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Biomolecules

Biomolecules, also called biological molecule, any of numerous substance that are produced by cells and living organisms. Biomolecules have a wide range of sizes and structures and perform a vast array of functions.

The four major types of biomolecules are carbohydrates, lipids, nucleic acids and proteins.

Carbohydrates

These are naturally occurring organic substances, present in both plants and animals. Initially these are produced in plants by a process known as **photosynthesis**. In this process, sunlight is absorbed by a green pigment called **chlorophyll** (present in the green plants).

The photochemical energy obtained is used to convert carbon dioxide and water into carbohydrates and oxygen.

$$x \text{CO}_2 + y \text{H}_2\text{O} \xrightarrow{\text{Sunlight}} \text{C}_x(\text{H}_2\text{O})_y + x \text{O}_2$$

Animals do not synthesis carbohydrates.

Earlier, it was believed that carbohydrates are the substances with general formula $C_x(H_2O)_y$, i.e. hydrates of carbon. However, a number of compounds have been discovered which are carbohydrates by chemical behaviour, but do not possess the formula $C_x(H_2O)_y$.

e.g. Rhamnose $(C_6H_{12}O_5)$ and deoxyribose $(C_5H_{10}O_4)$.

Similarly, all compounds possessing to the formula $C_x(H_2O)_y$ are not necessarily carbohydrates, e.g. HCHO, CH_3COOH etc. Hence, this definition has been changed now.

According to modern definition "optically active polyhydroxy aldehydes or polyhydroxy ketones or compounds which can be hydrolysed to one of these are called **carbohydrates**."

IN THIS CHAPTER

- Carbohydrates
- α-Amino Acids
- Proteins
- Enzymes
- Vitamins
- Nucleic Acids

Classification of Carbohydrates or Saccharides

On the basis of number of simplest molecules (monomers) produced upon hydrolysis, carbohydrates are classified as follows



On the basis of reducing activity, carbohydrates can be classified as follows

- (i) **Reducing sugars** These are contain free functional group and reduce Fehling's solution and Tollen's reagent. These include all the monosaccharides.
- (ii) Non-reducing sugars These have bonded functional groups and cannot reduce Fehling's solution or Tollen's reagent. These include oligosaccharides and polysaccharides.

Monosaccharides : General Features

These are the simplest carbohydrates which cannot be hydrolysed to smaller molecules. All these are polyhydroxy compounds containing either an aldehydic (—CHO) group, i.e. **aldoses** (the aldehydic group being monovalent is present at the end of the chain) or a ketonic (>C=O) group, i.e. **ketoses** (the ketonic group is present next to terminal carbon atom).

The simplest monosaccharides are **trioses** such as glyceraldehyde (aldose), dihydroxyacetone (ketose) and aldotetrose such as erythrose and threose.



Note Ketotriose are not considered as a monosaccharide because it is optically inactive.

However, the naturally occurring monosaccharides are pentoses (5C-atoms) and hexoses (6C-atoms). Out of these, the most common are ribose, 2-deoxyribose, glucose (aldoses) and fructose (ketose).



Configuration of Carbohydrates

Glyceraldehyde is a simplest saccharide exists in two enantiomeric forms.



These two forms serve as a reference point for designating and drawing all other monosaccharides.

These monosaccharides having the same configuration as of D-glyceraldehyde at the asymmetric carbon, which is adjacent to — CH_2OH group but the most distant from carbonyl group (aldehyde or ketone group) are designated as D-form and those having the same configuration as of L-glyceraldehyde are designated as L-forms. The natural glucose and fructose exists in D-forms.

Epimers

A more selective term, **epimer** is used to designate diastereomers that differ in configuration at only one chiral centre.

Thus, glucose is epimeric with D-(+)-mannose and D-(+)-galactose as shown below



Ring Structure of Monosaccharides

The ring form of monosaccharides is favoured in aqueous solution. Structures of pentoses and hexoses are cyclic involving five or six membered rings containing an oxygen atom.

The five membered ring containing an oxygen atom because of its similarity with **furan** is called the **furanose form** and the six membered ring containing an oxygen atom because of its similarity with **pyran** is called the **pyranose form**.



During ring formation, reaction between an aldehyde and an alcohol forms a **hemiacetal**. A **hemiketal** is an analogous product formed by reaction of a ketone with an alcohol.

Formation of a hemiacetal or a hemiketal,



(where, R' = H or R)

If aldehyde (i.e. R' = H) \longrightarrow hemiacetal,

If ketone (i.e. R' = R) \longrightarrow hemiketal

As a result of ring formation

Carbon number 1-(C₁) becomes asymmetric (chiral) and hence, monosaccharides exist in two stereoisomeric forms, α and β -form. In the α -form, the —OH at C₁ is towards right while in the β -form, the —OH at C₁ is towards left.



A pair of stereoisomers which differ in configuration only around C_1 carbon are called **anomers** and the C_1 is called the **anomeric carbon** (or glycosidic carbon).

Some important monosaccharides are as follows

1. **Glucose** $(C_6H_{12}O_6)$

Glucose is a monosaccharide, aldohexose and reducing sugar. It is found in ripe grapes (hence named grape-sugar), honey and most sweet fruits. It is also a normal constituent of blood and found in the urine of diabetics.

The blood normally contains 65 to 110 mg of glucose per 100 mL (hence named blood sugar). In the combined state, it occurs in glucosides, disaccharides and polysaccharides.

Methods of Preparation

 (i) From sucrose Cane sugar (sucrose) on acid hydrolysis in the presence of alcohol, gives a mixture of glucose and fructose.

$$\begin{array}{c} C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6 \\ \text{Sucrose} & \text{Glucose} & \text{Fructose} \end{array}$$

Glucose being less soluble in alcohol than fructose separates out by crystallising on cooling (fractional crystallisation).

(ii) From starch Glucose is obtained on a large scale by the hydrolysis of starch with dilute H_2SO_4 or dilute HCl under pressure.

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

After neutralisation with $CaCO_3$ and filteration, filterate is decolourised by boiling with animal charcoal and then concentrated under reduced pressure and finally crystallised.

(iii) From lactose or maltose

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$$\begin{array}{c} C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6\\ Lactose & Glucose \\ \end{array} \\ \begin{array}{c} C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} 2C_6H_{12}O_6\\ Maltose & Glucose \end{array}$$

Physical Properties of Glucose

- Glucose is a white crystalline solid (m.p. 146°C). It also occurs in the form of monohydrate, $C_6H_{12}O_6 \cdot H_2O$ (m.p. 86°C).
- Glucose is readily soluble in water, sparingly soluble in alcohol and insoluble in ether.
- It is optically active and dextrorotatory (hence named dextrose). It shows mutarotation (The change in specific rotation of an optically active compound in solution with time, to an equilibrium value is called **mutarotation**)
- It has a very sweet taste but about three fourth as sweet as sucrose (cane-sugar).

Chemical Reactions of Glucose

- (i) Reduction
 - (a) On reduction with ${\rm NaBH}_4$ or Na-Hg, glucose yields sorbitol.

$$\begin{array}{c} \text{CHO} & \text{CH}_2\text{OH} \\ (\text{CHOH})_4 + 2[\text{H}] & \xrightarrow[\text{NaBH}_4 \text{ or}]{} & \text{NaBH}_4 \text{ or} \\ | & \text{CH}_2\text{OH} \\ \text{CH}_2\text{OH} & \text{CH}_2\text{OH} \\ \text{Glucose} & \text{Sorbitol} \end{array}$$

(b) On reduction with HI and red P, it gives a mixture of *n*-hexane and 2-iodohexane.

$$\begin{array}{ccc} \mathrm{C_6H_{12}O_6} & \xrightarrow{\mathrm{Red} \ P/\mathrm{HI}} & \mathrm{CH_3CH_2CH_2CH_2CH_2CH_3} \\ & & & & \\ \mathrm{Glucose} & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\$$

(ii) **Reaction with hydroxylamine** Glucose forms glucose oxime with hydroxylamine.

$$\begin{array}{ccc} CHO & CH = NOH \\ | & & \\ (CHOH)_4 \xrightarrow{NH_2OH} & | \\ | & \\ CH_2OH & CH_2OH \\ Glucose & Glucose oxime \end{array}$$

(iii) **Reaction with hydrogen cyanide** An addition product, glucose cyanohydrin is formed.



(iv) **Reaction with phenyl hydrazine** When treated with equimolar quantities of phenyl hydrazine, glucose yields a phenyl hydrazone.



However, when glucose is warmed with excess of phenyl hydrazine a crystalline product, glucosazone is formed.



Osazone formation is given by only α -hydroxy aldehyde and α -hydroxy ketones. (glucose, fructose and mannose form the same osazone, i.e. glucosazone). Glucosazone is a yellow crystalline solid, sparingly soluble in water and has sharp melting point. Due to these properties, it is used to identify glucose.

- (v) **Oxidation**
 - (a) With bromine water, glucose gives gluconic acid.

$$\begin{array}{ccc} \mathrm{CHO} & \mathrm{COOH} \\ | & & | \\ (\mathrm{CHOH})_4 + [\mathrm{O}] \xrightarrow{\mathrm{Br}_2 \cdot \mathrm{H}_2 \mathrm{O}} & (\mathrm{CHOH})_4 \\ | & & | \\ \mathrm{CH}_2 \mathrm{OH} & & \mathrm{CH}_2 \mathrm{OH} \\ \mathrm{Glucose} & & \mathrm{Gluconic acid} \end{array}$$

(b) Glucose on oxidation with Fehling's solution and Tollen's reagent gives coloured precipitate and gluconic acid.

$$\begin{array}{ccc} \text{CHO} & \text{COOH} \\ | & | \\ (\text{CHOH})_4 + \text{Cu}^{2^+} \text{ or } \text{Ag}^+ \longrightarrow & (\text{CHOH})_4 + \text{Cu}_2 \text{O} \downarrow \\ | & \text{Red ppt.} \\ | & \text{Red ppt.} \\ \text{CH}_2 \text{OH} & \text{CH}_2 \text{OH} & \text{or} \\ \text{Glucose} & \text{Gluconic acid} & \text{Ag} \downarrow \\ & & \text{Silver mirror} \end{array}$$

(c) On oxidation with strong acids like nitric acid, glucose gives **glucaric (saccharic) acid**.

$$\begin{array}{c} \text{CHO} & \text{COOH} \\ | \\ (\text{CHOH})_4 + 3[\text{O}] & \xrightarrow{\text{HNO}_3} & (\text{CHOH})_4 \\ | \\ \text{CH}_2\text{OH} & \text{COOH} \\ \text{Glucose} & & \text{Glucaric acid} \\ (\text{saccharic acid}) \end{array}$$

(vi) **Reaction with acetyl chloride** Glucose reacts with acetyl chloride to form glucose **penta-acetate**.

$$\begin{array}{ccc} CHO & CHO \\ | \\ (CHOH)_4 + 5CH_3COCl & \xrightarrow{ZnCl_2} & (CHOCOH_3)_4 + 5HCl \\ | \\ CH_2OH & CH_2OCOCH_3 \\ Glucose & Glucose \\ pentaacetate \end{array}$$

(vii) Reaction with PCl_5 Glucose reacts with PCl_5 to form penta-chloroglucose.

$$\begin{array}{ccc} \mathrm{CHO} & \mathrm{CHO} \\ | & | \\ (\mathrm{CHOH})_4 + 5\mathrm{PCl}_5 \longrightarrow & (\mathrm{CHCl})_4 & + 5\mathrm{POCl}_3 \\ | & | & + 5\mathrm{HCl} \\ \mathrm{CH}_2\mathrm{OH} & \mathrm{CH}_2\mathrm{Cl} \\ \mathrm{Glucose} & & \mathrm{Penta-chloroglucose} \\ & & (\mathrm{glucose \ pentachloride}) \end{array}$$

(viii) **Reaction with methanol** D-(+)-glucose treated with methanol in presence of dry HCl gas, reacts with its one mole only and yields monomethyl ether which is actually a mixture of α - and β - forms indicating that one of the —OH group is different from others.

