ST. LAWRENCE HIGH SCHOOL

A JESUIT CHRISTIAN MINORITY INSTITUTION

STUDY MATERIAL FOR CHEMISTRY (CLASS-12)

TOPIC-BIOMOLECULES (PART-1)

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Biomolecules are the organic compounds which form the basis of life, i.e., they build up the living system and responsible for their growth and maintenance.

The sequence that relates biomolecules to living organism is

Biomolecules → Organelles → Cells → Tissues → Organs → Living organism.

Carbohydrates

Optically active polyhydroxy aldehydes (aldcses) or ketones (ketoses) or compounds which on hydrolysis give these units are known as carbohydrates. They are also called saccharides

(Latin Saccharum = sugar) due to sweet taste of simpler members.

Depending upon their behaviour towards hydrolysis, carbohydrates can be of following three types

Monosaccharides

These cannot be hydrolysed to simpler molecules and further subdivided into tetroses, pentoses or hexoses depending upon the number of carbon atoms. These are also called homopolysaccharides.

- **Aldotetroses** Erythrose, Threose
- **Aldopentoses** Xylose, Ribose,
- **Aldohexoses** Glucose, Galactose,
- **Ketohexoses** Fructose

All naturally occurring monosaccharides belong to D-series.

killiani synthesis is used to convert an aldose into next higher aldose.

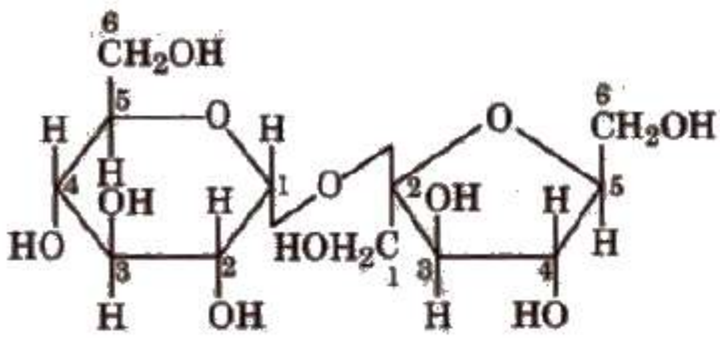
Oligosaccharides

(Greek oligos = few). On hydrolysis, they generally give two to nine monosaccharides (same or different) and are further classified as disaccharides, e.g., sucrose, maltose, lactose, trisaccharides and so on. $C_{12}H_{22}O_{11}$ is a disaccharide because it gives two monosaccharides.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

The bond formed between two monosaccharides is called a glycosidic bond and normally it is (1, 4) bond.

Sucrose is most abundant in plants and known as cane sugar or table sugar or invert sugar as equimolar mixture of glucose and fructose is obtained by hydrolysis of sucrose.



Structure of sucrose

Trisaccharides Raffinose ($C_{18}H_{32}O_{16}$)

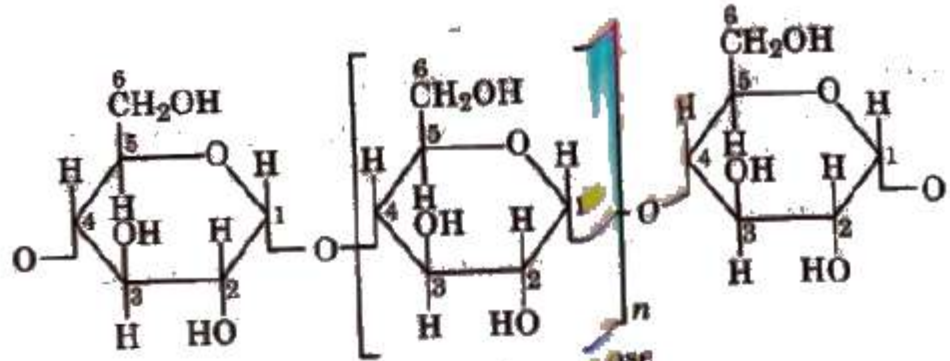
$$(C_{18}H_{32}O_{16}) + 2H_2O \xrightarrow{H^+} \text{Glucose} + \text{Fructose} + \text{Galactose}$$

Polysaccharides
These are polymers of monosaccharides. Examples are starch, cellulose, glycogen, etc.

