

CARBOHYDRATES, AMINO ACIDS & POLYMERS

□ Introduction :

Complex organic compound which governs the common activities of the living organism are called biomolecules. Living systems are made up of various complex biomolecules like carbohydrates, proteins, nucleic acids, lipids, etc.

In addition, some simple molecules like vitamins and mineral salts also play an important role in the functions of organisms.

CARBOHYDRATES

Carbohydrates are primarily produced by plants and form a very large group of naturally occurring organic compounds. Some common examples are cane sugar, glucose, starch, etc. Most of them have a general formula, $C_x(H_2O)_y$, and were considered as hydrates of carbon from where the name carbohydrate was derived. For example, the molecular formula of glucose ($C_6H_{12}O_6$) fits into this general formula, $C_6(H_2O)_6$. But all the compounds which fit into this formula may not be classified as carbohydrates. Rhamnose, $C_6H_{12}O_5$ is a carbohydrate but does not fit in this definition. Chemically, **the carbohydrates may be defined as optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis**. Some of the carbohydrates, which are sweet in taste, are also called sugars. The most common sugar, used in our homes is named as sucrose whereas the sugar present in milk is known as lactose.

□ Classification of Carbohydrates :

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

1. Monosaccharides :

A carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone is called a **monosaccharide**. Some common examples are glucose, fructose, ribose, etc.

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

Different Types of Monosaccharides

Carbon Atom	General term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

2. Oligosaccharides :

Carbohydrates that yield two to ten monosaccharide units, on hydrolysis, are called oligosaccharides. They are further classified as disaccharides, trisaccharides, tetrasaccharides, etc., depending upon the number of monosaccharides, they provide on hydrolysis. Amongst these the most common are disaccharides. The two monosaccharide units obtained on hydrolysis of a disaccharide may be same or different.

For example, sucrose on hydrolysis gives one molecule each of glucose and fructose whereas maltose gives two molecules of glucose only.

3. Polysaccharides :

Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides. Some common examples are starch, cellulose, glycogen, gums, etc. Polysaccharides are not sweet in taste, hence they are also called non-sugars.

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

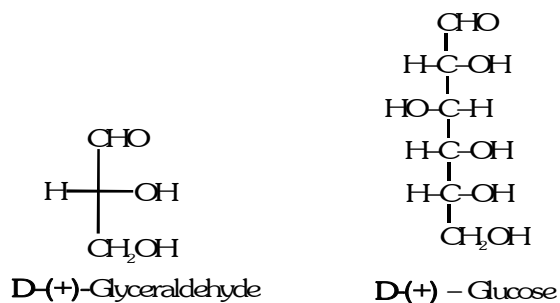
In disaccharides, if the reducing groups of monosaccharides i.e., aldehydic or ketonic groups are bonded, these are **non-reducing sugars e.g. sucrose**. On the other hand, sugars in which these functional groups are free, are called reducing sugars, for example, maltose and lactose.

□ Configuration in monosaccharides :

Glucose is correctly named as D(+)-glucose. 'D' before the name of glucose represents the configuration whereas '+' represents dextrorotatory nature of the molecule. It may be remembered that 'D' and 'L' have no relation with the optical activity of the compound. The meaning of D- and L- notations is given as follows. The letters 'D' or 'L' before the name of any compound indicate the relative configuration of a particular stereoisomer. This refers to their relation with a particular isomer of glyceraldehyde. Glyceraldehyde contains one asymmetric carbon atom and exists in two enantiomeric forms as shown below.



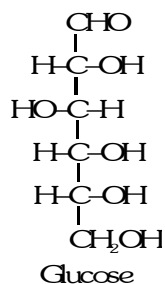
All those compounds which can be chemically correlated to (+) isomer of glyceraldehyde are said to have D-configuration whereas those which can be correlated to (-) isomer of glyceraldehyde are said to have L- configuration. For assigning the configuration of monosaccharides, it is the lowest asymmetric carbon atom (as shown below) which is compared. As in (+) glucose, -OH on the lowest asymmetric carbon is on the right side which is comparable to (+) glyceraldehyde, so it is assigned D-configuration. For this comparison, the structure is written in a way that most oxidised carbon is at the top.



GLUCOSE (ALDOHEXOSE)

□ Structure of Glucose :

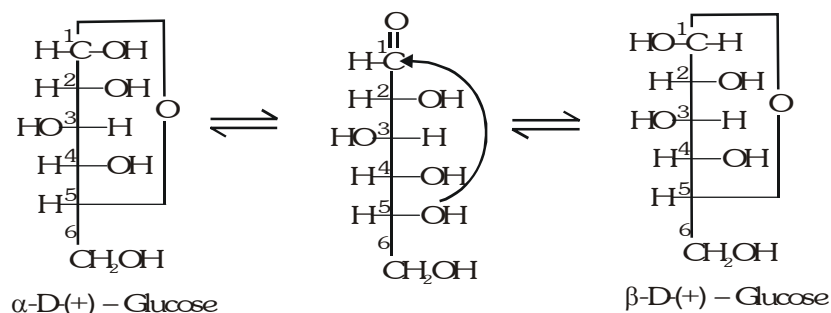
Its molecular formula was found to be $C_6H_{12}O_6$.



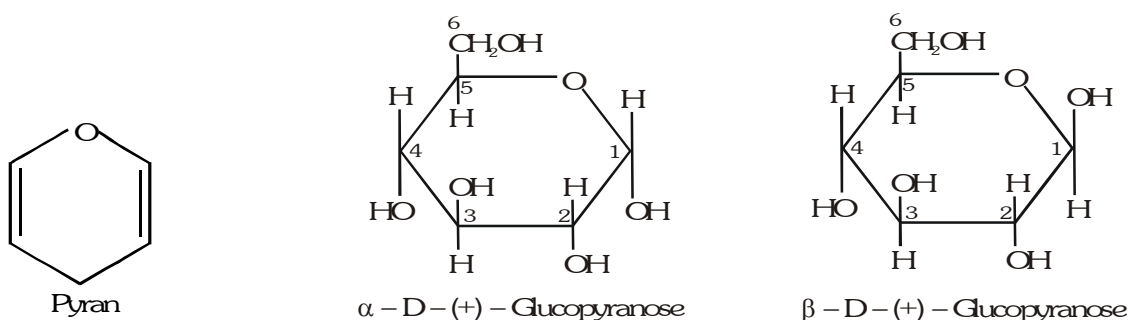
◆ Cyclic structure of Glucose :-

Glucose is found to exist in two different crystalline forms which are named as α and β . The α -form of glucose (m.p. 419 K) is obtained by crystallisation from concentrated solution of glucose at 303 K while the β -form (m.p. 423 K) is obtained by crystallisation from hot and saturated aqueous solution at 371 K.

It was found that glucose forms a six-membered ring in which $-\text{OH}$ at C-5 is involved in ring formation. This explains the absence of $-\text{CHO}$ group and also existence of glucose in two forms as shown below. These two cyclic forms exist in equilibrium with open chain structure.

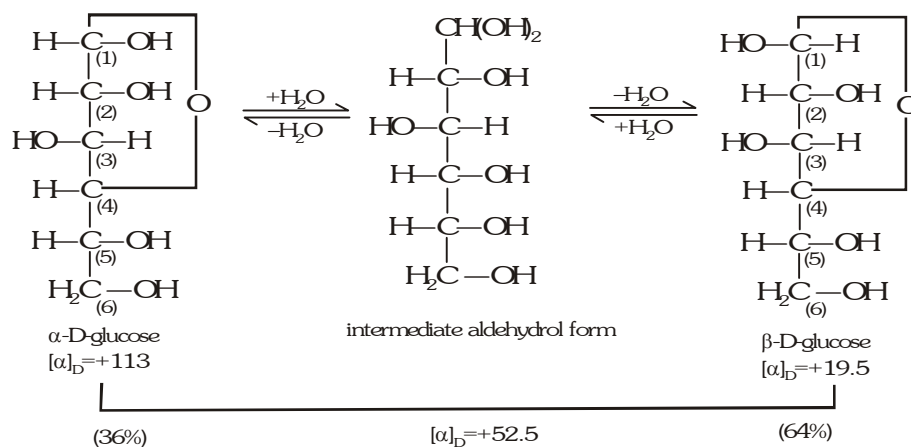


The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C_1 , called anomeric carbon (the aldehyde carbon before cyclisation). Such isomers, i.e., α -form and β -form, are called **anomers**. The six membered cyclic structure of glucose is called **pyranose structure** (α - or β -), in analogy with pyran. Pyran is a cyclic organic compound with one oxygen atom and five carbon atoms in the ring. The cyclic structure of glucose is more correctly represented by Haworth structure as given below.



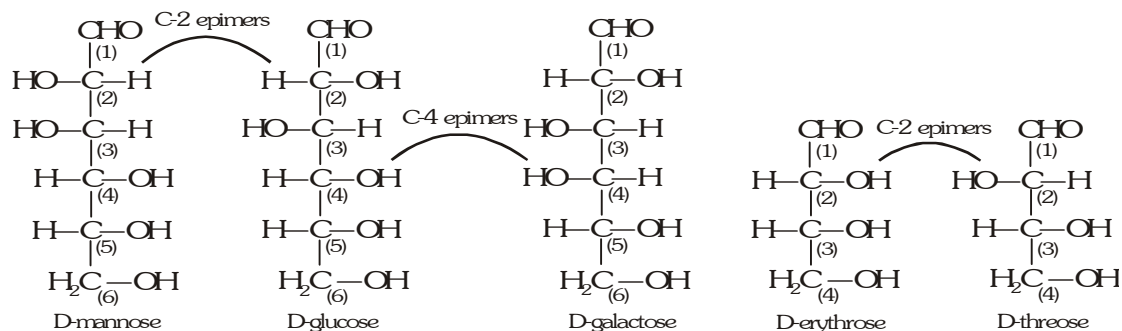
◆ Mutarotation :

The ring structures for glucose also explains the mutarotation by the fact that the change in specific rotation is due to the interconversion of the α -form [$(\alpha)_D = +113$] of glucose to β -[$(\beta)_D = +19.5$] and vice versa through the aldehydrol structure (hydrate of aldehyde) till an equilibrium is reached between two structures. The specific rotation value of this equilibrium mixture consisting of 36% α -glucose and 64% β -is $+52.50$.