TTO

$$C_{6}H_{11}O_{5} - \underbrace{OH + H}OCH_{3} \xrightarrow{Dry HCl} C_{6}H_{11}O_{5}OCH_{3} + H_{2}O$$

$$\begin{array}{c} \alpha \cdot \text{and}\beta \cdot \text{methyl} \\ \text{glucoside} \end{array}$$



(ix) **Reaction with conc. HCl** On treatment with conc. HCl, glucose forms hydroxyl methyl furfural which further produces laevulic acid.



(x) **Reaction with metallic hydroxides** Glucose reacts with metallic hydroxides like $Ca(OH)_2$, $Ba(OH)_2$, $Sr(OH)_2$ etc., to form metallic glucosates, which are soluble in water.

 $C_6H_{11}O_5 - OH + HO - Ca - OH \rightarrow$

$$C_6H_{11}O_5 - O - Ca - OH + H_2O$$

Calcium glucosate

(xi) **Reaction with periodic acid** Periodic acid splits glucose into formic acid and formaldehyde.

$$(CHO) (CHOH)_4 \xrightarrow{HIO_4 \text{ or } H_5IO_6} 5HCOOH + HCHO Formic acid + HCHO Formic acid + HCHO Glucose}$$

(xii) **Fermentation** Glucose when fermented by zymase, yields ethanol.

$$\begin{array}{ccc} C_{6}H_{12}O_{6} & \xrightarrow{Zymase} & 2C_{2}H_{5}OH + 2CO_{2} \uparrow \\ Glucose & & Ethanol \end{array}$$

(xiii) **Dehydration** On strong heating or on treating with warm conc. H_2SO_4 , glucose is dehydrated to give a black mass (sugar carbon) or black carbon.

$$C_6H_{12}O_6 \xrightarrow{\text{Conc. } H_2SO_4} 6C + 6H_2O$$

(xiv) **Reaction with alkalies** When warmed with conc. alkali, glucose first turns yellow, then brown and finally gives a resinous mass.

A dilute solution of glucose when warmed with dilute alkali is converted into an optically inactive solution of D-(+)-glucose, D-(+)-mannose and D-(-)-fructose. This is known as **Lobry-de-Bruyn-van Ekenstein rearrangement**,



Structure of Glucose

- The molecular formula of glucose is found to be $C_6 H_{12} O_6.$
- Formation of 2-iodohexane and *n*-hexane (Reaction (i)-b) indicates that six carbon atoms in glucose are present in a straight chain.
- Formation of glucose penta acetate Reaction-(vi) indicates the presence of five —OH groups. Since, it exists as a stable compound, five —OH groups should be attached to different carbon atoms.
- Formation of glucose oxime and glucose cyanohydrin (reaction (iii) and (iv)) respectively confirms the presence of carbonyl group in glucose.
- Formation of gluconic acid in presence of mild oxidising agent like $\rm Br_2/H_2O$ (Reaction (ii)-a) indicates that glucose contains an aldehydic group. Since aldehydic group is monovalent, it must be present on the end of the chain.

On the basis of point discussed above, it was suggested that glucose has an **open chain structure**.

The open chain structure, for the first time, was proposed by **Baeyer**. It contains one —CHO group, one 1° alcoholic group and four 2° alcoholic groups as,



There are four dissimilar chiral carbon atoms in the molecule, but a definite configuration to these asymmetric centres has not been assigned.

The configuration of D-glucose was proved by **Emil Fischer.**

$$\begin{array}{c} H & 1 \\ |2 \\ H - C - OH \\ |3 \\ HO - C - H \\ |4 \\ H - C - OH \\ |5 \\ H - C - OH \\ 6 \\ CH_2OH \\ D - (+) - glucose \end{array}$$

Evidence Against Open Chain Structure

However, there are some evidences which do not support the open chain structure of glucose. These are

- Even though an aldehyde group is present, the glucose does not react with $NaHSO_3$, NH_3 , 2,4-DNP and Grignard reagent.
- Glucose does not respond to Schiff's reagent test.
- Glucose penta-acetate does not react with hydroxylamine. It indicates the absence of free —CHO group in glucose.
- Glucose exists in two stereoisomeric forms, i.e. α and β anomers.

 α -glucose (m.p. 146°C) with specific rotation +111° is obtained by crystallising glucose from alcohol or acetic acid solution whereas β -glucose (m.p. 150°C) with specific rotation 19.2° is obtained by crystallising glucose from pyridine solution.

- An aqueous solution of glucose shows mutarotation, i.e. if either of the two forms is dissolved in water and allowed to stand, the specific rotation of the solution changes gradually until a final value of $+52.5^{\circ}$ is reached. It means that the specific rotation gradually decreases from $+111^{\circ}$ to $+52.5^{\circ}$ in case of α -glucose and increases from $+19.2^{\circ}$ to $+52.5^{\circ}$ in case of β -glucose. This phenomena is known as **mutarotation**.
- **Cyclic structure of glucose** This behaviour could not be explained by the open chain structure for glucose. It was proposed that one of the —OH groups may add to the —CHO group to form a cyclic hemiacetal structure.

According to **Fischer**, glucose forms a stable cyclic hemiacetal between —CHO group and the —OH group of the fifth carbon atom in pyranose structure.



Fischer projections are not the best way to show the structure of a glucose. The cyclic structure of glucose is more correctly represented by **Haworth projection formula**.



The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C-1 called **anomeric carbon**. Such isomers, i.e. α -form and β -form are called **anomers**.

Sametimes, glucose is illustrated as a **chair form** because it is a more accurate representation of bond-angles of the molecule, (Reeves, 1950).



In β -anomer, the glycosidic hydroxyl group is equatorial and as a general rule, the configuration with greatest number of large groups in equatorial orientation is the most stable form.

Thus, β -anomer predominates in the equilibrium mixture. The **boat form** of glucose is unstable.

2. Fructose

The important ketohexose is D-(–)-fructose (also known as **laevulose**). In the free state, it is present along with honey and most sweet fruits (berries, melons etc.), hence named as **fruit sugar**.

In the combined state, fructose is present in sucrose and insulin. It is the sweetest monosaccharide.

Some methods of preparation of fructose are

(i) By hydrolysis of cane sugar with dilute acids.

$$\begin{array}{ccc} \mathrm{C}_{12}\mathrm{H}_{22}\mathrm{O}_{11} \ + \ \mathrm{H}_{2}\mathrm{O} \ & \stackrel{\mathrm{H}^+,\,\Delta}{\longrightarrow} \ & \mathrm{C}_{6}\mathrm{H}_{12}\mathrm{O}_{6} \ + \ & \mathrm{C}_{6}\mathrm{H}_{12}\mathrm{O}_{6} \\ \mathrm{Cane\ sugar} \ & \mathrm{D}\text{-}(+)\text{-}\mathrm{glucose} \ & \mathrm{D}\text{-}(-)\text{-}\mathrm{fructose} \end{array}$$

The solution having equal molecules of D-glucose and D-fructose is termed as **invert sugar** and the process is known as **inversion**.

(ii) By calcium fructosate

$$C_6H_{11}O_5 \longrightarrow Ca \longrightarrow Ca \longrightarrow C_6H_{12}O_6 + CaCO_3$$

Fructose

(iii) From insulin

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{HCl}} nC_6H_{12}O_6$$

(Insulin is a polysaccharide which occurs in dahlia tubers and Jerusalem artichokes).

Physical Properties

- Fructose is colourless crystalline compound (m.p. 102°).
- It is soluble in water and insoluble in benzene and ether.
- It is less soluble in water than glucose. Like glucose, it also shows **mutarotation**.

Chemical Properties

The chemical reactions of fructose are almost similar to those of glucose. The only different behaviour are oxidation and reduction. These are as follows

(i) **Reduction** On reduction with $NaBH_4$ or $Na-Hg/H_2O$, fructose forms a mixture of sorbitol and mannitol.



Note The reduction of glucose with $NaBH_4$ forms D-sorbitol while that of fructose forms a mixture of D-sorbitol and D-mannitol (they differ in configuration).

(ii) Oxidation Fructose is not oxidised by mild oxidising agent like Br₂ water. However, when oxidised with nitric acid, fructose is converted into a mixture of trihydroxy glutaric, glycollic and tartaric acids.



Since a mixture of acids each containing fewer carbon atoms than fructose is obtained, the carbonyl group in fructose must be a ketonic group.

(iii) Reducing nature Unlike ketones, fructose can reduce Fehling's solution and Tollen's reagent. This is probably due to formation of an equilibrium mixture of glucose, mannose and fructose in alkaline solution.

(iv) Action of conc. HCl

$$\begin{array}{ccc} C_{6}H_{12}O_{6} & \xrightarrow{HCl} & H_{3}C \cdot CO \cdot CH_{2} \cdot CH_{2} \cdot COOH + \begin{array}{c} HCOOH \\ Formic \ acid \end{array} \\ \begin{array}{c} Laevulinic \ acid \end{array} + H_{2}O \end{array}$$

Structure of Fructose

Some major structure of fructose are discussed below

1. Open Chain Structure

The open chain structure of fructose may be represented as below

$$\begin{array}{c} \mathrm{CH}_2 - \mathrm{C} - \overset{*}{\mathrm{C}} \mathrm{H} - \overset{*}{\mathrm{C}} \mathrm{H} - \overset{*}{\mathrm{C}} \mathrm{H} - \overset{*}{\mathrm{C}} \mathrm{H} - \mathrm{CH}_2 \\ | & | & | & | & | \\ \mathrm{OH} & \mathrm{O} & \mathrm{OH} & \mathrm{OH} & \mathrm{OH} & \mathrm{OH} \end{array}$$

The structure contains three asymmetric carbon atoms and eight optically active forms but only six are known. The configuration of D-(–)-fructose is



2. Cyclic Structure

Fructose also has a cyclic structure in aqueous solution, i.e. intramolecular hemiketal. It also exhibit mutarotation.



