

# <u>Objectives</u>

After studying this Unit, you will be able to

- explain the characteristics of biomolecules like carbohydrates, proteins and nucleic acids and hormones;
- classify carbohydrates, proteins, nucleic acids and vitamins on the basis of their structures;
- explain the difference between DNA and RNA;
- describe the role of biomolecules in biosystem.



"It is the harmonious and synchronous progress of chemical reactions in body which leads to life".

A living system grows, sustains and reproduces itself. The most amazing thing about a living system is that it is composed of non-living atoms and molecules. The pursuit of knowledge of what goes on chemically within a living system falls in the domain of *biochemistry*. Living systems are made up of various complex biomolecules like carbohydrates, proteins, nucleic acids, lipids, etc. Proteins and carbohydrates are essential constituents of our food. These biomolecules interact with each other and constitute the molecular logic of life processes. In addition, some simple molecules like vitamins and mineral salts also play an important role in the functions of organisms. Structures and functions of some of these biomolecules are discussed in this Unit.

## 14.1 Carbohydrates

Carbohydrates are primarily produced by plants and form a very large group of naturally occurring organic compounds. Some common examples of carbohydrates are cane sugar, glucose, starch, etc. Most of them have a general formula,  $C_x(H_2O)_v$ , and were considered as hydrates of carbon from where the name carbohydrate was derived. For example, the molecular formula of glucose  $(C_6H_{12}O_6)$  fits into this general formula,  $C_6(H_2O)_6$ . But all the compounds which fit into this formula may not be classified as carbohydrates. For example acetic acid (CH<sub>3</sub>COOH) fits into this general formula, C<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> but is not a carbohydrate. Similarly, rhamnose,  $C_6H_{12}O_5$  is a carbohydrate but does not fit in this definition. A large number of their reactions have shown that they contain specific functional groups. Chemically, the carbohydrates may be defined as optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis. Some of the carbohydrates, which are sweet in taste, are also called sugars. The most common sugar, used in our homes is named as sucrose whereas the sugar present in milk is known as lactose. Carbohydrates are also called saccharides (Greek: *sakcharon* means sugar).

Carbohydrates are classified on the basis of their behaviour on hydrolysis. They have been broadly divided into following three groups.

- (i) *Monosaccharides*: A carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone is called a monosaccharide. About 20 monosaccharides are known to occur in nature. Some common examples are glucose, fructose, ribose, etc.
- (ii) Oligosaccharides: Carbohydrates that yield two to ten monosaccharide units, on hydrolysis, are called oligosaccharides. They are further classified as disaccharides, trisaccharides, tetrasaccharides, etc., depending upon the number of monosaccharides, they provide on hydrolysis. Amongst these the most common are disaccharides. The two monosaccharide units obtained on hydrolysis of a disaccharide may be same or different. For example, one molecule of sucrose on hydrolysis gives one molecule of glucose and one molecule of fructose whereas maltose gives two molecules of only glucose.
- (iii) *Polysaccharides*: Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides. Some common examples are starch, cellulose, glycogen, gums, etc. Polysaccharides are not sweet in taste, hence they are also called non-sugars.

The carbohydrates may also be classified as either reducing or nonreducing sugars. All those carbohydrates which reduce Fehling's solution and Tollens' reagent are referred to as reducing sugars. All monosaccharides whether aldose or ketose are *reducing sugars*.

Monosaccharides are further classified on the basis of number of carbon atoms and the functional group present in them. If a monosaccharide contains an aldehyde group, it is known as an aldose and if it contains a keto group, it is known as a ketose. Number of carbon atoms constituting the monosaccharide is also introduced in the name as is evident from the examples given in Table 14.1

Carbon atoms	General term	Aluenyue	Netone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

Table	14.1:	Different	Types	of	Monosaccharides
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14.1.2.1 Glucose

14.1.1

14.1.2

**Monosaccharides** 

**Classification of** 

Carbohydrates

Preparation of Glucose Glucose occurs freely in nature as well as in the combined form. It is present in sweet fruits and honey. Ripe grapes also contain glucose in large amounts. It is prepared as follows:

1. From sucrose (Cane sugar): If sucrose is boiled with dilute HCl or  $H_2SO_4$  in alcoholic solution, glucose and fructose are obtained in equal amounts.

