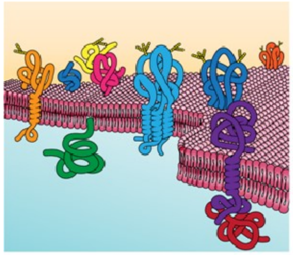


UNIT 2

CARBOHYDRATES AND LIPIDS

Structure

Gly

2.1 INTRODUCTION

In the previous unit you have learnt about the structure of the cell, various organelles present in the cell and the functions of these organelles. A proper understanding of the cell is possible only when we correlate the structure with chemical composition and functions of various cellular organelles. Amongst the chemicals there are important biomolecules and water which are of key significance and therefore called the molecules of life. In fact, Unit 2dealswith these molecules wherein in the first section only an overview and introductory picture of these molecules is given. Water being the most abundant of the cell molecules, the concept of its ionisation with reference to hydrogen ion concentration is discussed in detail. The structures of simple organic molecules like sugars, amino acids, nucleotides and lipids have been discussed.

The unit is dedicated to carbohydrates and lipids which are the energy providing molecules in living systems. The broad classification of both the molecules is given with the presumption that you have read about the basic structure and chemistry of these molecules in your undergraduate programs. Therefore, the significant derivatives of these molecules have been dealt from the function point of view and their use to chemists who might be interested in getting into the related further studies. The important derivatives of carbohydrates and lipids have been given with their structural and biological significance. The structure and function of the cell membrane is covered in detail keeping in view its diverse functions and the central role in cellular biology. The biological functions of both the biomolecules are listed.

In the next unit you will study about other very important biomolecules, viz., proteins and nucleic acids.

Expected Learning Outcomes

After studying this unit, you will be able to:

- list different types of molecules and their percent mass present in a cell;
- state the properties of water, pH and calculate pH;
- define buffers and state their significance in the living organisms;
- describe briefly the structure of monomeric sugars, amino acids, nucleotides and fatty acids;
- classify carbohydrates into different types on the basis of size of the molecules and the functional groups;
- draw the structures of mono-, oligo- and polysaccharides;
- draw and explain the important derivatives of carbohydrates;
- state the biological importance of carbohydrates in the living systems;
- define and classify lipids on the basis of their structure and function;
- draw the structure of fatty acids as part of glycerides;
- describe the structural features of lipid derivatives and lipid aggregates;
- state the biological importance of lipids in the living systems; and
- describe the structure and function of biomembranes.

2.2 MOLECULES OF LIFE: AN OVERVIEW

Cells in different tissues of an organism vary in their structure and function. Consequently, cells are of many types, such as muscle cells, blood cells, nerve cells in animals and meristematic cells and vascular cells in plants. Yet all the cells show considerable uniformity in their basic biochemical make-up. In other words, the chemical components of various types of cells are very similar and it is only the arrangement of components that causes a great diversity among cells, and consequently among tissues and organisms. Cells contain various simple as well as complex molecules. Table2.1 gives molecular composition of a cell.

Table 2.1: Molecular Composition of a Cell

	Percent of total mass		
Types of molecules	Bacterial cell	Mammalian cell	Number of types of molecules in a bacterium
Water (H_2O)	70	70	1
Macromolecules (proteins)	15	18	3000
RNA	6	1.1	300
DNA	1	0.25	1
Sugars and precursors	3	2.0	200
Lipids and precursors	2	5	50
Amino acids and precursors	0.4	--	100
Nucleotides and precursors	0.4	--	200
Inorganic ions (like Na^+, Mg^{2+}, Ca^{2+}, PO_4^{3-})	01	1	20
Other small molecules (like vitamins)	0.2	3	500

In a living system, a large number of organic molecules are present. Diversity of organic molecules is due to the property of the carbon atom which in association with itself and with other atoms forms an unlimited number of compounds with different properties. Four major classes of organic compounds found in biological systems are: carbohydrates, proteins, nucleic acids and lipids. In the following subsection let us revise the basic information about some of these molecules briefly.

2.2.1 Organic Molecules in Living Systems

Carbohydrates: Carbohydrates form the most abundant class of organic compounds. They are the compounds containing carbon, hydrogen and oxygen. The hydrogen and oxygen in these compounds are generally present in the ratio of two to one atom as in water.

The carbohydrates can be divided into classes based on the size of the molecules. The **monosaccharides,** the basic units of carbohydrates are simple sugars having the general formula $C_nH_{2n}O_n$ where n can vary from three to eight. Depending on the number of carbon atoms, they are called as trioses (C_3), tetroses (C_4), pentoses (C_5), hexoses (C_6) and so on. The structures of some of these are given in Fig. 2.1. The **disaccharides,** consist of two monosaccharide units joined together. The **oligosaccharides** include the sugars with up to 10 monosaccharide units. The **polysaccharides** are also made up of monosaccharides joined together but may contain thousands of units.

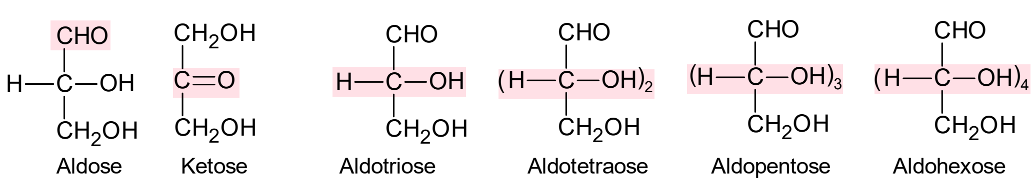


Fig. 2.1: Structures of some monosaccharides with different number of carbon atoms.

Glucose, fructose, galactose, ribose and deoxyribose are examples of monosaccharides. Sucrose, lactose and maltose are examples of disaccharides. The table sugar or sucrose is composed of glucose and fructose, whereas milk sugar or lactose is composed of glucose and galactose. It is interesting to note that the milk sugar lactose can be digested by the enzymes produced in the intestine of children (lactase) but in several groups of adults this enzyme is missing. The deficiency of this enzyme causes intolerance of lactose and hence of milk. It is found that the percentage of lactose intolerance is more in adult populations which have not consumed milk and dairy products in childhood than those who have consumed these. Starch, cellulose and glycogen (all composed of glucose) are examples of polysaccharides.

You will study in detail about the different carbohydrates in Section 2.3 of this unit.

Proteins: Proteins are complex diverse and high molecular weight polymers found in the cell. The **monomeric** units of proteins are amino acids.

Monomer: The basic subunit from which, by repetition polymers are made. For example, amino acids are the monomers of proteins, glucose is the monomer of glycogen.

Amino acids join each other in a specific manner to form an unbranched, linear polymers known as polypeptides. Thousands of proteins that are present in a body are made-up of only 20 different naturally occurring amino acids. Amino acids are important not only in the synthesis of proteins but also in general metabolism.

In each amino acid, the alpha carbon atom is attached to a carboxyl group, an amino group and a side chain. Presence of both a positively and a negatively charged group in the same molecule of amino acid is known as "zwitterion" (German: *Zwitter* = hybrid, both). The variation in the different amino acids is due to the presence of a side chain (R) attached to the alpha carbon atm. On the basis of the side chains, i.e., polar, non-polar, uncharged polar, positively or negatively charged polar groups, amino acids are classified into four groups.

You will study the role of proteins in Unit 3 of this block.

Nucleic Acids: The nucleic acids are large complex polymers like proteins. There are two types of nucleic acids viz., the ribonucleic acid (RNA) and the deoxyribonucleic acid (DNA) found within the cell. They are made-up of four types of nucleotides. Each nucleotide is made of a sugar, a phosphate and a nitrogenous base. There are only 2 kinds of sugars in nucleotides: ribose and 2-deoxyribose. There are five types of nitrogenous bases: cytosine, thymine, uracil, adenine and guanine. The nucleotides are joined together by a specific linkage (5' $\rightarrow$ 3' phosphodiester linkage) to form a linear, unbranched chain of polynucleotides.

The structures of DNA, RNA and the role of nucleic acids are dealt in Unit 3 of this block.

Lipids: Lipids are heterogenous groups of compounds usually formed by the combination of a fatty acids with glycerol. Fatty acids are the characteristic components of lipids present in both animal and vegetable fats such as ghee, coconut oil and mustard oil. Fatty acids are long linear chain organic compounds containing 4-24 carbon atoms. Nearly all fatty acids in nature have an even number of carbon atoms, but those with 16 and 18 carbon atoms are most abundant in oil. Fatty acids have a single carboxyl group and a long, non-polar hydrocarbon chain. The presence of non-polar chain makes lipids insoluble in polar solvents such as water. The long hydrocarbon chain may be fully saturated with carbon atoms joined by single covalent bonds or it may be unsaturated with double bonds between carbon atoms. The details of structure and types oflipids and their role in the biological membrane is explained in Section 2.12 of this unit.

It is needless to say that water is very essential for the sustenance of life for all. In the following subsection let us study the role of water in living systems.

2.2.2 Water in Living Systems

Water is the most abundant of all the molecules in a living cell and is very essential for life as is clear from the molecular composition given in Table 2.1. It is difficult to imagine the existence of any form of life in which water can be replaced by any other molecule. Uniqueness of water lies in its structure, capacity as an excellent solvent and role as a medium in which all the biochemical reactions occur.

Chemical reactions in the body are very sensitive to changes in the pH as most chemical reactions of life occur at neutral pH. Blood and most of the body fluids have pH values about 7.4 except for the stomach contents which have a pH value about 2.0. The pH of a solution is measured in terms of its hydrogen ion (H^+) concentration, which indicates whether a solution is acidic or basic.

Ionisation of Water

The unique properties of water are due to its molecular structure. In water two hydrogen atoms are covalently held to an oxygen atom and hence dissociation of hydrogen is very difficult. Consequently, pure water exhibits very little ionisation. In pure water, for every 550 million undissociated molecules, one molecule of water dissociates into one hydrogen ion (H^+) and one hydroxy ion (OH^-) as per the following reaction.

$$H_2O \rightleftharpoons H^+ + OH^-$$

The equilibrium constant between the dissociated molecules may be represented as follows:

$$\frac{[H^+]\,[OH^-]}{[H_2O]} = K_{eq} \qquad \ldots (2.1)$$

K_{eq} = equilibrium dissociation constant. H^+, OH^- and H_2O in brackets indicate **molar** concentrations.

The molar concentration of water in one litre of water is 1000/18 = 55.5, therefore, Equation 2.1 can be written as follows.

$$55.5 \times K_{eq} = [H^+]\,[OH^-] \textbf{ or } K_w = [H^+]\,[OH^-] \qquad \ldots (2.2)$$

Where K_w is the ionic product of water and is estimated = 1.0×10^{-14} at 25°C.

One **mole** of a substance means 6.023×10^{23} molecules of that substance.

Since the concentration of both H^+ and OH^- is exactly equal, the concentration of each ion is given as below.

$$[H^+] = [OH^-] = 1 \times 10^{-7} \text{ moles/litre}$$

Taking logarithm of the quantities we get,

$$-\log K_w = -\log [H^+] - \log [OH^-]$$

Since, -log K_w at 25°C is 14, the Equation 2.3 may be simplified as

$$[H^+] + [OH]^- = 14$$

You know that all the biochemical reactions take place at a specific pH. The **pH scale** is based on ionic product of water (K_w). You are familiar with this concept but we recall it for the benefit of all.

Hydrogen Ion Concentration (pH)

The acidity or basicity of a solution can be calculated in terms of its hydrogen ion concentration. Concentration of hydrogen in a solution is generally represented in terms of **pH**. The pH is defined as the negative logarithm of hydrogen ion concentration. The concept of pH is very useful in understanding the change in hydrogen ion concentration in and around the cellular environment.

You know how we can calculate of pH from hydrogen ion concentration. For example, a hydrogen ion concentration of 10^{-7} moles/litre means,

$$\text{pH} = -\log [H^+]$$

$$= -\log [10^{-7}] = 7.0$$

It is important to note that pH may vary only between 0 and 14 and 7.0 is the neutral pH value. The pH scale along with the pH of some common substances is listed in Table 2.2.

Table 2.2: The pH scale with examples

	$[H^+]$ (M)	pH	$[OH^-]$ (M)	Examples
	1.0	0	10^{-14}	1 M HCl
	10^{-1}	1	10^{-13}	Gastric juice
	10^{-2}	2	10^{-12}	Lemon juice
Acids	10^{-3}	3	10^{-11}	Vinegar
	10^{-4}	4	10^{-10}	Tomato juice
	10^{-5}	5	10^{-9}	Black coffee
	10^{-6}	6	10^{-8}	Rain water
Neutral	10^{-7}	7	10^{-7}	**Pure water**
	10^{-8}	8	10^{-6}	Sea water
	10^{-9}	9	10^{-5}	Baking soda
Bases	10^{-10}	10	10^{-4}	Alkaline desert ponds
	10^{-11}	11	10^{-3}	Liquid soap

	10^{-12}	12	10^{-2}	Household ammonia (or Lime water)
	10^{-13}	13	10^{-1}	
	10^{-14}	14	1.0	1 M NaOH

When we neutralise an acid with a base, the change in pH would be very large, say from a highly acidic pH of 2.0, to a neutral pH of 7.0. This pH change may be very damaging in body fluids such as blood besides affecting the other biochemical reactions. It is very essential to actually prevent even minor fluctuations of pH in blood. The pH values of some important organelles and body fluids are listed in Table 2.3. The living organisms manage this change with the help of buffer solutions which is recalled in the following paragraph.