3. The Haworth Projection Formulae

The cyclic structure of D-(–)-fructose is represented as,



However, in the combined state (such as in sucrose) fructose exists in the furanose form.



In solution, fructose exists as an equilibrium mixture of 70% fructopyranose and about 22% fructofuranose as well as small amounts of the three other forms, including the acylic structure (i.e. D-(+)-glucose, D-(+)-mannose and D-(-)-fructose)

Oligosaccharides : General Features

Molecules of these carbohydrates are made up of a small number of monosaccharide units joined together by

glycosidic bonds
$$\left(\begin{array}{c} | & | \\ -C \\ -O \\ -C \\ - \end{array} \right)$$
. Glycosidic bonds are

established during the condensation of monosaccharides. The process is called dehydration.

These are further classified into disaccharides, trisaccharides, tetrasaccharides etc., depending upon the number of monosacharides, they peroxide on hydrolysis. Some important oligosaccharides are as follows

Some important ongosaccharities are as iono

1. Sucrose $(C_{12}H_{22}O_{11})$

It is commercial sugar, which is also called **cane sugar** because most of it is obtained from sugarcane (16-20%). It is also present in sugarbeet (10-15%), pineapple (10-12%), apricot banana, mango and honey. It is formed by condensation of any molecule and formations.







Properties

- It is a colourless, odourless, crystalline substance having m.p. 180°C. It is very soluble in water but insoluble in alcohol and ether. It is dextro-rotatory with a specific rotation + 66.5°.
- On hydrolysis with dilute acids or invertase or sucrose, it gives an equimolar mixture of D-(+)-glucose and D-(-)-fructose.

. . .

$$\begin{array}{c} C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Acid or}} C_6H_{12}O_6 + C_6H_{12}O_6 \\ (+)\text{-sucrose} \\ [\alpha]_D = +66.5^{\circ} \\ \end{array} \xrightarrow{\text{D-}(+)\text{-glucose}} D_{-}(-)\text{-fructose} \\ [\alpha]_D = +52.7^{\circ} \\ [\alpha]_D = -92.4^{\circ} \end{array}$$

Since, D-(–)-fructose has a greater specific rotation than D-(+)-glucose, the resulting mixture is laevorotatory. Because of this, the hydrolysis of cane sugar is known as **the inversion of cane sugar** and the mixture is known as **invert sugar**. Due to the presence of fructose, invert sugar is sweeter than sucrose. Invert sugar is used to coat chocolate. Sweetening power of common sugars : Fructose >

Invert sugar > Sucrose > Glucose > Maltose > Lactose

- On heating (200°C), sucrose melts and on cooling forms a glassy yellow solid known as **barley sugar**. When heated above its melting point, it loses water and gives a brown substance known as **caramel**. On further heating sucrose gets charred to almost pure carbon (sugar charcoal).
- Sucrose on acetylation gives sucrose octaacetate. This shows the presence of eight —OH groups in sucrose.
- Sucrose does not form oxime or osazone. It shows the absence of >C=0 group.
- Sucrose does not reduces Tollen's reagent and Fehling's solution. It shows the absence of —CHO group in sucrose.
- **Fermentation** In the presence of yeast, it yields ethanol and carbon dioxide.

$$\begin{array}{c} \mathbf{C}_{12}\mathbf{H}_{22}\mathbf{O}_{11} + \mathbf{H}_{2}\mathbf{O} & \xrightarrow{\text{Invertase}} & \mathbf{C}_{6}\mathbf{H}_{12}\mathbf{O}_{6} + \mathbf{C}_{6}\mathbf{H}_{12}\mathbf{O}_{6} \\ \mathbf{C}_{6}\mathbf{H}_{12}\mathbf{O}_{6} & \xrightarrow{\text{Zymase}} & \mathbf{2C}_{2}\mathbf{H}_{5}\mathbf{O}\mathbf{H} + \mathbf{CO}_{2} \\ \text{Glucose} & \xrightarrow{\text{Ethanol}} \end{array}$$

• With conc. H₂SO₄, sucrose loses water to give sugar charcoal (charring of sugar).

$$\begin{array}{rcl} \mathrm{C}_{12}\mathrm{H}_{22}\mathrm{O}_{11} + \mathrm{H}_{2}\mathrm{SO}_{4} & \longrightarrow & 12\mathrm{C} + 11\mathrm{H}_{2}\mathrm{O} \\ \\ \mathrm{C} + 2\mathrm{H}_{2}\mathrm{SO}_{4} & \longrightarrow & 2\mathrm{SO}_{2} + \mathrm{CO}_{2} + 2\mathrm{H}_{2}\mathrm{O} \end{array}$$

A small amount of sulphurdioxide is also observed due to reduction of the acid.

2. Lactose ($C_{12}H_{22}O_{11}$)

It occurs in the milk of all animals (milk-sugar). It is a white crystalline solid (with m.p. 203°C), soluble in water and is dextrorotatory. It is hydrolysed by dilute acid or enzyme lactose, to an equimolar mixture of D-(+)-glucose and D-(+)-galactose. Lactose is a reducing sugar, forms an oxime and osazone and undergoes mutarotation. It gets hydrolysed by emulsin also, an enzyme which specifically hydrolyses β -1,4-glycosidic linkage.



Representation of β -1,4-glycosidic linkage

3. **Maltose** ($C_{12}H_{22}O_{11}$)

It is obtained by partial hydrolysis of starch by diastase enzyme present in malt, i.e. sprouted barley seeds (hence named **maltose** or **malt sugar**).

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{Diastase}} nC_{12}H_{22}O_{11}$$

Maltose

Properties

• Maltose is a white crystalline solid (with m.p. 160°-165°C), soluble in water and dextrorotatory.



Representation of α -1,4-glycosidic linkage

• Maltose is a reducing sugar. It reduces Fehling's solution Tollen's reagent, it forms an oxime and an osazone and undergoes mutarotation. It indicates that at least one aldehyde group is free in it. (Free aldehyde group can be produced at C-1 of second glucose in solution which shows reducing property).

Example 1. What are the functional groups present in the structure of maltose ? (JEE Main 2020)

- (a) One ketal and one hemiketal
- (b) One acetal and one ketal
- (c) One acetal and one hemiacetal
- (d) Two acetals

Sol. (c) The functional groups present in the structure of maltose is one acetal and one hemiacetal. It is illustrated in following structure.



Polysaccharides : General Features

It composed of large number of monosaccharides units joined together by glycosidic linkages. These are used as food storage or structural material. Some important polysaccharide are as follows

1. Starch

It is a polymer of α -glucose. It is found in cereals, roots, tubers etc. It is the most important dietary source. It consists of two cmponents, i.e. amylose and amylopectin. Amylose is water soluble component which constitutes about 15-20% of starch. It is a long unbranched chain with 200-10000 α -D-(+)-glucose units held by C₁-C₄ glycosidic linkage.

Whereas amylopectin is insoluble in water and constitutes about 80-85% of starch. It is a

branched chain polymer of α -D-glucose units in which chain is formed by C_1 - C_4 glycosidic linkage whereas branching occurs by C_1 - C_6 glycosidic linkage.





Representation of glycosidic linkage in amylopectin and amylose

2. Cellulose

It occur exclusively in plants. It is predominant constitutent of cell wall of plant cells. It is a straight chain polysaccharide composed of β -D-glucose units joined by glycosidic linkage between C_1 of the glucose and C_4 of next glycose.



3. Glycogen

It is known as **animal starch** because its structure is similar to amylopectin and is more highly branched. It is stored in animal body and present in liver, muscles and brain. In need of glucose, enzymes break the glycogen down to glucose. It is also found in yeast and fungi.

B. α-Amino Acids

Bifunctional organic compounds containing carboxylic and amino group either at the same carbon atom or at the nearby carbon atoms are called **amino acids**. These are the monomers of proteins. Usually, amino acids have primary amino group but proline is a **secondary amine**.

Natural proteins can be broken down into about 20 different α -amino acids (19 α -amino acids and 1 α -imino acid). These molecules differ in the nature of the *R*-group attached to the alpha carbon. *R*-group can be

- An aliphatic side chain
- A hydroxyl group containing side chain
- A sulphur atom containing side chain
- A side chain containing acidic (carboxylic) group or amides group
- A side chain containing basic groups

A side chain containing aromatic ring





Stereochemistry of α -Amino Acids

With exception of glycine, all common naturally occurring α -amino acids have asymmetric α -carbon atom. The chiral amino acids found within naturally occurring proteins have only one enantiomeric form, which has the following configuration.

$$H_3 \stackrel{+}{N} \xrightarrow{COO^-} H$$

This configuration is S in all cases except for **cysteine**.

D and L-Configuration for α -amino Acids

It refers to the configuration of the α -carbon regardless of the number of asymmetric carbons in the molecule. D-amino acid has an amino group on right and hydrogen on left when —COOH group is up and side chain is at lower position in a Fischer projection of the α -carbon whereas a L-amino acid has amino group on left. Naturally occurring amino acids have L-configuration.



Classification

- I. On the basis of relative number of amino and carboxyl groups present, amino acids are classified as follows
- Acidic amino acids These are contain more number of carboxylic groups than amino groups, e.g. asp, glu etc.
- **Basic amino acids** These are contain more number of amino groups than carboxyl groups, e.g. lys, arg etc.
- Neutral amino acids These are contain equal number of amino group and carboxyl group, e.g. gly, ala etc.
- II. On the basis of requirement in human diet, amino acids are classified into following types
- Human body can synthesis 10 out of 20 amino acids found in proteins, these are called **non-essential** or **dispensable amino acids** while the remaining ten, which the human body cannot synthesis, are called **essential** or **indispensable amino acids**.
- These essential amino acids are required for the growth of the body and their deficiency causes disease like **kwashiorkor**.
- The essential amino acids are : Arginine, Valine, Methionine, Leucine, Threonine, Phenylalanine, Histidine, Isolucine, Lysine and Tryptophan.

Example 2. W	hich of the fol	lowing is not a	an essential
amino acid?			(JEE Main 2020)
(a) Leucine	(b) Valine	(c) Lysine	(d) Tyrosine

Sol. (d) Tyrosine is not an essential amino acid and remaining all are essential amino acid.

Amino acids which are synthesised by the body, are called non-essential. On the otherhand, those amino acids which cannot be synthesised in the human body and are supplied in the form of diet are called essential amino acids the ten essential amino acids. Valine, leucine, isoleucine, arginine lysine, threonine, methionine, phenylalanine, trpropham, histidine are essential amino acid.