◆ **Epimers :**

Many common sugars are closely related, differing only by the stereochemistry at a single carbon atom. For example, glucose and mannose differ only at C-2, the first asymmetric carbon atom. Sugars that differ only by the stereochemistry at a single carbon are called epimers, and the carbon atom where they differ is generally stated. If the number of a carbon atom is not specified, it is assumed to be C-2. Therefore, glucose and mannose are 'C-2 epimers' or simply 'epimers'. The C-4 epimer of glucose is galactose and the C-2 epimer of erythrose is threose.



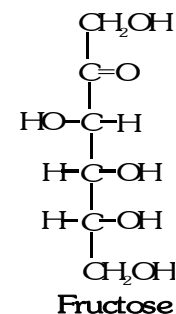
FRUCTOSE (KETOHEXOSE)

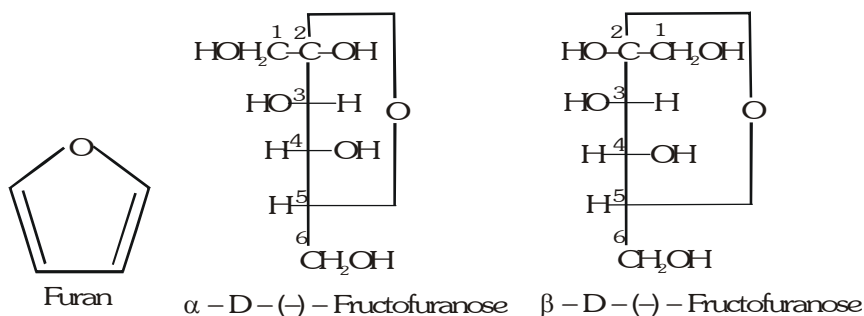
□ **Structure of Fructose :**

Fructose also has the molecular formula $C_6H_{12}O_6$ and on the basis of its reactions

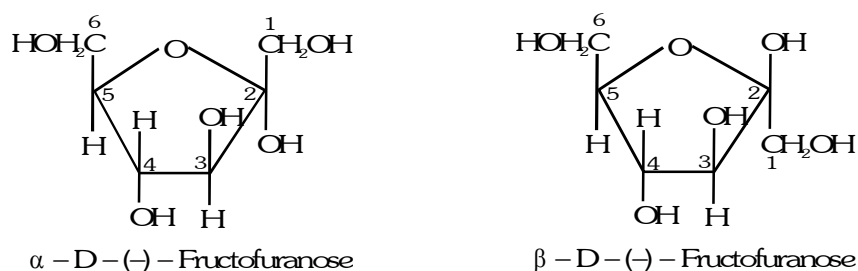
it was found to contain a ketonic functional group at carbon number 2 and six carbons in straight chain as in the case of glucose. It belongs to D-series and is a laevorotatory compound. It is appropriately written as D-(-)-fructose. Its open chain structure is as shown.

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





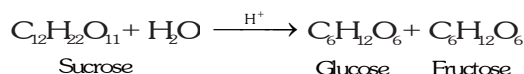
The cyclic structures of two anomers of fructose are represented by Haworth structures as given.



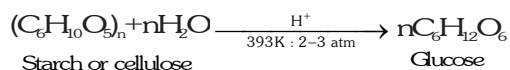
□ **Glucose (Aldohexose) :**

◆ **Preparation of Glucose :**

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

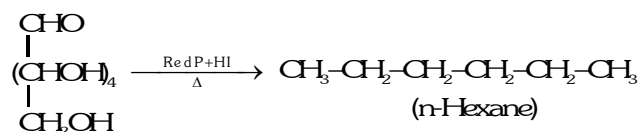


- (b) **From starch :** Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute H_2SO_4 at 393 K under pressure.

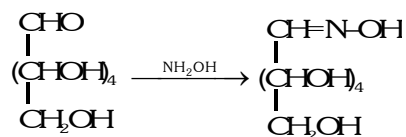


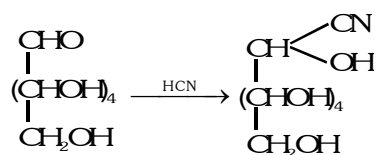
◆ **Reactions of glucose :**

- (i) On prolonged heating with Red P/HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.

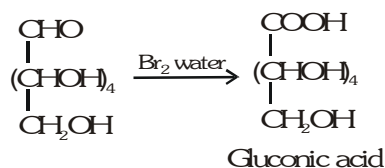


- (ii) Glucose reacts with hydroxylamine to form an oxime and adds a molecule of hydrogen cyanide to give cyanohydrin. These reactions confirm the presence of a carbonyl group ($>\text{C} = \text{O}$) in glucose.

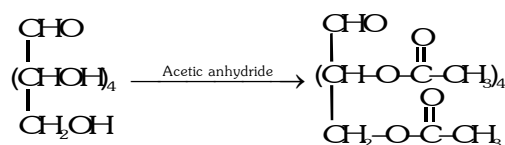




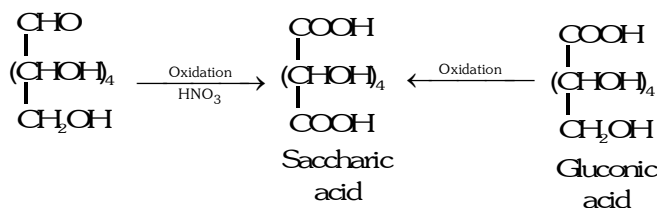
- (iii) Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehydic group. (Aldohexose)



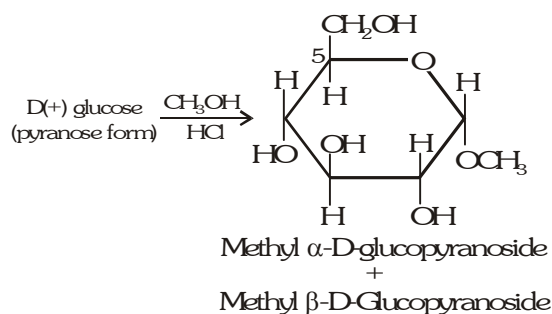
- (iv) Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five -OH groups. Since it exists as a stable compound, five -OH groups should be attached to different carbon atoms.



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



- (vi) **Glucoside formation** : Glucose reacts with methyl alcohol in the presence of hydrochloric acid gas forming two isomeric (α and β) methyl glucosides. This reaction indicates the presence of a ring structure in glucose in which free -CHO group is not present but it is converted into (-CHOH) group.

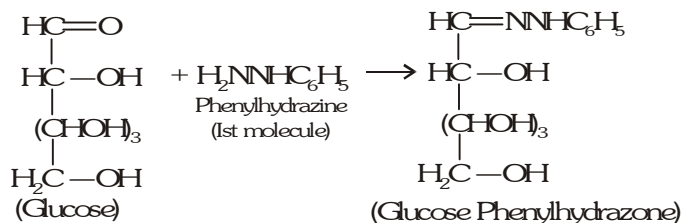


Carbohydrate acetals, generally are called glycosides and an acetal of glucose is called glucoside.

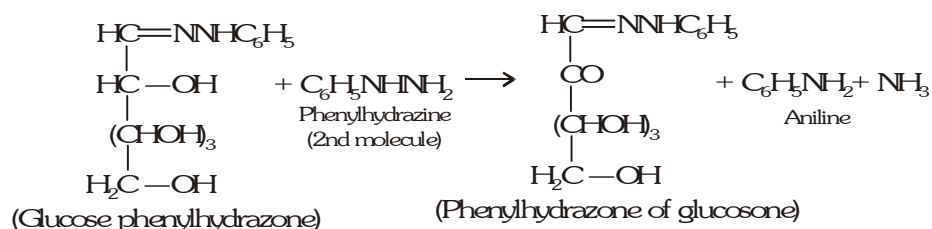
- (vii) **Action of phenylhydrazine** : Like the normal aldehydes, glucose reacts with phenylhydrazine in equimolecular proportion to form phenylhydrazone but unlike the normal aldehydes, glucose reacts with excess of phenylhydrazine (three molecular proportions) to form glucosazone.

According to Fischer, glucosazone formation takes place in the following steps :

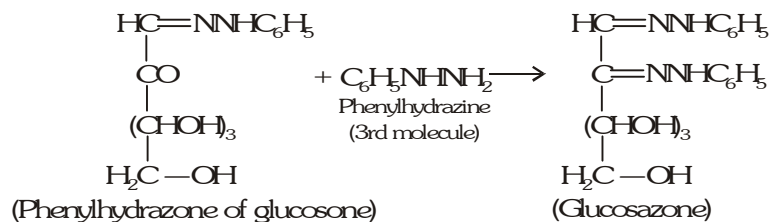
- (a) One molecule of phenylhydrazine reacts with the aldehydic group of glucose to form glucose phenylhydrazone.



- (b) The second molecule of phenylhydrazine oxidizes the secondary alcoholic group (–CHOH–) adjacent to the aldehydic group to a ketonic group and itself is reduced to aniline and ammonia.



- (c) The new keto group reacts with the third molecule of phenylhydrazine to form glucosazone.

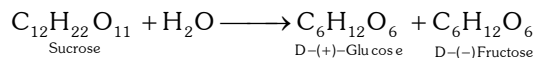


Glucosazone is a yellow crystalline compound, sparingly soluble in water and has a sharp melting point. On account of these properties, it is used in the identification of glucose.

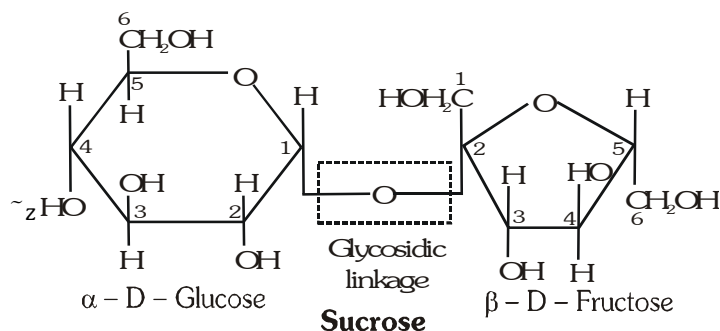
□ Disaccharides :

The two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule. Such a linkage between two monosaccharide units through oxygen atom is called **glycosidic linkage**.

