10. BIOMOLECULES

The molecules present in living system like carbohydrates, proteins, nucleic acids, lipids, vitamins etc. which are essential for the growth and maintenance of our body are called Biomolecules.

Carbohydrates

These are the hydrates of carbon and most of them have a general formula They can be defined as optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis. Some of the carbohydrates are crystalline, water soluble and sweet in taste. They are called sugars. Carbohydrates which are not crystalline, water insoluble and have no sweet taste are called non-sugars. Carbohydrates are also called 'Saccharides'.

Classification of carbohydrates

1) Based on their behaviour on hydrolysis:

Based on this, carbohydrates are classified into three types:

1) Monosaccharides: These are carbohydrates which cannot be hydrolysed into simpler units of polyhydroxyaldehydes or ketones. E.g. glucose, fructose, ribose, galactose etc.

2) Oligosaccharides: These are carbohydrates which give two to ten monosaccharide units on hydrolysis. They are further classified as disaccharides, trisaccharides, tetrasaccharides etc. E.g. Sucrose, maltose, lactose.

Sucrose on hydrolysis gives one molecule each of glucose and fructose, maltose gives two molecules of glucose while lactose gives one molecule each of glucose and galactose.

3) Polysaccharides: These are carbohydrates which give a large number of monosaccharide units on hydrolysis. E.g. starch, cellulose, glycogen etc.

II) Based on their reducing character:

Based on this, carbohydrates are of two types — reducing sugar and non-reducing sugar. Carbohydrates which contain free aldehydic or ketonic groups are called reducing sugars, while those which do not contain free aldehydic or ketonic group are called non-reducing sugars. All monosaccharides are reducing sugars. Disaccharides like maltose and lactose are reducing while sucrose is non-reducing.

III) Based on the functional group and no. of carbon atoms: A monosaccharide containing an aldehyde group is known as aldose, while a monosaccharide containing a ketonic group is known as ketose. Monosaccharides containing 3 carbon atoms are called triose, 4 carbon atoms are called tetrose etc.

MONOSACCHARIDES

Glucose (C6H1206)

Glucose is an aldohexose and is also known as dextrose. It is the monomer of starch, cellulose. It is probably the most abundant organic compound on earth.

Methods of preparation

1. From sucrose (Cane sugar): If sucrose is boiled with dilute HCI or H2S04 in alcoholic solution, glucose and fructose are obtained in equal amounts.

C H 12 22 O 11 +H20 c 6 H 12 O 6 + C H 6 12 O6

Sucrose Glucose Fructose

2. From starch: Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute H2S04at 393 K under pressure.

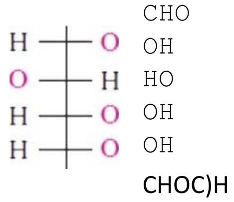
(C6H1005 + nH20 $\xrightarrow{H^+}$ 393K: 2-3 atmnC6H1206

Starch or cellulose Glucose

Structure ofglucose

1. Molecular formula of glucose is C6H1206.
2. On continuous heating with HI, glucose forms n-hexane. This indicates that all the six carbon atoms in glucose are in a straight chain.
3. Glucose reacts with hydroxylamine to form an oxime and adds a molecule of hydrogen cyanide to give cyanohydrin. These reactions confirm the presence of a carbonyl group (>C = O) in glucose.
4. On oxidation using mild oxidising agents like bromine water, Glucose gives gluconic acid (six carbon carboxylic acid). This indicates that the carbonyl group present is an aldehydic group.
5. Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five —OH groups. Since it exists as a stable compound, five —OH groups should be attached to different carbon atoms.
6. On oxidation with nitric acid, glucose gives saccharic acid (a dicarboxylic acid). This indicates the presence of a primary alcoholic (—0H) group in glucose.

Based on the above information, Fischer proposed an open chain structure for glucose as follows:



D- Glucose (Open chain structure)

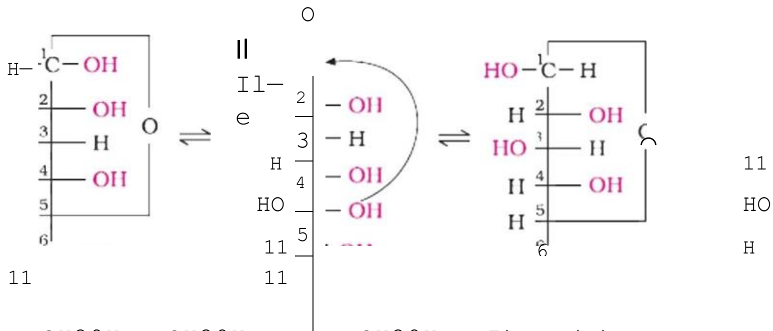
But this open chain structure cannot explain the following observations:

I. Glucose does give 2,4-Dinitrophenyl hydrazine test (2,4-DNP test or Borsche's test), Schiff's test and does not give addition product with NaHS03.