(a) cystine (b) cysteine (c) methionine (d) cytosine



Zwitter Ion Structure

• Amino acids contain the —COOH group, which is acidic and the —NH₂ group which is basic. In the solid state, an amino acid ordinarily exists as a **Zwitter ion** or as **a dipole ion**, formed by the transfer of a proton from a —COOH group to an —NH₂ group.

$$\begin{array}{cccc} R & R \\ | & | \\ H_2 N - C - COOH \longrightarrow H_3 N^+ - C - COO^- \\ | & | \\ H & H \\ Amino acid & Zwitter ion form \end{array}$$

• Modern researches have proved that the acidic properties of amino acids are due to $-NH_3^+$ group (which can donate a proton) and basic properties are

due to the $-\dot{\mathbf{C}}$ $-\mathbf{O}^{-}$ group (which can accept a proton) in a Zwitter ion or 'inner salt'.

• A Zwitter ion behaves like a polar molecule. Within the molecule, there is a positive charge at the nitrogen atom of the amino group and a negative charge at the oxygen atom of the carboxyl group. Overall, the Zwitter ion has no net charge.

Isoelectric Point

In aqueous solution, Zwitter ions are stable only over a certain pH range. At high H^+ ion concentration (low pH), the $-COO^-$ group picks up a proton and forms a cation (due to the presence of NH_3^+ group) with a positive charge. At low H^+ ion concentration (high pH), the NH_3^+ group loses a proton and forms an anion (due to the presence of $-COO^-$ group) with a negative charge.

$$\begin{array}{c} \mathrm{NH}_{3}^{+} - \mathrm{CH}_{2}\mathrm{COOH} \xleftarrow{\mathrm{H}^{+}}_{\mathrm{Less \ pH}} \mathrm{NH}_{3}^{+} - \mathrm{CH}_{2} - \mathrm{COO^{-}}_{\mathrm{Zwitter \ ion}} \\ & \xrightarrow{\mathrm{More \ pH}} \mathrm{NH}_{2} - \mathrm{CH}_{2} - \mathrm{COO^{-}}_{\mathrm{Anion}} \end{array}$$

Note The amino acid can never exist as an uncharged compound at any pH. In fairly acidic medium, it exists as cation while in fairly basic medium it exists as an anion. At physiological pH (\approx 7.3), an amino acid exists as a dipolar ion called **Zwitter ion** or **inner salt**.

The point (pH range) at which the amino acid molecule has equal positive and negative charges is called the **isoelectric point.** At this point, the amino acids do not migrate in an electric field. All amino acids do not have the same isoelectric point. Neutral amino acids have isoelectric point from pH 5.5 to 6.3 (e.g. glycine = 6.1). Acidic amino acids have isoelectric point around 3 (e.g. aspartic acid = 3) and basic amino acids have isoelectric points from pH 7.6 to 10.8 (e.g. Lysine = 9.7)

Amino acids usually shows their lowest solubility in a solution at the isoelectric point. Since, there is a highest concentration of dipolar ion. This property has been used in the separation of different amino acids obtained from the hydrolysis of proteins.

 α -amino acids have protonated —NH₃⁺ group which exerts a strong electron withdrawing inductive effect (-*I* effect) and therefore, increases acid strength. That's why the carboxylic acid groups of the amino acids are so much more acidic (pK_a = 2) than a carboxylic acid such as acetic acid (pK_a = 4.76). If an amino acid has amino group and one carboxyl group such as alanine, it has two pK_a values.

The isoelectric point of this amino acid has the average value of the both pK_a values.

$$\begin{array}{ccc} \text{H}_{3}\text{C} & -\text{CH} & -\text{COOH} \leftarrow \boxed{\text{p}K_{a} = 2.34} \\ & & & \\ & &$$

The isoelectric point, pI = $\frac{2.34 + 9.69}{2} = 6.02$

The pI of an amino acid that has an ionisable side chain is the average of the pK_a values of the similarly ionising group.

C. Proteins

The term protein is derived from the Greek word 'proteios' means 'first rank' because the proteins are ranked first amongst the natural polymer essential for the growth and maintenance of life. These are the polymers of amino acids (specifically α -amino acids) and make up to 15% by mass of our body. The chief sources of proteins are pulses, cheese, milk, egg, peanut, fish, meat etc. The protein content of these sources are

Source	Protein percentage
Soyabean (pulse)	-54%
Meat	-22%
Egg	-14%
Wheat	-12%
Milk	-4%
Egg Wheat Milk	-14% -12% -4%

Examples of Some Proteins and their Biological Functions

Class of proteins	Example	Function
Structural proteins	Collagen	Connective tissue
Enzymes	DNA polymerase	Replicate and repair DNA
Transport protein	Haemoglobin	Transportation of respiratory gases $(O_2 \text{ and } CO_2)$
Contractile protein	Active myosin	Responsible for contraction of muscles
Protective proteins	Antibodies	Complex with foreign proteins
Hormones	Insulin	Regulate glucose metabolism
Toxins	Snake venom	Incapcitate prey

Proteins are important components of most foods. In the digestive system, proteins are broken down into small molecules called α -amino acids. These molecules are reassembled in cells to form other proteins required by the body.

Features of Proteins

- A pure protein is tasteless, odourless and colourless. Chromoproteins are coloured. Most of proteins are hydrophilic. They do not have sharp melting point.
- All proteins on partial hydrolysis give peptide of varying molecular masses, which on complete hydrolysis gives α-amino acids.

 $\text{Proteins} \xrightarrow{\text{Hydrolysis}} \text{Peptides} \xrightarrow{\text{Hydrolysis}} \alpha\text{-amino-acids}$

• All the proteins are laevorotatory due to the presence of asymmetric carbon in α-amino acids.

Peptide Bond and Protein Structure

Amino acids may be joined together by an amide linkage called **peptide linkage** (—CO—NH—). A water molecule is always eliminated in forming a peptide linkage.

The parts of amino acids in a peptide (after liberation of water molecules) are called **amino acid residues**.



- Peptide are amides formed by the condensation of amino group of one α -amino acid with the carboxyl group of another molecule through peptide linkage, with the elimination of a molecule of water.
- The molecule derived from two amino acids containing a single peptide linkage is called a **dipeptide**, that derived from three amino acids is termed as a **tripeptide**. The peptides having 2-10 amino acid residues are called **oligopeptides** while those with greater than 10 amino acid residues are called **polypeptides**.
- **Polypeptide** with molecular weight greater than 10,000 u is termed as a **protein**. Proteins generally have more than 70 amino acid residues, but a polypeptide with fewer α -amino acids may also called a **protein** if it has a well defined conformation characteristic of a protein such as insulin (contains 51 amino-acids).
- Polypeptides are amphoteric in nature because of the presence of terminal ammonium and carboxylate ions as well as the ionised side chains of amino acid residues. Therefore, like α -amino acids, they neutralise both acids as well as bases and possess isoelectric point. At isoelectric points, polypeptides have least solubility and hence can be separated.

Composition of Proteins

An approximate composition of proteins is as follows

Carbon	-50-53%	Hydrogen	-6-7%
Oxygen	-23-25%	Sulphur	-1%
Nitrogen	-16 - 17%	Hydrogen	-6-7%

Other elements such as phosphorus in nucleoproteins, iron in haemoglobin and iodine in thyroid are also present.

Structure of Proteins

On the basis of different configuration or conformations, there are mainly four types of structure of protein. These are as follows

1. Primary Structure

The number and sequence of amino acids in the polypeptide chain constitute the primary structure. It shows how the atoms in protein molecule are joined to one another through covalent bonds to form chains.

Fredrick Sanger, in first time determine the sequence of amino acid sequence of a protein (i.e. insulin) and for this work he was awarded Nobel prize (in 1958). The nature and the sequence of the amino acids determine the three dimensional structure and properties of proteins.

Determination of sequence of amino acids in a peptide chain. It can be determined either by analysing the products of partial hydrolysis or by end group analysis.

 (i) Partial hydrolysis In partial hydrolysis method, dilute acids or enzymes are used to break the polypeptide chain into small fragments. By knowing the structures of these small fragments, the sequence of amino acids in a polypeptide chain is determine.
 For example, partial hydrolysis of a tetra peptide containing Ala, Gly, Phe and Val yields a tripeptide Gly-Phe-Val and a dipeptide Ala-Gly.

Tetrapeptide $\xrightarrow{\text{Hydrolysis}}$ Gly-Phe-Val + Ala-Gly

Since, dipeptide shows that Ala is linked to Gly, the amino acids in the tetrapeptide are linked in the following sequence.

Cleavage at 1. gives tripeptide and at 2. gives dipeptide.

(ii) Terminal residue analysis or end group analysis Peptide structures are written in such a way that the amino group is at the left and carboxy group is at the right. Hence, the amino end is called the N-terminal and carboxy end is called C-terminal. Amino groups of all amino acids except N-terminal amino acid and carboxy group of all amino acids except C-terminal amino acid are involved in amide bond formation.

In other words, amino group is free at the N-terminal end and carboxy group is free at the C-terminal end.



The primary structure of proteins dissolved in water is not disrupted by heating above 80°C. The difference in chemical and biological properties of various proteins and peptides arise due to the difference in their primary structure. e.g. In haemoglobin (blood protein) which carries oxygen, there are 574 amino acid units in a definite sequence but the replacement of only one α -amino acid results in defective haemoglobin. This is the cause of a disease, called **sickle cell anaemia**.

In the patients suffering from this disease, the defective haemoglobin precipitates causing the cells to sickle shaped and sometimes even makes them burst leading ultimately to death. Normal haemoglobin has-Val-His-Leu-Thr-Pro-Glu-Lys.

On the other hand, sickle cell haemoglobin structure. Val-his-Leu-Thr-Pro-Val-Glu-Lys structure.

2. Secondary Structure

Most of the long polypeptide chain are folded or coiled to produce specific three-dimensional structures. These are called **secondary structure** and give idea about shape of the conformation of the protein molecule. Depending upon the size of *R* groups, three major types of secondary structure (α -helix, β -conformation, β -pleated sheet and triple-helix) have been identified.



These are as follows

(i) α -helix In α -helix, the size of *R* groups is quite large and H-bonds are formed between the >C=O of one amino acid and the (>N-H) of the fourth amino

acid residue in the chain. Only right handed α - helix exists in nature, since it is more stable than left handed helix. In this form, there are 3.6 amino acid residues per complete turn. The rise along the central axis is 1.5 Å per residue.

 The structure is stabilised by intramolecular hydrogen bonds between an amide hydrogen (N—H group) and the carbonyl oxygen (C=O group) of the fourth amino acid residue away in the peptide chain.

- Although, the hydrogen bond is fairly weak, their large number stabilises the structure. The imino acid, proline along with amino acids glycine, serine do not fit into the normal α-helix. They disrupt the α-helical structure and cause sharp bends in the direction of the chain. They are called helix-breakers. α-helix is found in both fibrous and globular proteins. Fibrous proteins such as α-keratin in hair, nail, wool, skin, beaks, claws and myosin in muscle have α-helix structure.
- Globular proteins also contain segments of α -helix, because of the α -helical structure, human hair fibres are stretchable and elastic to some extent. When hair is stretched, the H-bonds are broken but when the stretching force is removed, the H-bonds reformed again.
- (ii) β -conformation (β -pleated sheet) it results from hydrogen bonding between two peptide chains. In this conformation, the polypeptide chains lie side by side in a *zig-zag* manner with alternate —*R* groups on the same side situated at fixed distances apart. The chains may be parallel or anti-parallel.