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



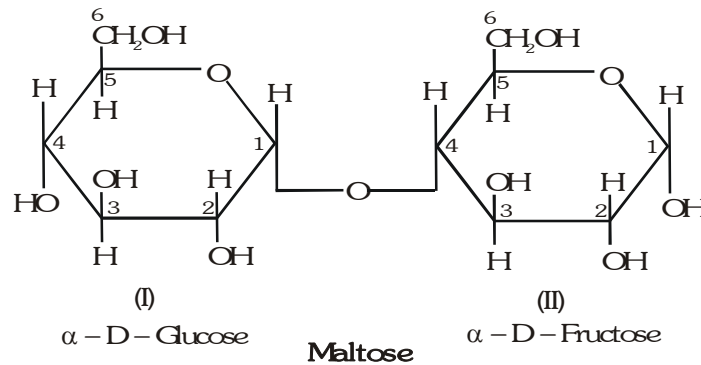
These two monosaccharides are held together by a glycosidic linkage between C1 of α-glucose and C2 of β-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non reducing sugar.



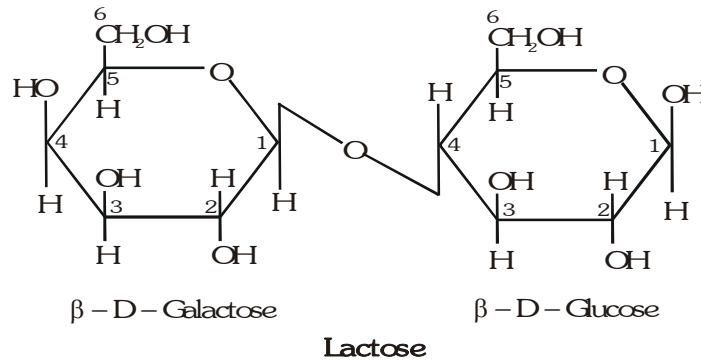
Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (-) and the product is named as invert sugar.

Sucrose is dextrorotatory, its specific rotation being $+66.5\%$, D-glucose is also dextrorotatory, $[\alpha]_D = +53$, but D-fructose has a large negative rotation, $[\alpha]_D = -92$. Since D-fructose has a greater specific rotation than D-Glucose, the resulting mixture is laevorotatory. Because of this the hydrolysis of sucrose is known as the inversion of sucrose and the equimolecular mixture of glucose and fructose is known as invert sugar or invertose.

- (ii) **Maltose** : Another disaccharide, maltose is composed of two α -D-glucose units in which C-1 of one glucose (I) is linked to C-4 of another glucose unit (II). The free aldehyde group can be produced at C-1 of second glucose in solution and it shows reducing properties so it is a reducing sugar.



- (iii) **Lactose** : It is more commonly known as milk sugar since this disaccharide is found in milk. It is composed of β -D-galactose and β -D-glucose. The linkage is between C-1 of galactose and C-4 of glucose. Hence it is also a reducing sugar.

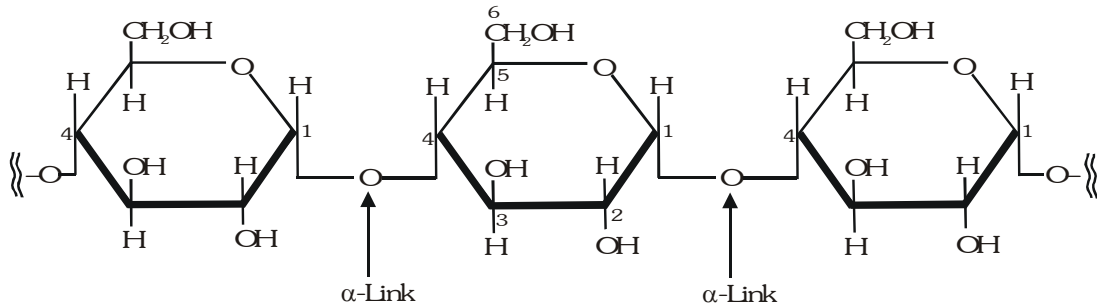


□ Polysaccharides

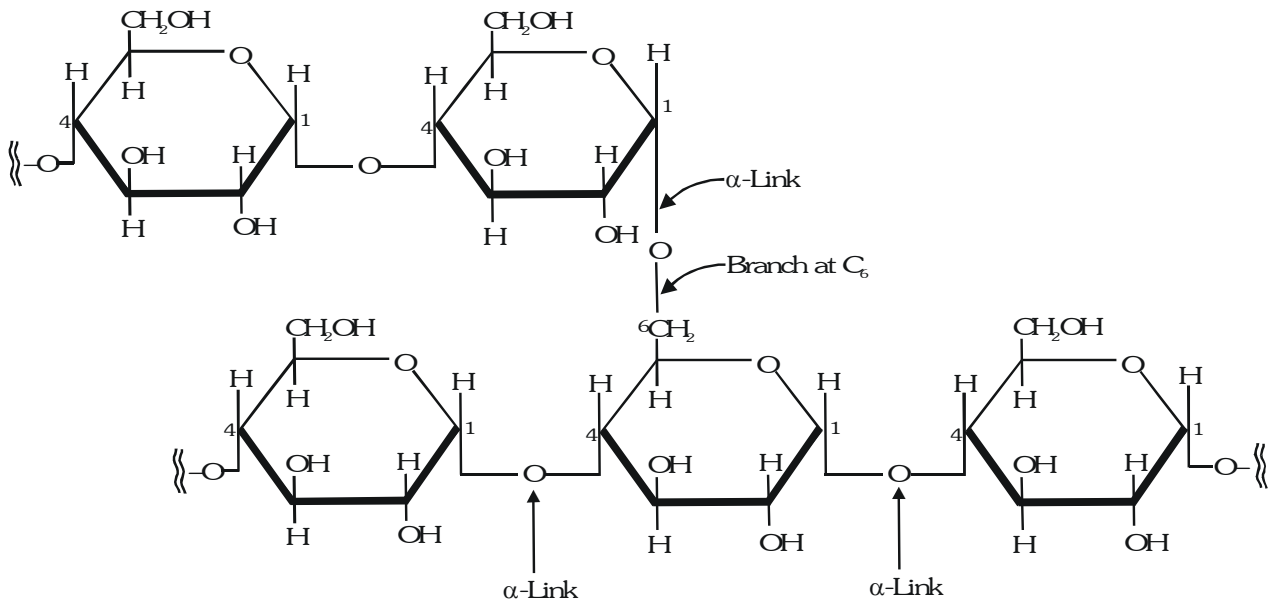
Polysaccharides contain a large number of monosaccharide units joined together by glycosidic linkages. They mainly act as the food storage or structural materials.

- (i) **Starch** : Starch is the main storage polysaccharide of plants. It is the most important dietary source for human beings. High content of starch is found in cereals, roots, tubers and some vegetables. It is a polymer of α -glucose and consists of two components :

Amylose and **Amylopectin**. Amylose is water soluble component which constitutes about 15-20% of starch. Chemically amylose is a long unbranched chain with 200-1000 α -D-(+)-glucose units held by C1- C4 glycosidic linkage. Amylopectin is insoluble in water and constitutes about 80-85% of starch. It is a branched chain polymer of α -D-glucose



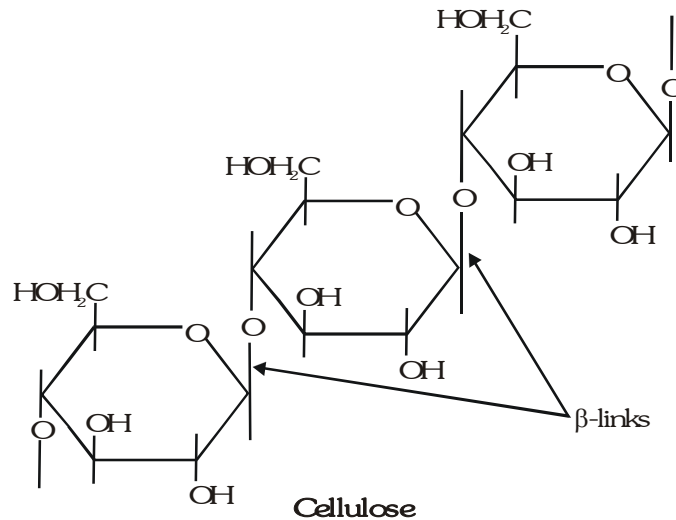
Amylose



Amylopectin

units in which chain is formed by C1–C4 glycosidic linkage whereas branching occurs by C1–C6 glycosidic linkage.

- (ii) **Cellulose** : Cellulose occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. It is a predominant constituent of cell wall of plant cells. Cellulose is a straight chain polysaccharide composed only of β -D-glucose units which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.

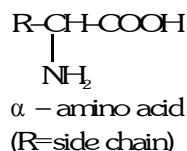


Cellulose

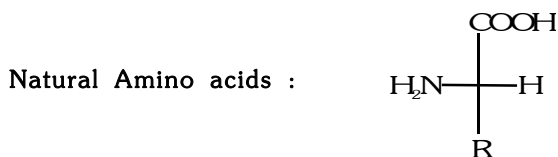
(iii) **Glycogen** : The carbohydrates are stored in animal body as glycogen. It is also known as animal starch because its structure is similar to amylopectin and is rather more highly branched. It is present in liver, muscles and brain. When the body needs glucose, enzymes break the glycogen down to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

AMINO ACIDS

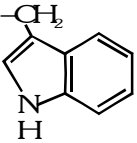
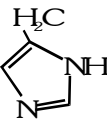
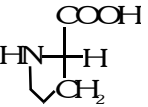
Amino acids contain amino ($-\text{NH}_2$) and carboxyl ($-\text{COOH}$) functional groups. Depending upon the relative position of amino group with respect to carboxyl group, the amino acids can be classified as α , β , γ , δ and so on. Only α -amino acids are obtained on hydrolysis of proteins. They may contain other functional groups also.



All α -amino acids have trivial names, which usually reflect the property of that compound or its source. Glycine is so named since it has sweet taste (in Greek *glykos* means sweet) and tyrosine was first obtained from cheese (in Greek, *tyros* means cheese.).



