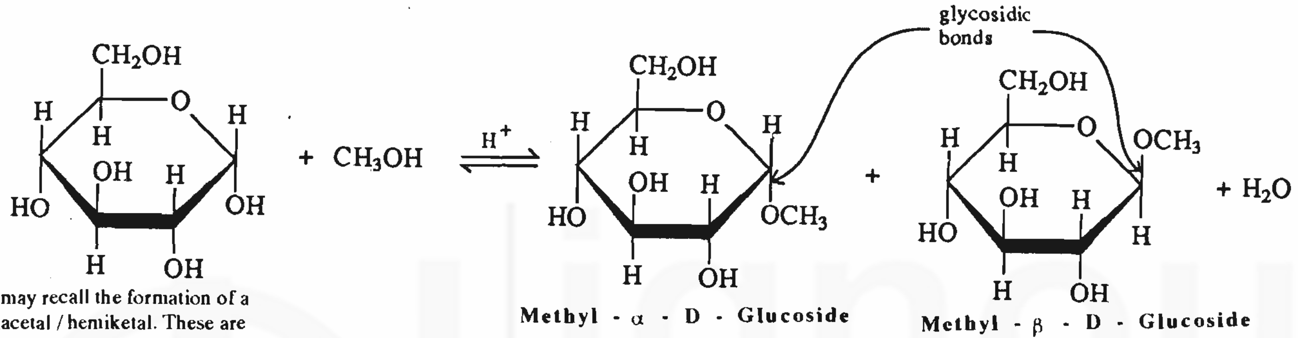


$$\begin{array}{l}CHO\\|\\CHOH\\ \wr\end{array} \xrightarrow{3C_6H_5HN.NH_2} \begin{array}{l}CH{=}NNHC_6H_5\\|\\C{=}NNHC_6H_5\\ \wr\end{array} + C_6H_5NH_2 + NH_3$$

Osazone formation is typical of all carbohydrates with an-hydroxy aldehyde or α-hydroxy ketone function.

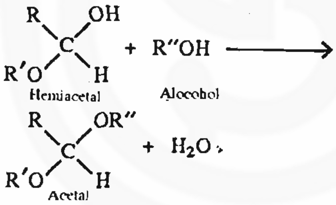
Phenylhydrazine is a powerful reagentin the study of sugars and osazone formation provides an easy identification of different sugars through their characteristic-crystalline forms and melting points. An osazone, more importantly, alsogives anideaof configuration of various sugars. For example, (+)-glucose and (+)-mannose give the same ozasone, which means that they are epimeric at C-2, as ozasone formation destroys the chirality only at C-2 of an aldose. (-)-Fructose also forms an osazone which is identical with that obtained from (+)-glucose, thereby, implying that (-)-fructose has similar configuration as (+)-glucose at C-3, C-4 and C-5.

A very important reaction of monosaccharides is the formation of acetals, more commonly known as **glycoside formation**. For example, D-glucose (a hemiacetal) combines with a molecule of methanol in the presence of an acid to form an acetal. In this reversible reaction, the anomeric hydroxyl group (C-1, –OH) condenses with an alcohol to form α and β glycosides. The bond that connects the anomeric carbon to the acetal oxygen, is known as the glycosidic bond:



The acid catalysed condensation of α–D-glucose with methanol to form an anomeric pair of methyl-D-glucosides. D-Glucose in solution will be a mixture of , α, β and linear structures

You may recall the formation of a hemiacetal / hemiketal. These are basically not very stable and can react with one more molecule of an alcohol to form a stable cetal/ketal, with the elimination of a water molecule.



These bonds are labelled α and β, depending on whether the oxygen atom in the acetal (glycoside) is below or above the plane of the sugar ring. Glycosides can be hydrolysed to monosaccharides and alcohols, with dilute acids or enzymes. Glycosides do not undergo mutarotation, nor are they readily oxidised. Both these properties require the presence of a free –OH group at the anomeric carbon.

The acetal/ketal (or glycoside) formation is an important reaction, because it helps in understanding the structure of oligo- and polysaccharides in which the constituent monosaccharide units are held together by glycosidic bonds. Generally, C-1 (anomeric carbon) of one monosaccharide reacts with the –OH on C-4 or C-6 of another monosaccharide molecule. This will be clear from the representations in Fig.2.5.