In a parallel chain β -pleated sheet, the N-atoms point in the same direction, while in the antiparallel chain β -pleated sheet, alternate chains are oriented in the same direction. The anti-parallel structure permits maximum hydrogen bonding. The β -conformation is found in fibrous proteins.

Keratin protein (present in hair) has parallel
 β-pleated sheet structure while the silk protein,
 fibroin has anti-parallel β-pleated sheet structure.



β-pleated structure

(iii) **Triple helix** In this structure, three loosely coiled helical polypeptide chains can wind around each other to form a stiff cable. It is very strong and relatively rigid. The triple helix is found mainly in collagen, the major structural protein of skin, bones, teeth, tendons and cartilage. It can be seen that the triple helix structure is more extended and stabilised by hydrogen bonds between the chains, while in α -helix, it is between the amino acid residues in the same chain.



A protein may have the different secondary structures through out its length. Some parts may have α -helix structure, while other may have β -pleated sheet structure. Some parts of the chain may even have no secondary structure at all. These structureless parts are called **random coils** and the arrangement is called **random coil arrangement**. This type of structure is flexible, changing and statistically random. Synthetic polylysine exists as a random coil.

3. Tertiary Structure

The tertiary structure of a protein has its three dimensional shape that arises from further foldings of its polypeptide chains, foldings superimposed on the coils of the α -helixes. These folding brings together **active amino acids**, which are otherwise scattered along the chain, and may form a distinctive **cavity** or **cleft** in which the substrate is bound.

In proteins consisting of a single polypeptide chain, the tertiary structure determines the overall shape of the molecule. So, proteins are called **fibrous proteins** when they form thin, long threads and **globular proteins**, if very compact.

The tertiary structure is specific to a given amino acid sequence and is called the native shape of the protein. Thus, primary structure of a protein dictates its tertiary structure.

4. Quaternary Structure

It is shown by proteins containing more than one polypeptide chain. Two or more polypeptide chains may associate to give rise to the quaternary structure. These are held together by non-covalent forces such as hydrogen bonds, electrostatic interactions and van der Waals' interactions.

If the protein consists of identical units it is said to have a **homogeneous quaternary structure**. If the units are dissimilar, the protein is said to have a

heterogeneous quaternary structure, e.g. haemoglobin which consists of two α chains and two β chains.



Classification of Proteins

Proteins can be classified on the basis of their chemical composition and functions or on the basis of their physical properties.

- Based on the molecular structure and the function they perform, proteins can be further classified as
 - (i) Fibrous proteins These are long and thread like molecules and tend to lie side by side to form fibres. They are held together by intermolecular H-bonding and hence insoluble in water, e.g. keratin (in hair, skin, nails, horn and wool), fibroin (in silk) and myosin (in muscle).
 - (ii) Globular proteins These are folded with spheroidal shapes. The folding takes place in such a way that the lipophilic parts are turned inward and hydrophilic parts tend to move towards the surface, Hydrogen bonding is chiefly intramolecular. Hence, they are soluble in water, acids, bases and salts, e.g. albumin (in eggs), haemoglobin (in blood), all enzymes and most hormones (insulin).
- On the basis of their physical properties, proteins can be classified as,
 - (i) **Simple proteins** These are give only amino acids on hydrolysis, e.g. albumin, globulins etc.
 - (ii) Conjugated proteins These are contain a non-protein part (prosthetic group). The prosthetic group in a protein controls its biological functions. The common prosthetic group in the proteins are tabulated below

Examples of Some Conjugated Proteins

Name of protein	Prosthetic group
Glyco-protein	Sugars (carbohydrates)
Nucleo-protein	Nucleic acid
Lipo-protein	Lipid
Phospho-proteins	Phosphoric acid
Chromo-protein	Pigments having metals Cu, Fe (haemoglobin)

(iii) Derived proteins These are obtained by the hydrolysis of higher proteins with acids, alkalies or enzymes.

e.g. Peptones, proteases and denatured proteins.

Denaturation of Proteins

A protein that is in a biologically inactive form is said to be in a denatured state. The conformational change that produces this state is called **denaturation of proteins**. Denatured proteins usually forms large aggregates that are precipitated from solution. This process is called **coagulation**.

During denaturation no peptide bonds are broken, i.e. chemical composition or primary structure remains unaffected.



The relatively weak, non-covalent interactions are disrupted in the denaturation of a protein.

Some following factors can bring about the denaturation of proteins are

- (i) Heat When you fry or boil an egg, you bring about a denaturation of egg proteins. That's the reason why bacteria are destroyed at high temperatures that exist in an autoclave is that their proteins are denatured.
- (ii) Exposure to organic solvents Organic solvents such as ethanol and rubbing alcohol can denature proteins. Alcohol is rubbed on the skin, before an injection to kill surface bacteria by denaturing bacteria proteins and preventing infection.
- (iii) Exposure to acid and bases Strong acids and bases can denature proteins by disrupting salt bridges and hydrogen bonds. Prolonged treatment with strong acids will bring about hydrolysis of peptide bonds of a protein.
- (iv) Exposure to salts of heavy metal ions Cation of metals such as Hg²⁺, Ag⁺ and Pb²⁺ interfere with the disulphide bonds and salt bridges that stabilise the protein structure and bring about denaturation.

Hence, mercury and lead are poisonous to the human system as they denature proteins in the body.

The first aid treatment for a person who has ingested a heavy metal is to give a large dose of egg whites or milk, both of which are rich in proteins. The proteins in them form complexes with the heavy metals in the stomach, temporarily preventing absorption of the metals into the blood. The patient should later be given an emetic to get rid of the poison.

Test for Proteins

With the help of following tests, presence of proteins can be detected by these methods.

 (i) Biuret test Protein is gently warmed with 10% solution of NaOH and then a drop of dil. CuSO₄ solution is added. Formation of reddish-violet colour indicates the presence of peptide linkage



This test is also given by the compound biuret, obtained by urea on heating.

- (ii) **Xanthoprotic test** Certain proteins give yellow colour with conc. HNO_3 . This yellow colour is same which is formed on skin when skin comes in contact with conc. HNO_3 .
- (iii) Millon's test When Millon's reagent (a solution of mercurous and mercuric nitrates in nitric acid containing some nitrous acid) is added to a protein solution, a white precipitate is obtained. On heating, it turns to red precipitate or colour.
- (iv) Ninhydrin test When a protein is boiled with a dilute solution of ninhydrin, a violet colour is obtained. This test is given by all proteins.
- (v) Nitroprusside test When sodium nitroprusside is added to proteins containing —SH group, a violet colour is obtained.

5. Enzymes

Kuhne (1878) coined the term enzyme. **Buchner** in (1897, 1903) isolated enzyme (including zymase from yeast for the first time). **Sunner** found that enzymes are proteinaceous. He crystallised the first enzyme, urease from jack bean.

An enzyme is a specialised protein produced within an organism which is capable of catalysing a specific chemical reaction. Since, the enzymes act as catalyst, they are sometimes referred to as **biocatalysts**. A catalyst alters the rate of a chemical reaction, usually without undergoing any change itself. In this respect an enzyme differs from a normal catalyst. The enzyme may participate in a reaction by combining with the substrate. Ultimately, it is set free.

Some examples of enzymes along with the reaction, catalyse are given in tabulated form below

Enzymes and their Reaction Catalyse

Enzymes	Reaction catalyse
Amylase	Starch to <i>n</i> glucose
Maltase	Maltose to (2) glucose
Lactase	Lactose to glucose + galactose
Invertase	Sucrose to glucose + fructose
Pepsin	Proteins to amino acids
Trypsin	Polypeptides to α-amino acids
Urease	Urea to ammonia + CO_2
Nuclease	DNA, RNA to nucleotides
Carbonic anhydrase	H_2CO_3 to $H_2O + CO_2$
DNA polymerase	Deoxyribonucleotide triphosphate to DNA
RNA polymerase	Ribonucleotide triphosphate to RNA

Nomenclature of Enzymes

Enzymes are generally named by adding **ase** to the root indicating the substrate on which the enzyme acts. This system was provided by **Duclau** (X) (1883). Thus, **fumarase** catalyses the conversion of fumaric acid to malic acid.

Classification of Enzymes

The International Union of Biochemistry report of 1962 (revised in 1964) contains a scheme for the classification of enzymes. Enzymes have been divided into following six groups, *viz*.

- (i) Oxidoreductases These are include a large number of enzymes (221 are listed). These are bring about the main energy yielding reactions of living tissue. Oxidoreductases include oxidases and dehydrogenases. It act by transferring electrons and hydrogen ions.
- (ii) Transferases These are concerned with the transfer of a group of atoms from one molecule to another. Oxidoreductases and transferases together represent over half the enzymes known.
- (iii) Hydrolases Complex molecules undergo cleavage, and the elements of $\rm H_2O$ are added across the bond cleaved by the action of hydrolases.
- (iv) Lyases These may work in two ways. A group of atoms may be removed from the substrate leaving double bonds, or groups may be added to double bonds without hydrolysis, oxidation or reduction. The enzymes act on the following bonds :

$$C-C, C-O, C-N, C-S and C-X$$

- (v)**Isomerases** These are catalyse reactions which bring about intramolecular rearrangement of atoms in substrates.
- (vi) Ligases (Synthetases) These are catalyse reactions in which the pyrophosphate bond of ATP is broken down and linkage takes place between two molecules. These enzymes form the following bonds : C—O, C—S, C—N and C—C.

Types	of	Rea	ctions	Shown	by	Enzymes
	~			~ ~ ~ ~ ~	$\sim J$	

Enzymes	Reactions
Oxidoreductases	Oxidation-reduction reactions
Transferases	Group transfer reactions
Hydrolases	Hydrolytic reactions (addition of H_2O)
Lyases	Addition or loss of groups to double bonds
Isomerases	Isomeration reactions
Ligases	Synthesis by condensation of two groups requiring ATP

In another system of classification, the name of the enzyme is derived from its substrate.

e.g. Carbohydrases, proteases, dehydrogenases, oxidases, decarboxylases, hydrases, isomerases, transferases, amidases and esterases.

Mechanism of Enzyme Action

Lock and key and induced fit models both explain the enzyme specificity and its mechanism.

In **1894**, **Fischer** suggested **a lock** and **key** concept to explain the working of an enzyme. According to this mechanism, an enzyme catalysed reaction involves the following steps.