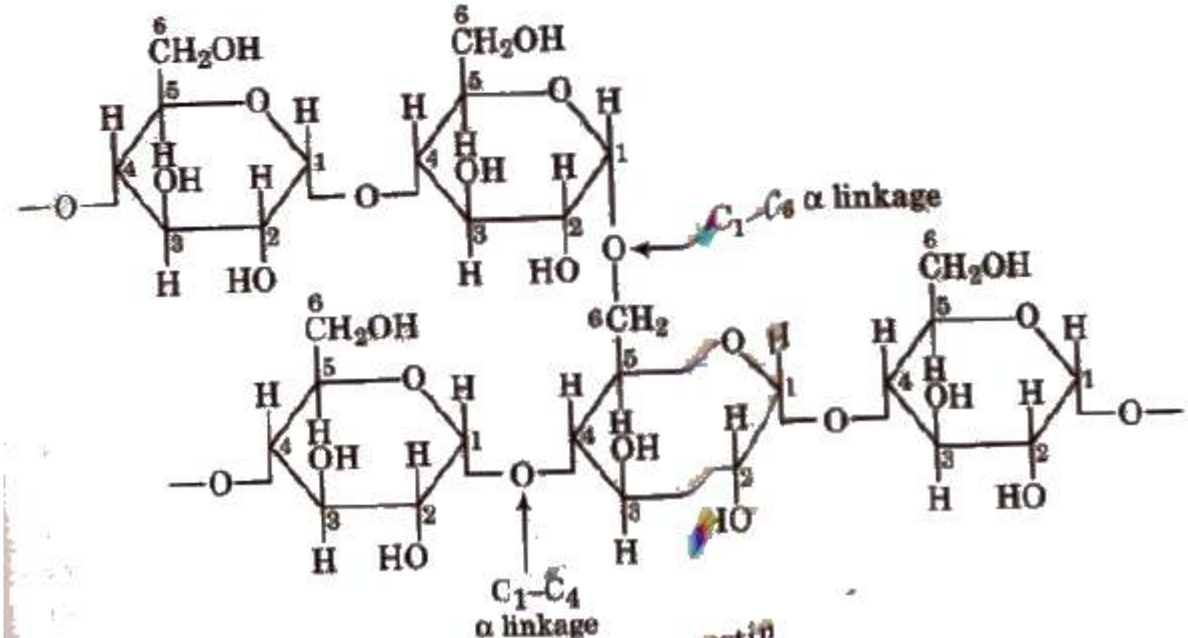
1. Starch, $(C_6H_{10}O_5)_N$
It is a polymer of a-glucose and a major reserve food in plants. It turns blue with iodine. It is a mixture of two components:

1. Amylose (20%), an unbranched water soluble polymer.
2. Amylopectin (80%), a branched water insoluble polymer.

Sources of starch are potatoes, wheat, rice, maize, etc.