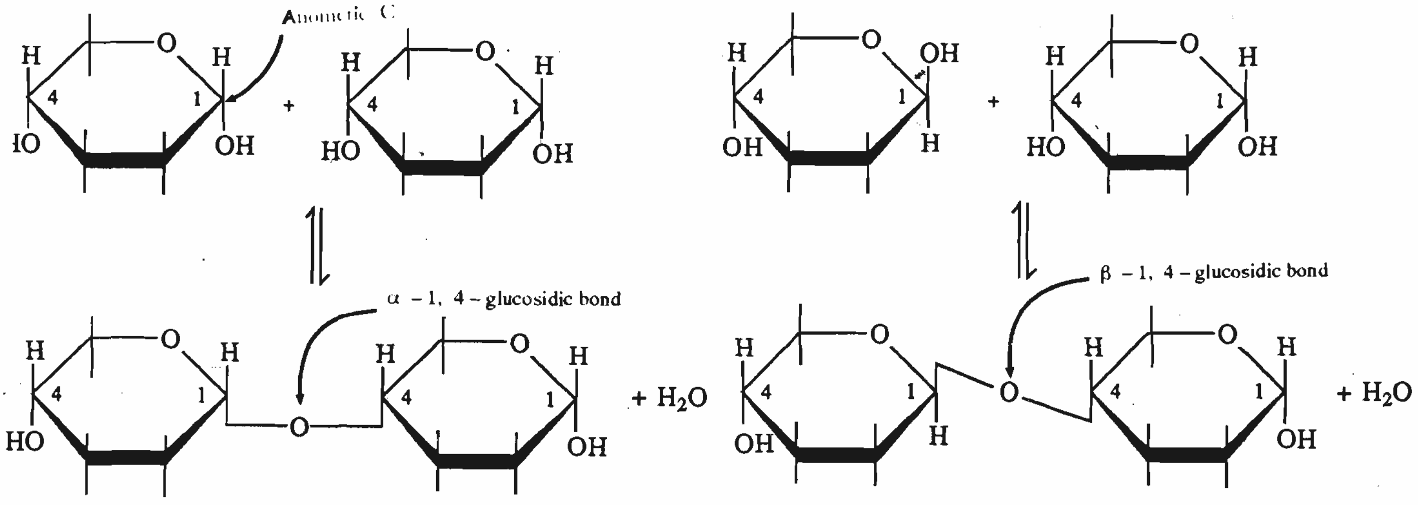


Fig.2.5: The other groups on the sugar rings have been omitted for the sake of convenience and clarity

As is clear from reactions of Fig.2.5, the acetal linkage is a C-1 and C-4 bond and can be termed as α-1,4-glycosidic or β-1, 4- glycosidic bond, depending on whether the starting hemiacetal has an α or a β–OH group. Besides, you would observe that the resulting disaccharide (or polysaccharide, as the case may be) has only one anomeric carbon (C-1) left intact, and, therefore, the disaccharide/polysaccharide can exist in either an α or β anomeric form.

Now try the following SAQs first, and then we shall describe other carbohydrates.

When the hemiacetal is glucose in acetal formation, the resultant acetal linkage is referred to as glucosidic bond, i.e., an acetal bond to glucose. However, generally, this bond is called a glycosidic bond, i.e., an acetal bond in any carbohydrate and not just glucose.

The bond between C-1 of glucose and the oxygen atom of methanol is called a glycosidic bond-specifically, an *O*-glycoosidic bond.

SAQ 6

Match the following in A with those given in B

A	B
1) D-Sorbitol	a) Anomeric carbon
2) L-Ascorbic acid	b) A disaccharide
3) Glycoside	c) A sugar lactone
4) C-1 of glucose	d) Sugar alcohol

SAQ 7

How are monosaccharide units held together in a disaccharide? Can a di/polysaccharide exist in α and β anomeric forms?

………

………

………

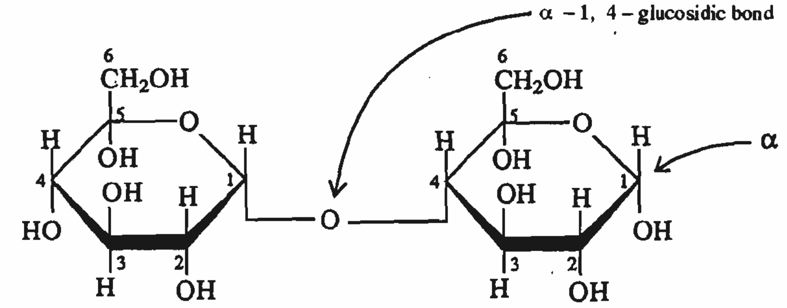
………

2.4 DISACCHARIDES

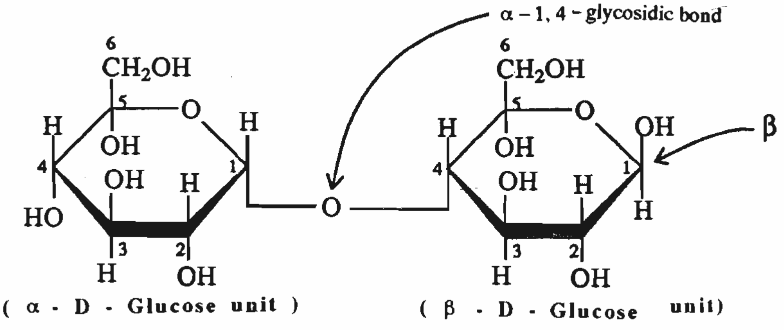
The disaccharides are the most commonly occurring oligosaccharides in nature and on hydrolysis yield two monosaccharide molecules. Maltose, lactose and sucrose are the three widely found disaccharides and each has a molecular formula of $C_{12}H_{22}O_{11}$. Now let us study these carbohydrates briefly. We shall mainly describe the nature of monosaccharides and the linkages which hold them together.

2.4.1 Maltose

Maltose or malt sugar exists in small amounts in nature. It is obtained mainly by the incomplete hydrolysis of starch, glycogen or dextrins. This disaccharide is made up of two glucose units (or residues), linked through the C-1 hydroxyl of one residue in α-form and C-4 hydroxyl of the other, by an α,1,4-glycosidic bond. Maltose undergoes mutarotation and its solution has an equilibrium mixture of α and β maltose (with a small quantity of the aldehyde form of maltose). It is a reducing sugar.