Step 1 Binding of enzyme (E) to the substrate (S) to form an enzyme substrate complex.

$$E + S \longrightarrow (ES)$$

Step 2 Product formation in the complex.

$$(ES) \longrightarrow EP$$
Enzyme substrate complex Enzyme product

Step 3 Release of the product from the enzyme.



In **induced fit** mechanism, the active site undergoes a change in its conformation in presence of a substrate to allow

a better fit between the active site and the substrate. It means that enzymes are highly specific for the reaction that they catalyse. It is shown in below



Features of Enzymes

Some important features of enzymes are discussed below

- (i) Specificity Enzymes show striking specificity. These catalyse have specific reactions of specific substrates. Some enzymes are so specific that they catalyse only one type of substrate molecule.
 e.g. The enzyme chymotrypsin catalyses the hydrolysis of acetyl, L-phenyl-alanine methyl ester, but is inert to the D isomer.
- (ii) Required in small amount Only one enzyme can catalyse a large number of substrate molecules. In other words, enzymes are required in very small amounts.
- (iii) **Activation energy** Enzymes alter the speed of a chemical reaction. They lower the energy of activation of a reaction, thus enabling it to occur at ordinary physiological temperatures.



Change in activation energy (A.E.) (A) Reaction without enzyme, (B) Reaction with enzyme.

Factors Affecting Enzyme Activity

- (i) Effect of temperature Enzyme action is greatly affected by temperature. If the temperature is increased by 10°C, the rate of most chemical reactions is doubled. However, at 40-60°C, there is loss of enzyme activity because denaturation of proteins occurs at this temperature.
- (ii) pH At optimum pH, the activity of enzyme is maximum. For most enzymes, the effective pH range is 4–9. Below and beyond these limits, denaturation of enzymes takes place. The optimum pH for pepsin is 2.0 and for trypsin is 8.0.
- (iii) **Ions** Enzyme activity is affected by H⁺ ion concentration and other ionic concentrations.

Some enzymes require a loosely bound cation such as Mg^{2^+} .



(C) Effect of temperature on the rate of enzymatic reaction. On represents the point of thermal denaturation of the enzyme (44-45 $^{\circ}$ C). (*D*) Effect of pH on the rate of enzyme reaction.

(iv) Concentration Enzyme concentration affect the rate of a reaction. If the substrate concentration is increased, the rate of enzyme reaction also increases. Beyond a certain point, however, the enzyme becomes saturated with substrate molecules. Further increase in reaction velocity occurs only if the enzyme concentration is increased.

For example, during starvation the supply of the substrate (glucose) decreases and glycolysis is depressed. Conversely, increase in glucose concentration accelerates the rate of reaction upto the point when enzyme is saturated with glucose.

(v) Inhibitors Certain compounds (e.g. drugs, poisons) combine with an enzyme but do not serve as substrates. They block reaction by the enzyme and function as inhibitors. The inhibitors usually resemble the substrate in structure. The enzyme and the inhibitor form an enzyme-inhibitor complex which is inactive.



Mechanism of enzyme action inhibition.

- Inhibition may be **competitive** or **non-competitive**. In **competitive inhibition**, both inhibitor and substrate molecules compete for binding with the enzyme. If the inhibitor is in sufficiently high concentration, it displaces the substrate molecules. For example, sulphanilamide is a competitive inhibitor for a bacterial enzyme that incorporates *p*-amino benzoic acid into folic acid.
- Competitive inhibition can be reversed by increasing the concentration of the substrate. In **non-competitive inhibition**, the inhibitors (poisons) react with the various functional groups of the enzyme. They inhibit the normal reactions catalysed by the enzyme and result in death. Non-competitive inhibition cannot be reversed by increasing the concentration of the substrate.

6. Vitamins

These are essential dietary factors required by an organism in minute quantities. These are not utilised in cell building or as energy source but they act as catalysts (coenzymes) in biological processes.

Note Vitamins are not synthesised in the body and hence should be supplied in diet. Their deficiency causes specific diseases (avitaminosis).

Classification of Vitamins

These are classified into two groups

- (i) **Fat soluble vitamins** These are vitamin A, D, E and K.
- (ii) Water soluble vitamins These are vitamin B and vitamin C. Water soluble vitamins must be supplied regularly in diet because they are excreted in urine and cannot be stored in our body (except B₁₂).
- Vitamins catalyse biological reactions in very low concentration, therefore the daily requirement of any vitamin for any individual is extremely small.
- The sources and diseases caused by the deficiency of different vitamins are tabulated below

Vitamins : Sources and Deficiency Diseases

Name of vitamin	Sources	Deficiency disease
Vitamin A (Retinol or Axerophthol, $C_{20}H_{30}O$)	Fish liver oil	Xerophthalamia (hardening of cornea)
Vitamin B_1 (Thiamine or Aneurin, $C_{12}H_{18}N_4SOCl_2$)	Green vegetables, milk	Beri-Beri (disease of nervous system)
Vitamin B_2 (Riboflavin or Lactoflavin, $C_{17}H_{20}N_4O_6)$	Vegetables, milk, liver, egg white, kidney	Dark red tongue dermatitis, cheilosis
Vitamin $\rm B_3$ (Pantothenic acid, $\rm C_9H_{17}O_5N)$	All food, more in yeast, liver, kidneys tomatoes	Dermatities in cocks, retarded body and mental growth
Vitamin B_5 (Nicotinic acid or Niacin, (C_5H_4N — COOH)	Fresh meat, liver, fish, cereals, milk, pulses	Pellagra, dermatities
Vitamin B_6 (Pyridoxine or adermin, $C_8H_{11}O_3N$)	Grams, molasses, egg yolk meat	Severe dermatitis, convulsions
Vitamin H (Biotin, $C_{10}H_{16}N_2O_3S$)	Yeast, liver, kidney milk	Dermatitis, loss of hair and paralysis
Vitamin B_{12} (Cyanocobalamine, $C_{63}H_{88}O_4$ $N_{14}PCo$)	Liver of ox, sheep, pig, fish etc.	Pernicious anaemia
Vitamin C (Ascorbic acid, $C_6H_8O_6$)	Citrus fruits, green vegetables	Scurvy
Vitamin K (K ₁ and K ₂) (Phylloquinone, $C_{13}H_{46}O_2$)	Cereals, leafy vegetables	Hemorrhagic conditions, increased blood clotting time
Vitamin D (Ergocalciferol, $C_{28}H_{44}O$)	Synthesized in skin cells in the presence of sunlight, liver, egg yolk, meat and milk	Rickets with osteomalacia, soft and fragile teeth

Note Provitamins are the biologically inactive compounds which have almost similar structure as vitamins and can be converted into active vitamins.

Example 4. Match the following :

	(i)	Riboflavin	(A)	Beri-beri	
	(ii)	Thiamine	(B)	Scurvy	
	(iii)	Pyridoxine	(C)	Cheilosis	
	(iv)	Ascorbic acid	(D)	Convulsions	
(a) (i)-	-(C), (ii)-(D), (iii)-(A), (iv)	-(B)	(JEE	Main 2020)
(b) (i)-	-(C), (ii)-(A), (iii)-(D), (iv)	-(B)		
(c) (i)-	(c) (i)-(D), (ii)-(B), (iii)-(A), (iv)-(C)				
(d) (i)	-(A), (ii)-(D), (iii)-(C), (iv)	-(B)		

Sol. (b) (i) Riboflavin - (C) Cheilosis (ii) Thiammine - (A) Beri-beri (iii) Pyridoxine - (D) Convulsions (iv) Ascorbic acid - (B) Scurvy

Thus, the correct option is (b).

Nucleic Acids

Nucleic acids are present in all living organisms, whether plants, animals or virus. These are generally associated with proteins (in eukaryotes) to form **nucleoproteins**. These are responsible in the biosynthesis of proteins and for the transmission of heredity characters. The genetic information coded in nucleic acids helps to know the structure of all proteins including enzymes and all metabolic activities of living organisms.

Classification of Nucleic Acids

There are two types of nucleic acids, **deoxyribose nucleic acid** (DNA) and **ribose nucleic acid** (RNA). DNA is found predominantly in the nucleus, whereas RNA is predominant in the cytoplasm. DNA is the genetic material of most organisms, including many viruses. Some viruses, however, have RNA as their genetic material.

1. Deoxyribose Nucleic Acid (DNA)

It is present in the cells of all plants, animals, prokaryotes and in a number of viruses. In prokaryotes (e.g. *Escherichia coil*, a bacterium), the genetic material consists of a single giant molecule of DNA without any associated proteins. DNA is present mainly in the chromosomes. It has also been reported in cytoplasmic organ cells like mitochondria and chloroplasts. The DNA of most plants and animals and many viruses (polyoma virus, small-pox virus, bacteriophages T_2 , T_4 and T_6) is double stranded. In bacteria and in higher plants and animals both DNA and RNA are present. Viruses usually contain either DNA or RNA.

Structure of DNA

The widely accepted molecular model of DNA is the **double helix structure**, proposed by **Watson** and **Crick** (1953). The DNA molecule consists of two helically twisted strands. Each strand consists of alternating

molecules of deoxyribose (a pentose sugar) and phosphate groups.

The two strands are intertwined in a clockwise direction, i.e. in a right hand helix, and run in opposite directions. Each successive nucleotide turns 36 degrees in the horizontal plane. The width of the DNA molecule is 20 Å. The twisting of the strands result in the formation of **deep** and **shallow spiral grooves**.



Chemical Composition of Nucleic Acids

Nucleic acids are biopolymers made of nucleotides joined together to form a long chain. Hence, these are called **polynucleotide**. Each nucleotide consists of the pentose sugar, deoxyribose, a phosphate group and nitrogenous base which may be either a purine or pyrimidine. Deoxyribose and a nitrogenous base together form a **nucleoside**.

A nucleoside and a phosphate together form a **nucleotide**. **Nucleoside** = deoxyribose + nitrogenous base

Nucleotide = deoxyribose + nitrogenous base + phosphate = nucleoside + phosphate

Nucleotide may be represented as,



(i) **Deoxyribose** is a pentose sugar with five carbon atoms. Four of the five carbon atoms plus a single atom of oxygen form a five-membered ring. The fifth carbon atom is outside the ring and forms a part of a $-CH_2$ group.

The four atoms of the ring are numbered 1' , 2' , 3' and 4'. The carbon atom of $-CH_2$ is numbered 5'.



(ii) Nitrogenous bases are of two types, *viz*, pyrimidines and purines. The pyrimidines are single ring compounds, with nitrogen in position 1 and 3 of a 6-membered benzene ring.

The two most common pyrimidines of DNA are **cytosine** (C) and **thymine** (T). The purines are double ring compounds. A purine molecule consists of a 5-membered imidazole ring joined to a pyrimidine ring at positions 4 and 5. The two most common purines of DNA are **adenine** (A) and **guanine** (G).

The structure of these bases are follows :



• Two purines would occupy too much space, while two pyrimidines would occupy too little. Because of the purine-pyrimidine pairing, the total number of purines in a double-stranded DNA molecule is equal to the total number of pyrimidines.