Structure of amylose

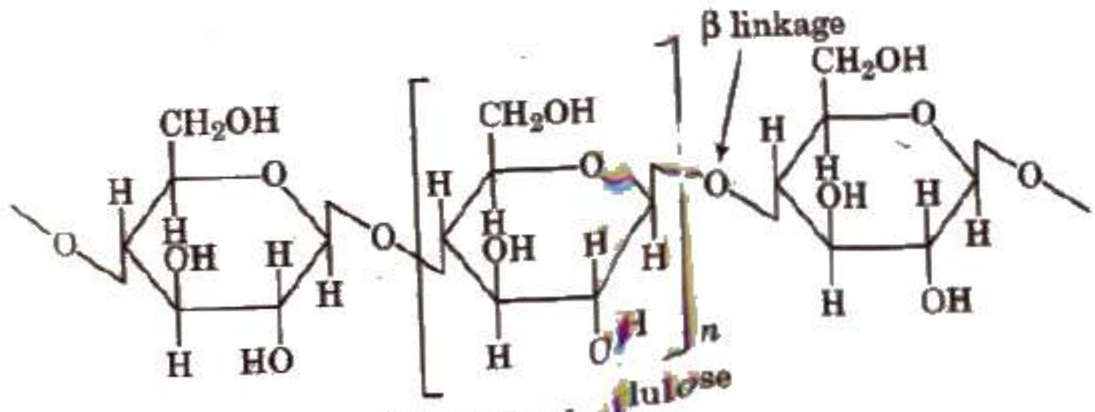


Structures of amylopectin

2. Cellulose, $(C_6H_{10}O_5)_n$

It is the most abundant and structural, polysaccharide of plants. It is important food source of some animals It is a polymer of D (+) β-glucose.

The chief sources of cellulose are wood (Contains 50% cellulose rest being lignin, resins, etc) and cotton (contains 90% cellulose rest being fats and waxes).



Structure of cellulose

Several materials are obtained from cellulose:

1. **Mercerised cotton** Cellulose treated with cone. sodium hydroxide solution acquire silky lustre. It is called mercerissd cotton.
2. **Gun cotton** It is completely nitrated cellulose (cellulose nitrate), highly explosive in nature and is used in the manufacture of smokeless gun powder, called blasting gelatin.
3. **Cellulose acetate** It is used for making acetate rayon and motion picture films.
4. **Cellulosexanthate** It is obtained by treating cellulose with sodium hydroxide and carbon disulphide and is the basic material for VISCOSE rayon.

Oligosaccharides and heteropolysaccharides are also called heteropolysaccharides.

Reducing and Non-reducing sugars

Based upon reducing and non-reducing properties, carbohydrates are classified as reducing and non-reducing sugars. Carbohydrates reducing Fehling reagent or Tollen's reagent are termed as reducing carbohydrates. e.g., All monosaccharides and disaccharides (except sucrose). But carbohydrates which do not reduce such reagents are known as non-reducing carbohydrates. e.g., sucrose and polysaccharides.

Sugars and Non-sugars

On the basis of their, taste, carbohydrates are classified as sugars and non-sugars. The monosaccharides and oligosaccharides having sweet taste are collectively known as sugars. Polysaccharides which are insoluble in water and not sweet in taste, are non-sugars.

Glucose

Dextrose, grape sugar, corn sugar, blood sugar ($C_6H_{12}O_6$).

Manufacture

By hydrolysis of starch with hot dil mineral acids and by hydrolysis of sucrose.

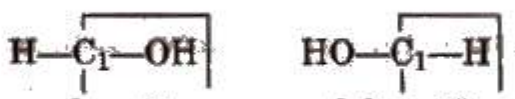
$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{starch or cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\text{393 K; 2-3 bar}]{H^+} \underset{\text{glucose}}{n\,C_6H_{12}O_6}$$

Extra glucose is stored in liver as glycogen.

α and β glucose

In intermolecular hemiacetal formation (cyclic structure), -CHO is converted into -CHOH which can have two configurations as shown below.



α-form (i) β-form (ii)

Glucose having (i) configuration about C_1 is the α-glucose and having (ii) configuration about C_1 is β-glucose.

The carbon C_1 is known as anomeric carbon and these compounds are called anomers. Both the forms are optically active. ex-D-glucosehas specific rotation +111.5° and β-D-glucose has specific rotation + 19.5°.