α-Maltose

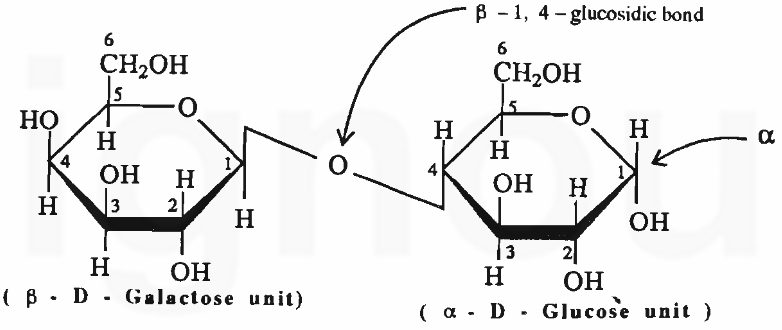


β-Maltose

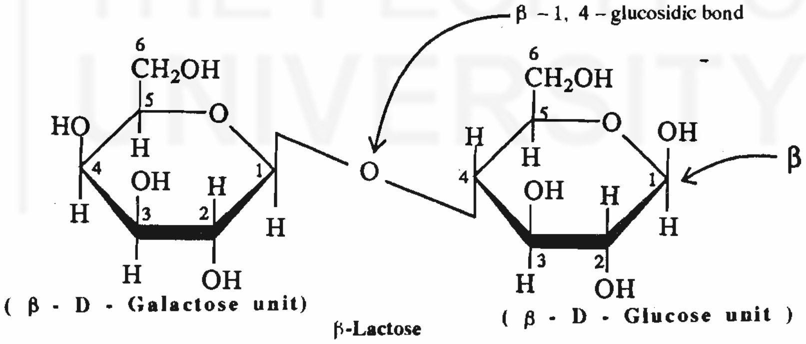
2.4.2 Lactose

Lactose or milk sugar is a disaccharide present in the milk of mammals and is synthesised in the mammary glands after child birth, from glucose and galactose under hormonal regulation. Cow's milk contains on an average 4% lactose while human milk contains 6-8%. It is a white powder that is nearly tasteless. It is, therefore, used in special high calorie diets.

Lactose is formed by the condensation reaction between anomeric hydroxyl of β-galactose and C-4 hydroxyl of glucose, in a β-1,4- glycosidic link. Lactose also undergoes mutarotation and is a reducing sugar.



α-Lactose



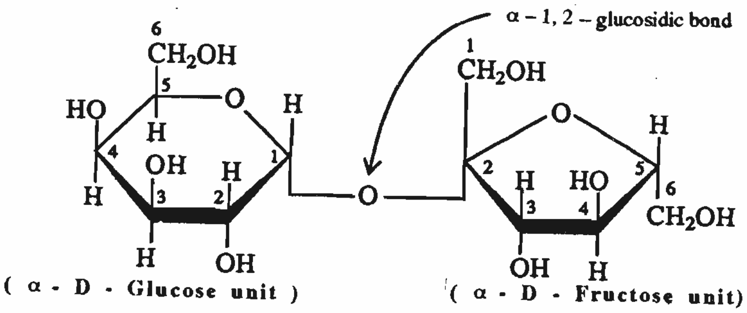
β-Lactose

2.4.3 Sucrose

Sucrose (table sugar, cane sugar, beet sugar) is the most widely employed sweetening agent and is found in higher plants (e.g., in juices of fruits, vegetables) and also in honey. It is commercially obtained from sugar cane or sugar beet. Upon hydrolysis, sucrose yields one molecule each of glucose and fructose. In comparison to maltose and lactose, it has properties which are unique. It does not undergo mutarotation and is a nonreducing sugar. This is because, α-glucose and α-fructose are held in an α-1,2 glycosidic link instead of the more common 1,4-glycosidic bond. As a result the anomeric carbons of both the constituent sugars are involved in the linkage formation. Therefore, none of these is available for mutarotation or for undergoing oxidation reaction.

Sweetness of sugars is measured relative to the sweetness of sucrose, which has been assigned a value of 100. The sweetness valueof other sugars relative to sucrose are as follows:

	Relative sweetness value
Lactose	16
Galactose	32
Maltose	33
Glucose	74
Sucrose	100
Fructose	173



Sucrose

Sucrose Sucrose can be hydrolysed, by acids or enzymes found in intestines and in yeast, to a mixture of fructose and glucose. This mixture is known as invert sugar.

SAQ 8

Which of the following is the correct structure of sucrose? Tick [√] mark your answer

a) 1-α-D-glucosyl-4-fructose [ ]

b) 1-β-D-glucosyl-2-fructose [ ]

c) 1-α-D-glucosyl-2-fructose [ ]

2.5 POLYSACCHARIDES

We have already described monosaccharides and disaccharides in sections 2.3 and 2.4. You have been introduced to some general reactions of monosaccharides as well, including the glycosidic bond formation. This helped you in understanding the formation of disaccharides also. Now let us describe polysaccharides with emphasis on the linkages that hold the monosaccharide units in them. Polysaccharides, also known as glycans, are large polymers of hundreds or thousands of monosaccharide units held together by glycosidic linkages. The polysaccharide chains may be linear or branched and may be composed of only one type of monosaccharide (homopolysaccharide, e.g., starch) or two or more types of monosaccharides (heteropolysaccharides, e.g., in cell wall). In nature, polysaccharides are employed as part of the structural tissues (known as **structural polysaccharides**) or may be used for storing energy (known as **storage polysaccharides**). Polysaccharides are not sweet and do not mutarotate. They are generally unreactive as most of their hemiacetal groups are bonded in the glycosidic bonds. We shall now describe more about some storage polysaccharides.