2. The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free —CHO group.

3. The existence of two different anomeric forms of glucose (a and ß form).

In order to explain the above, it was proposed that one of the —OH groups may add to the —CHO group and form a cyclic hemi-acetal structure. The —OH at C5 is involved in ring formation. (1,5 — oxide ring).



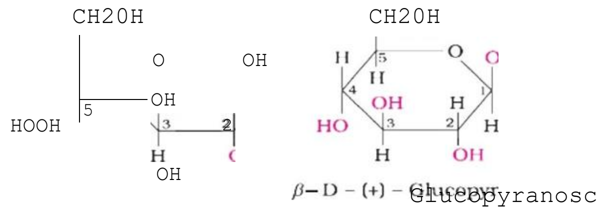
CH20H CH20H CH20H a-I) - (+) -

Glucose [J -D- (+) - Glucose

Thus the two cyclic forms exist in equilibrium with the open chain structure. The two cyclic hemiacetal forms of glucose differ only in the configuration at first carbon (anomeric carbon). So they are called anomers. These are stereo isomers which differ only in the configuration at the first carbon.

The Pyranose structure of Glucose (Haworth Structure)

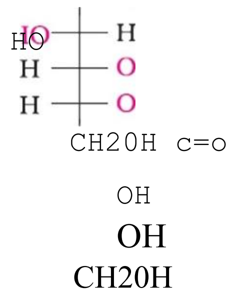
The six membered cyclic structure of glucose is called Pyranose structure. The anomeric forms of glucose can be represented as follows:



α–D– (+) – Glucopyranose β–D – (+) – Glucopyranose

Fructose ($C_6H_{12}O_6$)

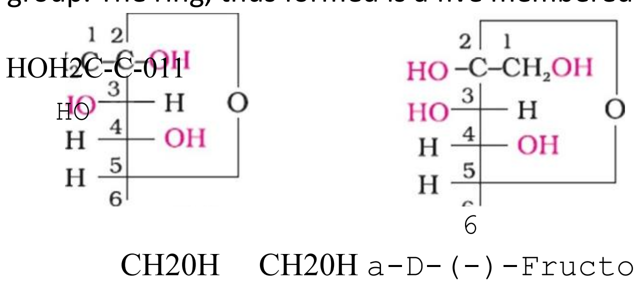
Fructose is a ketohexose. It has also the molecular formula $C_6H_{12}O_6$. On the basis of its reactions, it was found to contain a ketonic group at 2[nd] carbon and six carbons in straight chain. It is laevorotatory and can be written as D-(—)-fructose. Its open chain structure is:



D — (—) — Fructose

Ring Structure of fructose

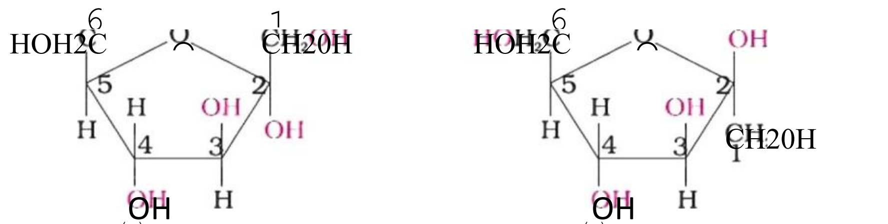
Fructose also exists in two cyclic forms which are obtained by the addition of —OH at C5 to the Carbonyl group. The ring, thus formed is a five membered ring (2,5-oxide ring structure).



a-D-(-)-Fructose   ß-D-(-)-Fructose

Haworth structure (Furanose structure) of Fructose

The cyclic structure of fructose is analogous to the heterocyclic compound furan and is called furanose structure.



α-D-(–)-Fructofuranose β-D-(–)-Fructofuranose

Assigning D, L Notation

Assigning D, L Notation

D, L notation is assigned based on the structure of Glyceraldehyde. Glyceraldehyde contains one asymmetric carbon atom and exists in two enantiomeric forms as shown below:

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        CHO                    CHO

    H       OH             HO       H

        CH2OH                  CH2OH
 (+) — Glyceraldehyde   (—) — Glyceraldehyde
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(+)-Glyceraldehyde with the —OH group on right side is assigned as D-Glyceraldehyde and (-) Glyceraldehyde with the —OH group on left side is assigned as L-Glyceraldehyde.