Thus, A / T = 1 and G/C = 1

or, A + G = C + T (Chargaff's rule).

(iii) **Phosphate group** In the DNA strand, the phosphate groups alternate with deoxyribose. Each phosphate group is joined to carbon atom 3 of one deoxyribose and to carbon atom 5 of another.

Thus, each strand has a 3 end and a 5 end. The two strands are oriented in opposite direction. The 3 end of one strand corresponds to the 5 end of the other. Consequently the oxygen atoms of deoxyribose point in opposite directions. **Example 5.** Which one of the following bases is not present in DNA ? (JEE Main 2014)

- (a) Quinoline
- (b) Adenine
- (c) Cytosine
- (d) Thymine

Sol. (a) DNA contains four nitrogenous pyramidine bases, adenine, guanine, cytosine, thymine. While quinoline is an alkaloid, hence, it is not present in DNA.

2. Ribose Nucleic Acid (RNA)

It is the genetic material of mainly viruses. It can be single stranded or double stranded.

Chemical Composition of RNA

RNA, like DNA is also a polymer of nucleotide which in turn obtained from nucleoside, chemical which when combines with phosphate.

Here, the point of difference is that the sugar present in nucleoside is ribose sugar instead of deoxyribose sugar. Nucleoside = ribose + nitrogenous base

Nucleotide = ribose + nitrogenous base + phosphate These are classified into

(i) **Ribose** The pentose sugar of RNA has an identical structure with deoxyribose sugar except that there is an —OH group instead of H on carbon atom 2'.



- (ii) Nitrogenous base are divided into two types : pyrimidines and purines. Purine bases are same as that in DNA but pyrimidine bases are cytosine (C) and uracil (U). (In RNA uracil replaces thymine).
- (iii) Phosphate is same as DNA.

Note There are viruses, called retroviruses, in which information flows from RNA to DNA. The virus that causes AIDS is a retrovirus.

Types of RNA

RNA are divided into three types.



(i) *m*-RNA It makes 3-5% of total cellular RNA.
 The *m*-RNA comes out with proteins into the cytoplasm and normally swim as spherical balls along

with the same untill these are required. These RNA + protein spherical balls are called **informosomes**.



(ii) *r*-RNA It makes 80% of total cellular RNA. These RNA is the basic constituent of ribosomes. It is developed from *r*-DNA in the case of prokaryotes while in the case of eukaryotes, it is developed from the nucleolar organiser region of chromosome.

The various r-RNAs present in different units of ribosome are as follows

Prokaryotes (70 S)

 $30 \text{ S} \longrightarrow 16 \text{ S} r$ -RNA; $50 \text{ S} \longrightarrow 23 \text{ S}$ and 5 S r-RNA Eukaryotes (80S)

40S —>18 S r-RNA; 60 S —> 28-29 S, 5.85 S, 5 S r-RNA

Chloroplast and Mitochondria (55 S)

 $30\mathrm{S} \longrightarrow 12\text{-}13~\mathrm{S}\,r\text{-}\mathrm{RNA}; 40~\mathrm{S} \longrightarrow 16\text{-}17~\mathrm{S}\,r\text{-}\mathrm{RNA} + 5~\mathrm{S}$



(iii) **t-RNA** It makes 10-20% of total cellular RNA with sedimentation coefficient of 3.8 S. These RNA contains 73-93 nucleotides with in the structure given below



Structure of t-RNA

The above structure is called clover leaf model and was fully worked out by Holley *et al.* of yeast alanine *t*-RNA.

The function of *t*-RNAs is to align the required amino acids according to the nucleotide sequence of *m*-RNA.

The Genetic Code

Nucleic acids control heredity on molecular level. The double helix of DNA is reponsible for the hereditary information of the organisms. The information is stored as the sequence of bases along the polynucleotide chain. DNA preserve the hereditary informations and use it.

- It done these things through two properties
- (i) DNA molecules can duplicate themselves (replication).
- (ii) DNA molecules can control the synthesis of proteins in an exact and specific way. Synthesis of a polypeptide chain is controlled by a particular gene. The gene, which is almost always a segment of a DNA strand, transcribes an *m*-RNA which acts as an intermediate in conveying information from the sequence of amino acids in the polynucleotide chain. Each amino acid is specified by a sequence of three bases known as codon of *m*-RNA.

Each *t*-RNA molecules has a sequence of three bases known as **anticodon**, which reads a codon of *m*-RNA. *t*-RNA molecules thus serve as adaptors in protein synthesis by reading of *m*-RNA codons in a sequence.

Practice Exercise

ROUND I Topically Divided Problems

Carbohydrates

- **1.** The two functional groups present in a typical carbohydrate are
 - (a) -OH and -COOH (b) -CHO and -COOH
 - (c) $\Sigma = 0$ and -OH (d) -OH and -CHO
- **2.** Which is not true for carbohydrates?
 - (a) General formula is $\mathbf{C}_{n}\mathbf{H}_{2n}\mathbf{O}_{n}$
 - (b) Glucose is the most common monomer of carbohydrates
 - (c) Fructose is the sweetest of all sugars
 - (d) Do not conjugate with lipids
- **3.** Identify the product '*C*' in the following series of reactions

Glucose
$$\xrightarrow{\text{HCN}} A \xrightarrow{\text{H}_2\text{O}} B \xrightarrow{\text{HI}} C$$

- (a) heptanoic acid (b) hexanoic acid
- (c) α -methyl caproic acid (d) None of these
- **4.** The two forms of D-glucopyranose obtained from the solution of D-glucose are called

(a)	isomer	(b)	anomer
(c)	epimer	(d)	enantiomer

5. Consider the following reagents

I. Br $_2$ water II. Tollen's reagent

III. Fehling's solution

Which can be used to make distinction between an aldose and a ketose ?

- (a) I, II and III (b) II and III (c) I only (d) II only
- 6. If α -D-glucopyranose is reacted with acetic anhydride at 373 K, the major product is the β -isomer of the pentaacetate. It is attributed to (a) isomerisation of α -D into β -D-glucose at 373 K
 - (b) opening of glucopyranose ring
 - (c) Both the statements are correct
 - (d) None of the statement is correct
- 7. Number of stereo-centers present in linear and cyclic structures of glucose are respectively (JEE Main 2019)
 (a) 4 and 5 (b) 4 and 4 (c) 5 and 4 (d) 5 and 5
- **8.** When glucose reacts with bromine water the main product is
 - (a) acetic acid(b) saccharic acid(c) glyceraldehyde(d) gluconic acid
- **9.** Which of the following statements is correct?

[JEE Main 2020]

- (a) Gluconic acid is obtained by oxidation of glucose with HNO_3
- (b) Gluconic acid is a dicarboxylic acid
- (c) Gluconic acid can form cyclic (acetal/hemiacetal) structure
- (d) Gluconic acid is a partial oxidation product of glucose



10. Which of the following pairs represents anomers ?

- **11.** Which of the following statement is not true for glucose? (JEE Main 2020)
 - (a) The penta-acetate of glucose does not react with hydroxylamine to give oxime
 - (b) Glucose exists in two crystalline forms α and β
 - (c) Glucose gives Schiff's test for aldehyde
 - (d) Glucose reacts with hydroxylamine to form oxime
- **12.** Which of the following reagent is used to identify fructose?
 - (a) Neutral FeCl₃ (b) CHCl₃/alc. KOH
 - (c) Ammonical AgNO₃ (d) Iodine
- **13.** Which of the following pairs give positive Tollen's test?
 - (a) Glucose, sucrose (b) Glucose, fructose
 - (c) Hexanal, acetophenone (d) Fructose, sucrose
- **14.** D-fructose is used for sweetening cold drinks but not hot ones because
 - (a) it is not a true carbohydrate
 - (b) on heating it converts into pyranose form
 - (c) on heating it converts into furanose form
 - (d) on heating it gets decomposed of D-fructose

- **15.** Given, $[\alpha]_D = +52.7^\circ$ for D-glucose and $[\alpha]_{D} = -92.40$ for D-fructose. The specific rotation of invert sugar is
 - (-72.55° (c)
- **16.** Which one of the following statements is not true ? (JEE Main 2020, 6 Sep.)
 - (a) Lactose contains α -glycosidic linkage between C₁ of galactose and C_4 of glucose
 - (b) Lactose is a reducing sugar and it gives Fehling's test
 - (c) Lactose $(C_{11}H_{22}O_{11})$ is a disaccharide and it contains 8 hydroxyl groups
 - (d) On acid hydrolysis, lactose gives one molecule of D-(+)-glucose and one molecule of D-(+)-galactose
- $\xrightarrow{\text{HOH/H}^+} \text{glucose + fructose}$ **17.** A
 - HOH/H^+ B glucose + glucose
 - HOH/H^+ glucose + galactose C

The disaccharides A, B and C respectively are

- (a) lactose, sucrose, maltose
- (b) sucrose, maltose, lactose
- (c) sucrose, lactose, maltose
- (d) maltose, sucrose, lactose
- **18.** A non-reducing sugar "*A*" hydrolyses to give two
 - reducing monosaccharides. Sugar A is [JEE Main 2021]
 - (a) galactose (b) fructose
 - (c) glucose (d) sucrose
- **19.** Amylopectin is composed of (JEE Main 2019) (a) β -D-glucose, C₁—C₄ and C₂—C₆ linkages (b) α -D-glucose, C₁-C₄ and C₂-linkages (c) $\beta\text{-}D\text{-}glucose, C_1\text{---}C_4$ and $C_1\text{---}C_6$ linkages (d) α -D-glucose, C₁—C₄ and C₁—C₆ linkages
- **20.** Which of the given statements is incorrect about glycogen? (JEE Main 2019) (a) It is straight chain polymer similar to amylose
 - (b) Only α -linkages are present in the molecule
 - (c) It is present in animal cells
 - (d) It is present in some yeast and fungi
- **21.** Glycogen is a branched chain polymer of α -D-glucose units in which chain is formed by C₁— C₄ glycosidic linkage whereas branching occurs by the formation of C_1 — C_6 glycosidic linkage. Structure of glycogen is simple to
 - (NCERT Exemplar)
 - (a) amylose (b) amylopectin
 - (c) cellulose (d) glycogen

(NCERT Exemplar)

a) –39.7°	(b) -145.1
c) -19.9°	(d) -72.55

- **22.** A compound gives negative test with ninhydrin and positive test with Benedict's solution. The
 - compound is
 - (a) a protein (b) an amino acid (c) a lipid
 - (d) a monosaccharide

Amino Acids

- **23.** Which one of the following is involved in the formation of nicotinamide and indole-3-acetic acid? (a) Lysine
 - (b) Tryptophan
 - (c) Tyrosine
 - (d) Glutamic acid
- 24. At intermediate pH values of about 6.0, an amino acid behaves as a dipolar ion or Zwitter ion. On decreasing and increasing the pH values, the amino acid becomes
 - (a) basic and acidic respectively
 - (b) acidic and basic respectively
 - (c) remains in the state of a neutral molecule
 - (d) loses its optical activity with the exception of glycine
- **25.** Which of the following has an imino (>NH) group instead of amino group $(-NH_2)$?
 - (a) Proline (b) Isoleucine (c) Tryptophan

(d) Serine

COOH

26. When
$$H_2N \longrightarrow H$$
 is acylated using Ac_2O

- (a) its configuration is retained
- (b) its configuration is inverted
- (c) it becomes unstable
- (d) no reaction takes place

27. In an electric field, if an amino acid migrate towards cathode, the pH of the solution is said to be (a) less than pI (b) more than pI

- (c) equal to pI (d) 7
- **28.** Which of the following is the major solute species in a solution of lysine at pH = 10.5 (pI = 9.6)?