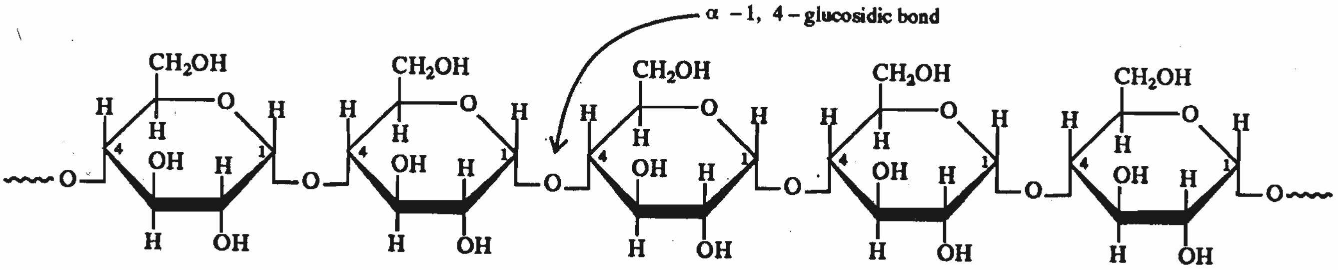
2.5.1 Storage Polysaccharides

Starch is the principal storage polysaccharide in plants. It not only serves as a reserve food in plants but is also a major source of carbohydrates for human beings. It is a glucose polymer and when excess glucose enters a plant cell, it is linked by an enzyme to the end of starch molecules. In case of shortfall of glucose in the cell, starch is hydrolysed within the cell to release glucose. Dietary starches are present in potatoes, rice, wheat, corn and many other plant sources.

Natural starch $(C_6H_{10}O_5)_n$, is a mixture of two components, namely, **amylose** and **amylopectin**. The proportion of amylose and amylopectin varies in starches from different sources, but usually consists of 25% amylose and 75% amylopectin. Amylose (molecular weight 50,000-60,000) consists of D-glucose units linked in a linear manner by α-1,4-glycosidic bonds:

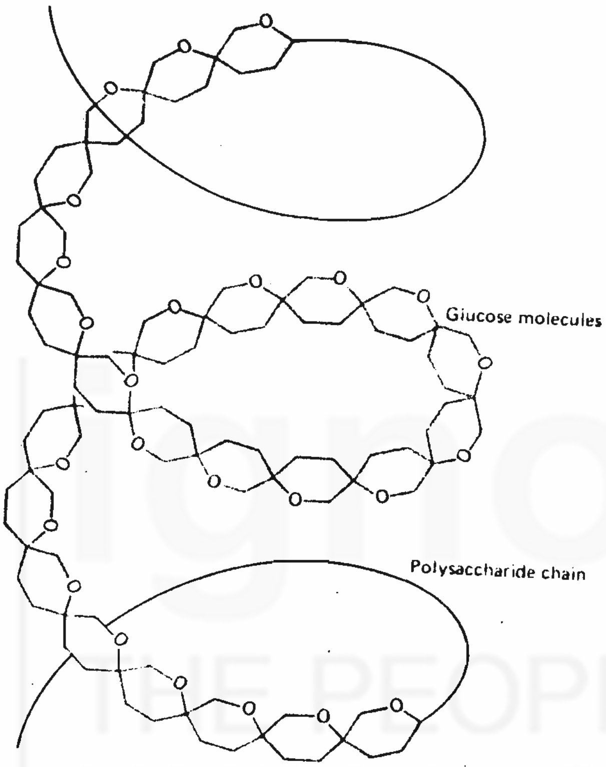
A solution of iodine and KI is used to test for the presence of starch and the degree to which it is hydrolysed. Starch-iodine complexes range in colour from blue black to red. Amylose gives a blue black colour and amylopectin a red colour with iodine.

Partial hydrolysis of starch by acids, enzymes or dry heat, produces polysaccharides known as **dextrins**. Dextrins get sticky when wet and are, therefore, employed as adhesives. The golden colour of bread crust is due to the formation of dextrins.



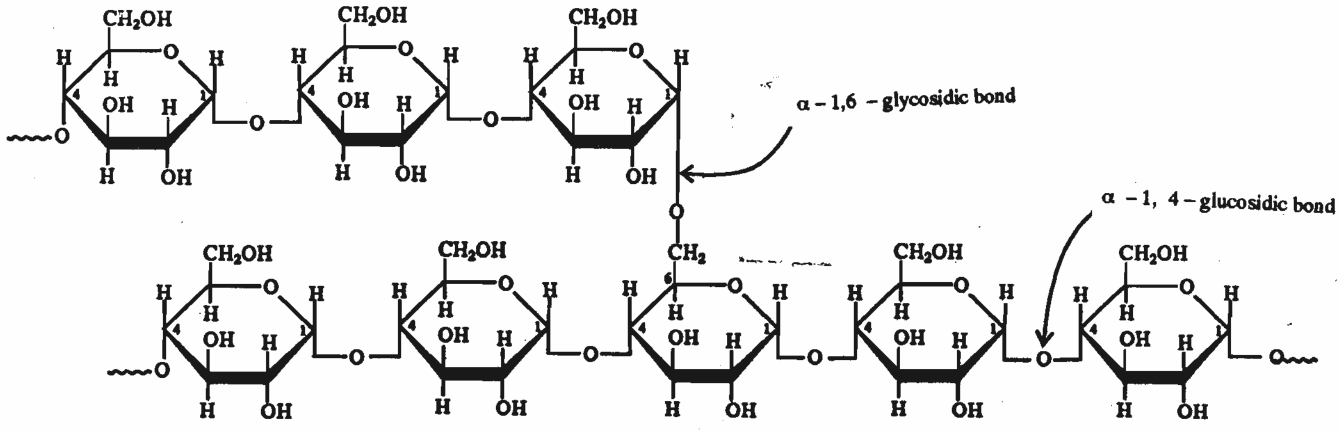
A segment of amylose molecule

The average chain length is 300-350 glucose units. you would observe that due to α-1,4 linkage, amylose has a nonreducing as well as a reducing end. In solution amylose assumes a helical structure as shown below. It is soluble in hot water, which is due to the formation of a colloidal suspension.