For assigning the configuration of a monosaccharide, first write the compound in such a way that the most oxidisable carbon (like —CHO group) is at the top. Then compare the configuration of the lowest asymmetric carbon atom of the compound with glyceraldehyde. If the —OH group is on the right side, the compound is assigned as D-configuration and if it is on the left side, the compound is assigned as L&Q0figuration.

DISACCHARIDES:

These are carbohydrates which on hydrolysis give two monosaccharide units. Important disaccharides are Sucrose, Maltose and Lactose.

1. Sucrose (C12H22011) [Cane sugar or Grape sugar]:

It is formed by the combination of 2 monosaccharides a-D-glucose and ß-D-fructose. So sucrose (Cane sugar) on hydrolysis gives an equimolar mixture of D-(+)-glucose and D-(-)-fructose.

$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 \quad C_6H_{12}O_6$

Sucrose D(+)Glucose ($+52.5^0$) D(-)Fructose (-92.4^0)

Sucrose is dextro rotatory but after hydrolysis it gives dextro rotatory glucose and laevo rotatory fructose. Since the laevo rotation of fructose (-92.4^0) is more than dextro rotation of glucose ($+52.5^0$), the mixture is laevo rotatory. So the process is called inversion of cane sugar and the product formed is called invert sugar.

In sucrose, the two monosaccharides [D-(+)-glucose and D-(-)-fructose] are held together by a glycosidic linkage between Cl of a-D-glucose and C2 of ß-D-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non-reducing sugar.

Glycosidic linkage: The C-O-C linkage formed between monosaccharide units during the formation of a disaccharide or polysaccharide is called Glycosidic linkage.

2. Maltose (C12H22011) [Malt sugar]:

It is formed by the combination of two a-D-glucose units in which Cl of one glucose is linked to C4 of another glucose unit. The free aldehyde group can be produced at Cl of second glucose in solution and so it is a reducing sugar.

3. Lactose (C12H22011) [Milk Sugar]:

It is formed by the combination of ß-D-galactose and ß-D-glucose. The glycosidic linkage is between Cl of galactose and C4 of glucose. Free aldehyde group can be produced at Cl of glucose unit in solution and hence it is a reducing sugar.

POLYSACCHARIDES:

These are carbohydrates which on hydrolysis give a large number of monosaccharide units. They are natural polymers.

Important polysaccharides are Starch, Cellulose and Glycogen.

1. Starch, $(C6H1005)n$:

It is the main storage polysaccharide of plants. It is a polymer of a-glucose and consists of two components — Amylose and Amylopectin.

Amylose is water soluble component which constitutes about 15-20% of starch. Chemically amylose is a linear polymer of a-D-(+)-glucose units with Cl - C4 glycosidic linkage.

Amylopectin is insoluble in water and constitutes about 80-85% of starch. It is a branched chain polymer of a-D-glucose units in which chain is formed by Cl- C4 glycosidic linkage and branch is formed by Cl- C6 glycosidic linkage.

2. Cellulose, $(C6H1005)n$:

It is the main constituent of cell wall of plants. Cellulose is a straight chain polysaccharide of BD-glucose units which are joined by CI - C4 glycosidic linkage.

3. Glycogen: The carbohydrates are stored in animal body as glycogen. It is also known as animal starch because its structure is similar to amylopectin. It is present in liver, muscles and brain. It is also found in yeast and fungi.

No.	Sugar	Reducing character	Monosaccharides	Glycosidic linkage
1.	Sucrose	Non-reducing sugar	One units each of a-Dglucose and ß-D-fructose	Cl of a-glucose and C2 of ß-fructose (C. G)
2.	Maltose	Reducing sugar	2 units of a-D-glucose	Cl of one a-glucose and C4 of another aglucose (Cl — C4)
3.	Lactose	Reducing sugar	One units each of ß-Dgalactose and ß-Dglucose	Cl of galactose and C4 of glucose
4.	Cellulose	Non-reducing	ß-D-glucose	Cl of one glucose and C4 of another glucose
5.	Starch	Non-reducing	a-D-glucose	It contains two components — amylose and amylopectin. Amylose is a linear polymer of a-D-glucose (Cl-C4) and amylopectin is a branched chain polymer of a-D-glucose (Cl-C4 & Cl-C6)

Uses of carbohydrates

Carbohydrates are used as storage molecules as starch in plants and glycogen in animals. Cell wall of bacteria and plants is made up of cellulose. Carbohydrates are used as raw materials for many important industries like textiles, paper, lacquers and breweries. Carbohydrate in the form of wood is used for making furniture etc.