Name of the amino acids	Characteristic feature of side chain. R	Three letter symbol	One letter of code
1. Glycine	H	Gly	G
2. Alanine	$-\text{CH}_3$	Ala	A
3. Valine*	$(\text{H}_3\text{C})_2\text{CH}-$	Val	V
4. Leucine*	$(\text{H}_3\text{C})_2\text{CH}-\text{CH}_2-$	Leu	L
5. Isoleucine*	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{CH}- \\ \\ \text{CH}_3 \end{array}$	Ile	I
6. Arginine*	$\begin{array}{c} \text{HN}=\text{C}-\text{NH}(\text{CH}_2)_3- \\ \\ \text{NH}_2 \end{array}$	Arg	R
7. Lysine*	$\text{H}_2\text{N}-(\text{CH}_2)_4-$	Lys	K
8. Glutamic acid	$\text{HOOC}-\text{CH}_2-\text{CH}_2-$	Glu	E
9. Aspartic acid	$\text{HOOC}-\text{CH}_2-$	Asp	D
10. Glutamine	$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CH}_2-\text{CH}_2- \end{array}$	Gln	Q
11. Asparagine	$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CH}_2- \end{array}$	Asn	N
12. Threonine*	$\text{H}_3\text{C}-\text{CHOH}-$	Thr	T

13. Serine	HO-CH ₂ -	Ser	S
14. Cysteine	HS-CH ₂ -	Cys	C
15. Methionine*	H ₃ C-S-CH ₂ -CH ₂ -	Met	M
16. Phenylalanine*	C ₆ H ₅ -CH ₂ -	Phe	F
17. Tyrosine	(p) HO-C ₆ H ₄ -CH ₂ -	Tyr	Y
18. Tryptophan*		Trp	W
19. Histidine*		His	H
20. Proline		Pro	P

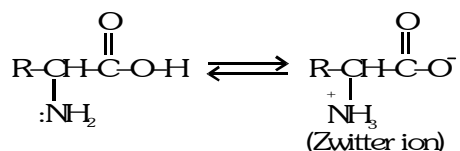
◆ essential amino acid, a = entire structure

□ Classification of Amino Acids :

Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule.

◆ The amino acids, which can be synthesised in the body, are known as **non-essential amino acids**. On the other hand, those which cannot be synthesised in the body and must be obtained through diet, are known as **essential amino acids**.

Amino acids are usually colourless, crystalline solids. These are water-soluble, high melting solids and behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule.



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.

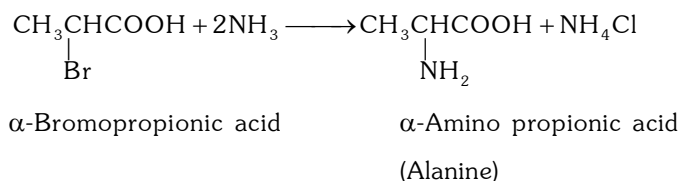
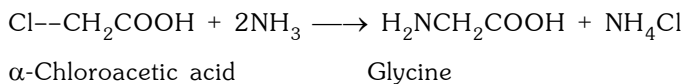
In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.

Except glycine, all other naturally occurring α -amino acids are optically active, since the α -carbon atom is asymmetric. These exist both in 'D' and 'L' forms. Most naturally occurring amino acids have L-configuration. L-Aminoacids are represented by writing the $-\text{NH}_2$ group on left hand side.

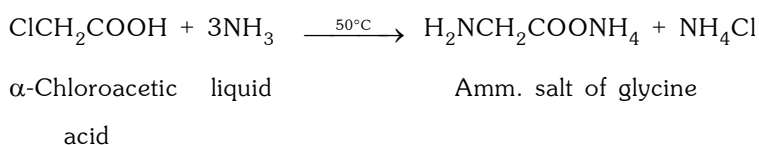
□ **Methods of Preparation of α -amino acid :**

1. **Amination of α -halo acids :**

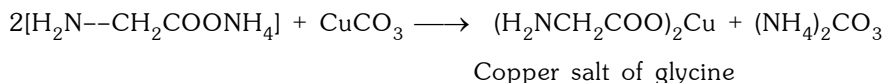
α -Chloro or α -bromo acids on treatment with excess of liquid or concentrated ammonia forms the respective amino acids.



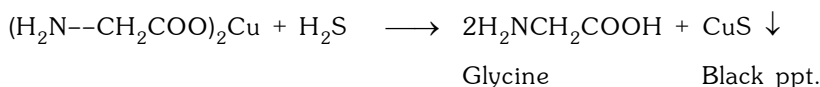
◆ **Lab preparation of glycine :**



The ammonium salt so obtained is boiled with copper carbonate and cooled when blue colour needles of copper salt of glycine are obtained.

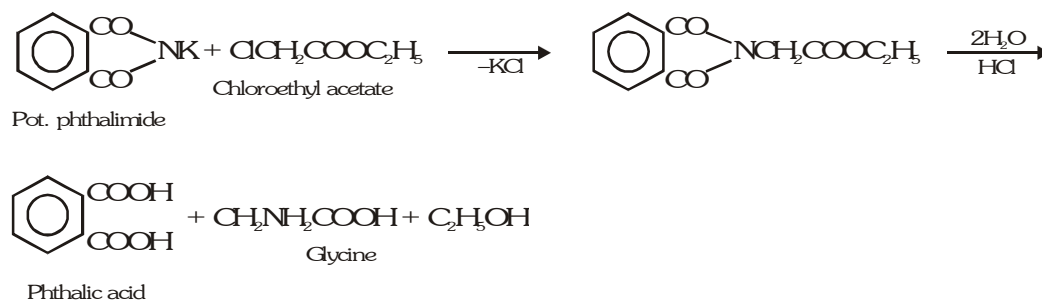


It is now dissolved in water and H_2S is passed till whole of the copper precipitates as copper sulphide leaving glycine as the aqueous solution.



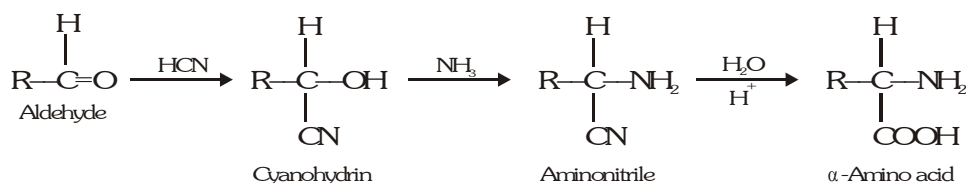
2. **Gabriel phthalimide synthesis :**

α -Halogenated acid or ester combines with potassium phthalimide. The product on hydrolysis gives α -amino acid.



3. **Strecker synthesis :**

An aldehyde reacts with HCN and ammonia or NH_4CN and the product on hydrolysis yields α -amino acid.



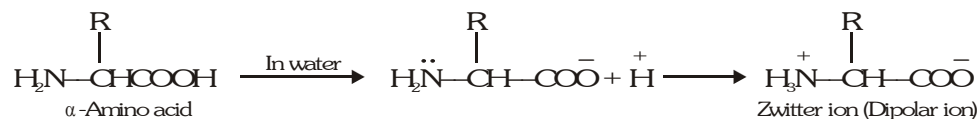
4. From natural proteins :

Natural proteins are hydrolysed with dil. HCl or H₂SO₄ at 250 C in an autoclave when a mixture of α -amino acids is obtained. This mixture is esterified and the various esters are separated by fractional distillation. The esters are then hydrolysed into respective α -amino acids.

◆ Properties :

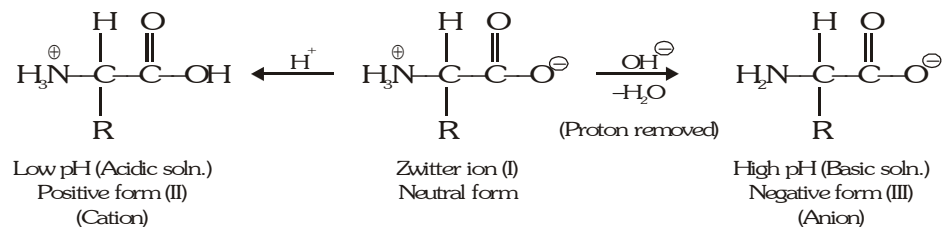
- (i) Amino acids are colourless, crystalline substances having sweet taste. They melt with decomposition at higher temperature (more than 200 C). They are soluble in water but insoluble in organic solvents.
- (ii) Except glycine, all the α -amino acids are optically active and have an asymmetric carbon atom (α -carbon atom). Hence, each of these amino acids can exist in two optical isomers. In proteins, however, only one isomer of each is commonly involved.
- (iii) **Zwitter ion and isoelectric point :**

Since the -NH₂ group is basic and -COOH group is acidic, in neutral solution, it exists in an internal ionic form called a Zwitter ion where the proton of -COOH group is transferred to the -NH₂ group to form inner salt, also known as dipolar ion.



The Zwitter ion is dipolar, charged but overall electrically neutral and contains both a positive and negative charge.

Therefore, amino acids are high melting crystalline solids and amphoteric in nature. Depending on the pH of the solution, the amino acid can donate or accept proton.