Table 2.3: pH values of some important organelles and body fluids

Cellular Organelles and Body Fluids	pH
Mitochondria matrix	7.5
Cytosol	7.2
Nucleus	7.2
Blood	7.4
Peroxisomes	7.0
Urine	6.0
Saliva	6.3-6.8
Human skin	5.5
Lysosomes	4.5
Gastric juice	1

Buffer Solutions and Types

A buffer solution is the one which resists changes in pH upon the addition of small amounts of a strong acid or strong base. Thus, the function of a buffer solution is to maintain effectively the pH of a solution, by neutralising the acid or base added to it. A buffer solution is made up of two components, one of which is a free acid or a weak base and the other is its salt. Two types of buffer solutions are generally prepared. These are given below.

Type I Buffer Solution or Acidic Buffer: It consists of a weak acid and its salt with a strong base. Some examples of buffer solutions of this type are:

Weak acid	Salt
Acetic acid (CH_3 COOH)	Sodium acetate (CH_3COONa)
Carbonic acid ($H_2CO_3^{2-}$)	Sodium bicarbonate ($NaHCO_3^{2-}$)
Sodium dihydrogen phosphate (NaH_2PO_4)	Disodium hydrogen phosphate (Na_2HPO_4)

Type II Buffer Solution or Basic Buffer: It consists of a weak base and its salt with a strong acid. An example of this type is ammonium hydroxide (NH_4OH) which is a weak base and ammonium chloride (NH_4Cl) which is the salt.

Buffers play important roles in maintaining the pH of cells and cellular organelles to carry out their biological processes. The important biological buffers in the human body are phosphate buffer and bicarbonate buffer. The phosphate buffer is an intracellular buffer in the cells which is maximally effective at pH 6.86 and it has buffering range from 5.9 to 7.9. The bicarbonate buffer is a physiological buffer system in human blood which plays a crucial role to maintain the blood at pH 7.4.

You should get familiar with another concept associated with water and that is the electrolyte balance.

2.2.3 Water and Electrolyte Balance

It is known that nearly three-fourth of our body weight is accounted for by fluid i.e., water. In fact, it is 70% of the body's weight. The distribution of water in the body is given as: **plasma** (5%), **Interstitial fluid (IF)** i.e., fluid in between the cells (15%) and **Intracellular fluid (ICF)** i.e., fluid inside the cell (50%). The plasma and interstitial fluid together form the **Extracellular fluid (ECF).** This distribution can be depicted as given in Fig 2.3.

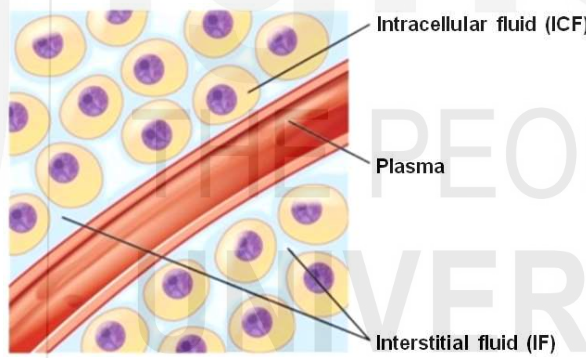


Fig. 2.3: Fluid compartments in the human body.

In the human body, sources of water are water and other beverages consumed, water content of solid foods and water formed due to metabolic changes. The total intake of water, however, depends on a number of factors. In a healthy condition, it mainly depends on external temperature, as one of the functions of water is to regulate the body temperature. We feel thirsty when the intake of water is inadequate for the body. The thirst is easily quenched by drinking water. However, thirst associated with dehydration, is a sign of lack of salts as well. Humans cannot distinguish between "salt-hunger" and "water-hunger", as animals do. So, along with water, electrolytes too, have to be replaced.

Water is excreted from the body through four channels: skin, lungs, kidneys and intestines. Salts accompany water in sweat, urine and intestinal secretions. Water balance is bound up with the distribution of Na^+ and K^+ ions. Other factors include acid-base equilibrium, intermediary metabolism of proteins, carbohydrates and fats, external temperature and the effect of some hormones. You will read more about the water balance in the body in unit 4 of this block.

You are familiar with the term **electrolyte**. An electrolyte is a solution that contains ions and passes the current through the movement of those ions. The electrolytic solutions mainly include soluble salts, acids, and bases dissolved in a polar solvent, such as water. It can be said that these are the inorganic constituents which ionise and provide positively and negatively charged ions. These constitute a small fraction in the body but are very significant. For example, mineral elements such as iron and iodine form parts of special proteins such as hemoglobin and thyroxine respectively. Similarly, ions such as H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, OH^-, HCO_3^-, Cl^-, HPO_4^{2-} and SO_4^{2-}, are essential for the elasticity and irritability (excitability) of muscles and nerves, permeability of cell membranes, etc.

The concentration of electrolytes in the three fluid compartments is maintained within narrow ranges especially by the interstitial fluid and blood plasma which manage the fluctuations in the cell. However, dehydration may result due to less intake of water, or extensive loss of water or both.

The electrolytes help in,

- rapid chemical reactions between various compounds.
- providing the right degree of acidity to gastric secretion.
- maintenance of proper alkalinity of pancreatic and intestinal secretions.
- enhancing the activity of many enzymes by providing an optimal pH, e.g., Mn^{2+}, Mg^{2+} and K^+ are essential for this purpose.
- controlling pH of body fluids through buffering action.
- regulating the passage of water into and out of cells by exerting osmotic pressure.

In the next section you will study about the very important biomolecules that are responsible for providing energy towards the various functions of the cell. You have been introduced to these molecules in the previous section, these are carbohydrates, and you know these are very essential in our diet.

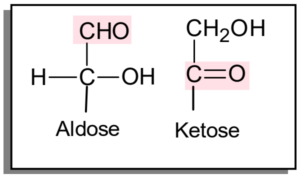
You can try to answer the following SAQ before proceeding further.

SAQ1

Calculate the pH of an aqueous solution in which 0.5 (cm^3) of dilute hydrochloric acid has been added to 1 dm^3 (1000 cm^3) of pure water.

Assume that this dilute hydrochloric acid has the concentration of 2 moles/dm^3 (2 moles/ litre =M) and is completely ionised in solution.

2.3 MONOSACCHARIDES



In Subsection 2.2.1 you read that depending on the number of carbon atoms which varies from 3-8, the monosaccharides have been classified into some groups. These are further divided into two sub-groups depending on the presence of aldehyde or keto group in the molecule namely, **aldoses** and **ketoses**, respectively. Individual aldoses and ketoses are called trioses, tetroses, pentoses, hexoses, etc., containing 3, 4, 5, 6 carbon atoms respectively in a molecule. The classification of carbohydrates indicating these features along with representative examples of each type is given in Fig. 2.4.

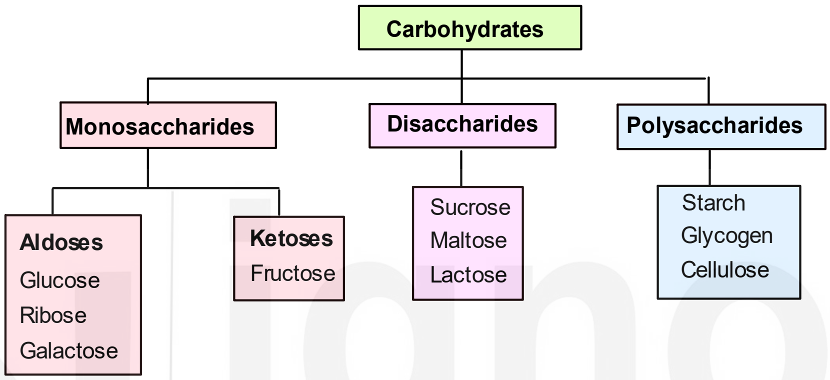


Fig. 2.4: Classification of carbohydrates.

The monosaccharides can exist as open chain structures or in the ring form. The aldohexose, D-glucose and the ketohexose, D-fructose are the most common monosaccharides occurring in nature. Their open and ring structures are given in Fig. 2.5.You may observe here that the hydroxyl groups pointing towards right in the Fischer representation (open chain form) are directed downwards and the ones pointing towards the left are directed upwards in the Haworth representation (cyclic form). In this representation the α–anomeric hydroxyl is directed downwards and the β-anomeric hydroxyl is directed upwards.

Furan

You know that the chiral carbon in a molecule is represented by an asterisk (*).

The number of stereoisomers is equal to 2^n, where n is the number of chiral carbon atoms.

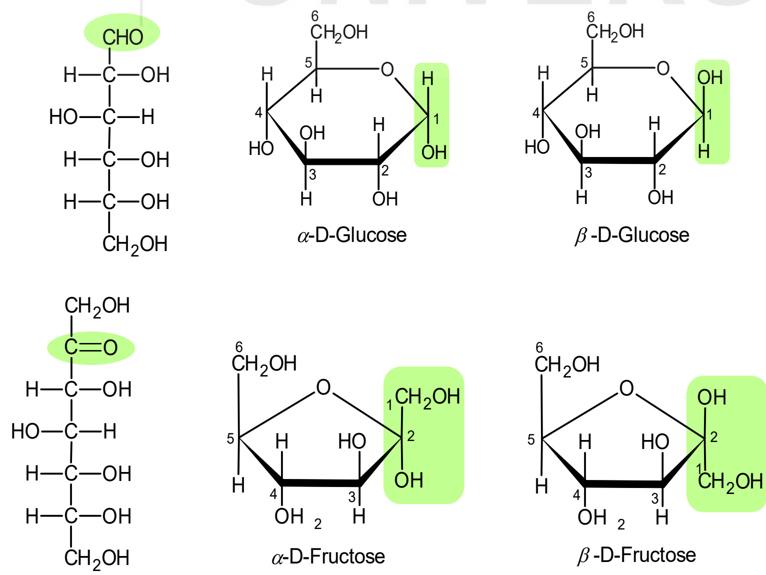
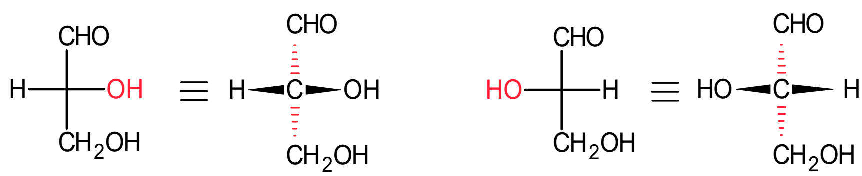


Fig. 2.5: Open and Ring structures of monosaccharides.

The aldopentose D-ribose and D-deoxyribose are components of nucleotides and the nucleic acids (DNA and RNA) about which you will read in Unit3 in detail. All the monosaccharides (whether aldoses or ketoses) are reducing in nature as these reduce Fehling's, Benedict's and Tollen's reagents. These are optically active due to the presence of one or more chiral carbon atoms. The Fischer projection of the two enantiomers of glyceraldehyde, a simple monosaccharide (aldotriose)is shown in Fig. 2.6.



D-Glyceraldehyde L-Glyceraldehyde

Fig. 2.6: Fischer projection of the enantiomers of glyceraldehydes.

The structure of glyceraldehyde in which the OH group attached to the chiral atom is towards the right in Fischer projection is arbitrarily called as **D-glyceraldehyde** and the one in which it points to the left (the mirror image) is called as **L-glyceraldehyde**. Higher sugars have two or more chiral carbon atoms and therefore, have a larger number of stereoisomers. Here you might like to recall the concepts of chirality studied in the stereochemistry course.

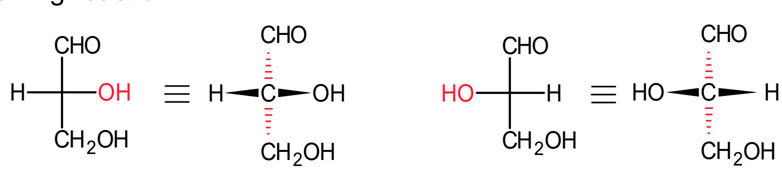
2.3.1 Derivatives of Monosaccharides

The monosaccharides undergo a number of reactions to form the derivatives of monosaccharides. These react with alcohol to form **glycosides**. For example, in the reaction of glucose with an alcohol, *α*-glucoside is formed as the major product. D-galactose as well as D-glucose exist in nature as their 2-amino derivatives and are commonly referred to as **amino sugars.** The replacement of one or more hydroxy groups by hydrogen produces a**deoxy sugar**. Let us study about these derivatives of monosaccharides in the following paragraphs.

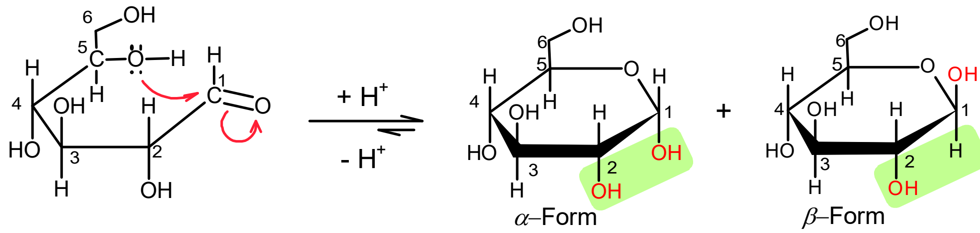
Glycosides

You would recall that an aldehyde reacts with equivalent molesof an alcoholto form a hemiacetal; the hemiacetal reacts with second equivalent molesof alcohol to forman acetal. Since monosaccharides (aldoses and ketoses) contain both alcoholic group and aldehyde or keto group within the same molecule, the two groups combine intramolecularly to give a cyclic hemiacetal. Five and six membered cyclic hemiacetals of aldoses and ketoses are quite stable. For example, in D-glucose, the hemiacetal will be formed between the aldehyde group at C-1 and alcoholic group at C-5. The carbonyl carbon of D-glucose, which has no chirality, becomesasymmetric followingcyclisation and the resultant diastereoisomers are formed, i.e., *α*-form and *β*-form as shown in the following reaction.