Amylose - helical structure

Amylopectin (molecular weight larger than 500,000) is a highly branched glucose polymer. The linear chains have glucose molecules bonded by α-1,4-glycosidic links. Branching occurs every 20-24 glucose units on an average and is a result of α-1,6- bonds between the glucose units. Amylopectin molecules are significantly larger than amylose molecules, and are insoluble in hot water.

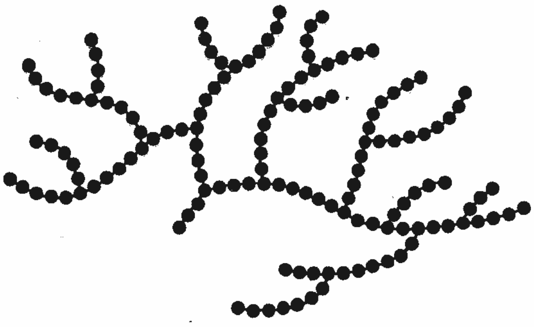


Segment of amylopectin

Amylose is hydrolysed by an enzyme, amylase, present in saliva and pancreatic juice, to a mixture of maltose and glucose. β- Amylase, hydrolyses amylose from the nonreducing end to yield successive units of maltose only. Amylopectin, resists hydrolysis with and β–amylase at branch points and also at α-1,6-linkages, resulting in a highly branched core of amylopectin called the **limit dextrin**, as one of the products of digestion.

Glycogen is also hydrolysed by α and β amylases to glucose. maltose and limit dextrin.

Glycogen is the storage form of glucose in animals and is the equivalent of plant starches. It is mainly concentrated in the liver and muscles. A well nourished body has enough glucose in the form of glycogen, to supply it with energy for about 18 hours. Glycogen is similar in structure to amylopectin, except that the branching occurs much more frequently every 8-10 glucose units. Most glycogen molecules have molecular weights higher than one million.



Glycogen
Each circle in the above chain represents a D-glucose unit, linked by α-1 , 4, bonds in the main chain and by α-1,6-bonds at the branches.

When required for metabolism in the body, glucose units are removed one by one from glycogen, by a process of phosphorylation (i.e., bond rupture with the addition of a molecule of phosphoric acid) in the presence of an enzyme, glycogen phosphorylase, to yield glucose-1-phosphate. This is utilised for the metabolic needs of the body.

$$\underset{\text{Glycogen having } n \text{ glucose units}}{G_n} + \underset{\text{Phosphate ion}}{HPO_4^{2-}} \rightarrow \text{Glucose} - 1 - \text{phosphate} + \underset{\text{Glycogen having } n-1 \text{ glucose units}}{G_{n-1}}$$

SAQ 9

Tick [√] mark the appropriate statement.

Limit dextrin is

a) Product left after digestion of starch by amylase. [ ]

b) Highly branched portion of amylose. [ ]

c) Nonreducing end of amylopectin. [ ]

SAQ 10

Polysaccharides do not mutarotate, why?

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We shall now describe a common structural polysaccharide.

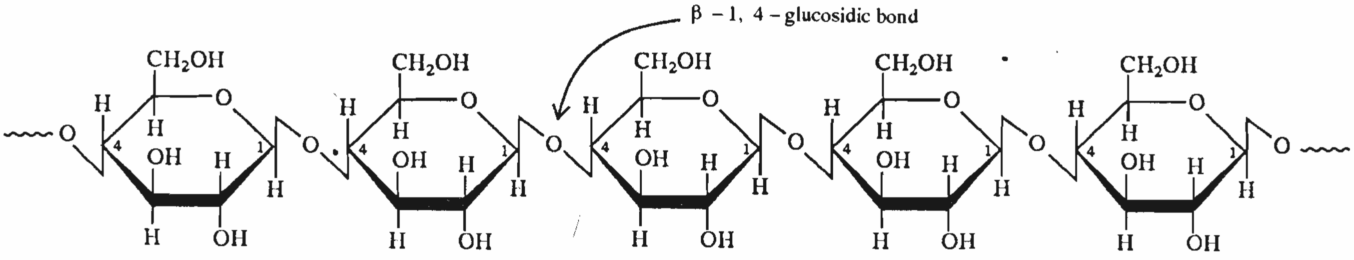
2.5.2 Cellulose: A Structural Polysaccharide

Cellulose is a structural polysaccharide and the rigid cell wall of plants is composed

The difference between amylose and cellulose is in the nature of the glycosidic bond holding glucose units together. In amylose it is α-1,4 link, while in cellulose it is a β-1,4-linkage.

primarily of this substance. It constitutes nearly one half of the carbon in the biosphere. Cellulose occurs almost in pure form in cotton (98%) and to a lesser extent in jute (50-70%) and wood (40-50%). Cellulose molecules are insoluble in water, due to their size and structure.

Cellulose is a linear polymer of D-glucose units bonded by β-1,4-linkages as shown below. It has a molecular formula of $(C_6H_{10}O_5)_n$, where $n = 500$ to 5,000, depending on the source, method of extraction and treatment.



Segment of cellulose chain

Unlike starch, it is highly resistant to acidic or enzymatic hydrolysis. However, rumen bacteria in grazing animals and also termites, possess an enzyme, cellulase, which hydrolyses cellulose to glucose. Other animals, such as man, lack this enzyme and cannot utilise cellulose as a source of energy. Any cellulose we eat, therefore, passes through the digestive tract undigested, providing the roughage we require for proper elimination.

Cellulose is a valuable commercial compound and as cotton it is used in clothing. On chemical treatment, cellulose forms a wide variety of products, such as celluloid, rayon, guncotton (an explosive), cellulose acetate, methyl and ethyl cellulose, etc. These derivatives are useful plastics that can be spun into fibres and spread into films. Cellulose in wood is also used to manufacture paper and a number of paper products.