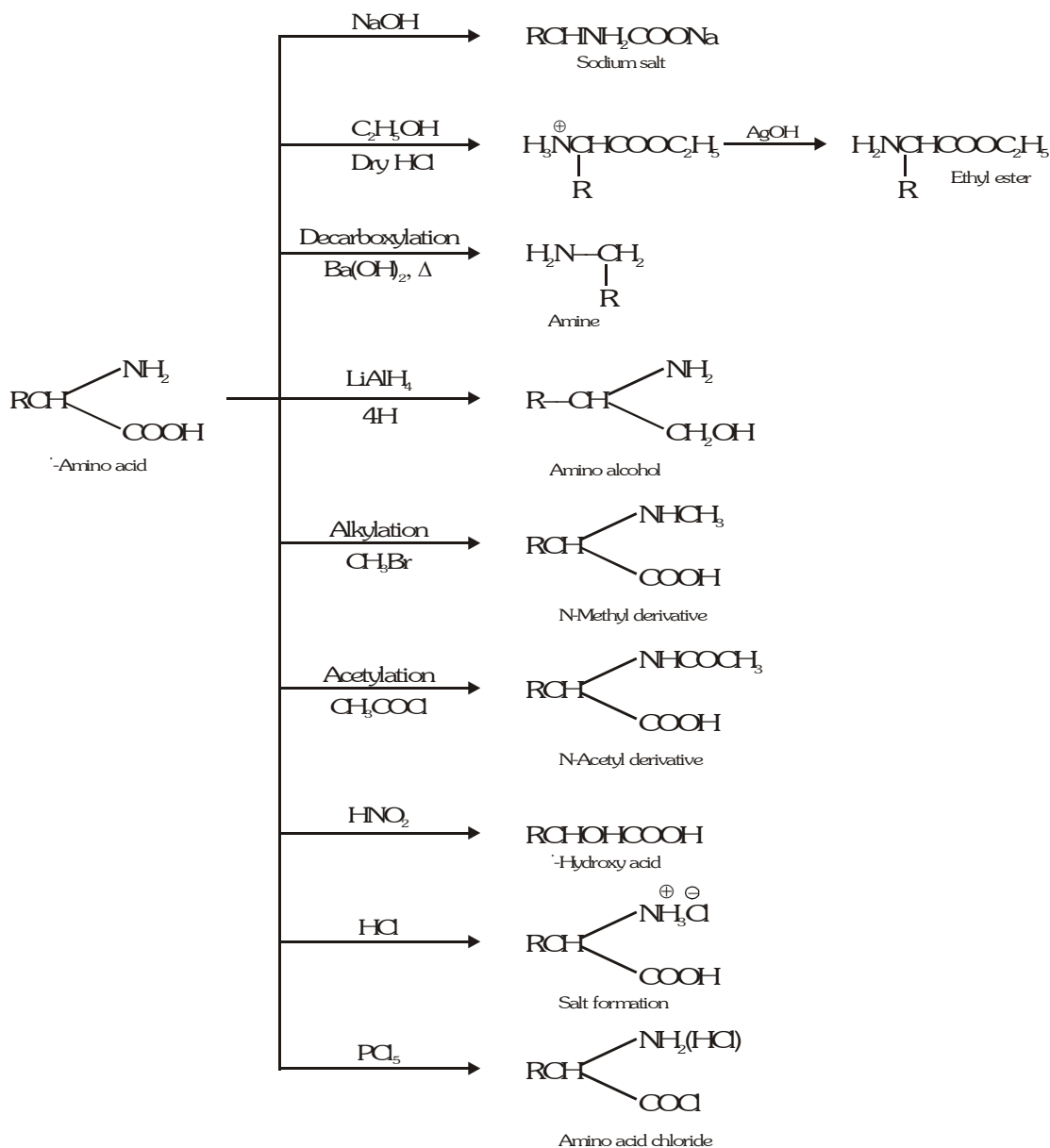


When an ionised form of amino acid is placed in an electric field, it will migrate towards the opposite electrode. Depending on the pH of the medium, following three things may happen :

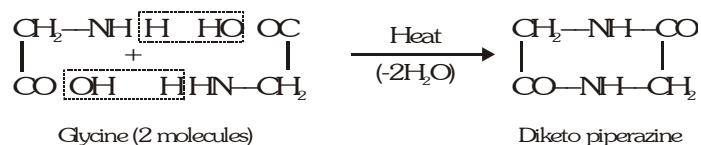
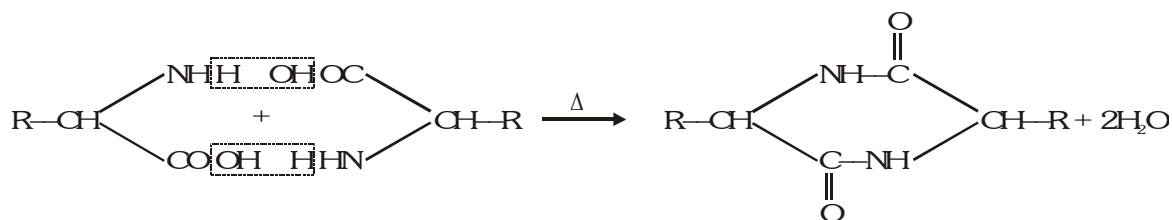
- (i) In acidic solution (low pH), the positive ion moves towards cathode [exist as cation, structure (II)].
- (ii) In basic solution (high pH), the negative ion moves towards anode [exist as anion, structure (III)]
- (iii) The Zwitter ion does not move towards any of the electrodes [neutral dipolar ion, structure (I)].

The intermediate pH at which the amino acid shows no tendency to migrate towards any of the electrodes and exists the equilibrium when placed in an electric field is known as isoelectric point. This is characteristic of a given amino acid and depends on the nature of R-linked to α -carbon atom.

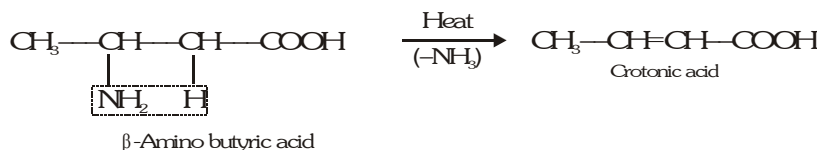
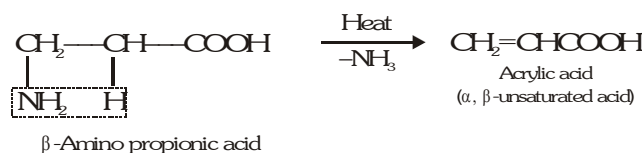
(A) As regards the chemical properties, α -amino acids show the reactions of -NH₂ group, -COOH group and in which both the groups are involved. A summary of chemical properties is given below :



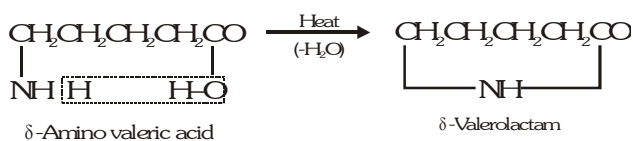
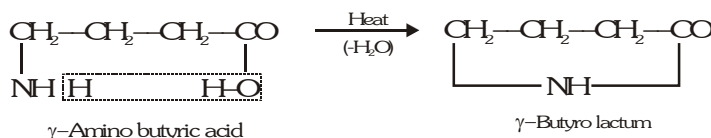
- Action of heat :** α -Amino acids lose two molecules of water and form cyclic amides.



β -Amino acid lose a molecule of ammonia per molecule of amino acid to yield α, β -unsaturated acids.



γ -Amino acids and δ -amino acids undergo intramolecular dehydration to form cyclic amides called Lactams.



These lactams have stable five or six membered rings.

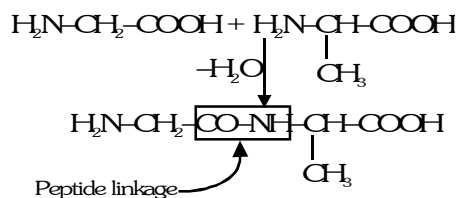
PROTEINS

The word protein is derived from Greek word, “**proteios**” which means primary or of prime importance.

All proteins are polymers of α -amino acids.

□ Structure of Proteins :

Proteins are the polymers of α -amino acids and they are connected to each other by **peptide bond** or **peptide linkage**. Chemically, peptide linkage is an amide formed between $-\text{COOH}$ group and $-\text{NH}_2$ group.



Glycylalanine [Gly-Ala]

The reaction between two molecules of similar or different amino acids, proceeds through the combination of the amino group of one molecule with the carboxyl group of the other. This results in the elimination of a water molecule and formation of a peptide bond $-\text{CO}-\text{NH}-$.

◆ **Proteins** can be classified into two types on the basis of their molecular shape.

- (a) **Fibrous proteins** : When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre- like structure is formed. Such proteins are generally insoluble in water. Some common examples are **keratin** (present in hair, wool, silk) and **myosin** (present in muscles), etc.

(b) **Globular proteins** : This structure results when 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 and shape of proteins can be studied at four different levels, i.e., primary, secondary, tertiary and quaternary.

◆ **Primary structure of proteins** : Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of that protein. Any change in this primary structure i.e., the sequence of amino acids creates a different protein.

◆ **Secondary structure of proteins** : The secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two different types of structures viz. α -helix and β -pleated sheet structure. These structures arise due to the regular folding of the backbone of the polypeptide chain due to hydrogen bonding between $>C=O$ and $-NH-$ groups of the peptide bond.

α -Helix is one of the most common ways in which a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw (helix) with the $-NH$ group of each amino acid residue hydrogen bonded to the $>C=O$ of an adjacent turn of the helix.

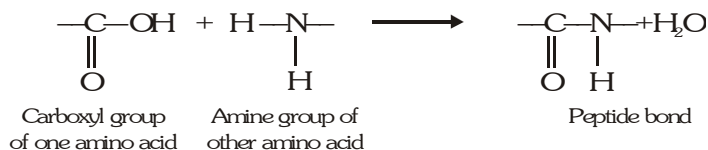
In β -structure all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by intermolecular hydrogen bonds.

◆ **Tertiary structure of proteins** : The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. The main forces which stabilise the 2 and 3 structures of proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.

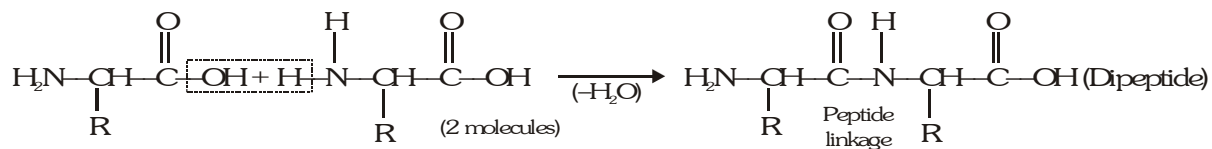
◆ **Quaternary structure of proteins** : Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. Subunits with respect to each other is known as quaternary structure.

□ Formation of proteins–Peptide bond :

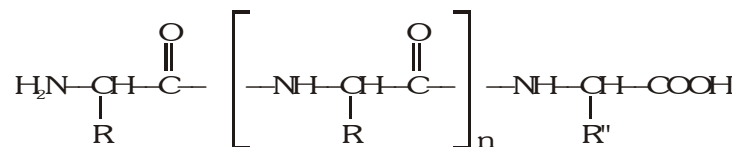
Proteins are formed by joining the carboxyl group of one amino acid to the α -amino group of another amino acid. The bond formed between two amino acids by the elimination of water molecule is called a peptide linkage or bond. The peptide bond is simply another name for amide bond.