Amino acids

These are compounds containing amino group (-NH2) and carboxyl (-COOH) group. Depending upon the relative position of amino group with respect to carboxyl group, the amino acids can be classified as a, ß, V, 6 and so on. The simplest amino acid is glycine (H2N-CH2-COOH). Except glycine, all other naturally occurring a-amino acids are optically active, since the a-carbon atom is asymmetric.

Amino acids are generally represented by a three letter symbol. (e.g. 'Gly' for glycine, 'Ala' for alanine etc). Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule. Amino acids having equal number of amino and carboxyl groups are neutral; those containing more number of amino groups are basic and those containing more number of carboxyl groups are acidic.

For e.g. glycine, alanine, valine etc. are neutral, arginine, lysine etc. are basic and glutamic acid, aspartic acid etc. are acidic.

Essential and Non-essential Amino acids: Our body requires 20 amino acids. Among these some are synthesized in the body and the remaining should be obtained through our diet.

The amino acids which can be synthesised in the body are known as non-essential amino acids. E.g.: Glycine, Alanine, Glutamic acid, Aspartic acid, Glutamine, Serine, Cysteine and Proline.

The amino acids which cannot be synthesised in the body and must be obtained through diet, are known as essential amino acids.

E.g.: Valine, Leucine, Isoleucine, Arginine, Lysine, Threonine, Methionine, Phenylalanine, Tryptophan and Histidine.

In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as zwitter ion. This is neutral but contains both positive and negative charges. In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.

R— CH—C O H c—o-

\+

12 NY 13

(Zwitter ion)

Most naturally occurring amino acids have L-configuration. L-Aminoacids are represented by writing the —NH2 group on left hand side.

Peptides and polypeptides

A peptide is formed by the combination of a-amino acid molecules. Chemically peptide linkage is an amide formed between —COOH group and -NH2 group. When two molecules of amino acids combine, the amino group of one molecule reacts with —COOH group of another molecule by losing one water molecule to form a -CO-NH- linkage, commonly called peptide linkage.

The peptide formed between two amino acid molecules is called a dipeptide.

H2N-CH2-COOH + H2N-CH2-COOH H2N-CH2-CO-NH-CH2-COOH

Glycine Glycine Glycylglycine (Gly-Gly)

The peptide formed by the combination of 3 amino acid molecules is called a tripeptide. When the number of amino acid molecules is more than 10, the product is called a polypeptide. A polypeptide with more than 100 amino acid residues and molecular mass greater than 10,000u is called a protein. [Polypeptides having less than 100 amino acid units are also called protein, if they have a well-defined structure. E.g. Insulin (It contains only 51 aminoacids)].

Proteins

Proteins are the polymers of a-amino acids. The word protein is derived from Greek word, "proteios" which means prime importance.

Classification of proteins

Based on the molecular shape, proteins are classified into 2 types:

a) Fibrous proteins: They have fibre - like structure. Here the linear polypeptide chains are held together by H-bond and disulphide bond. They are generally insoluble in water.

   E.g. Keratin (present in hair, wool, silk etc.) and myosin (present in muscles).

b) Globular proteins: Here the chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. Insulin and albumins are the common examples of globular proteins.

Structure of proteins

Structure of proteins can be studied at four different levels. They are primary, secondary, tertiary and quaternary structure.

1. Primary structure: It gives the sequence of amino acid molecules in a polypeptide chain of protein. Any change in the primary structure creates a different protein.
2. Secondary structure: The secondary structure of protein refers to the shape in which a long polypeptide chain can exist. There are two different types of secondary structures- a-helix and ß-pleated sheet structure. These structures arise due to the regular folding of the backbone of the polypeptide chain due to hydrogen bonding between >CO and —NH— groups of the peptide bond.
3. Tertiary structure: The tertiary structure represents overall folding of the polypeptide chains.
   i.e., further folding of the secondary structure. It gives rise to two major molecular shapes fibrous and globular.

4. Quaternary structure: Some of the proteins contain two or more polypeptide chains called sub-units. The spatial arrangement of these sub-units is known as quaternary structure.