> Hemiacetal is formed by the pyranose and hemiketal is formed by a furanose

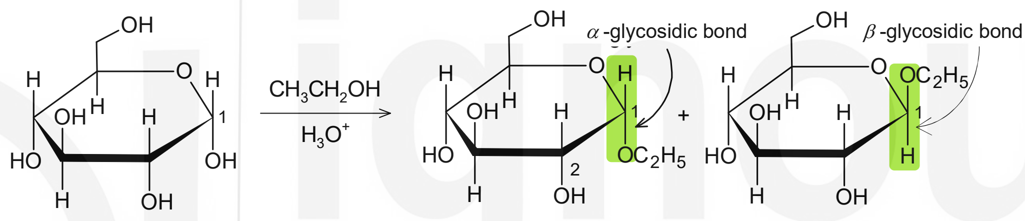


D-Glyceraldehyde L-Glyceraldehyde



Open chain aldehyde form of D-Glucose **Cyclic hemiacetal (two stereoisomers)**

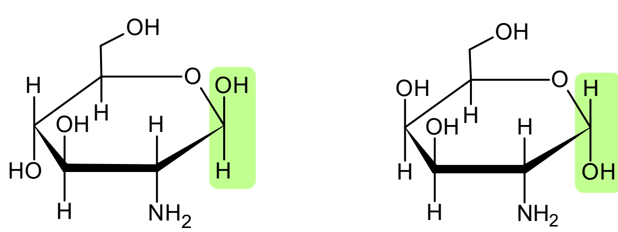
Further, the cyclic hemiacetal (or hemiketal) formed by a monosaccharide can react with an alcohol to form an acetal (or ketal). The acetal (or ketal) of a sugar iscalled a **glycoside**, and the bond between the carbon and the alkoxy oxygen is called a **glycosidic bond**. Glycosides are named by replacing the "e" ending of the sugar's name with "ide." Thus, a glycoside of glucose is a glucoside, a glycoside ofgalactose is a galactoside, etc. If the pyranose or furanose name is used, the acetal is called a **pyranoside** or a **furanoside**. It is observed when single anomer of glucose is treated with alcohol it gives both α-glucoside and β-glucoside as is clear from the following reaction.



α–D-Glucose Ethyl-α–D-glucoside Ethyl-β–D-glucoside

Amino Sugars

D-galactose as well as D-glucose exist in nature as their 2-amino derivatives and are commonly referred to as **amino sugars.** Amino sugars are formed when one of the hydroxy group(–OH) of sugar is replaced by the amino group (–NH_2).Glucose formsβ-D-glucosamine and by a similar reaction galactose forms β-D-galactosamine. Along with its acetylated derivative,β-D- N- acetyl glucosamine, the amino sugar,β-D-glucosamine is found in many oligosaccharides and polysaccharides, for example, in chitin, which forms exoskeleton of insects and crustaceans. Similarly, β-D-galactosamine is an important component of cartilage. Muramic acid and N- acetylneuraminic acid (NANA also known as sialic acid) are two important examples of amino sugars as components of polysaccharides of bacterial cell walls and cell membranes in higher organisms. The structures of β-D-glucosamine andβ-D-galactosamine are given below.



β–D–Glucosamine **α–D–Galactosamine**

Deoxy Sugars

When one or more hydroxy groups of a monosaccharide are replaced by hydrogen, it is called as a **deoxy sugar**. For example,**2-deoxy ribose** is one such derivative in which the hydroxy at C2 is replaced by H. It is a constituent of the DNA strand i.e., the genetic material in living organisms. **Fucose** is deoxy derivative of glucose in which CH_2OH becomes CH_3. It is secreted in the mother's milk, helps in the development of immune system of new born babies and also involved in nerve transmission. It is a common constituent of mammals, insects and plant cell surface. **Rhamnose** is the deoxy derivative of mannose which occurs naturally as L-sugar. It is more commonly found in plants and bacteria than animals. The structures of the mentioned deoxy sugars are given in Fig. 2.7.

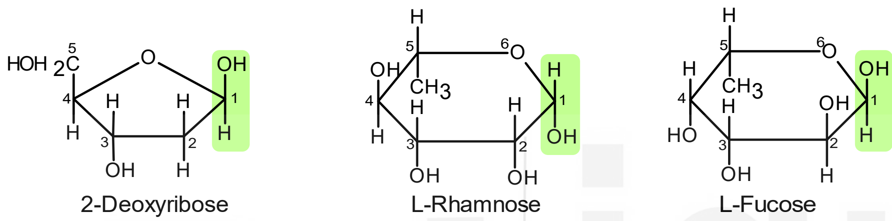
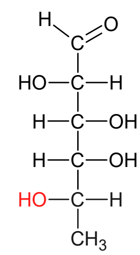


Fig. 2.7: Structures of deoxysugars



Open chain structure of L-Fucose

SAQ 2

a) General empirical formula of carbohydrates is _________.

b) Two major functions of carbohydrates are ______.

c) Two types of functional groups present in monosaccharides are keto _______________.

d) The number of carbon atoms present in the smallest carbohydrate is ____.

2.4 DISACCHARIDES

Disaccharides are the most commonly occurring oligosaccharides in nature. These yield two monosaccharide molecules on hydrolysis. A disaccharide is formed when two monosaccharides get connected by a glycosidic bond formed between them. Let us take the example of linking of a molecule of *α*-D-glucose with a molecule of *β*-D- glucose to give a molecule of maltose, a disaccharide. In this process the α-hydroxyl group of the *α*-D- glucose residue reacts with the C-4 hydroxyl of the second residue with the elimination of a water molecule to give the disaccharide as shown below in Fig. 2.8.

Maltose is also known as malt sugar and is obtained mainly by incomplete hydrolysis of starch and glycogen.

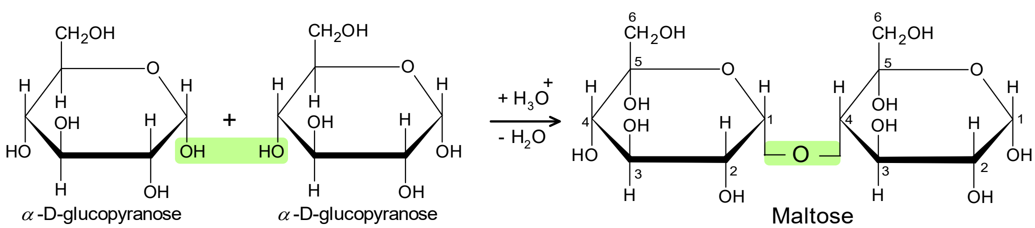


Fig. 2.8: Formation of maltose.

The linkage formed between the two monosaccharides is called as a glycosidic linkage and is represented as *α* (1→4) glycosidic linkage. This nomenclature highlights the fact that the linkage is between the C-1 atom of first residue and the C-4 of the second residue and secondly the *α*-anomer of the first residue is involved. If the *β*-anomer of the first residue gets into a glycosidic linkage with the C-4 hydroxyl of the second residue then the linkage will be named as *β*(1→4) glycosidic linkage. For example, in cellobiose, another disaccharide, two *β*-D-glucose residues are linked by *β* (1→4) glycosidic linkage as shown in Fig. 2.9.

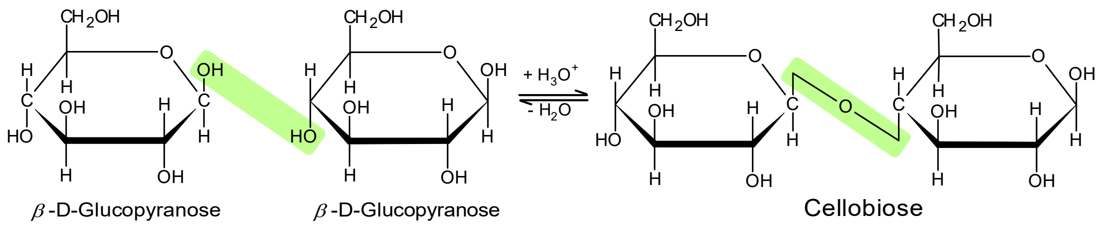
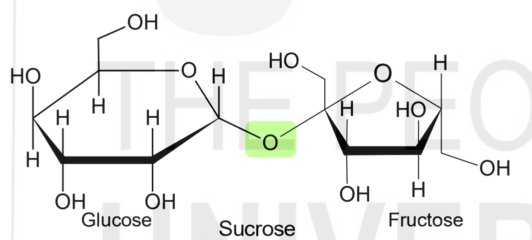


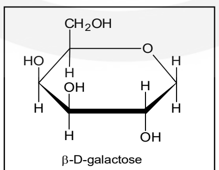
Fig. 2.9: Formation of cellobiose.

Sucrose is the most widely employed sweetening agent and is found in higher plants e.g., in juices of fruits, vegetables and also in honey.

The disaccharides do not necessarily contain two molecules of the same monosaccharide linked together. The two constituent monosaccharides may be different as in the case of lactose (the milk sugar) which is formed by linking of *β*-D-galactose and *β*-D-glucose through *β*(1→4) glycosidic linkage and is synthesised in the mammary glands after childbirth, from galactose and glucose under hormonal regulation. Sucrose (the common sugar) is another disaccharide which is made up of a molecule each of glucose and fructose.



SAQ 3



Draw the structure of lactose showing the linkage between the two monosachharides involved. The structure of *β*-D-galactose is given here for your reference.

2.5 POLYSACCHARIDES

As the name implies, polysaccharides are large, high molecular weight molecules formed by the condensation of a large number of molecules of monosaccharides joined together by glycosidic bonds. The monosaccharide units are either all identical as in starch, or of different types like in cell walls.

These are called the **homopolysaccharides** and **heteropolysaccharides** respectively. The polysaccharide chains may be linear or branched. These are generally unreactive as most of their hemiacetal groups are in the glycosidic bonds.The different possible arrangements of monosaccharides in homo- and heteropolysaccharides are shown in Fig. 2.10.

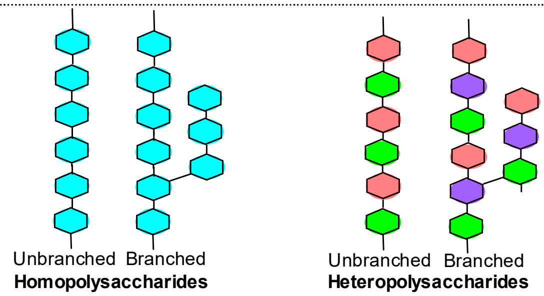


Fig. 2.10: Homo- and heteropolysaccharides.

In nature, polysaccharides are employed as part of structural tissues known as **structural polysaccharides** or may be used for storing energy known as **storage polysaccharides**.

The homopolysaccharides that are composed exclusively of glucose units are known as **glucosans** and include the following carbohydrates.

Starch: It is the carbohydrate reserve form in plants which is a glucose polymer. In case of shortage of glucose in the cell, starch is hydrolysed within the cell to release glucose. Dietary starch is present in potatoes, rice, wheat, corn and many other plant sources.

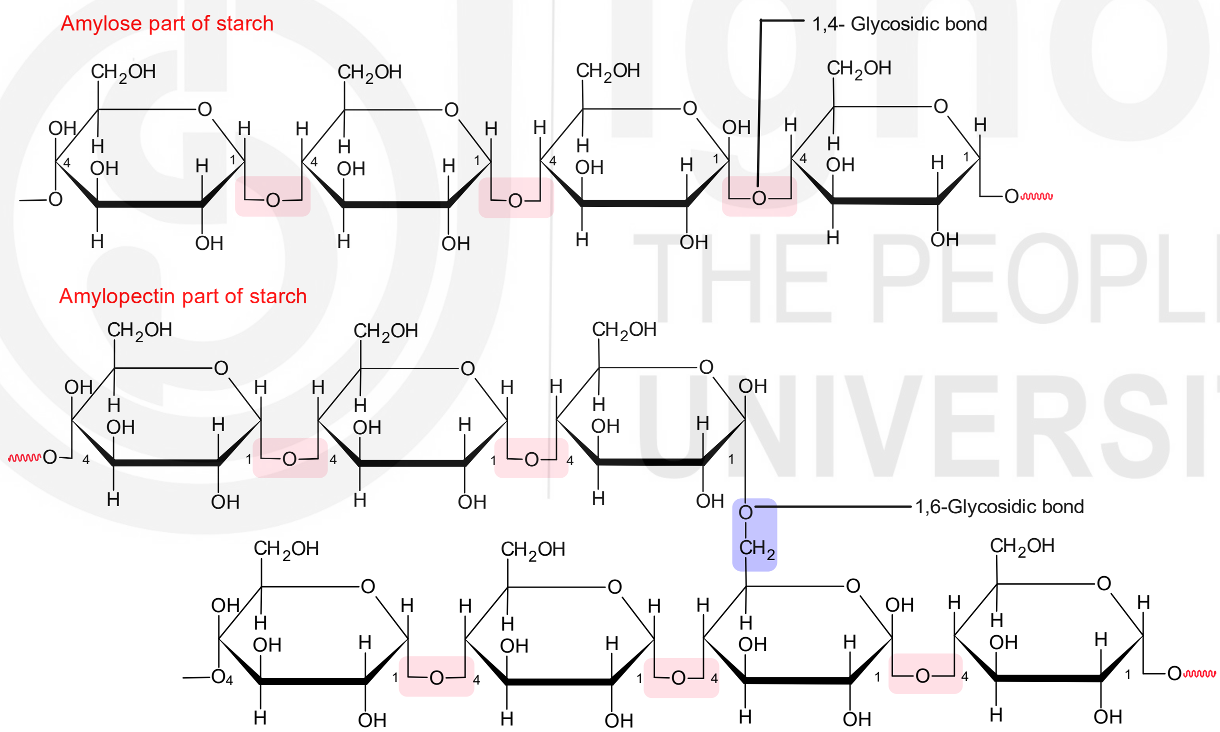


Fig. 2.11: A portion of amylose and amylopectin constituents of starch.