The product formed by linking amino acid molecules through peptide linkages, $-\text{CO}-\text{NH}-$, is called a peptide. Peptides are further designated as di, tri, tetra or penta peptides accordingly as they contain two, three, four or five amino acid molecules, same or different, joined together in the following fashions.



When the number of amino acid molecules is large, the product is termed polypeptide which may be represented as,



The formation of a protein linking together different amino acids is not a random process. Each molecule of a given protein has the same sequence of the amino acids along its polypeptide chain. In fact, it is this very sequence that imparts to a protein its own specific properties. Even a change of just one amino acid can drastically change the properties of entire protein molecule. Haemoglobin consists of 574 amino acid units in its molecule in a definite sequence. When only one specific amino acid in the sequence is changed, it becomes a defective haemoglobin which loses its specific property of carrying oxygen in blood stream and results in a disease called sickle cell anaemia.

Normal haemoglobin,

--Val--His--Leu--Thr--Pro--Glu--Glu--Lys--

Sickle cell haemoglobin

--Val--His--Leu--Thr--Pro--Val--Glu--Lys--

Composition of proteins : Composition of a protein varies with source. An approximate composition is as follows :

Carbon 50–53%; hydrogen 6–7%; oxygen 23–25%; nitrogen 16–17%; sulphur about 1%. Other elements may also be present, e.g., phosphorus (in nucleoproteins), iodine (in thyroid proteins) and iron (in haemoglobin).

Denaturation of Proteins :

Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. When a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called **denaturation** of protein. The coagulation of egg white on boiling is a common example of denaturation. Another example is curdling of milk which is caused due to the formation of lactic acid by the bacteria present in milk.

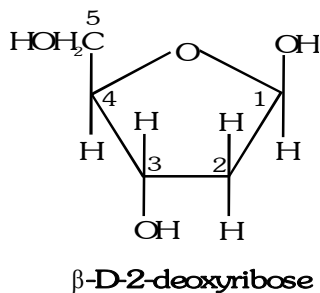
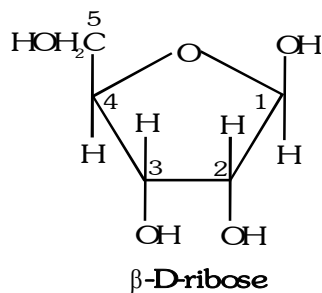
NUCLEIC ACIDS

□ Introduction :

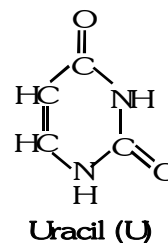
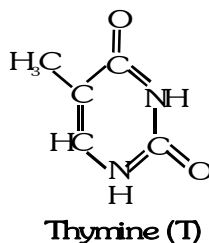
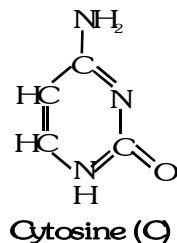
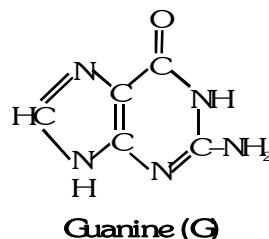
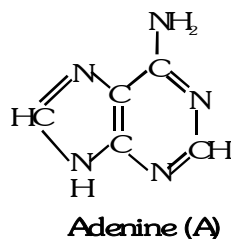
Every generation of each and every species resembles its **ancestors** in many ways. How are these characteristics transmitted from one generation to the next? It has been observed that nucleus of a living cell is responsible for this transmission of inherent characters, also called **heredity**. The particles in nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called **nucleic acids**. These are mainly of two types, the **deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA)**. Since nucleic acids are long chain polymers of **nucleotides**, so they are also called polynucleotides.

□ Chemical composition of Nucleic Acids :

Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds (called bases). In DNA molecules, the sugar moiety is β -D-2-deoxyribose whereas in RNA molecule, it is β -D-ribose.

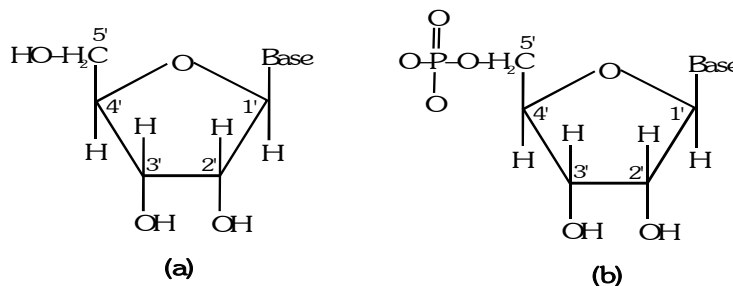


DNA contains four bases viz. **adenine** (A), **guanine** (G), **cytosine** (C) and **thymine** (T). RNA also contains four bases, the first three bases are same as in DNA but the fourth one is uracil (U).



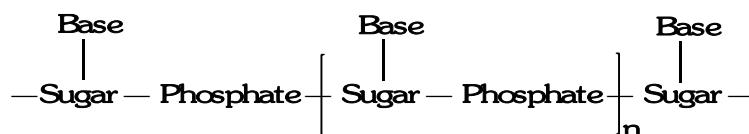
□ **Structure of Nucleic Acids :**

A unit formed by the attachment of a base to 1' position of sugar is known as **nucleoside**. In nucleosides, the sugar carbons are numbered as 1', 2', 3', etc. in order to distinguish these from the bases. When nucleoside is linked to phosphoric acid at 5'-position of sugar moiety, we get a nucleotide.



Structure of (a) a nucleoside and (b) a nucleotide

Nucleotides are joined together by phosphodiester linkage between 5' and 3' carbon atoms of the pentose sugar. Biomolecules A simplified version of nucleic acid chain is as shown below. Fig.



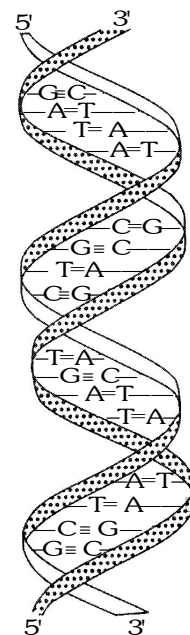
Information regarding the sequence of nucleotides in the chain of a nucleic acid is called its primary structure. Nucleic acids have a secondary structure also. James Watson and Francis Crick gave a double strand helix structure for DNA (Fig.).

Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.

In secondary structure of RNA, helices are present which are only single stranded. Sometimes they fold back on themselves to form a double helix structure. 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)**.

Biological Functions of Nucleic Acids

DNA is the chemical basis of heredity and may be regarded as the reserve of genetic information. DNA is exclusively responsible for maintaining the identity of different species of organisms over millions of years. A DNA molecule is capable of self duplication during cell division and identical DNA strands are transferred to daughter cells. Another important function of nucleic acids is the protein synthesis in the cell. Actually, the proteins are synthesised by various RNA molecules in the cell but the message for the synthesis of a particular protein is present in DNA.



Double strand helix structure for DNA

POLYMERS AND POLYMERISATION

- ◆ A polymer may be defined as a high molecular weight compound formed by the combination of a large number of one or more types of small molecular weight.
- ◆ The small unit (s) of which polymer is made is known as monomer.
- ◆ The polymerisation may be defined as a chemical combination of a number of similar or different molecules to form a single large molecules.
- ◆ A polymer which is obtained from only one type of monomer molecules is known as homopolymer.
Example: polythene, PVC, PAN, Teflon, Buna rubber etc.
- ◆ A polymer which is obtained from more than one type of monomer is known as a co-polymers for example- Buna- S, Dacron , Nylon-66, Bakelite etc.

□ Classification of polymers :

(1) Classification based upon origin (source) :

- (a) Natural polymers (b) Semi-Synthetic polymers (c) Synthetic polymers

(a) Natural polymers: These are of natural origin or these are found in plants and animals.

Natural polymers also called as biopolymers.

Example Proteins (Polymers of amino acids), Polysaccharides (Polymers of mono saccharides), rubber (Polymers of isoprene) silk, wool , starch , cellulose, enzymes, natural rubber, haemoglobin etc.

(b) Semi Synthetic polymers :

Examples Nitro cellulose, cellulose acetate, cellulose xanthate, etc.

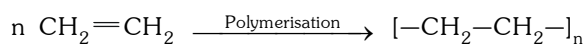
(c) Synthetic Polymers : These are artifical polymers. For example Polythene, nylon, PVC, bakelite, dacron.

(2) Classification based upon synthesis :

(a) Addition Polymers : These are polymers formed by the addition together of the molecules of the monomers to form a large molecule without elimination of any thing.

The process of the formation of addition polymers is called addition polymerisation.

For example



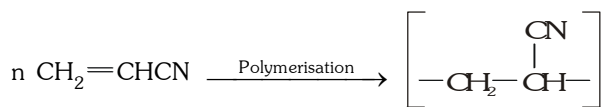
Ethene

Polythene



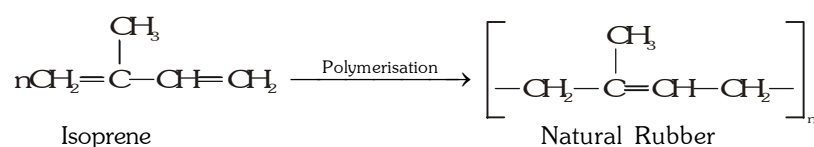
vinyl chloride

PVC



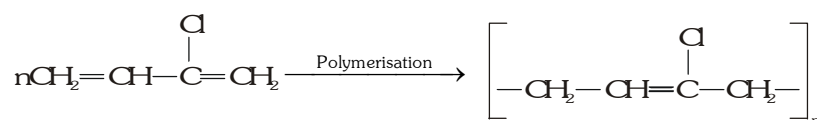
Vinyl cyanide

Orlon



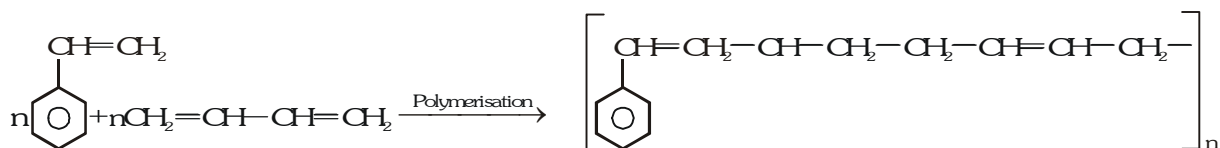
Isoprene

Natural Rubber



Chloroprene

Neoprene Rubber



Styrene 1, 3-Butadiene

Styrene butadiene rubber (SBR)

(b) **Condensation polymers** : Condensation polymers are formed by the combination of monomers with the elimination of simple molecules such as water or alcohol. This process is called condensation polymerisation.