Mutarotation

When either of the two forms of glucose is dissolved in water, there is a spontaneous change in specific rotation till the equilibrium value of +52.5°. This is known as mutarotation.

$$\underset{+111.5^\circ}{\alpha\text{-D(+) Glucose}} \rightleftharpoons \underset{+52.5^\circ}{\text{Equilibrium mixture}} \rightleftharpoons \underset{+19.5^\circ}{\beta\text{-D-(+) Glucose}}$$

Properties of glucose

Glucose has one aldehyde group, one primary hydroxyl ($-CH_2OH$) and four secondary hydroxyl (-CHOH) groups and gives the following reactions:

(i) **Glucose on acetylation with acetic anhydride gives a pentaacetate confirming the presence of five hydroxyl groups in glucose.**

$$\underset{\text{glucose}}{\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}} + 5(CH_3CO)_2O \longrightarrow \underset{\text{pentacetyl glucose}}{\begin{array}{c} CHO \\ | \\ (CHOCOCH_3)_4 \\ | \\ CH_2OCOCH_3 \end{array}} + 5CH_3COOH$$

(ii) **Glucose reacts with hydroxylamine to give monoxime and adds with a molecule of hydrogen cyanide to give a cyanohydrin.**

$$\underset{\text{glucose}}{CH_2OH(CHOH)_4CHO} \xrightarrow{HCN} \underset{\text{glucose cyanohydrin}}{CH_2OH(CHOH)_4CH{<}^{OH}_{CN}}$$

$$\xrightarrow[-H_2O]{NH_2OH} \underset{\text{glucose oxime}}{CH_2OH(CHOH)_4\,CH{=}NOH}$$

These reactions confirm the presence ofa carbonyl group in glucose.

(iii) Glucose reduces ammoniacal silver nitrate solution (Tollen’s reagent) to metallic silver and also Fehling’S solution or Benedict solution to reddish brown cuprous oxide (Cu_2O) and itself gets oxidised to gluconic acid. This confirms the presence of an aldehydic group in glucose.
(iv) With mild oxidising agent like bromine water, glucose is oxidised to gluconic acid. Glucose on oxidation with nitric acid gives saccharic acid.

$$HOOC{-}(CHOH)_4{-}COOH \xleftarrow{HNO_3} HOCH_2(CHOH)_4CHO$$

saccharic acid — glucose

$$HOCH_2(CHOH)_4CHO \xrightarrow{Br_2/H_2O} HOCH_2{-}(CHOH)_4{-}COOH$$

gluconic acid

(v) Glucose on prolonged heating with HI forms *n*-hexane, suggesting that all the 6 carbon atoms in glucose are linked linearly.

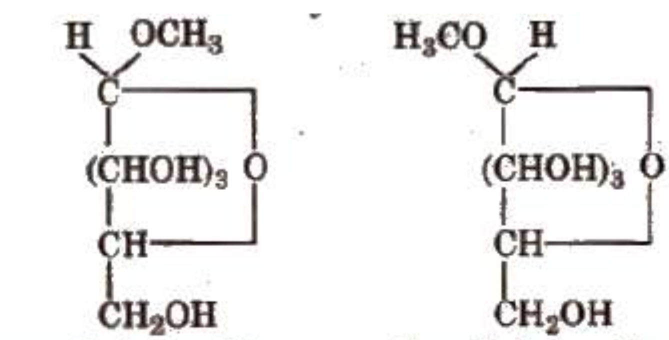
$$HOCH_2{-}(CHOH)_4{-}CHO \xrightarrow{HI,\ \Delta} H_3C{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

However, with Na/Hg and water, glucose is reduced to sorbitol $HOH_2C(CHOH)_4CH_2OH$.

(vi) D-glucose reacts with three molecules of phenyl hydrazine to give osazone (glucosazone).

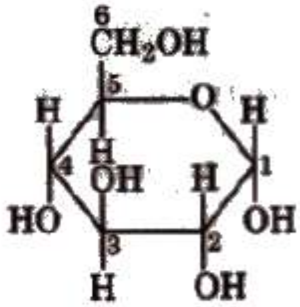
$$\begin{array}{c} CHO \\ | \\ CHOH \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \\ \text{glucose} \end{array} \xrightarrow[-2H_2O]{3C_6H_5NHNH_2} \begin{array}{l} CH{=}NNHC_6H_5 \\ | \\ C{=}N\cdot NHC_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \\ \text{glucosazone} \end{array}$$

(vii) Glucose on reaction with methyl alcohol in the presence of dry HCl(g) forms α and β-methyl glycosides. The reaction occurs only at the OH of hemiacetylic carbon.