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$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose

Glucose Fructose

2. From starch: Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute  $H_2SO_4$  at 393 K under pressure.

$$\begin{array}{rcl} (C_{6}H_{10}O_{5})_{n} + nH_{2}O & \xrightarrow{H^{+}} & nC_{6}H_{12}O_{6} \\ \\ \text{Starch or cellulose} & & \text{Glucose} \end{array}$$

Structure of Glucose Glucose is an aldohexose and is also known as dextrose. It is the monomer of many of the larger carbohydrates, namely starch, cellulose. It is probably the most abundant organic compound on earth. It was assigned the structure given below on the basis of the following evidences:

- 1. Its molecular formula was found to be  $C_6H_{12}O_6$ .
- 2. On prolonged heating with HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.

$$\begin{array}{c} \textbf{CHO} \\ (\textbf{CHOH})_4 & \xrightarrow{\text{HI, } \Delta} & \textbf{CH}_3 - \textbf{CH}_2 - \textbf{CH}_2 - \textbf{CH}_2 - \textbf{CH}_2 - \textbf{CH}_3 \\ \downarrow \\ \textbf{CH}_2 \textbf{OH} & (n-\text{Hexane}) \end{array}$$

3. Glucose reacts with hydroxylamine to form an oxime and adds a molecule of hydrogen cyanide to give cyanohydrin. These reactions confirm the presence of a carbonyl group (>C = O) in glucose.

$$\begin{array}{c|c} CHO & CH=N-OH & CHO & CH \\ (CHOH)_4 & \stackrel{NH_2OH}{\longrightarrow} & (CHOH)_4 & (CHOH)_4 & \stackrel{HCN}{\longrightarrow} & (CHOH)_4 \\ (CHOH)_4 & \stackrel{HCN}{\longrightarrow} & (CHOH)_4 & \stackrel{I}{\longrightarrow} & (CHOH)_4 \\ (CHOH)_2OH & CH_2OH & CH_2OH & CH_2OH \end{array}$$

4. Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehydic group.



5. Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five –OH groups. Since it exists as a stable compound, five –OH groups should be attached to different carbon atoms.



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# diacose

CHO

(CHOH)<sub>4</sub>

CH<sub>2</sub>OH Glucose

6. On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (-OH) group in glucose.



The exact spatial arrangement of different —OH groups was given by Fischer after studying many other properties. Its configuration is correctly represented as **I**. So gluconic acid is represented as **II** and saccharic acid as **III**.

CHO	СООН	СООН
H — OH	H — OH	H — OH
HO — H	<u>НО</u> —— Н	НО — Н
H — OH	H — OH	Н — ОН
H — OH	H — OH	Н —— ОН
CH <sub>2</sub> OH	CH <sub>2</sub> OH	СООН
I	П	III

Glucose is correctly named as D(+)-glucose. 'D' before the name of glucose represents the configuration whereas '(+)' represents dextrorotatory nature of the molecule. It should be remembered that 'D' and 'L' have no relation with the optical activity of the compound. They are also not related to letter 'd' and 'l' (see Unit 10). The meaning of D- and L- notations is as follows.

The letters 'D' or 'L' before the name of any compound indicate the relative configuration of a particular stereoisomer of a compound with respect to configuration of some other compound, configuration of which is known. In the case of carbohydrates, this refers to their relation with a particular isomer of glyceraldehyde. Glyceraldehyde contains one asymmetric carbon atom and exists in two enantiomeric forms as shown below.



(+) Isomer of glyceraldehyde has 'D' configuration. It means that when its structural formula is written on paper following specific conventions which you will study in higher classes, the –OH group lies on right hand side in the structure. All those compounds which can be chemically correlated to D (+) isomer of glyceraldehyde are said to have D-configuration whereas those which can be correlated to 'L' (–) isomer of glyceraldehyde are said to have L—configuration. In L (–) isomer –OH group is on left hand side as you can see in the structure. For assigning

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the configuration of monosaccharides, it is the lowest asymmetric carbon atom (as shown below) which is compared. As in (+) glucose, —OH on the lowest asymmetric carbon is on the right side which is comparable to (+) glyceraldehyde, so (+) glucose is assigned D-configuration. Other asymmetric carbon atoms of glucose are not considered for this comparison. Also, the structure of glucose and glyceraldehyde is written in a way that most oxidised carbon (in this case –CHO) is at the top.