Proteins, starch, cellulose etc. are the example of natural condensation polymers.

Two main synthetic polymers of condensation types are polyesters (Terylene or dacron) and poly amides (Nylon-66)

(3) **Classification based upon mechanism** :

(a) **Chain growth polymerisation** : These polymers are formed by the successive addition of monomer units to the growing chain having a reactive intermediate (Free radical, carbocation or carbanion). Chain growth polymerisation is an important reaction of alkenes and conjugated dienes.

Ex : Polythene, poly propylene, teflon, PVC, poly styrene are some examples of chain growth polymers.

(b) **Step growth Polymerisation** : These polymers are formed through a series of independent steps. Each steps involves the condensation between two monomers leading to the formation of smaller polymer.

Ex : Nylon, terylene, bakelite etc.

(4) **Classification based upon structure :**

- (a) **Linear polymers :** These consist of extremely long chains of atoms and are also called one dimensional polymers. Examples - Polyethylene , PVC, Nylon, Polyester.
- (b) **Three dimensional polymers :** Those polymers in which chains are cross linked to give a three dimensional network are called three dimensional polymers . Example- Bakelite.

(5) **Classification based upon molecular forces :**

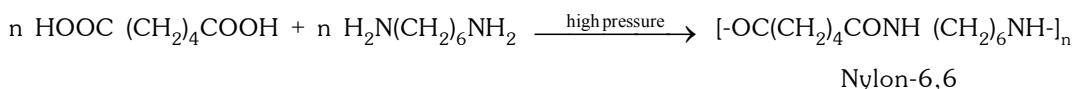
- (a) **Elastomers :** These are the polymers having very weak intermolecular forces of attraction between polymer chains.

Elastomers possesses elastic character.

Vulcanised rubber is very important example of an elastomer.

- (b) **Fibres :** These are the polymers which have bit strong intermolecular forces such as hydrogen bonding.
Ex. Nylon - 6, 6, Nylon-6,10, Terylene.

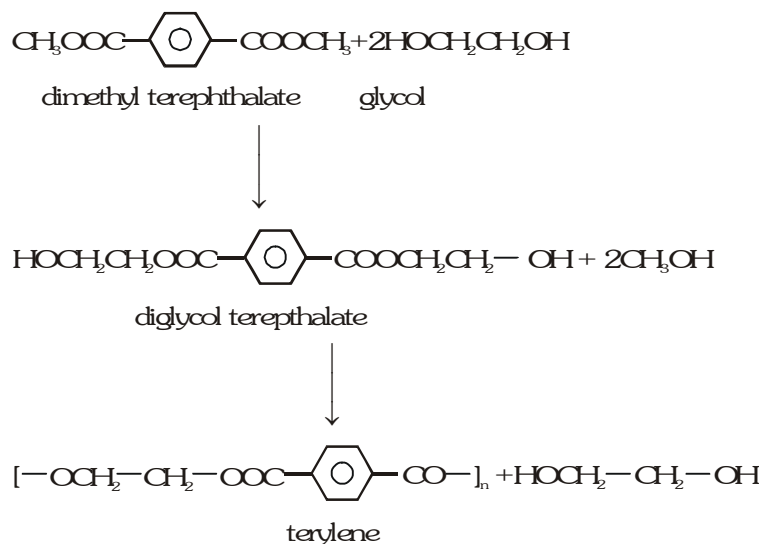
- ◆ **Nylon - 6,6 :** It is obtained by condensation polymerisation of hexamethylene diamine (six carbon) and adipic acid (a dibasic acid having six carbon)



- ◆ **Nylon - 6,10 :** It is obtained by condensation polymerisation of hexamethylene diamine (6C) and sebacic acid (10C)

- ◆ **Terylene :** (Dacron, teron, cronar, mylar)

It is a polyester fibre made by the esterification of terephthalic acid with ethylene glycol.



- (c) **Thermoplastics :** A thermo plastic polymer is one which softens on heating and becomes hard on cooling.

Polyethylene, polypropylene, polystyrene are the example of thermo plastics.

- (d) **Thermo setting polymers or resin :** A thermo setting polymer becomes hard on heating. Bakelite , Aniline aldehyde resin, urea formaldehyde polymer.

MONOMERS AND POLYMERS

S.N.	Monomer	Polymer	Type of Polymers
1.	$\text{CH}_2=\text{CH}_2$ (Ethylene)	Poly ethene	Addition polymer
2.	$\text{CH}_2=\text{CHCH}_3$ (Propylene)	Poly propylene	Addition homo polymer
3.	$\text{CH}_2=\text{CHCl}$ (Vinyl chloride)	Polyvinyl chloride (PVC)	Homopolymer, chain growth
4.	$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$ (Styrene)	Polystyrene (styron)	Addition homo polymer, linear chain
5.	$\text{CH}_2=\text{CH}-\text{CN}$ (Acrylonitrile)	Ployacrylonitrile (PAN), Orlon	Addition homopolymer
6.	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ (1,3 Butadiene)	BUNA rubbers	Addition copolymer
7.	$\text{CH}_2=\text{CHOCOCH}_3$ (Vinyl acetate)	Poly vinyl acetate (PVA)	Addition homopolymer
8.	$\text{CF}_2=\text{CF}_2$ (Tetrafluoro ethylene)	Teflon	Chain growth homopolymer (Nonstick cookwares)
9.	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ \\ \text{CH}_3 \end{array}$ (Isoprene)	Natural Rubber	Additon homopolymer
10.	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ \\ \text{Cl} \end{array}$ (Chloroprene)	Neoprene (Artificial Rubber)	Addition homopolymer
11.	Ethylene Glycol + dimethyl terephthalate	Terylene or Dacron (Polyester)	Copolymer, step growth
12.	Hexamethylene diamine + adipic acid	Nylon-6,6 (Polyamide)	Copolymer, step growth linear
13.	Formaldehyde + urea	Urea formaldehyde resin	Copolymer, step growth
14.	Formaldehyde + Phenol	Bakelite	Copolymer, step growth thermo setting polymer
15.	Maleic anhydride + methylene glycol	Alkyl plastic	
16.	Methyl methacrylate	Poly methyl meth acrylate (PMMA)	Addition homopolymer
17.	Ethylene Glycol	Glyptal or Alkyds + Phthalic acid	Copolymer, linear step growth, thermo plastic
18.	Melamine + formaldehyde	Melamine formaldehyde resin	Copolymer, step growth thermosetting polymer
19.	Hexamethylene diamine + sebasic acid	Nylon - 6,10	Copolymer, step growth linear
20.	6 - Aminohexanoic acid	Nylon - 6	Homopolymer, step growth linear

POINTS TO BE REMEMBER

- ❖ Monosaccharides which differ in configuration at C_1 in aldoses and C_2 in ketoses are called anomers. thus, α -D-glucose and β -D-glucose are anomers and so are α -D-fructose and β -D-fructose.
- ❖ The C_1 carbon atom in aldoses and C_2 carbon atom in ketoses around which the configuration of anomers differs is called anomeric or the glycosidic carbon.
- ❖ Monosaccharides which differ in configuration at a carbon atom other than the anomeric carbon are called epimers. Thus, glucose and mannose which differ in Configuration at C_2 are called C_2 -epimers while glucose and galactose which differ in configuration at C_4 are called C_4 epimers.
- ❖ All monosaccharides (aldoses and ketoses) and disaccharides except sucrose reduce fehling's solution, Benedict's solution and Tollen's reagent and hence are called reducing sugars. Others (sucrose, starch, cellulose) which do not reduce these reagents are called non-reducing sugars.
- ❖ Although starch and cellulose both contain an aldehydic group at the end of the chain but still they do not reduce Tollen's reagent. (The reason being that due to high molecular weights of these polysaccharides their reducing properties are marked and hence no detectable reducing properties are observed).
- ❖ The spontaneous change of specific rotation with time to an equilibrium value is called mutarotation. All reducing carbohydrates i.e. monosaccharides (glucose, fructose, mannose etc.) and disaccharides (maltose, lactose etc.) undergo mutarotation in aqueous solutions.
- ❖ Since glucose (grape sugar) is dextrorotatory, it is also called dextrose. Similarly, fructose being laevorotatory is also called laevulose.
- ❖ α -Amino acids are the building blocks of proteins or proteins are the condensation polymers of α -amino acids.
- ❖ All the α -amino acids forming proteins have L- configuration while all the naturally occurring carbohydrates have D-configuration.
- ❖ Keratin in skin, hair, nails and wool, collagen in tendons, fibroin in silk and myosin in muscles are all fibrous proteins and have linear structures.
- ❖ Enzymes, hormones (insulin, thyroglobulin), antibodies, haemoglobin, fibrinogen, albumin etc. are all globular proteins. These have folded structures. The folding of globular proteins occurs due to (i) disulphide bridges, (ii) intramolecular H-bonding (iii) van der Waals' interactions and (iv) dipolar interactions.
- ❖ Insulin is a protein or peptide hormone. It consists of 51 amino acids arranged in two polypeptide chains containing 21 and 30 α -amino acid residues respectively. The two peptide chains are held together by two cystine disulphide cross-links.
- ❖ The disease sickle cell anaemia is caused by defective haemoglobin which is obtained by replacement of just one amino acid (i.e., glutamic acid by valine) in the sequence of the protein haemoglobin.
- ❖ Enzymes are biological catalysts. Chemically all enzymes are globular proteins.
- ❖ DNA contains 2-deoxy D-(-) ribose as the pentose sugar while RNA contains D-(-) ribose as the sugar.
- ❖ Both DNA and RNA contain the same two purine bases, i.e. adenine and guanine. The pyrimidine bases are however, different Whereas DNA contains cytosine and thymine, RNA contains cytosine and uracil
- ❖ Waxes are the esters of long chain fatty acids with long chain alcohols.