Starch is composed of two constituents namely, **amylose**, a polysaccharide with linear chains which is made up of D-glucose units joined by $\alpha(1 \rightarrow 4)$ glucosidic linkages (as in maltose) and **amylopectin**, a polysaccharide which is made of main chains that are identical to those of amylose with side chains joining these by $\alpha(1 \rightarrow 6)$ glucosidic linkages. The side chains have the same structure as the main chains and are 20 to 25 glucose residues long. A portion of amylose and amylopectin constituents of starch are shown in Fig. 2.11.

Glycogen: It is the storage form of glucose in animals and is mainly concentrated in the liver and muscles. Its structure is the same as that of amylopectin; however, glycogen is branched to a greater degree and therefore contains more α(1→6) glucosidic linkages. The average length of chainsvaries from 10 to 15 glucose residues. When required for metabolism in the body, glucose units are removed one by one from glycogen by a process of phosphorylation in the presence of the enzyme glycogen phosphorylase to give glucose 1-phosphate. This is then utilised for the metabolic needs of the body.

Cellulose: It is mainly responsible for the structure of cell walls of plants and consists of long chains made up of D-glucose units joined by β(1→4) glycosidic bonds. These chains are closely attached to one another by hydrogen or van der Waals type of bonds, thus forming compact and insoluble fibrous structures which permit the industrial use of cellulose as in the paper fibres and fabrics. A segment of cellulose molecule is shown in Fig. 2.12.

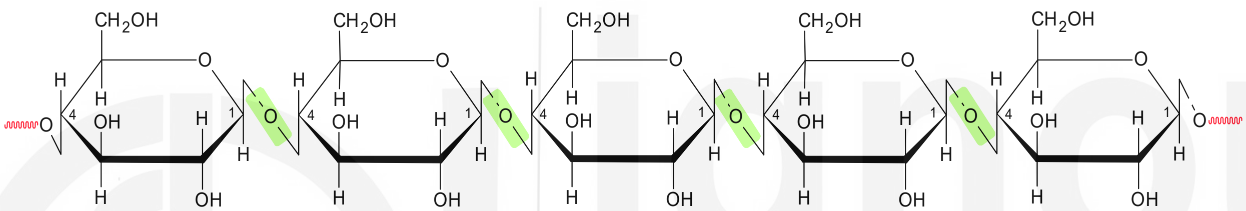


Fig. 2.12: A segment of cellulose molecule.

Our body can digest all the polysaccharides discussed above, except cellulose. The reason for this lies in the glycosidic linkages involved in linking the monosaccharides in these polymeric molecules. You would have noticed that amylose, amylopectin, and glycogen have α (1→ 4) or α (1→ 6) glycosidic linkages which are broken down in our body with the help of an enzyme called α-amylase. Our body does not have any enzyme to break the β (1→ 4) glycosidic linkages found in cellulose. Think of a scenario in which our body had the enzyme, β-amylase, found in the grazing animals and we had to compete with them for the grass.

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

In the next section you will study about the carbohydrates which are linked to other biomolecules and fulfil important roles in the living beings. Before proceeding try to answer the following SAQ.

SAQ 4

Fill in the blank spaces with appropriate words.

a) The polysaccharide ______is a plant food reserve.

b) Branching points in starch and glycogen are due to formation of______glycosidic bonds between glucose residues.

c) In amylopectin, the side chains have ______glucose residues.

d) The polysaccharide ______ is found in plant fibres.

2.6 GLYCOCONJUGATES

In the preceding sections, we have described polysaccharides essentially made up of hexose monomer units. Oligosaccharides and polysaccharides also exist in covalent linkage with lipids and proteins to form complexes known as **glycoconjugates**. Glycoconjugates are believed to be more dynamic and information rich than proteins and nucleic acids. These carry the information for communication between cells and their surroundings, labelling and targeting proteins for transport from their site of synthesis to action, cell-cell recognition, blood clotting, wound healing, immune response and many more. 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.

The complex polysaccharides are important as intercellular substances and exist either free or in combination with proteins or lipids.

Glycoconjugates are divided into the following broad classes:

1. Glycoproteins
2. Glycolipids
3. Glycosaminoglycans
4. Proteoglycans

Let us discuss the structure and role of these glycoconjugates in the following subsections.

2.6.1 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 and lipid bilayers are glycoproteins. In general, glycoproteins consist of a core protein to which the carbohydrates like glucose, galactose, mannose, fucose, N-acetylgalactosamine, N-acetylglucosamine and N-acetylneuraminic acid (NANA) are covalently linked. These carbohydrates in glycoproteins form glycosidic bond with amino acid residues of the proteins by O- or N-glycosidic bonds and are therefore divided into two types: O- linked and N- linked. The details of the structures are beyond the scope of this course. In case you wish to get the details, may look into any Biochemistry book.

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 in 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.

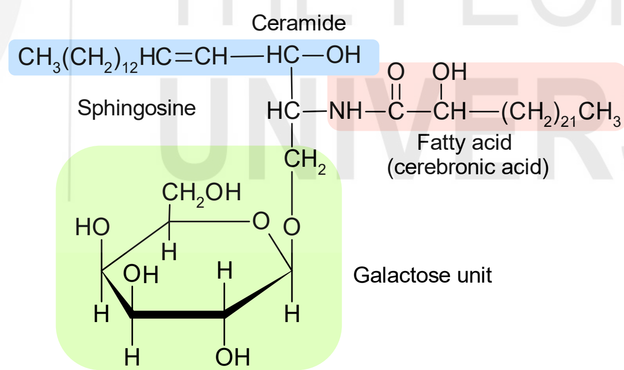
2.6.2 Glycolipids

Glycolipids are the membrane lipids found in animals and plants to which oligosaccharides are attached. These oligosaccharides act as cell surface markers by providing specific sites for recognition by carbohydrate-binding proteins. Gangliosides are the lipids found on the outer surface of eukaryotic cell membranes and are associated with oligosaccharides containing sialic acid and other monosaccharides. These oligosaccharides act as cell markers helping in cell recognition and cell to cell communication.

Glycolipids are widely distributed in most tissues of the body and particularly in the nervous tissue, such as the brain. In the plasma membrane these contribute to cell surface carbohydrates, which function as cell membrane receptors, and are involved in recognition mechanism. The major glycolipids of the animal tissues are the glycosphingolipids**.** These contain ceramide which is the combination of sphingosine and fatty acid. When the terminal primary-OH group of sphingosine in ceramide is bonded to a sugar residue then a cerebroside is formed.

Ceramides help to restore the skin's moisture. These are used in moisturizers and in anti-aging cream.

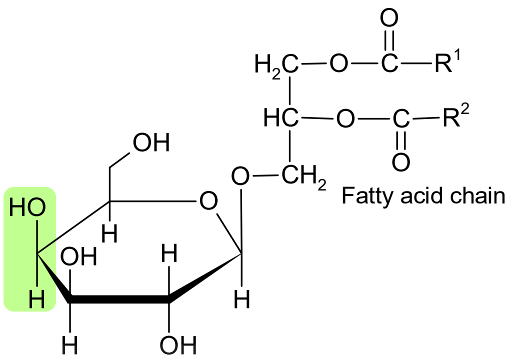
For example, the structure of galactocerebroside or galactosylceramide is given in Fig. 2.13.



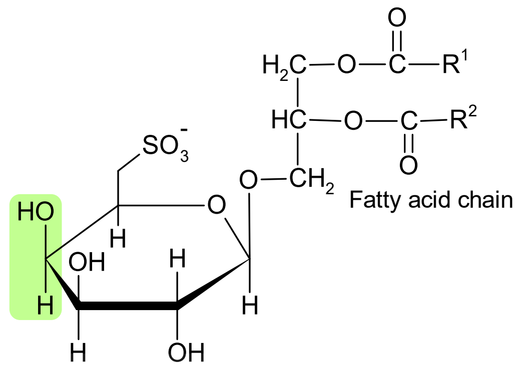
2.13: Structure of galactocerebroside.

Galactosylceramide has a characteristic 24 carbon fatty acids, as a constituent part. The sugar molecule in the cerebroside can be sulphated in some cases. These sulphated glycolipids are known as **sulphatides.** Some highly complex glycosphingolipids are derived from glucosyl-ceramide and are called **gangliosides.** These are present in nerve tissues.

Another type of glycolipids are glyceroglycolipids. In these cases the sugar and fatty acid residues are attached to a glycerol molecule. Glyceroglycolipids include the galactolipids and the sulpholipids. Both the lipids are part of chloroplast membranes and play important roles in plant development and photosynthesis. Galactolipids have one or two galactose residues linked to terminal of diacylglycerols by a glycosidic linkage. A specific example of a galactolipid is **mono-galactosyl-diglyceride** (MGDG). Sulfolipids contain a sulphonated glucose residue attached to diacylglycerol by a glycosidic linkage. A specific example of a galactolipid is **sulfo-quinovosyl diacylglycerol** (SQDG). The structures of MGDG and SQDG are given Fig. 2.14.



Galactose unit



Galactose unit

Fig. 2.14: Mono-galactosyldiglyceride **Sulfo-quinovosyldiacylglycerol.**

Blood group antigens (A, B, O) are oligosaccharides which determine the blood group types in humans. In fact, these oligosaccharides exist as both glycoproteins as well as glycolipids. Let us study the blood group substances in the following section.

2.6.3 Blood Group Substances

Blood group substances were the first-discovered and well-understood for all membrane-bound carbohydrates. These are chiefly found on the surface of erythrocytes but can also be found on proteins and lipids in other parts of the body where these act as markers called **antigens** as they can cause an immune response. 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 showing the type of bonds and the bond with the surface of the erythrocyte in general can be represented as given below.

α-1,3 Bond β-1,3 Bond β-1...Bond with OH of erythrocyte

Last monosaccharide — D-Galactose (Gal) — *N*-acetyl-D-glucosamine (NAGlu) — Cell wall

L- Fucose (Fuc)

The carbohydrate composition of A, B, and O blood groups as per the above is shown in Fig. 2.15. The last monosaccharide (at nonreducing end) in the 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 N-acetylgalactosamine and D-galactose as the terminal sugars.

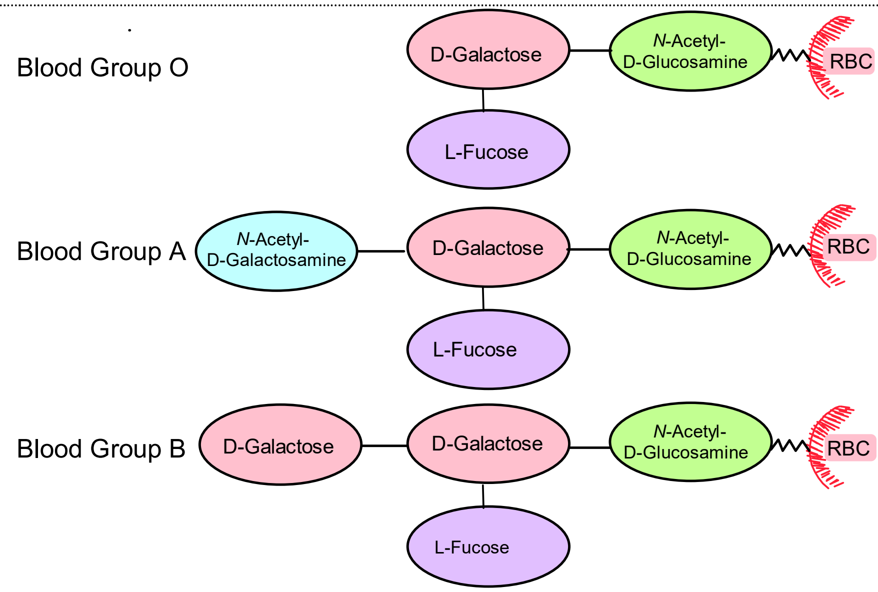


Fig. 2.15: Carbohydrate composition in blood groups.

Glycosaminoglycans (GAGs) 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 alternative β-D-glucuronic acid and *N*-acetylglucosamine which are linked by β-1,3' bonds. The repeating units are, in turn, joined by β-1, 4' bonds as shown in Fig. 2.16.

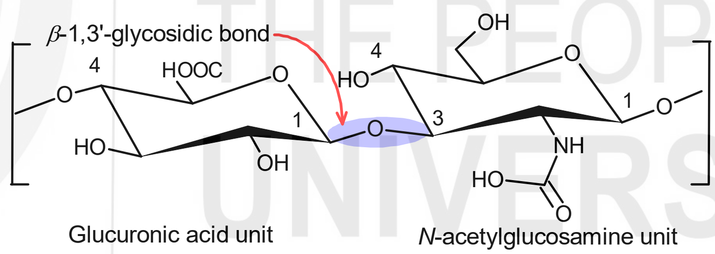


Fig. 2.16: A section of Hyaluronic acid.

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.

2.6.4 Proteoglycans

These include diverse group of molecules which are composed of proteins and glycosaminoglycans. The two components may be linked covalently or non-covalently. These form the ground substance in extracellular matrix.