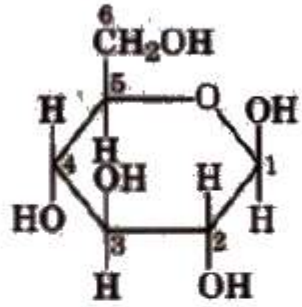


α-methyl glucoside β-methyl glucoside

Cyclic structure of glucose Given by Haworth and Hirst.

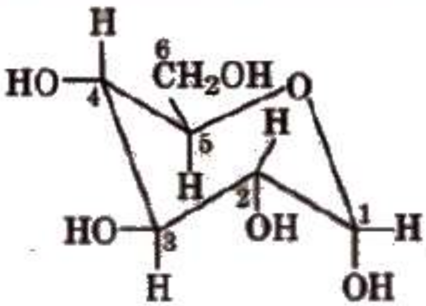


α-D (+) glucose

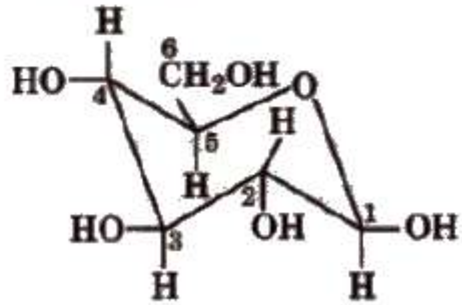


β-D (+) glucose

Glucose is sometimes illustrated as a chair form :



α-anomer



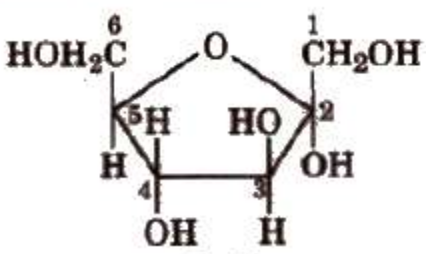
β-anomer

Fructose Fruit Sugar ($C_6H_{12}O_6$)
Manufacture
By hydrolysis of inulin.

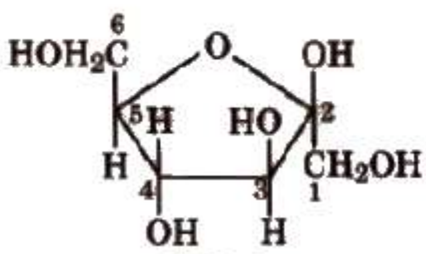
$$\underset{\text{inulin}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H^+} \underset{\text{fructose}}{nC_6H_{12}O_6}$$

Structure

Fructose has furanose structure, *i.e.*, ring structure consisting of four C atoms and one O atom.



α-D (–)
fructofuranose



β-D (–)
fructofuranose

α and β-fructose
The two forms have different configuration about C_2.

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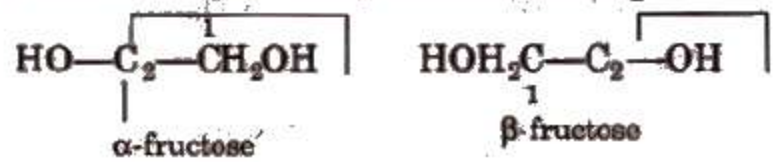


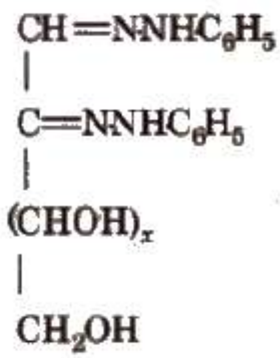
Fructose does not reduce Br_2 water.