COMPETITION WINDOW

- ❖ Both glucose and fructose reduce Tollen's reagent, fehling's solution, Benedict's solution etc.
- ❖ All monosaccharides and reducing disaccharides (maltose, lactose etc.) react with three molecules of $C_6H_5NHNH_2$ to form crystalline osazones which are used for their identification and characterization. Further all monosaccharides which differ in configuration at C_1 and C_2 give the same osazone, i.e. glucose and fructose.

- ❖ Both starch and cellulose are condensation polymers of glucose. Whereas glucose is a polymer of α -glucose, cellulose is polymer of β -glucose.
- ❖ Starch is a mixture of two components, i.e. amylose and amylopectin. Whereas amylose is a linear polymer, amylopectin has branched chain structure.
- ❖ Amylose gives a blue colour with iodine solution due to the formation of an inclusion complex.
- ❖ Sucrose is non-reducing disaccharide.
- ❖ In lactose, glucose unit is in the reducing form.
- ❖ Proteins are the condensation polymers of α -amino acids.
- ❖ $-\text{CO}-\text{NH}-$ is called the peptide bond.
- ❖ At isoelectric point, the amino acids primarily exist as the neutral dipolar or zwitterion and hence have the minimum solubility.
- ❖ In amino acids. $-\text{COO}^{\ominus}$ group acts as the base while $-\text{NH}_3^{\oplus}$ acts as the acid.
- ❖ During denaturation, the primary structure of proteins remains intact while secondary and tertiary structures are destroyed.
- ❖ The pH of the gastric juice (containing strong HCl) is 2 which causes denaturation of proteins in the stomach.
- ❖ Haemoglobin is a globular protein and the red colour of haemoglobin is due to the iron-protoporphyrin complex called the heme.
- ❖ The bicarbonate/carbonic acid system, i.e. $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ acts as the buffer and maintains the pH of blood between 7.36–7.42.

GOLDEN KEY POINTS

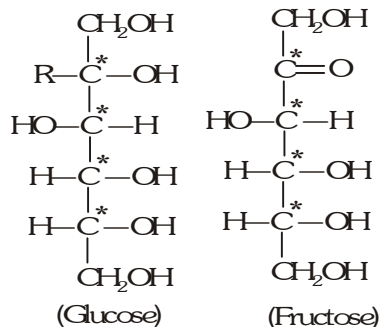
- ❖ Plastics have high molecular weight ranging from 20,000 (nylon) to 2,50,000 (PVC)
- ❖ Thermo plastics are linear polymers (nitrocellulose, polyethene, perspex)
- ❖ Plasticizers fit between the polymer chains and thus weaken the attraction between the chains there by increasing the flexibility.
- ❖ Nylon-6(USA) or perlonl (Germany) is prepared by prolonged heating of caprolactum at 540K.
- ❖ Saran is a copolymer of vinylidene chloride (85%) and vinyl chloride (15%).
- ❖ Dynel is a copolymer of acrylonitrile (40%) and vinyl chloride (60%). It is used in making water softener bags, cloth blankets and dyenets etc.
- ❖ Aspirin is used to prevent heart attacks besides being antipyretic and analgesic agents.
- ❖ Soaps, detergents and phospholipids are called surfactants since they lower the surface tension of water.
- ❖ All surfactants consist of two characteristic groups, i.e., apolar head group which is water-soluble (hydrophilic group) and a non-polar hydrocarbon tail which is oil-soluble (lyophilic or lipophilic group).
- ❖ Sodium soaps are hard while potassium soaps are soft. Therefore, washing soaps are mostly sodium soaps while liquid soapshaving creams and toilet soaps are potassium salts.
- ❖ Like soaps, detergents of the type, linear benzene sulphonate (LBS) in which the phenyl group is randomly attached to the various secondary positions of a long straight chain or n-alkyl hydrogen sulphates are 100% biodegradable.
- ❖ Unlike soaps, detergents can be used in hard water. The reason being that magnesium and calcium salts of detergents are soluble in water while those of soaps are insoluble in water.
- ❖ Sulpha drugs are effective against bacterial infections.
- ❖ Congo red (azo dye) and martius yellow (nitro dye) are also called direct dyes.

SOLVED EXAMPLES

Ex 1. Chiral carbon atoms in glucose and fructose are -

- (A) 3 in each (B) 4 in each
(C) 2 in glucose and 4 in fructose (D) 4 in glucose and 3 in fructose

Sol. (D)



Carbon atoms marked * are chiral carbons.

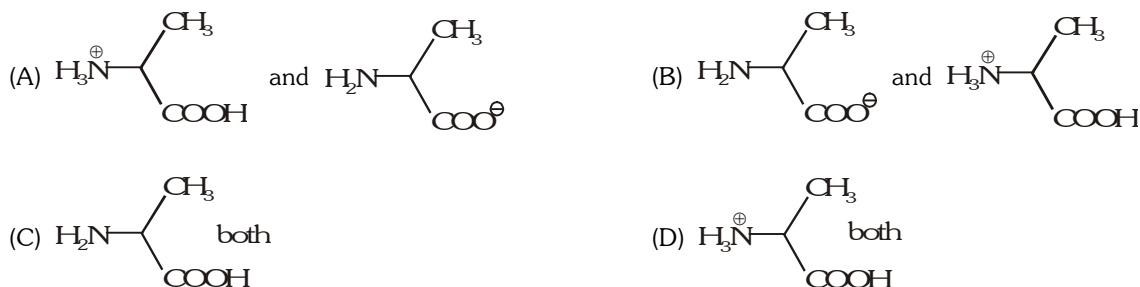
Ex 2. An organic compound is found to contain C, H and O as elements. It is soluble in water, chars with conc. sulphuric acid and also gives purple colour and Molisch reagent. The Fehling solution test is negative but it forms a blue colour with iodine. The organic compound should be -

- (A) glucose (B) fructose (C) starch (D) meso-tartaric acid

Sol. (C)

Charring with Conc. H_2SO_4 and purple colour with Molisch reagent shows it to be a carbohydrate. As Fehling solution test is negative, it could not be glucose and fructose. Since it gives blue colour with iodine, so it is starch which forms a blue starch-iodine complex.

Ex 3. Structures of alanine at pH = 2 and pH = 10 are respectively :



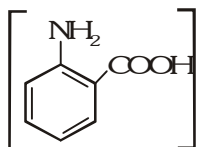
Sol. (A)

Ex 4. Which of the following does not exist as a Zwitter ion -

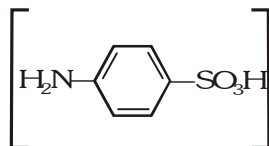
- (A) glycine (B) sulphanilic acid (C) anthranilic acid (D) Alanine

Sol. (C)

Glycine and Alanine are α -amino acids and exist as zwitter ion structures. In anthranilic acid lone pair of electrons on the $-\text{NH}_2$ group is donated towards the benzene ring. As a result, character of $-\text{COOH}$ group and basic character of $-\text{NH}_2$ group decreases. Thus the weakly acidic $-\text{COOH}$ group cannot transfer a H^+ ion to the weakly basic $-\text{NH}_2$ group. As a result, anthranilic acid does not exist as a zwitter ion. On the other hand in sulphanilic acid.



$-\text{SO}_3\text{H}$ group is a much stronger acidic group as compared to $-\text{COOH}$ group and donates a proton to weakly basic $-\text{NH}_2$ group to form a zwitter ion.



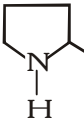
Ex 5. Ketones do not reduce fehling solution and Tollen's reagents, but fructose with a keto group reduces it. This is due to -

- (A) $>\text{CH}-\text{OH}$ group which is oxidized to keto group
 (B) Enolisation of keto group of fructose and then its interconversion to aldehyde group in the presence of OH^\ominus of the reagent
 (C) Lohbry de Bruy Van Ekenstein rearrangement
 (D) Epimerisation and Ruff's degradation

Sol. (D)

Ex 6. The structural feature which distinguishes proline from other natural α -amino acids is -

- (A) It is optically inactive (B) It contains an aromatic group
 (C) It is a dicarboxylic acid (D) It contains secondary amino group

Sol. (D) proline is  so it is a secondary amine.

Ex 7. Starch is polymer of -

- (A) fructose (B) glucose (C) lactose (D) none

Sol. (b) Starch is homopolysaccharide of glucose having 24-30 glucose units.

Ex 8. The commonest disaccharide has the molecular formula -

- (A) $\text{C}_{10}\text{H}_{18}\text{O}_9$ (B) $\text{C}_{10}\text{H}_{20}\text{O}_{10}$ (C) $\text{C}_{11}\text{H}_{22}\text{O}_{11}$ (D) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

Sol. (D)

The most common disaccharide is sucrose, whose molecular formula is $\text{C}_{12}\text{H}_{22}\text{O}_{11}$.

Ex 9. The structure of glycine (amino acid) is $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$ (zwitter ion). Select the correct statement of the following-

- (A) Glycine, as well as other amino acids are amphoteric
 (B) The acidic functional group in amino acids is $-\text{NH}_3^+$
 (C) The basic functional group in amino acids is $-\text{CO}_2^-$
 (D) All the statements are correct

Sol. (D)

Glycine and all other amino acids are amphoteric because of the presence of $-\text{NH}_2$ and $-\text{CO}_2\text{H}$ group both. The amino acid exists as Zwitter ion and basic group is $-\text{CO}_2^-$.

Ex 10. Sugars are characterised by the preparation of osazone derivatives. Which sugar have identical osazones-

- (A) Glucose and lactose (B) Glucose and fructose
 (C) Glucose and arabinose (D) Glucose and maltose

Sol. (B)

The reaction with phenyl hydrazone gives same osazone because glucose and fructose differ only on carbon atoms 1 and 2 which are involved in osazone formation.

Ex.11 In which of the following sets do the carbohydrates contain disaccharides only ?

- (A) maltose, lactose, starch (B) maltose, sucrose, lactose
 (C) sucrose, lactose, cellulose (D) maltose, lactose, mannose

Sol. (B)