Proteoglycans have structure like a bottle brush. Fig. 2.17 shows the structure of a proteoglycan, where the backbone is made up of hyaluronic acid and core protein to which GAGs such as keratan sulphate and chondroitin sulphate are covalently attached like bristles. The covalent linkage to core protein is through –OH group of serine present in the sequence Ser-Gly-X-Gly where X is any amino acid. The monosaccharides in GAGs attached to protein remain extended because they are negatively charged and repel each other. The extended brush like structure and negatively charged GAGs allow the proteoglycans to retain lot of water and hence make them resistant to compression. This property also makes them suitable as a component of cartilage.

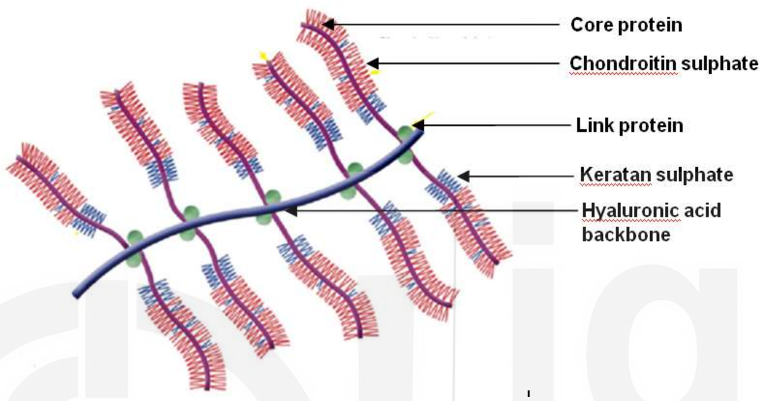


Fig. 2.17: Bottle brush like structure of proteoglycan.
(Source: themedicalbiochemistrypage.org/glycans.php)

In bacteria, the cell wall consists of framework of polysaccharides which are covalently linked to polypeptide chains. It is known as peptidoglycan or murein and provides protection to bacteria against environment. Antibiotic penicillin inhibits the enzymes which crosslink the peptidoglycan fibres in cell wall. As a result the cell wall cannot form and bacteria cannot multiply.

SAQ 5

How does type A blood differ from type O blood?

2.7 BIOLOGICAL FUNCTIONS OF CARBOHYDRATES

It is obvious that the carbohydrates perform a variety of functions in the living system. Some of these are listed below.

- All forms of carbohydrates are converted into glucose in the body which then forms the fuel to be burned to liberate energy. Carbohydrates provide about 17 kJ of energy per gram.
- Excess glucose is converted into glycogen and stored in liver and muscles, where it acts as a reserve source of energy.

- Carbohydrates containing proteins (glycoproteins) and lipids (glycolipids) are vital constituents of cell membranes, mitochondria, brain and nervous tissue.
- The pentose sugars, ribose and deoxyribose are required for the synthesis of ribonucleic acid (RNA) and deoxyribonucleic acid (DNA) respectively.
- Chitin, a polysaccharide forms the structural framework (tough shell structures) in certain invertebrates.
- Heparin an important heteropolysaccharide is a natural anticoagulant present in the body.
- Certain carbohydrates such as galactose, amino sugars, etc., are components of blood group proteins, such as the A, B, AB and O group proteins as discussed in the previous section.

As mentioned in the introduction of this unit, another important class of biological molecules responsible for the storage of energy and performing other important functions is lipids. We will discuss about its types, structure and biological functions in the following sections.

2.8 LIPIDS: CLASSIFICATION

Lipids are heterogenous groups of compounds usually formed by a fatty acid and glycerol.

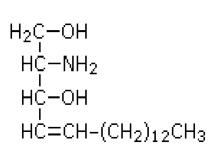
Lipids are a group of naturally occurring organic substances that are soluble in organic solvents such as ether, chloroform, benzene etc. and are highly hydrophobic (water hating) and thus water insoluble. Most of the lipids are derivatives of fatty acids. Lipids can be classified on the basis of their structure and function. These are explained briefly below.

The classification of lipids based on their structure is more meaningful for chemists to understand their chemistry. The different classes are explained briefly in the following paragraphs.

Fatty acids are carboxylic acids containing long hydrocarbon chains.

Simple lipids are esters of fatty acids with alcohols, such as glycerol. Oils and fats are common examples of this class of lipids. **Fats** are generally esters of **fatty acids** with **glycerol**, and any fat in the liquid state is known as **oil.** **Waxes** are also simple lipids and are esters of fatty acids with high molecular weight monohydric alcohols.

Complex lipids also are esters of fatty acids with alcohol. However, these contain some additional groups, such as a phosphate group or a carbohydrate moiety. This group contains the following types of lipids:



Sphingosine

- **Phospholipids:**These complex lipids contain a phosphate group, in addition to fatty acids and an alcohol. They frequently have nitrogen containing bases and other substituents as well. Phospholipids that contain glycerol as alcohol are known as **glycerophospholipids** and those containing **sphingosine** as the alcohol are known as **sphingophospholipids**.

- **Glycolipids:** These lipids contain a carbohydrate group, in addition to fatty acids and an alcohol as discussed in subsection 2.6.2. The sugar group in glycolipids is usually galactose and less frequently, glucose. The alcohol is either sphingosine or glycerol.

- **Other complex lipids:** This category comprises of lipids such as sulpholipids, aminolipids and lipoproteins.

Derived lipids are the third major class of lipids. These are obtained from the simple and the complex lipids by hydrolysis and include steroids, lipid soluble vitamins and prostaglandins.

Different structural classes of lipids have been grouped into three major groups based on their functions. These are explained in brief below.

Storage Lipids: Storage lipids serve as the principal form of energy reserves in the animals and plants. These include triglycerides and waxes.

Membrane Lipids: These constitute the major structural components of cell membranes and include phospholipids, glycolipids, sphingolipids and sterols.

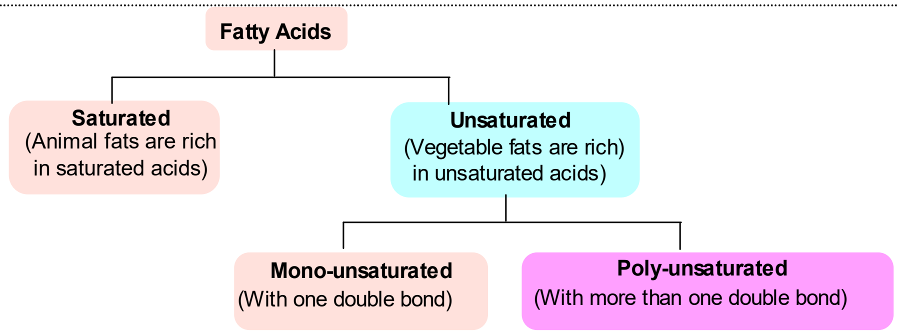
Specialized Lipids: This group includes lipids which are present in relatively smaller amounts but play specialized functions such as enzymes, cofactors, electron carriers, light absorbing pigments, hormones and intracellular messengers or signals. These include eicosanoids, steroid hormones, fat soluble vitamins A, D, E, K and conjugated dienes.

2.8.1 Fatty Acids

It was mentioned in Section 2.2 that the fatty acids have a single carboxyl group and a long, non-polar hydrocarbon chain. Fatty acids are generally named after the parent hydrocarbon, with –oic being substituted for the last –e in the name of hydrocarbon e.g., a fatty acid containing eight carbon atoms ($CH_3(CH_2)_6$–COOH) is called as octanoic acid and the one containing eleven carbon atoms is called undecanoic acid. The parent hydrocarbon chain contains no double bonds and is unbranched therefore these are called **saturated fatty acids**. In some fatty acids the chain contains one or more double bonds and therefore called **unsaturated fatty acids**. The unsaturated fatty acids with double bonds are named as–enoic acid, e.g., octadecenoic acid, commonly known as oleic acid is ($CH_3(CH_2)_7CH{=}CH(CH_2)_7$–COOH).

Fatty acids are the characteristic components of lipids present in both animal and vegetable fats such as ghee, coconut oil and mustard oil.

The unsaturated fatty acids, containing one double bond are called **monounsaturated fatty acids.** Those fatty acids having two or more double bonds are known as **polyunsaturated fatty acids (PUFA)**. Some of the PUFAs, such as linolenic, linoleic and arachidonic acids are not synthesised by higher animals and humans. These have to be supplied through dietary sources, being essential for normal health and the well-being of the organism. Such fatty acids are known as **essential fatty acids (EFAs).** The classification on the basis of presence or absence of double bond can be represented by the scheme given below.



A simplified nomenclature for these compounds specifies the chain length and the number of double bonds. The carbon atoms are numbered from the carboxyl carbon, which is designated as carbon atom 1. The carbon adjacent to the carboxyl carbon is the carbon atom 2 or α-carbon. Similarly, carbon atom 3 is also known as β-carbon, and the terminal methyl carbon is known as the ω-carbon or *n*-carbon atom. The total number of carbon atoms and the number of double bonds are written one after the other separated by a colon. For example 18:0 would mean that the fatty acid has total 18 carbon atoms and no double bond, whereas 18:1 would mean a fatty acid with 18 carbon atoms and one double bond. The positions of double bonds are specified by superscript numbers following Δ (delta). A 20-carbon fatty acid with one double bond between C-9 and C-10 and another between C-12 and C-13 (with C-1 being the carboxyl carbon) is designated 20:2 ($\Delta^{9,12}$).

There is also a common pattern in the location of double bonds in fatty acids. In most monounsaturated fatty acids the double bond is between C-9 and C-10 (Δ^9), and the other double bonds of polyunsaturated fatty acids are generally Δ^{12} and Δ^{15}. The double bonds of polyunsaturated fatty acids are almost never conjugated but are separated by methylene group.

The most commonly occurring fatty acids have even number of carbon atoms in an unbranched chain of 12 to 24 carbons. The structures of a saturated fatty acid viz., stearic acid and an unsaturated fatty acid viz., oleic acid are given in Fig. 2.18.

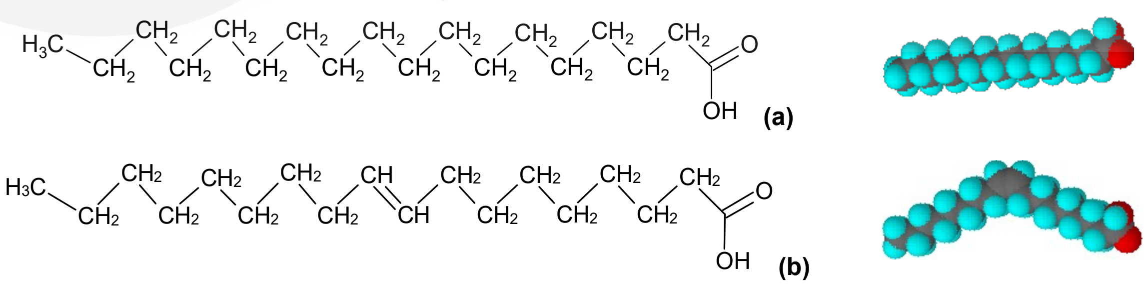


Fig. 2.18: Structures of a) stearic acid (saturated) and b) oleic acid (unsaturated-*Cis*) and their space filling models.

2.8.2 Triacylglycerol

The esters of the fatty acids are called **acylglycerols** and trisubstituted derivatives being neutral in nature are also called as **triglycerides or triacylglycerols**. The mono-, di- and triacylglycerols are formed by the reaction of a glycerol with one, two or three molecules of fatty acid respectively in which one -H or two -H or three -H of the hydroxy group of the glycerol are replaced by the acyl group of the fatty acid molecules.These molecules constitute the **fats**. Fats are the major form of simple lipids. As mentioned above, these are formed, when long chain carboxylic acids are linked to a molecule of an alcohol known as glycerol through ester bonds. Hence, fats are known as **glyceryl esters**. The reaction of a glycerol molecule with one or two or three molecules of fatty acids to form mono-, di- and triacylglycerolsis given in Fig. 2.19.

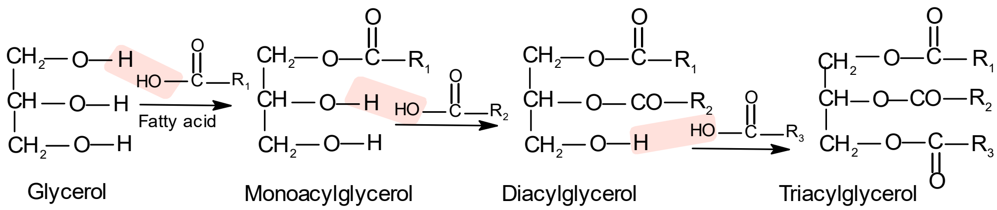


Fig. 2.19: Reaction between glycerol and fatty acid molecules.

Triacylglycerols from animal sources normally contain a higher percentage of saturated fatty acids and are solids at room temperatures. These are generally known as **fats**, while those from vegetable sources are rich in unsaturated fatty acids and are generally liquids at room temperature. These are known as **oils**. Pure oils and fats are colourless, odourless and tasteless. These are insoluble in water but can form emulsions in the presence of emulsifying agents, such as soaps and bile salts. The process of emulsification usually occurs during the digestion of fats and oils in the small intestine, in which the bile salts aid in emulsification process.

When a triacylglycerol is subjected to hydrolysis, the ester bonds are hydrolysed. Consequently, three molecules of fatty acids and one molecule of glycerol are obtained. This reaction can be catalysed by acids, alkalis or enzymes (lipases). Alkaline hydrolysis of a fat is also called **saponification,** since the fatty acids liberated would be present as their salts, which are soaps. An oil or fat can be characterised by the **saponification number**, which is the weight of KOH, in milligrams, required to completely saponify one gram of fat or oil. This is a measure of fatty acid component in a fat and a higher value indicates presence of mostly short chain fatty acids.