2.6 COMPLEX POLYSACCHARIDES

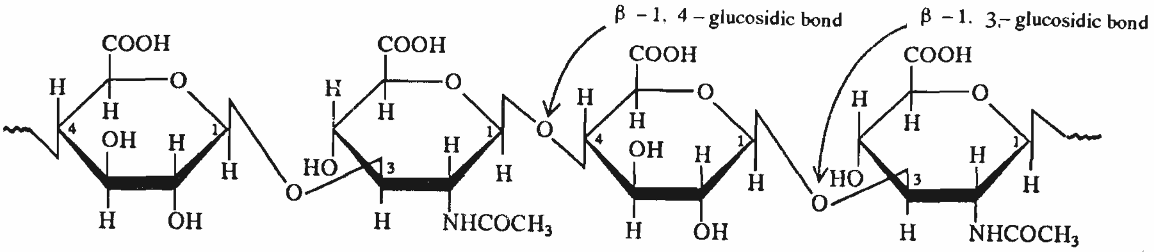
In the preceding sections, we have described polysaccharides essentially made up of hexose monomer units. In addition to these, there are many complex carbohydrate molecules that contain amino nitrogen, which is either acetylated or combined with sulphuric or phosphoric acid. These complex polysaccharides are important as intercellular substances and exist either free or in combination with proteins or lipids.

Let us describe the structure and role of some of these important complex molecules.

2.6.1 Glycosaminoglycans

The extracellular spaces, especially of connective tissues like cartilage, tendon, skin and the walls of blood vessels, consist of proteins collagen and elastin, embedded in a gel like matrix called the **ground substance**. This ground substance is mostly made up of complex polysaccharides called **glycosaminoglycans** or **mucopolysaccharides**. These complex molecules have a slimy, mucus like consistency, which makes them highly viscous and elastic.

Glycosaminoglycans are made up of alternating glucuronic acid and hexosamine residues. Hyaluronic acid is an example of a glycosaminoglycan. It is an important component of the ground substance present in the synovial fluid of joints and vitreous humour of eyes. It consists of about 250-25,000 repeating units of β-D-glucuronic acid and *N*-acetyl-β-D-glucosamine linked by β- 1,3 bonds. The repeating units are, in turn, joined by β-1,4 bonds as shown:



A section of hyaluronic acid

Hyaluronic acid tightly binds ions like Na^+, K^+ and Ca^{2+}. It is a rigid and highly hydrated molecule. In solution, it occupies a volume about 1000 times of that in its dry state. These properties make it highly suitable as an excellent biological shock absorber in the joints and also as a lubricant. Another glycosaminoglycan, chondroitin-4-sulphate is a major component of cartilage and other connective tissues. Its structure is similar to hyaluronic acid, except that the *N*-acetyl-D-glucosamine residue is replaced by *N*-acetyl-D-glucosamine-4-sulphate.

Dermatan sulphate present in the skin tissue, keratan sulphate found in the keratin of nails and hooves, and heparin are other examples of complex polysaccharides. Heparin is a variably sulphated glycosaminoglycan, consisting mostly of alternating α-1, 4 linked residues of D-glucuronate-2-sulphate and D-glucosamine sulphated at N and at C-6. It occurs almost exclusively in the arterial walls and inhibits blood clotting. It is, therefore, a widely used powerful blood anticoagulant.

2.6.2 Glycoproteins

Many proteins in the cells are covalently associated with carbohydrate molecules, resulting in a type of biomolecule known as glycoproteins. The carbohydrate content of such glycoproteins varies from 1% (e.g., in immunoglobulins) upto 85% (e.g., in blood group substances). These molecules occur in almost all forms of life and include most of the plasma proteins, enzymes, hormones, etc. Most of the proteins in membranes, e.g., lipid bilayers, are glycoproteins. In general, glycoproteins consist of a core protein to which the carbohydrates like glycosaminoglycans, or *N*-acetyl amino sugars are covalently linked.

Glycoproteins serve diverse functions, but in general they act as recognition sites for various biological interactions. Glycoproteins like immunoglobulins act as antibodies; γ- globulins fight infectious diseases, and mucin in saliva and gastric juice aids in the digestive process. Another glycoprotein, interferon, is produced by cells in response to viral infection. Some glycoproteins in the antarctic fishes protect them against freezing.

Antigens are foreign substances that invade the body and antibodies are substances that counteract them.

2.6.3 Blood Group Substances

Plasma membranes of animal cells are linked to a number of carbohydrates, and literally appear as "sugar coated". These carbohydrates, basically components of glycoproteins and glycolipids, are a part of the mechanism by which various cell types identify (recognise) each other and act as biochemical markers (antigenic determinants). These membrane bound carbohydrates contain as many as 4 to 20 monosaccharide units, predominant among which are D-galactose, L-fucose, *N*- acetyl-D-glucosamine and *N*-acetyl-D-galactosamine.

L-Fucose is an uncommon carbohydrate, where $-CH_2OH$ group is replaced by a $-CH_3$ group.

Blood group substances were the first-discovered and well- understood of all membrane-bound carbohydrates. They are chiefly found on the surface of erythrocytes, but can also be found on proteins and lipids in other parts of the body. In the ABO group system, put forth in 1900 by Karl Landsteiner, four blood groups have been identified. These are A, B, AB and O. The chemical basis for this classification is the relatively small, membrane bound carbohydrate. The carbohydrate composition on the erythrocytes of A, B, AB and O blood groups is shown in Fig.2.6 and 2.7.