Cyclic Structure of Glucose The structure (I) of glucose explained most of its properties but the following reactions and facts could not be explained by this structure.

- 1. Despite having the aldehyde group, glucose does not give Schiff's test and it does not form the hydrogen sulphite addition product with NaHSO $_3$ .
- 2. The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free —CHO group.
- 3. Glucose is found to exist in two different crystalline forms which are named as  $\alpha$  and  $\beta$ . The  $\alpha$ -form of glucose (m.p. 419 K) is obtained by crystallisation from concentrated solution of glucose at 303 K while the  $\beta$ -form (m.p. 423 K) is obtained by crystallisation from hot and saturated aqueous solution at 371 K.

This behaviour could not be explained by the open chain structure (I) for glucose. It was proposed that one of the —OH groups may add to the —CHO group and form a cyclic hemiacetal structure. It was found that glucose forms a six-membered ring in which —OH at C-5 is involved in ring formation. This explains the absence of —CHO group and also existence of glucose in two forms as shown below. These two cyclic forms exist in equilibrium with open chain structure.



The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called *anomeric carbon* 

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(the aldehyde carbon before cyclisation). Such isomers, i.e.,  $\alpha$ -form and  $\beta$ -form, are called **anomers**. The six membered cyclic structure of glucose is called **pyranose structure** ( $\alpha$ - or  $\beta$ -), in analogy with pyran. Pyran is a cyclic organic compound with one oxygen atom and five carbon atoms in the ring. The cyclic structure of glucose is more correctly represented by Haworth structure as given below.



 $\alpha$  – D – (+) – Glucopyranose  $\beta$  – D – (+) – Glucopyranose

**14.1.2.2 Fructose** Fructose is an important ketohexose. It is obtained along with glucose by the hydrolysis of disaccharide, sucrose. It is a natural monosaccharide found in fruits, honey and vegetables. In its pure form it is used as a sweetner. It is also an important ketohexose.

Structure of Fructose Fructose also has the molecular formula  $C_6H_{12}O_6$  and on the basis of its reactions it was found to contain a ketonic functional group at carbon number 2 and six carbons in straight chain as in the case of glucose. It belongs to D-series and is a laevorotatory compound. It is appropriately written as D-(–)-fructose. Its open chain structure is as shown.



It also exists in two cyclic forms which are obtained D - (-) - Fructose by the addition of —OH at C5 to the (C=O) group. The ring, thus formed is a five membered ring and is named as furanose with analogy to the compound furan. Furan is a five membered cyclic compound with one oxygen and four carbon atoms.



The cyclic structures of two anomers of fructose are represented by Haworth structures as given.







#### 14.1.3 Disaccharides

You have already read that disaccharides on hydrolysis with dilute acids or enzymes yield two molecules of either the same or different monosaccharides. The two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule. Such a linkage between two monosaccharide units through oxygen atom is called *glycosidic linkage*.

In disaccharides, if the reducing groups of monosaccharides i.e., aldehydic or ketonic groups are bonded, these are non-reducing sugars, e.g., sucrose. On the other hand, sugars in which these functional groups are free, are called reducing sugars, for example, maltose and lactose.

(*i*) *Sucrose*: One of the common disaccharides is **sucrose** which on hydrolysis gives equimolar mixture of D-(+)-glucose and D-(-) fructose.

$$C_{12} H_{22} O_{11} + H_2 O \longrightarrow C_6 H_{12} O_6 + C_6 H_{12} O_6$$
  
Sucrose D-(+)-Glucose D-(-)-Fructose

These two monosaccharides are held together by a glycosidic linkage between C1 of  $\alpha$ -D-glucose and C2 of  $\beta$ -D-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non reducing sugar.



Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (-92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (-) and the product is named as **invert sugar**.

(ii) *Maltose*: Another disaccharide, maltose is composed of two  $\alpha$ -D-glucose units in which C1 of one glucose (I) is linked to C4 of another glucose unit (II). The free aldehyde group can be produced at C1 of second glucose in solution and it shows reducing properties so it is a reducing sugar.



(iii) Lactose: It is more commonly known as milk sugar since this disaccharide is found in milk. It is composed of  $\beta$ -D-galactose and  $\beta$ -D-glucose. The linkage is between C1 of galactose and C4 of glucose. Free aldehyde group may be produced at C-1 of glucose unit, hence it is also a reducing sugar.