> Lipases are secreted along with digestive juices in an animal and are responsible for digestion of fats in thestomach.

The unsaturated fatty acids present in oil or fat can be catalytically reduced in the presence of hydrogen (hydrogenation). They can also be halogenated with bromine or iodine. The addition of halogen e.g., iodine is used to determine the degree of unsaturation of oil or a fat. The **iodine number** of a fat is defined as the weight of iodine in grams that can be taken up by 100 grams of fat or oil. A higher iodine number indicates a greater degree of unsaturation in the fat. The iodine numbers of coconut, olive, groundnut and safflower oils are about 8, 80, 91 and 140 respectively.

> The sodium salts of long chain fatty acids are called as soaps.

Unsaturated fatty acids can also be easily oxidised. When allowed to stand in contact with air, many oils and fats become rancid and develop unpleasant odours. This is because of the oxidation of double bonds, yielding short chain aldehydes and keto acids of higher volatility. This oxidative **rancidity** of oils can be prevented by the addition of antioxidants, like vitamin E.

SAQ 6

Fill in the blank spaces with appropriate answers in the following.

a) Essential fatty acids are termed so becausethese are ______________.

b) The degree of unsaturation is determined by determining the _________.

c) The __________________are examples of storage lipids.

d) Triacylglycerols are hydrolysed by ______ present in the digestive juices.

2.9 COMPLEX LIPIDS

As mentioned in the previous section, complex lipids contain some additional groups, such as a phosphate group, proteins or a carbohydrate moiety. Glycolipids have been dealt in the section pertaining to carbohydrates. The phospholipids and the lipoproteins are described in the following subsections.

2.9.1 Phospholipids

Phospholipids are the major lipid components of all biological membranes. These are so named because of the presence of a phosphate group. In addition, glycerol, fatty acids and nitrogenous bases are the key components of these molecules. Hence these are called **phospho-acylglycerols** (also called **phospho-glycerides**).These are similar to triacylglycerols except that a terminal OHgroup of glycerol is esterified with phosphoric acid rather than with a fatty acid. These phosphoglycerides may be considered as derivatives of phosphatidic acid, in which the phosphate group of phosphatidic acid is generally esterified with the hydroxy of a suitable alcohol such as ethanolamine, choline, and serine. Their structures are given in Fig. 2.20.

R^1 and R^2indicate fatty acid chain

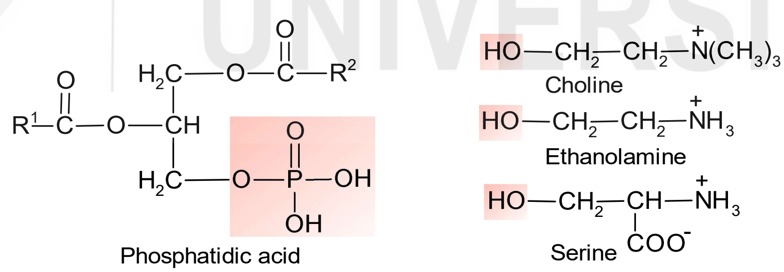


Fig. 2.20: General structure of phosphatidic acid and the related alcohols.

The phospholipids are further classified on the basis of the nature of polar substituted alcoholic group. These include (a) phosphatidic acid and phosphatidyl glycerols, (b) phosphatidyl choline, (c) phosphatidyl ethanolamine, (d) phosphatidyl inositol, (e) phosphatidyl serine, (f) lysophopholipids, (g) plasmalogens, and (h) sphingomyelins.

Sphingomyelins are phospholipids that do not contain glycerol but instead contain the complex amino alcohol, sphingosine. In the sphingomyelins, a choline unit is attached to sphingosine through a phosphate group, along with a single fatty acid attached to the nitrogen atom of sphingosine via an amide linkage. The structure of a sphingomyelin is shown in Fig 2.22.The structures of these phospholipids are given in Fig. 2.21.

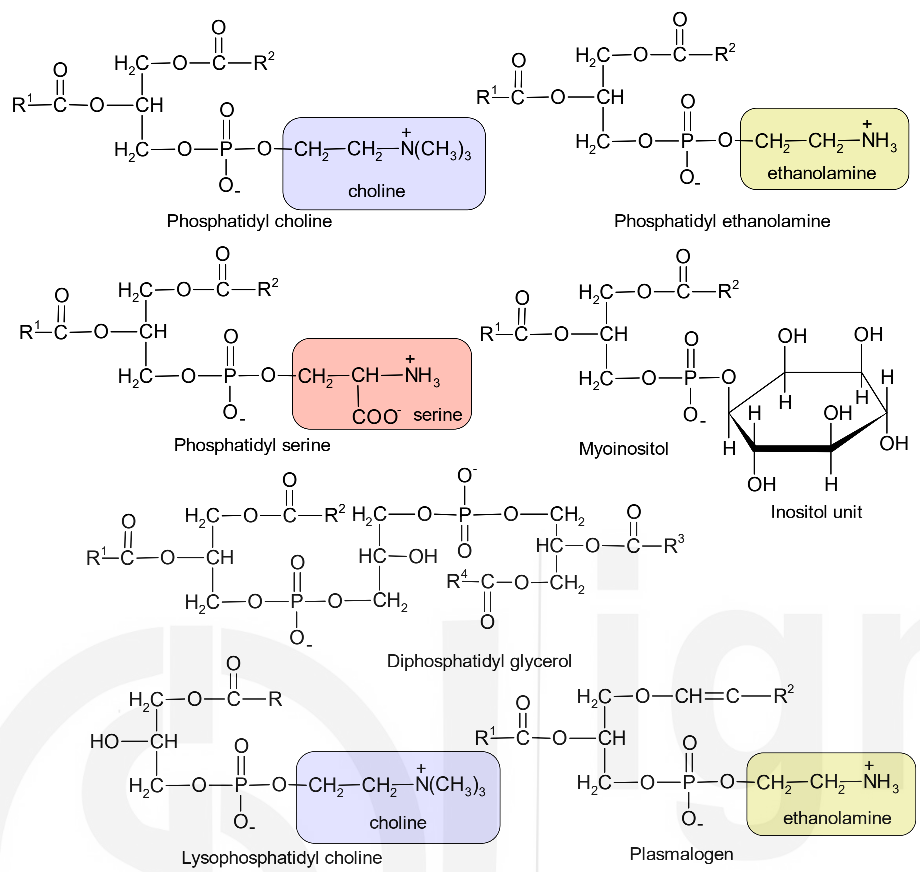


Fig. 2.21: Structure of Phospholipids.

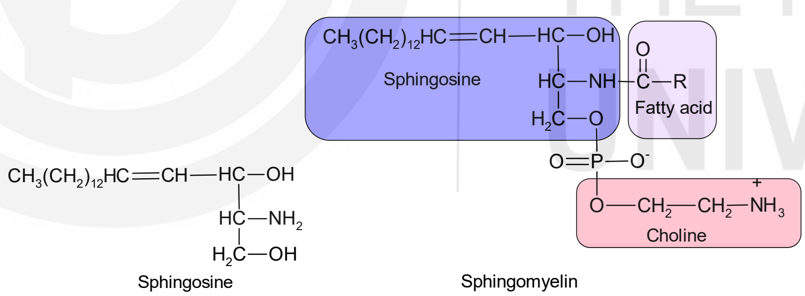


Fig. 2.22: Structure of sphingomyelin.

2.9.2 Lipoproteins

Lipids, being insoluble in water, cannot be transported in the free form in circulating blood plasma. Hence, these are transported in association with proteins. Such protein complexes with lipids are called **lipoproteins.** Lipoproteins are water miscible, and consist mainly of triacylglycerols, phospholipids, cholesterol, and one or more protein compounds called the **apolipoproteins.** Depending upon the composition and density of the lipoproteins four major groups of lipoproteins have been identified. They are the chylomicrons, very low density lipoproteins (VLDL), low density lipoproteins (LDL) and high density lipoproteins (HDL).

The apolipoprotein content of HDL is as high as 60% while in that of chylomicrons it is as low as 2%. The general structure of a typical lipoprotein is given in Fig. 2.23.

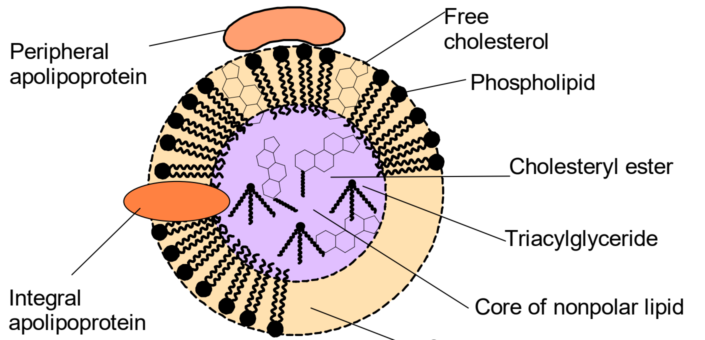


Fig. 2.23: General structure of a lipoprotein.

Chylomicrons and VLDL consists of a lipid core of mainly nonpolar triacylglycerols and cholesterl ester, surrounded by a single layer of phospholipids and cholesterol molecules. The apoliproprotein is present either on the surface of the lipid core or it could be an integral part of the complex. Free fatty acids are released in the tissues from the lipoproteins, by the action of enzyme **lipoprotein lipase.** Dietary triglycerides are partially hydrolysed in the small intestines mostly to 2-acyglycerols which are absorbed together with the free fatty acids in an emulsified form. These are reconverted into triacylglycerols and transported to liver as part of chylomicrons. In the liver they are processed into other higher density lipoproteins. They are then transported to the extra hepatic tissues. Different lipoproteins are recognised by different tissues by specific receptors found in the cells. Various abnormalities of lipid metabolism occur at the sites of production and utilisation of lipoproteins, causing various hypo or hyperlipoproteinemias. Hypercholesterolemia and atheroscelerosis are two such disorders seen in humans.

SAQ 7

Tick [✓] mark the option which correctly describes the function of lipoproteins.

a) Lipid solubilisation [ ]

b) Increase in density of lipoproteins [ ]

c) Stability of lipids [ ]

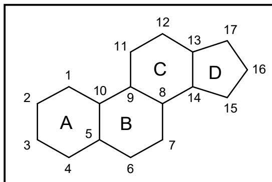
d) Carrier of lipids [ ]

2.10 DERIVED LIPIDS

The derived lipids are also called non-saponifiable lipids i.e.,these cannot be hydrolyzed by heating with alkali to yield soaps. Some of the members of this group are discussed in the following subsections.

2.10.1 Steroids

Steroids are the cyclic lipids which lack fatty acid chain and therefore, are non-saponifiable. They are derived from **four** fused and fully saturated rings called **sterane**. This system consists of 3 cyclohexane rings (A, B and C) fused in nonlinear or phenanthrene manner and a terminal cyclopentane ring (D). The sterane ring along with the conventional numbering of the carbon atoms is shown margin. Molecules containing sterane ring are known as sterols.



Steroid ring system

One of the commonly known steroids is **cholesterol**, which is widely distributed in body cells and is a major constituent of the plasma membrane and plasma lipoproteins.**Terpenes** are another large group of lipids which are made up of repeating "isoprenoids units" are the precursor of steroids.

Terpene molecules are derived by the condensation of **isoprene** units, which gives rise to such important compounds as carotenoids, from which vitamin A is derived, and cholesterol, from which several steroid hormones, bile acids and vitamin D are derived. The structures in Fig. 2.24 indicate the isoprene as the precursor to some of the steroids.

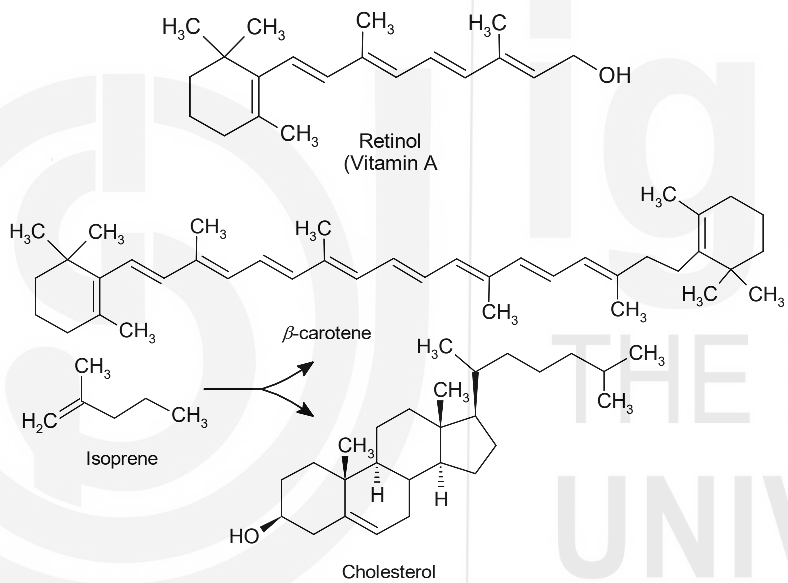


Fig. 2.24: Isoprene molecule as a precursor to the cholesterol and β-carotene.

Bile Salts

Bile is a yellowish brown or green fluid produced in the liver and stored in the gall bladder. Bile salts act like soaps and other emulsifiers. These contain both polar and nonpolar regions, helping to break fats in foods into smaller pieces, so that the food is hydrolysed more easily. The structure of a bile salt is shown in Fig. 2.25.