Epimers

Monosaccharides differing in configuration at a carbon other than anomeric carbon are called epimers, e.g., glucose and galactose differ in configuration at C_4, hence called epimers.

Osazones

Monosaccharides and reducing disaccharides react with excess of phenyl hydrazine to form crystalline substances of the structure



It is known as osazones glucose and fructose give same osazone.

Molisch Test for Carbohydrates

In aqueous solution of compound add solution of α-naphthol in alcohol and then cone. H_2SO_4 along the walls of the test tube. Purple coloured ring is obtained at the junction.

Relative Sweeteness of Some Sugars

Cane sugar is assumed to have a sweeteness of 10. The relative sweeteness of other sugars is

Lactose	:	1.6	Invert sugar : 12.6
Fructose	:	17.3	Maltose : 3.2
Saccharin	:	300 (an artificial sweetener)	
Glucose	:	7.4	

Amino Acids

The compounds containing amino group ($-NH_2$) and carboxylic group (-COOH) are called amino acids.

General formula
$$R-\underset{\underset{NH_2}{|}}{CH}-COOH$$

α-amino acid

R = H, alkyl or aryl group. Except glycine ($H_2N.CH_2COOH$), others are optically active in nature.

Classification of Amino Acids

(a) **α, β, γ-amino acids** Depending upon the position of $-NH_2$ *wrt* $-COOH$ group.

(b) **Neutral** Having one $-NH_2$ and one $-COOH$, *e.g.*, $NH_2 \cdot CH_2 \cdot COOH$ (glycine).

(c) **Acidic** Having one $-NH_2$ and two $-COOH$, *e.g.*,

$$HOOC \cdot CH_2 \cdot \overset{\overset{NH_2}{|}}{CH}-COOH \text{ (aspartic acid)}$$

(d) **Basic** Having two or more $-NH_2$ and one $-COOH$, *e.g.*,

$$H_2N(CH_2)_4-\overset{\overset{NH_2}{|}}{CH}-COOH \text{ (lysine).}$$

Essential and Non-essential Amino Acids

Human body can synthesise ten amino acids, called non-essential amino acids. The remaining ten amino acids required for protein synthesis are not synthesised by body and are called essential amino acids. They are

1. Phenylalanine
2. Histidine
3. Tryptophan
4. Valine
5. Methionine
6. Threonine
7. Arginine
8. Leucine
9. Isoleucine
10. Lysine

Nomenclature

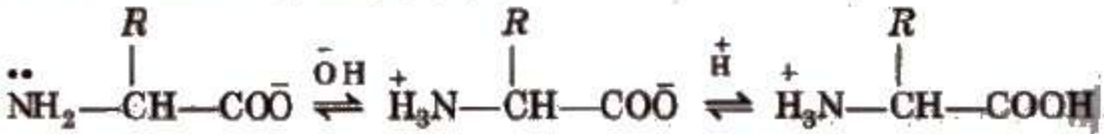
They are known by their common names and abbreviated by first three letters of their common names e.g., glycine as ‘gly’ and alanine a as ‘ala’.

Configuration of α-Amino Acids

L-amino acid (NH_2 on LHS)   D-amino acid (NH_2 on RHS)

Naturally occurring α-amino acids are L-amino acids. D-amino acids occur in some antibiotics and bacterial cell walls.