Denaturation of Proteins

When a protein is subjected to physical change (like change in temperature) or chemical change (like change in p ^{H}), it loses the biological activities. This process is called denaturation of protein. During denaturation, secondary and tertiary structures are destroyed, while primary structure remains unaffected.

E.g. coagulation of egg white on boiling, curdling of milk etc.

Enzymes

Enzymes are biological catalysts, which catalyse the different reactions taking place in living body. Almost all the enzymes are globular proteins. Enzymes are very specific in nature. A small amount of enzyme is required to catalyse a large amount of reactants.

E.g. for enzyme catalysis: The enzyme maltase catalyses the hydrolysis of maltose to glucose.

Vitamins

These are organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth. Vitamins are designated by alphabets A, B, C, D, etc. Some of them are further named as sub-groups e.g. Bl, B2, B6, B12, etc.

Classification of Vitamins

Vitamins are classified into two groups depending upon their solubility in water or fat.

i) Fat soluble vitamins: e.g. Vitamins A, D, E, & K. They are stored in liver and adipose (fat storing) tissues.
ii) Water soluble vitamins: e.g. Vitamins B & C. These vitamins are readily excreted through urine and cannot be stored (except vitamin B12) in our body.

Some vitamins and their deficiency diseases

Vitamin	Deficiency Disease
Vitamin A	Night blindness (Xerophthalmia)
Vitamin Bl	Beri-beri
Vitamin B2	Cheilosis
Vitamin B6	Convulsions
Vitamin B12	Pernicious anaemia
Vitamin C	Scurvy
Vitamin D	Rickets and osteomalacia
Vitamin E	Increased fragility of RBCs and muscular weakness
Vitamin K	Hemophilia (Increased blood clotting time)

Nucleic acids

Nucleic acids are long chain polymers of nucleotides and are responsible for transmission of heredity. These are mainly of two types - deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Since nucleic acids are long chain polymers of nucleotides, they are also called polynucleotides.

Nucleic acid contains a pentose sugar, phosphoric acid and a nitrogen base. In DNA, the pentose sugar is ß-D-2-deoxy ribose, while in RNA it is ß-D-ribose.

DNA contains 4 bases - Adenine (A), Guanine (G), Cytosine (C) and Thymine (T). [A, G, C &T]

RNA contains Adenine (A), Guanine (G), Cytosine (C) and Uracil (U). [A, G, C & U]

The pentose sugar combines with the base to form nucleoside, which combines with the phosphoric acid group to form nucleotide. The nucleotide units combine to form nucleic acid.

Structure of Nucleic Acids

Nucleic acids have two types of structures — primary structure and secondary structure.

Primary structure gives the sequence of nucleotides in a nucleic acid chain. The secondary structure of DNA was given by James Watson and Francis Crick. They gave a double strand helix structure for DNA. The two strands in the helix are complementary to each other. They are held together by hydrogen bonds between the bases. Adenine forms 2 hydrogen bonds with thymine while cytosine forms 3 hydrogen bonds with guanine.

RNA molecules are of three types and they perform different functions. They are named as messenger RNA (m-RNA), ribosomal RNA (r-RNA) and transfer RNA (t-RNA).

Differences between DNA and RNA

DNA	RNA
DNA is double stranded	RNA is single stranded
The pentose sugar is deoxy ribose	The pentose sugar is ribose
The nitrogen bases are Adenine, Guanine, Cytosine and Thymine.	The nitrogen bases are Adenine, Guanine, Cytosine and Uracil.

Biological functions of nucleic acids

The important functions of Nucleic acids are:

1. DNA is responsible for the transmission of hereditary characters from one generation to other.
2. Another important function of nucleic acids is protein synthesis. Hormones

Hormones are molecules that act as intercellular messengers. In terms of chemical nature, they are classified as steroids (e.g., estrogens and androgens), poly peptides (E.g. insulin and endorphins) and amino acid derivatives (e.g epinephrine and norepinephrine).

Functions of Hormones

They help to maintain the balance of biological activities in the body.

For example the hormones insulin and glucagon together regulate the glucose level in the blood. Epinephrine and norepinephrine mediate responses to external stimuli.

Thyroxine produced in the thyroid gland is an iodinated derivative of amino acid tyrosine. Abnormally low level of thyroxine leads to hypothyroidism. Increased level of thyroxine causes hyperthyroidism. Low level of iodine in the diet may lead to hypothyroidism and enlargement of the thyroid gland.

Testosterone is the major male sex hormone and estradiol is the main female sex hormone.