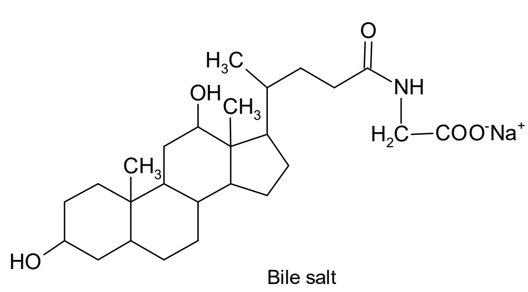


Fig. 2.25: Structure of a bile salt.

Steroid Hormones

Hormones are chemicals released by cells or glands in one part of the body that send out messages that affect cells in other parts of the body. Many hormones are steroids. The steroid hormones can be divided into five classes: viz., glucocorticoids, mineralocorticoids,androgens, estrogens, andprogestins. Glucocorticoids and mineralocorticoids are synthesized in the adrenal gland (located on the top of the kidney)and are collectively known as **adrenal-corticosteroids**. All adrenal corticosteroids have oxygen at C-11. Glucocorticoids, as their name suggests, are involved in glucose metabolism, as well as in the metabolism of proteins and fatty acids. Glucocorticoids such as cortisol andits derivatives, cortisone and prednisolone (synthetic) are powerful anti-inflammatory drugs used in the treatment of arthritis and asthma. The structures of the glucocorticoids are given in Fig. 2.26.

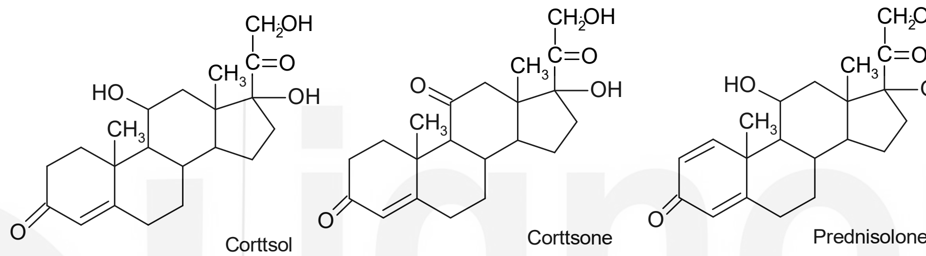


Fig. 2.26: Structures of glucocorticoids.

Mineralocorticoids regulate absorption of Na^+, Cl^- and HCO_3^- ions by the kidneys. Any abnormal change leads to increase in blood pressure. It also regulates the retention of water in the body. **Aldosterone** is an example of a mineralocorticoid and shown in Fig. 2.27.

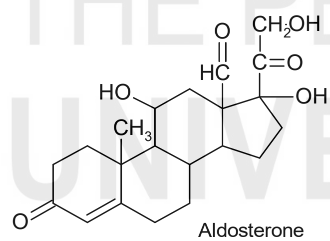


Fig. 2.27: Structure of aldosterone, a mineralocorticoid.

Estradiol and estrone are female sex hormones known as **estrogens**. These are secreted by the ovaries and are responsible for the development of female secondary sex characteristics. These also regulate the menstrual cycle. Progesterone is the hormone that prepares the lining of the uterus for implantation of a fertilized ovum and is essential for the maintenance of pregnancy. During pregnancy, it also prevents ovulation. The structures of estrogens are given in fig. 2.28.

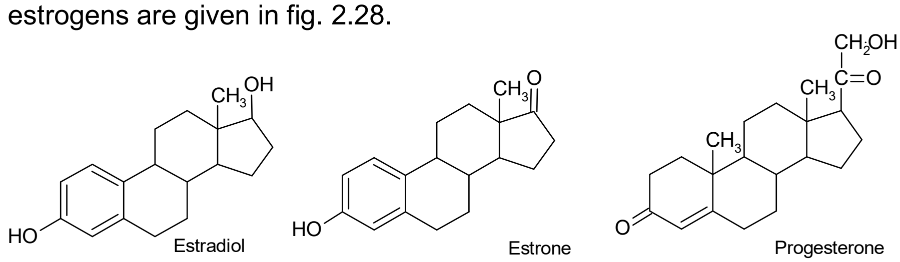


Fig. 2.28: Structures of estrogens.

Testosterone is a male hormone and is produced in the testes, Fig. 2.29. It regulates the production of sperm and aids in the development of male secondary sex characteristics.

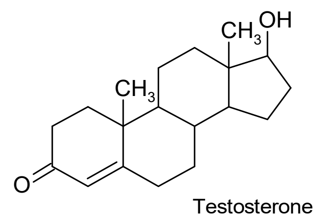


Fig. 2.29: Structure of testosterone.

You might have noticed that although the various steroid hormones have remarkably different physiological effects, but their structures are quite similar.

2.10.2 Eicosanoids

The polyunsaturated fatty acids (PUFAs) are essential for animals and human nutrition, because these are the precursors to a class of compounds collectively called **eicosanoids.** The eicosanoids comprise prostaglandins, thromboxane and leukotrienes. These are derived from arachidonic acid, which contains four double bonds. The structures of these three eicosanoids are depicted in Fig. 2.30.

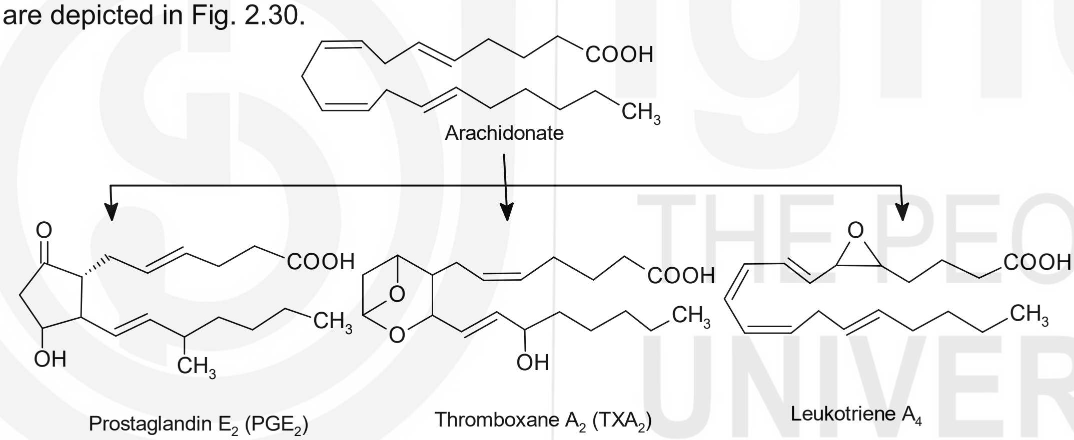


Fig. 2.30: Structure of eicosanoids.

As mentioned above, **prostaglandins** are a class of derived lipids. These act as defences against many sorts of changes in the body. Let us learn more about these molecules. Prostaglandinshave a cyclopentane ring and are so called because these were first isolated from the secretions of the prostrate gland. These exist in all tissues and act as local hormones and exert important physiological and pharmacological effects. Some important actions of prostaglandins are their effects on blood pressure, blood clotting, gastric secretions, contraction of the uterine muscles and reproduction.

Thromboxanes, first discovered in platelets, have a six membered ether ring called the oxane ring, and are derived from prostaglandins. These have potent effects on arterial walls of blood vessels and are implicated in several cardiovascular disorders.

Leukotrienes, the third group of eicosanoids, first found in leukocytes, are characterised by the presence of three conjugated double bonds. Leukotrienes cause vascular permeability. These attract and activate leukocytes and are important regulators of many diseases involving inflammatory reactions, such as asthma.

SAQ 8

Fill in the blank spaces in the following with appropriate words.

a) The steroid hormone which is responsible for the retention of water in our body is………...

b) Steroids lack …..………in their structure, therefore are non-saponifiable.

c) The …………..are precursors to the class of compounds called eicosanoids.

2.11 LIPID AGGREGATES

Amphipathic (having both polar and nonpolar groups) membrane lipids form various types of aggregated structures in contact with aqueous environment. All these structures expose hydrophilic polar head towards aqueous medium and maximize the contact among hydrophobic lipid chains, for example, soaps. Let us us look at these arrangements. Lipids arrange themselves into monolayers, micelles, liposomes or bilayers when exposed to an aqueous environment. Fig. 2.31 shows these arrangements.

Monolayers are formed when few lipid molecules are added to aqueous solution. This single layer formed at water-air interface exposes polar head towards water and hydrophobic tails towards air.

Micelles are spherical structures that contain anywhere from a few dozen to a few thousand amphipathic molecules. These molecules are arranged with their hydrophobic tails aggregated in the interior, where water is excluded, and their hydrophilic/polar head groups are at the surface, in contact with water as shown in Fig. 2.31 (a).

Amphipathic molecules form micelles at or above a specific concentration. This concentration is known as critical micelle concentration (CMC). Below CMC, these molecules exist as individual molecules.

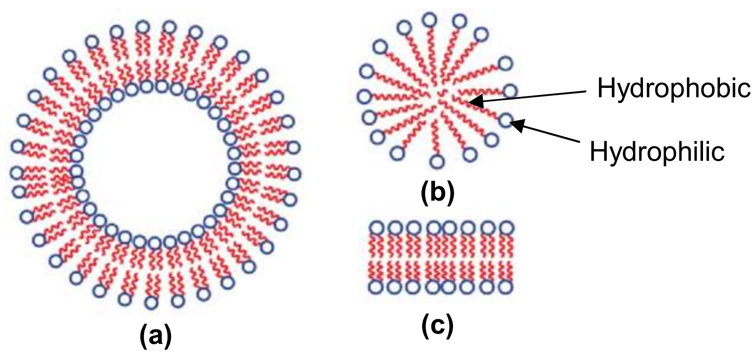


Fig. 2.31: Aggregation of lipids as a) Micelles, b) Bilayer, c) Liposome.

Bilayer is another type of lipid aggregate in water in which two lipid monolayers are arranged back-to-back to form a two-dimensional sheet as shown in Fig. 2.31(b). The hydrophobic portions in each monolayer interact with each other. The hydrophilic head groups interact with water at each surface of the bilayer. Because the hydrophobic regions at its edges are transiently in contact with water, the bilayer sheet is relatively unstable and spontaneously forms a third type of aggregate: it folds back on itself to form a hollow sphere, a vesicle or liposome.

Liposomes are the closed self sealing solvent filled vesicles bound by a single bilayer, Fig. 2.31 (c). By forming liposomes, bilayers lose their hydrophobic edge regions, achieving maximal stability in the aqueous environment. These bilayer vesicles enclose water, creating a separate aqueous compartment.

Liposomes have been widely used as models to study properties and functions of biological membranes. These are also used a vehicle for drug delivery since they are absorbed by many cells through fusion with the plasma membrane.

You will recall from the previous unit that all living cells are enveloped by a surface plasma membrane, composed primarily of lipids and proteins. Because of its diverse functions, the plasma membrane plays a central role in cellular biology. Even cellular organelles, such as mitochondria, nucleus, lysosomes and chloroplasts are bound by membranes. The membranes thus give individuality to cells separating them from the environment and permitting compartmentalisation of cellular functions.

You will learn about the structure and function of membranes in the following section.

2.12 BIOLOGICAL MEMBRANE

As mentioned earlier, membranes are mainly composed of lipids and proteins. Although most membranes contain approximately equal amounts of proteins and lipids, their ratio varies depending upon the tissue or organelle. Protein and lipid composition of some membranes is given in Table 2.4. As can be understood from the table the erythrocyte and retinal rod membranes have a protein to lipid ratio of 1:1, while in the myelin membrane of nerve cells it is 1:4, and the inner mitochondrial membrane has a ratio of 3:1.

Table 2.4: Lipid and protein composition of some membranes

Membranes	**% Dry weight**	
	Protein	**Lipid**
Myelin	18	79
Human RBC	49	43
Retinal rods	51	49
Mitochondria (Outer)	52	48
Mitochondria (inner)	76	24
Gram positive bacteria	75	25

Phospholipids are the most abundant lipid material in membranes, and in addition small amounts of cholesterol and glycolipids are also present. The predominant phospholipids of membranes are phosphatidylcholine, phosphatidylethanolamine, phosphatidylserine and sphingomyelin.

It was mentioned earlier that the fluid mosaic model is the widely accepted model that describes the structure of cell membranes. Let us understand it in the following subsection.

The lipid bilayer, recognised nearly 60 years ago by Gorter and Grendel, exists as a sheet in which hydrophobic region of the phospholipids are protected from the aqueous environment, while the hydrophilic regions are exposed to water.

2.12.1 Fluid Mosaic Model

The model describes the cell membrane as a lipid bilayer (two-molecules-thick layer consisting primarily of amphipathic phospholipids) in which protein molecules are embedded. The membrane is a quasi-fluid structure and the different components are held merely by noncovalent interactions. The lipid and protein molecules are free to perform lateral movements within the overall bilayer. The fluidity of the membrane is regulated by the cholesterol content, and the unsaturated fatty acid content of the phospholipids. The unsaturated fatty acid residues disrupt the highly ordered packing of fatty acid chains, and thus increase fluidity. It satisfactorily accounts for several of the observed properties of the plasma membrane.

A schematic representation of the fluid mosaic model is shown in Fig. 2.32 (a) while the structure of a typical phospholipid is shown in Fig. 2.32(b).