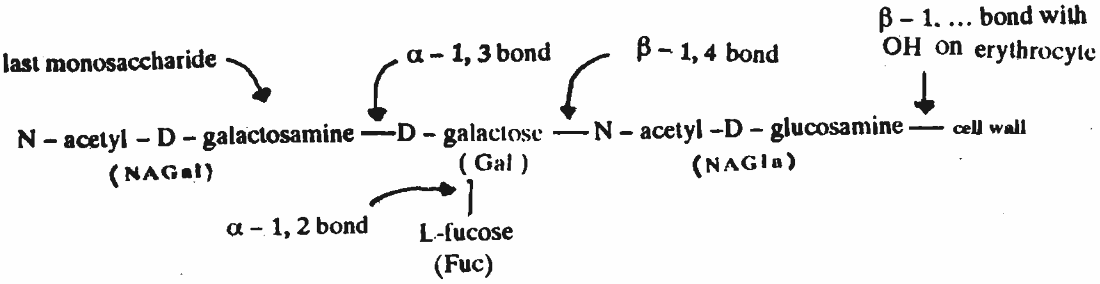
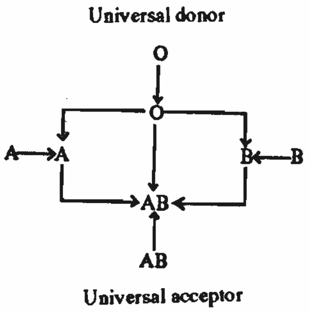
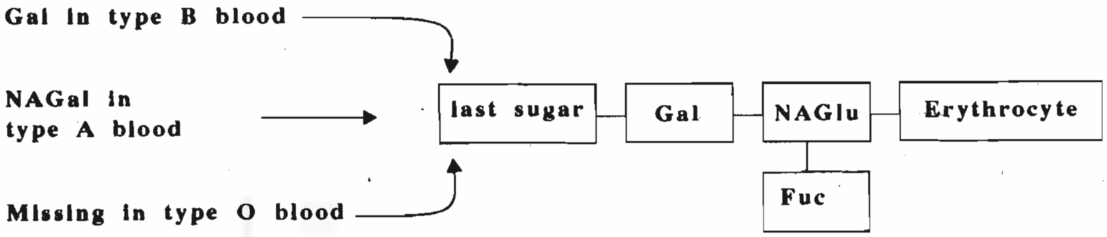


Fig.2.6: Carbohydrate composition of erythrocytes (of type A blood)

The ABO grouping is very important in blood transfusion. Blood from individuals of the same type can be mixed without clumping (agglutination) of erythrocytes. However, if serum of type A blood is mixed with type B blood or vice versa, the erythrocytes will clump. The following transfusion possibilities exist.



The last monosaccharide (at the nonreducing end) in this carbohydrate chain determines the ABO classification. In type A, the chain terminates in *N*-acetyl-D-galactosamine. In type B it terminates in D-galactose and in type O, the last sugar is missing completely, while type AB contains both *N*-acetylgalactosamine as well as D-galactose as the terminal sugars, as shown:



Last sugar in type AB is NaGal as well as Gal as shown:

SAQ 11

How does type A blood differ from type O blood?

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2.7 SUMMARY

- Carbohydrates are polyhydroxy aldehydes or ketones of the approximate composition $C_x(H_2O)_n$.
- Various monosaccharides, such as, ribose, fructose, glucose and mannose differ in their number of carbon atoms, the position of the carbonyl group and diastereomeric configuration.

- Sugars undergo intramolecular cyclisation to form hemiacetals or hemiketals and exist in two anomeric forms. The five and six membered rings that are formed are called furanoses and pyranoses, respectively.
- Sugars can be oxidised to uronic acids or aldonic acids or reduced to alditols. Sugars also form acetyl and ammo derivatives.
- Disaccharides and polysaccharides have glycosidic bonds, which hold the monosaccharide units together.
- The different disaccharides can be distinguished by the nature of the sugars present and the position and orientation of the glycosidic bond.
- Starch and glycogen, the chief storage polysaccharides, are branched glucose polymers with α-1,4 linkages in the chains and α-1,6 linkages at branch points.
- Cellulose the most important structural polysaccharide of plants is a linear polymer of D-glucose with β-1,4 linkages.
- Starch and glycogen are easily hydrolysed by acids and enzymes, while cellulose is resistant to acids and is hydrolysed only by cellulase.
- Complex polysaccharides are important as components of intercellular ground substances and may exist either free or complexed with proteins.
- The glycosaminoglycans-hyaluronic acid, chondroitin sulphate, keratan sulphate and heparin are high molecular weight polymers consisting of uronic acids, and sulphated or amino substituted acetyl sugars.
- Glycosaminoglycans are excellent shock absorbers and lubricatig compounds in tissues.
- The glycoproteins on the external surface of the erythrocyte membranes are important as blood group antigens.

2.8 TERMINAL QUESTIONS

1) Define the terms enantiomer, diastereomer, anomer and mutarotation, giving specific examples from carbohydrates.

2.) Name and give the structure of a naturally occurring (a) sugar alcohol, (b) amino sugar, (c) sugar phosphate, (d) deoxy sugar.

3) Name the storage polysaccharides present in animals and plants. Indicate the structural differences between them.

4) Why is maltose a reducing sugar and sucrose a non-reducing sugar?

5) Why is cellulose insoluble in water and why is it not used as an energy source by human beings?

6) Give the structures of sucrose, lactose and maltose. What are the sources of these common disaccharides?

7) How is the classification of polysaccharides related to their composition and function?