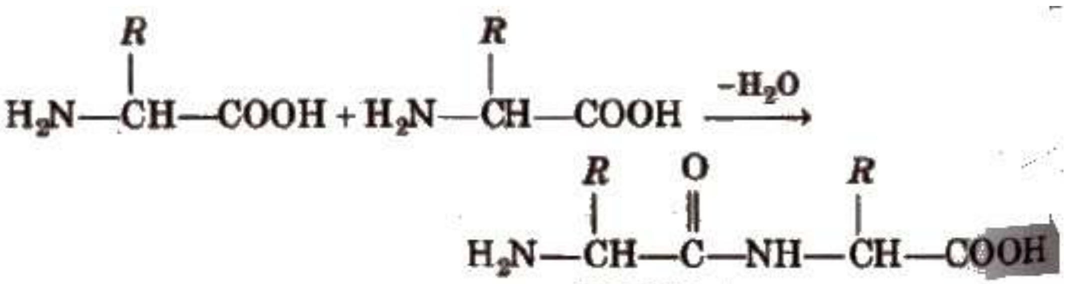
Structure of Amino Acids



as anion (high pH)   Zwitter ion, (isoelectric point)   as cation (low pH)

Peptides

Peptides are condensation products of two or more amino acids.



dipeptide

$-\overset{\displaystyle O}{\overset{\|}{C}}-NH-$ is known as peptide linkage and C—N as a peptide bond.

Two molecules of different amino acids can form two dipeptides.Three molecules of different amino acids can give six tripeptides.

Dipeptide has only one peptide bond, tripeptide has two peptide bonds and so on. Thus, a polypeptide made up of n-amino acids has (n – 1) peptide bonds.

Polypeptides
Condensation Products of many amino acids (‘In P xiucts of many amino acids (≈ 10000) is known as polypeptide and those polypeptides which have molecular mass above than 10000 are called proteins.

Proteins
They are linear polymers of a-amino acids.

Structure of Proteins
(a) Primary structure
It simply reveals the sequence of amino acids.

(b) Secondary structure α-helix structure maintained by hydrogen bonds or β-pleated sheet structure when R is small group.
(c) Tertiary structure The folding and superimposition of polypeptide chains forms a compact globular shape, termed as tertiary structure. It is stabilised by covalent, ionic, hydrogen and disulphide bonds.
The precise arrangement constitutes the quaternary structure.

Classification on the Basis of Hydrolysis Products
(i) Simple These yield only a-amino acids upon hydrolysis.
e.g., albumin.

(ii) Conjugated proteins These yield α-amino acids and non-protein part, called prosthetic group.

Protein	Prosthetic group
Nucleoproteins	Nucleic acid
Phospho proteins	Phosphoric acid
Glycoproteins	Carbohydrates
Metalioproteins	Metals
Lipoproteins	Lipids

(iii) Derived proteins These are obtained by partial hydrolysis of simple or conjugated proteins.
Proteins → Proteoses → Peptones → Polypeptides

Classification on the Basis Functions
1. **Structural proteins** Fibrous proteins
2. **Enzymes** Serve as biological catalyst e.g., pepsin, trypsin etc.
3. **Hormones** Insulin
4. **Contractile proteins** Found in muscles, e.g., myosin, actin.
5. **Antibodies Gamma** globulins present in blood.
6. **Blood protein** Albumms, haemoglobin and fibrinogen.

Haemoglobin is a globular protein. Its prosthetic group is heme. It Contains 574 amino acid units distributed in four polypeptide chains.

Two chains containing 141 amino acid residues each are called α-chains and the two chains containing 146 amino acid residues are called β-chains.

Sickle cell anaemia is caused by defective haemoglobin obtained by replacing only one amino acid, i.e., glutamic acid by valine.

Denaturation of Proteins

The process that changes the three dimensional structure of native proteins is called denaturation of proteins. It can be caused by Change in pH, addition of electrolyte, heating or addition of solvent like water, alcohol or acetone.

Tests of Proteins

(i) Biuret Test

Protein solution + NaOH + dil. $CuSO_4$ → pink or violet colour.

(ii) Millon's Test

Protein solution + Millon's reagent → pink colour

Millon's reagent is solution of mercuric nitrate and nitrite in nitric acid containing traces of nitrous acid.

(iii) Iodine reaction

Protein solution + iodine in potassium iodide solution → yellow colour.

(iv)Xanthoprotic test

Protein solution + conc. HNO_3 → yellow colour $\xrightarrow{NaOH}$ orange colour.

Enzyme

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