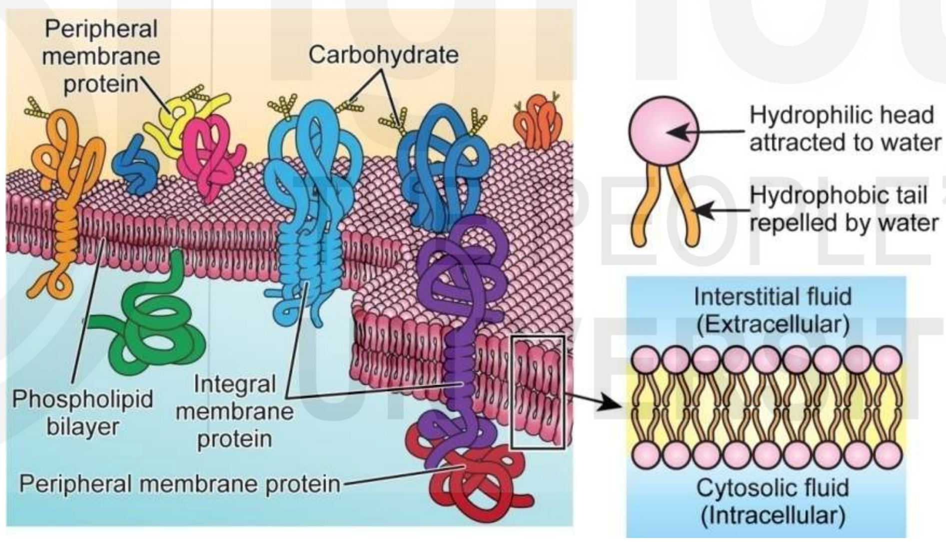


Fig. 2.32: (a) Fluid mosaic model of plasma membrane; (b) Structure of phospholipid.

According to the fluid mosaic model, the phospholipids of the membrane are arranged in a bilayer with their polar head groups on the exterior and the nonpolar hydrophobic tails tucked inside. The different proteins of the membrane are dispersed within this phospholipid bilayer and are free to move within the plane of the membrane. Some of the proteins may be present superficially embedded in the bilayer. The proteins are responsible for the diverse functions associated with the cell membrane, such as, selective transport, cell recognition, cell-cell communication, cell responses and motility.

Some of the main and distinguishing functions are as follows:

- The cell membrane forms a selective barrier between cells and their environment, and regulates the entry and exit of substances across the cell membrane. Thus, it is responsible for the maintenance of the internal environment, whose composition is strikingly different from that of outside.
- The cell membrane is also responsible for cell-cell communication and recognition. The cell surface proteins function as receptors recognising specific molecules such as hormone and other second messengers.
- Membranes also carry out specialised functions, such as membranes of the mitochondria and the chloroplast, which act as energy transducers. Retina rod cell membrane proteins, for instance, act as photoreceptors.

Let us understand the most important function of the membrane i.e. transport across the membrane.

2.12.2 Transport Across the Membrane

It has been mentioned that the major function of the cell membrane is to maintain the characteristic integrity of the cell by forming a selective barrier between the cell and its surroundings. It regulates the movements of various molecules into and out of the cell. For this purpose, the cell membrane is provided with various transport processes. There are three types of mechanisms followed by the cell in the transport process. These are briefly explained below.

Passive diffusion: In passive diffusion the molecules simply move or diffuse across a membrane and the rate of flow depends directly on the concentration gradient across the membrane.

Facilitated diffusion: It is the transport of molecular or ions across a membrane by carrier proteins in the membrane, driven by a concentration difference for the substance on the two sides of the membrane.

Active process or transport: It is similar to facilitated diffusion except that the molecules or ions move across the membrane against a concentration gradient which requires energy input.

In general, nonpolar molecules are transported more readily across the membrane than polar or charged molecules. Some substances move by passive diffusion while others like, glucose is transported by facilitated diffusion, involving specific proteins in the membrane. These mechanisms do not require energy. Most of the biomolecules are transported against a concentration gradient by active transport, a process that needs energy, as in the absorption of amino acids across the intestines. This is accomplished by the presence of specific transport protein and transport channels that act as selective gates for the entry and exit of molecules.

You may try to answer the following SAQ to check your understanding about the structure of plasma membrane.

SAQ 9

Make appropriate corrections in the following statements and write the correct versions:

a) Proteins exhibit free mobility in the lipid bilayer.

b) Lipid bilayers and micelles are formed by free fatty acids in water.

c) Membranes possess specific pores for transport of molecules.

d) Cholesterol is exclusively found in bacterial membranes.

2.13 BIOLOGICAL FUNCTIONS OF LIPIDS

The functions performed by lipids in the living system are many and varied in nature. Some of these include the following.

- Lipids are important dietary constituents. On oxidation, they provide about 38 kJ of energy per gram.
- Fat is a poor conductor of heat, so a thick layer of subcutaneous fat helps to prevent loss of heat (it acts as a thermal insulator).
- Lipids serve as packing and support material to the abdominal organs like the kidney.
- Fat represents the most concentrated form of stored energy, since it is associated with less water during storage, compared to carbohydrates and proteins. Upon oxidation, fats provide more body water.
- Polyunsaturated fatty acids (the essential fatty acids) have a cholesterol lowering effect and are thus a dietary means of preventing coronary heart disease. They are important structural components of the cell membrane and mitochondrial membrane.
- Cholesterol is the precursor molecule for the synthesis of bile acids, steroid hormones and vitamin D.

2.14 SUMMARY

Let us summarise the salient features regarding the structure and function of carbohydrates and lipids dealt in this unit.

- The cells in a living system consist of a large number of organic molecules that mainly include carbohydrates, proteins, nucleic acids and lipids. Out of all the types, carbohydrates are the most abundant. These are divided into different classes on the basis of their structure. Proteins are complex diverse and high molecular weight polymers found in the cell. The monomeric units of proteins are amino acids. Nucleic acids are made-up of four types of nucleotides. Each nucleotide is made of a sugar, a phosphate and a nitrogenous base. Lipids are heterogenous groups of compounds usually formed by the combination of a fatty acid with glycerol. Fatty acids are the characteristic components of lipids present in both animal and vegetable fats.

- Amongst all the types of molecules present in cells, water is the most abundant. It is a unique molecule due to its structure, capacity as an excellent solvent and its role as a medium in which all biochemical reactions occur. All the biochemical reactions take place at a specific pH in a solution i.e. at a particular hydrogen ion concentration. The concept of pH is very useful in understanding the change in pH in and around the cellular environment. The living organisms manage a change in pH with the help of buffer solutions. Besides this water plays a crucial role in the electrolyte balance of the body.

- The monosaccharides can exist as open chain structures or in the ring form and undergo a number of reactions to form their derivatives. The most important derivatives are glycosides formed by the reaction with alcohol, amino sugars which are the amino derivatives and the deoxy sugars formed by the replacement of one or more hydroxy groups by hydrogen. A disaccharide is formed when two monosaccharides get connected by a glycosidic bond formed between them. The disaccharides may contain two molecules of the same monosaccharide linked together or the two constituent monosaccharides may be different as in the case of lactose. The polysaccharides are large, high molecular weight molecules formed by the condensation of a large number of molecules of monosaccharides joined together by glycosidic bonds. The monosaccharide units are either all identical as in starch, or of different types like in cell walls. These are called the homopolysaccharides and heteropolysaccharides respectively.

- Oligosaccharides and polysaccharides exist in covalent linkage with lipids and proteins to form complexes known as glycoconjugates. These are believed to be more dynamic and information rich than proteins and nucleic acids. These carry the information for communication between cells and their surroundings, labelling and targeting proteins for transport from their site of synthesis to action, cell-cell recognition, blood clotting, wound healing, immune response and many more. Glycoconjugates are divided into glycoproteins, glycolipids, glycosaminoglycans and proteoglycans. Blood group antigens (A, B, O) are oligosaccharides which determine the blood group types in humans. In fact, these oligosaccharides exist as both glycoproteins as well as glycolipids. The carbohydrates are responsible for a number of biological functions like, these are the source of energy, are vital constituents of cell membranes, involved in the structural framework, function as natural anticoagulants, etc.

- Lipids are a group of naturally occurring organic substances usually formed by the combination of a fatty acids with glycerol and are soluble in organic solvents such as ether, chloroform, etc. and are highly hydrophobic thus, water insoluble. Lipids can be classified on the basis of their structure into simple, complex and derived types. On the basis of structure these are classified into storage, membrane and specialized types. The fatty acids have a single carboxyl group and a long, non-polar hydrocarbon chain. The esters of the fatty acids are called acylglycerols and trisubstituted derivatives being neutral in nature are also called as triglycerides. The complex lipids contain some additional groups, such as a phosphate group, proteins or a carbohydrate moiety. These are accordingly named as phospholipids, lipoproteins and glycolipids. Steroids, bile salts, steroid hormones, eicosanoids etc. belong to the class of derived lipids. Lipids arrange themselves into monolayers, micelles, liposomes or bilayers when exposed to an aqueous environment.

- The cellular organelles, such as mitochondria, nucleus, lysosomes and chloroplasts are bound by membranes. The membranes give individuality to cells separating them from the environment and permitting compartmentalisation of cellular functions. The fluid mosaic model is the widely accepted model that describes the structure of cell membranes. The cell membrane performs various functions like, it forms a selective barrier between cells and their environment, it is responsible for cell-cell communication also carry out specialised functions. The transport across the cell membrane involves the mechanism of passive diffusion, facilitated diffusion and active process or transport. The biological roles of lipids include prevention of loss of heat, packing and support materials, most concentrated form of stored energy, cholesterol lowering effect thus, a dietary means of preventing coronary heart disease, etc.

2.15 TERMINAL QUESTIONS

1. Ionisation of a base produces OH^- and not H^+ ions. Why does addition of a base such as KOH change the pH of a solution?

2. Which carbon atoms of glucose are commonly involved in glycosidic bond formation?

3. Cellulose, amylose, amylopectin and glycogen are all polymers of only one monosaccharide, i.e. glucose. How do these differ from each other in their structure? Give the reasons.

4. What is the difference between a saturated and an unsaturated fatty acid?

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

6. Name the storage polysaccharides present in animals and plants. Indicate the structural differences between the two.

7. Explain the information obtained by the saponification number, iodine number and rancidity of fats.

8. What are the major biological functions of lipids?

9. Describe the mechanisms of transport across the cell membrane.

10. Match the lipid functions in I with appropriate lipids in II.

I	II
a) Protection	i) Isoprenoids
b) Muscle contraction	ii) Leukotrienes
c) Precursor	iii) Prostaglandins
d) Inflammatory response	iv) Waxes

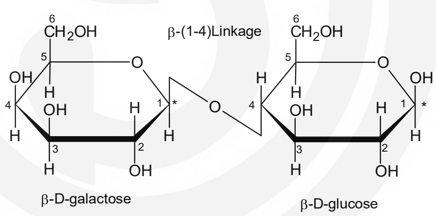
2.16 ANSWERS

Self Assessment Questions

1. Since HCl is completely ionised, concentration of H^+ions (in HCl) will be the same as the concentration of HCl, i.e., 2 moles/dm^3.
   - Since 0.5 cm^3 of the HC1 is added to 1 dm^3(1000 cm^3)of water, the concentration of H^+ions $[H^+]$= 0.5/1000 x2 mol/dm^3= 1×10^{-3}
   - pH = $-\log(10^{-3}) = 3$
   - The negligible contribution of 10^{-7}moles/dm^{3}from ionisation of water has been ignored.
2. a) $C_nH_2O_n$, n≥3

   b) structure and energy

   c) carbonyl (aldehyde or ketone) and hydroxyl

   d) 3
3. 

4. a) starch b) α (1→6) c) 25-30 d) cellulose
5. In type A blood the last monosaccharide in the carbohydrate chain is *N*-acetyl-D-galactosamine, whereas in type O blood it is missing.
6. a) essential components of diet and cannot be synthesised by our body.

   b) iodine number

   c) triglycerides and waxes

   d) lipases
7. d)
8. a) aldosterone

   b) fatty acid chain

   c) polyunsaturated fatty acids
9. a) Proteins exhibit lateral mobility in the lipid bilayer.

   b) Lipid bilayers and micelles are formed by phospholipids.

c) Membranes possess specific carrier proteins for transport of molecules.

d) Cholesterol is exclusively found in eukaryotic membranes.

Terminal Questions

1. The OH^- ions produced by ionisation of a base react with free H^+ ions present in a solution. The decrease in the concentration of H^+ ions is seen as an increase in pH.

$$KOH \longrightarrow K^+ + OH^-$$
$$OH^- + H^+ \longrightarrow H_2O$$

2. Carbon atom1and 4 or carbon atom1 and 6 of glucose are most often involved in glycosidic bond formation.

3. This is due to (i) branched or unbranched structures (ii) sequences of different lengths (iii)1- 4 or 1-6 glycosidic bond and(iv)different types(α or β) of glucose molecules.

4. In saturated fatty acids carbon atoms arejoined by single covalent bonds.Inunsaturated fatty acids at least one double bond is present between the two carbon atoms.

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

6. Glycogen and starch are the reserve polysaccharides in animals and plants respectively. Starch is a mixture of the linear polymer amylase (made of glucose units linked by α-1, 4'- glycosidic linkages) and branched polymer amylopectin (which consist 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).

7. The saponification number provides information about the average chain length of the fatty acids in the fat. The rancidity gives an idea about the number of free fatty acids present in a lipid sample. The iodine number of unsaturated fatty acids in a lipid, higher is its iodine number.

8. The biological roles of lipids include prevention of loss of heat, packing and support materials, most concentrated form of stored energy, cholesterol lowering effect thus, a dietary means of preventing coronary heart disease, etc.

9. The mechanism involves passive diffusion in which the molecules simply move or diffuse across a membrane and the rate of flow depends directly on the concentration gradient across the membrane.

   The other mechanism is facilitated diffusion which is the transport of molecular or ions across a membrane by carrier proteins in the membrane, driven by a concentration difference for the substance on the two sides of the membrane.

   Active transport is similar to facilitated diffusion except that the molecules or ions move across the membrane against a concentration gradient which requires energy input.

10. a) -iv b) -iii c) -i d) d-ii