2.9 ANSWERS

Self Assessment Questions

1) a) True b) True c) False d) False

2) a) D-Mannose b) L, D c) Stereoisomers d) D-Glucose

3) a) False b) True c) False d) True

4) In sugars the symbols D & L are used to denote the configuration at the chiral carbon, farthest from the carbonyl group. Whether a sugar is D or L enantiomer, is arrived at by making a comparison to the configuration of glyceraldehyde. Structure of D and L glucose are given in subsection 2.3.1.

5) a) Furfural b) Fructose and Mannose c) Gluconic acid d) Uronic acids

6) 1-d; 2-c; 3-b; 4-a.

7) In a di/polysaccharide, the constituent monosaccharide units are held by acetal linkages, known as glycosidic bonds. These are formed between C-1–OH of one sugar unit and usually the C-4 or C-6 –OH of another sugar molecule. These bonds can be or β glycosidic bonds, depending on the starting hemiacetal. The resulting di/polysaccharide does have one anomeric carbon left as such and the –OH group on it can have and β orientation, i.e., the di/polysaccharide can be in or β anomeric forms.

8) c

9) a

10) In polysaccharides, the anomeric carbon of the constituent sugar units is not free to mutarotate, as it is linked in a glycosidic bond with another sugar molecule.

11) In type A blood the last monosaccharide in the carbohydrate chain is *N*-acetyl-D-galactosamine, where as in type O blood it is missing.

Terminal Questions

1) Enantiomers are those stereoisomers whose structures are non-superimposable mirror images of each other, e.g. D- and L- glyceraldehydes and D- and L-glucoses. When a pair of stereoisomers have more than one chiral centres and their structures are not related to each other as an object and its mirror image, they are said to be diastereomers, e.g. D-mannose and D-galactose. Those monosaccharides and their derivatives which differ from each other with respect to the configuration around the anomeric carbon atom only (i.e. the carbon responsible for the aldehyde or keto function) are referred to as anomers, e.g. α- and β-glucoses or methyl-α-glucoside and methyl-β- glucoside. When a freshly prepared solution of a monosaccharide or a reducing di- (or oligo-) saccharide is allowed to stand, its optical activity changes gradually with time to a constant value. This phenomenon is called mutarotation. For example, a freshly prepared solution of the common commercial D-glucose shows a specific rotation equal to $+112.2^\circ$. With time it changes to $+52.7^\circ$.

2.) a) Mannitol b) Glucosamine c) Glucose-6-phosphate d) Deoxy ribose Their structures are given in subsections 2.3.4 and 2.3.5.

3) Glycogen and starch are the reserve polysaccharides in animals and plants respectively. While starch is a mixture of the linear polymer amylose (made of glucose units linked by α-1,4 glycosidic linkages) and branched polymer amylopectin (which consists of short α-1,4 glucose chains linked by α-1,6 glycosidic bonds and the branching is not extensive). Glycogen is similar to amylopectin in structure excepting that the branching is more frequent (at every 8-10 glucose units).

4) Although maltose is a glycoside, the second glucose unit has an –OH group on its anomeric carbon atom and its ring can open to give an aldehyde and hence acts as a reducing sugar. Sucrose, on the other hand has its α-D-glucose unit condensed with the anomeric hydroxyl of β-D-fructose. Since neither unit possesses an anomeric hydroxyl and the rings cannot open to give an aldehyde, the sugar is nonreducing.

5) Cellulose molecules are insoluble in water, due to their size and structure. In cellulose, glucose units are linked to each other by β-1,4 linkages to form large linear polymers. Human beings do not possess the enzyme required to hydrolyse this bond. Amylase present in human saliva and pancreatic juice are suited for the hydrolysis of α-1,4 glucosidic bonds only. Hence, the glucose present in cellulose is unavailable to human beings as an energy source.

6) Structures of maltose, lactose and sucrose are given in section 2.4. Sucrose is the major disaccharide present in sugarcane, lactose is present in milk and maltose is a product obtained during incomplete (enzymatic) hydrolysis of starch, glycogen or dextrins and is present naturally in barley malt.

7) Polysaccharides can be classified on the basis of their composition as homopolysaccharides (starch) and heteropolysaccharides (Peptidoglycan of cell wall). Functionally, two types of polysaccharides are distinguished, namely, storage polysaccharides like starch and glycogen, and structural polysaccharides, like cellulose and chitin.

UNIT 3 : LIPIDS

Structure

3.1 INTRODUCTION

In Unit 2 we described carbohydrates, an important class of biomolecules, which are a source of energy for the cell. These molecules also form part of the structure of the cell. Another class of biomolecules, namely lipids, which are extremely hydrophobic in nature, are essential constituents of all living cells. You will recall that we briefly introduced you to the structure of membranes in Unit 1. You learnt that lipids form part of the structure of cell membranes. These molecules also store energy for the cell, and, in addition, perform some other tasks also. In Unit 3 we will describe the biological importance of lipids and classify them into various types. We will also illustrate their chemical composition. Besides this you shall learn more about the structure and function of biomembranes. In the next unit we will describe nucleic acids. Like carbohydrates, nucleic acids are biopolymers and are important components of the cell.

Objectives

After studying this unit you should be able to:

- describe the main functions of lipids in the organism,
- classify lipids into various groups,
- describe the essential structural features and major functional roles of various classes of lipids, and
- describe the role of lipids in the formation and functioning of biomembranes.

3.2 BIOLOGICAL IMPORTANCE OF LIPIDS

Lipids constitute a very heterogeneous group of biological compounds, which have a common property of being sparingly soluble in water but being freely soluble in organic (lipophilic) solvents, such as ether, chloroform and benzene. They include such diverse compounds as fatty acids, acylglycerols, phosphoglycerides, steroids,