#### 14.1.4 Polysaccharides

Polysaccharides contain a large number of monosaccharide units joined together by glycosidic linkages. These are the most commonly encountered carbohydrates in nature. They mainly act as the food storage or structural materials.

(i) Starch: Starch is the main storage polysaccharide of plants. It is the most important dietary source for human beings. High content of starch is found in cereals, roots, tubers and some vegetables. It is a polymer of  $\alpha$ -glucose and consists of two components— **Amylose** and **Amylopectin**. Amylose is water soluble component which constitutes about 15-20% of starch. Chemically amylose is a long unbranched chain with 200-1000  $\alpha$ -D-(+)-glucose units held together by C1– C4 glycosidic linkage.

Amylopectin is insoluble in water and constitutes about 80-85% of starch. It is a branched chain polymer of  $\alpha$ -D-glucose units in which chain is formed by C1–C4 glycosidic linkage whereas branching occurs by C1–C6 glycosidic linkage.







*(ii) Cellulose*: Cellulose occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. It is a predominant constituent of cell wall of plant cells. Cellulose is a straight chain



polysaccharide composed only of  $\beta$ -D-glucose units which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.

(*iii*) *Glycogen*: The carbohydrates are stored in animal body as glycogen. It is also known as *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 break the glycogen down to glucose. Glycogen is also found in yeast and fungi.

Carbohydrates are essential for life in both plants and animals. They form a major portion of our food. Honey has been used for a long time as an instant source of energy by '**Vaids**' in ayurvedic system of medicine. Carbohydrates are used as storage molecules as starch in plants and **glycogen** in animals. Cell wall of bacteria and plants is made up of cellulose. We build furniture, etc. from cellulose in the form

14.1.5 Importance of Carbohydrates

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of wood and clothe ourselves with cellulose in the form of cotton fibre. They provide raw materials for many important industries like textiles, paper, lacquers and breweries.

Two aldopentoses viz. D-ribose and 2-deoxy-D-ribose (Section 14.5.1, Class XII) are present in nucleic acids. Carbohydrates are found in biosystem in combination with many proteins and lipids.

### Intext Questions

- **14.1** Glucose or sucrose are soluble in water but cyclohexane or benzene (simple six membered ring compounds) are insoluble in water. Explain.
- **14.2** What are the expected products of hydrolysis of lactose?
- **14.3** How do you explain the absence of aldehyde group in the pentaacetate of D-glucose?

14.2  $\mathcal{P}_{roteins}$  Proteins are the most abundant biomolecules of the living system. Chief sources of proteins are milk, cheese, pulses, peanuts, fish, meat, etc. They occur in every part of the body and form the fundamental basis of structure and functions of life. They are also required for growth and maintenance of body. The word protein is derived from Greek word, "**proteios**" which means primary or of prime importance. All proteins are polymers of  $\alpha$ -amino acids.

**14.2.1 Amino**<br/>AcidsAmino acids contain amino  $(-NH_2)$  and carboxyl (-COOH) functional<br/>groups. Depending upon the relative position of amino group with<br/>respect to carboxyl group, the amino acids can be<br/>alaccified as  $g = \frac{\beta}{2}$  and  $g = \frac{\beta}{2}$  and g

classified as  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and so on. Only  $\alpha$ -amino acids are obtained on hydrolysis of proteins. They may contain other functional groups also.

 $NH_2$   $\alpha$ -amino acid (R = side chain)

All  $\alpha$ -amino acids have trivial names, which usually reflect the property of that compound or

its source. Glycine is so named since it has sweet taste (in Greek *glykos* means sweet) and tyrosine was first obtained from cheese (in Greek, *tyros* means cheese.) Amino acids are generally represented by a three letter symbol, sometimes one letter symbol is also used. Structures of some commonly occurring amino acids along with their 3-letter and 1-letter symbols are given in Table 14.2.

					ÇO	OH
<b>Fable</b>	14.2:	Natural	Amino	Acids	H <sub>2</sub> N	Η

		R		
Name of the amino acids	Characteristic feature of side chain, R	Three letter symbol	One letter code	
1. Glycine	Н	Gly	G	
2. Alanine	– CH <sub>3</sub>	Ala	А	
3. Valine*	(H <sub>3</sub> C) <sub>2</sub> CH-	Val	V	
4. Leucine*	$(H_3C)_2CH-CH_2-$	Leu	L	