- **29.** Glutamic acid, $H_2N CH(CH_2CH_2COOH) \cdot COOH$ has pK_{a_1} , (α -COOH) = 2.2, pK_{a_2} (α - NH_3) = 9.8 and pK_{a_3} (*R* group COOH) = 4.3. The isoelectric point of glutamic acid is (a) 3.2 (b) 6 (c) 7.05 (d) 8.3
- **30.** For which of the following amino acid, Van-Styke estimation method is not applicable? (a) Alanine (b) Aspartic acid
 - (c) Serine (d) Proline
- **31.** Among the following compounds, most basic amino acid is (JEE Main 2019) (a) serine (b) asparagine (c) lysine (d) histidine
- **32.** The correct structure of histidine in a strongly acidic solution (pH = 2) is (JEE Main 2019)



33. Which of the following tests cannot be used for identifying amino acids ? (JEE Main 2019)

(a) Barfoed test	(b) Ninhydrin test
(c) Xanthoproteic test	(d) Biuret test

Proteins

34. Which one is a fibrous protein ?

(a) Globulin	(b) Collagen
(c) Hordein	(d) Glutin

- **35.** Casein contained in milk as a
 - (a) carbohydrate
 - (b) lipid
 - (c) protein
 - (d) important molecule

36. Aleurone grains are

- (a) starch (b) glycogen (d) protein (c) lipid
- **37.** Initiation of polypeptide chain is through
 - (a) lysine (b) glycine
 - (c) leucine (d) methionine
- **38.** Which of the following is not a function of proteins?
 - (a) Nail formation
 - (b) Skin formation
 - (c) Muscle formation
 - (d) Providing energy for metabolism

39.	The seco	ndary stru	cture of	protein	is stabil	ised by	y
					(JEE I	Main 20)21,

(a)	(a) peptide bond		(b) glycosidic bond		
(c)	hydrogen bonding	(d)	van der Waals' forces		

- **40.** A tripeptide is composed equally of L-valine, L-tyrosine and L-alanine (one molecule of each). How many isomeric tripeptide of this kind may exist? (a) 3 (b) 4 (c) 6 (d) 8
- **41.** Primary structure of protein is based upon the
 - (a) hydrogen bonding (b) van der Waals' forces
 - (c) ionic bonding (d) covalent bonding
- **42.** Each polypeptide in a protein has amino acids linked with each other in a specific sequence. This sequence of amino acids is said to be (NCERT Exemplar)
 - (a) primary structure of proteins
 - (b) secondary structure of proteins
 - (c) tertiary structure of proteins
 - (d) quaternary structure of proteins
- **43.** Denaturation of proteins leads to loss of its biological activity by
 - (a) formation of amino acids
 - (b) loss of primary structure
 - (c) loss of both primary and secondary structure
 - (d) loss of both secondary and tertiary structure
- **44.** A hexapeptide has the composition Ala, Gly, Phe, Val. Both the N-terminal and C-terminal units are Val. Cleavage of the hexapeptide by chemotrypsin gives two different tripeptides, both having Val as the N-terminal group. Among the products of random hydrolysis is a Ala-Val dipeptide fragment. What is the primary structure of the hexapeptide?
 - (a) Val-Glv-Phe-Val-Ala-Val
 - (b) Val-Ala-Phe-Val-Gly-Val
 - (c) Val-Gly-Ala-Val-Phe-Val
 - (d) Val-Phe-Val-Ala-Gly-Val
- **45.** The increasing order of pK_a of the following amino

acids in aqueous solution is Gly, Asp, Lys, Arg

- (a) Asp < Glv < Arg < Lvs(JEE Main 2019)
- (b) Arg < Lys < Gly < Asp
- (c) Gly < Asp < Arg < Lys
- (d) Asp < Gly < Lys < Arg
- **46.** The correct sequence of amino acids present in the tripeptide given below is (JEE Main 2019)



(a) Thr - Ser - Leu	(b) Leu - Ser - Thr
(c) Val - Ser - Thr	(d) Thr - Ser - Val

- **47.** Proteins can be classified into two types on the basis of their molecular shape, i.e. fibrous proteins and globular proteins. Examples of globular proteins are (NCERT Exemplar)
 - (a) Collagen (b) Keratin (c) Albumin (d) Myosin
- **48.** In fibrous proteins, polypeptide chains are held (NCERT Exemplar) together by
 - (a) van der Waals' forces
 - (b) disulphide linkage and hydrogen bonds
 - (c) electrostatic forces of attractions
 - (d) None of the above

Enzymes

- **49.** The enzyme which facilitates internal rearrangement in 3-phosphoglyceric acid to form 2-phosphoglyceric acid is
 - (a) aldolase
 - (b) triose phosphate isomerase
 - (c) phosphoglycero mutase
 - (d) pyruvate kinase
- **50.** The enzymes which have control site in addition to active site are called
 - (a) holozymes (b) coenzymes (c) apoenzymes (d) allosteric enzymes
- **51.** Enzymes, in the living systems
 - (a) provide energy
 - (b) provide immunity
 - (c) transport oxygen
 - (d) catalyse biochemical processes
- **52.** Which enzyme is present in saliva?
 - (a) Urease (c) Maltase (c) Lactase (d) Amylase
- **53.** Which of the following is present in animals like cow, buffaloes etc., to digest compound like paper cloth etc?
 - (a) Urease (b) Cellulase (c) Silicones (d) Sucrase
- **54.** The enzyme pepsin hydrolysis
 - (a) proteins to amino acids
 - (b) fats to fatty acids

(c) ptyalin

- (c) glucose to ethyl alcohol
- (d) polysaccharides to monosaccharides
- **55.** Pick out the one which does not belong to the family of enzyme
 - (a) pepsin (b) cellulose
 - (d) lipase

56. Identify the correct statement regarding enzymes.

- (a) Enzymes are specific biological catalysts that can normally function at very high temperatures $(T \sim 1000 \text{ K})$
- (b) Enzymes are normally heterogeneous catalysts that are very specific in their action
- (c) Enzymes are specific biological catalysts that cannot be poisoned
- (d) Enzymes are specific biological catalysts that possess well defined active sites

57. Which of the following terms are correct about

enzyme ?	(NCERT Exemplar)
(a) Proteins	(b) Dinucleotides
(c) Nucleic acids	(d) Biocatalysts

Vitamins

58.	Which of the following B group vitamins can be				
	stored in our body ?	(NCERT Exemplar)			
	(a) Vitamin B ₁	(b) Vitamin B_2			
	(c) Vitamin B ₆	(d) Vitamin B ₁₂			
50	$\mathbf{X}\mathbf{Y}1$: 1 , \mathbf{C} (1 , \mathbf{C}) 1 ; 1 , 1	1 1			

- **59.** Which of the following biomolecules contains non-transition metal ion?
 - (a) Vitamin B₁₂
 (b) Chlorophyll
 (c) Haemoglobin
 (d) Insulin
- **60.** Which of the following compounds is known as the antisterility factor?

(a)	a-tocop	herol	(b)	Retinol
(c)	Calcifer	ol	(d)	Pyridoxine

- **61.** Vitamin B_6 is known as
 - (a) pyridoxin(b) thiamine(c) tocopherol(d) riboflavin
- **62.** The best source of vitamin A is (a) wheat (b) beans (c) carrots (d) oranges

63. The deficiency of vitamin B_1 causes

(a) beri-beri	(b) dermatitis
(c) scurvy	(d) rickets

- **64.** The metal present in vitamin B_{12} is (a) iron (b) manganese (c) cobalt (d) mercury
- **65.** Which of the following acids is a vitamin?

	(NCERT Exemplar)
(a) Aspartic acid	(b) Adipic acid
(c) Ascorbic acid	(d) Saccharic acid

Nucleic Acids

66. Maximum amount of RNA is found in
(a) nucleolus
(b) chloroplast
(c) ribosomes
(d) cytoplasm

- 67. When adenine is attached to ribose sugar, it is called adenosine. To make a nucleotide from it, it would require(a) oxygenation(b) addition of a base
 - (c) addition of phosphate (d) hydrogenation
- **68.** Nucleotide pairs present in one turn of DNA helix are
 - (a) 4 (b) 10 (c) 8 (d) 9
- **69.** DNA and RNA contain four bases each. Which of the following bases is not present in RNA? (NCERT Exemplar)
 - (a) Adenine (b) Thymine (c) Uracil (d) Cytosine
- **70.** In biological systems, the RNA molecules direct the synthesis of specific proteins which are characteristics of each kinds of organisms. This process is known as
 - (a) transcription (b) mutation
 - (c) replication (d) translation
- 71. Charagaff's rule states that in an organism(a) amount of adenine (A) is equal to that of thymine(T) and amount of guanine (G) is equal to that of cytocine (C)
 - (b) amont of adenine (A) is equal to that of guanine (G) and the amount of thymine (T) is equal to that of guanine (G)
 - (c) amount of adenine (A) is equal to that of cytocine (C) and the amount of thymine (T) is equal to that of guanine (G)
 - (d) amount of all bases are equal
- **72.** In DNA, the complementary bases are,
 - (a) adenine and thymine; guanine and cytocine
 - (b) uracil and adenine; cytocine and guanine
 - (c) adenine and guanine; thymine and cytocine
 - (d) adenine and thymine; guanine and uracil
- **73.** The hydrogen bonding for the bases pairs of DNA are between
 - (a) amide carbonyl and ---NH₂ only
 - (b) amide N—H and cyclic amine nitrogen only
 - (c) alcohols and carbonyls only
 - (d) Both (a) and (b)
- 74. The presence or absence of hydroxy group on which carbon atom of sugar differentiates RNA and DNA (AIEEE 2011)
 (a) 1st
 (b) 2nd
 (c) 3rd
 (d) 4th
- **75.** Which of the following will react with CHCl₃ + alc. KOH ? (JEE Main 2020)
 - (a) Adenine and lysine
 - (b) Thymine and proline
 - (c) Adenine and thymine
 - (d) Adenine and proline

- 76. Which of the following statement is not true about RNA? (JEE Main 2019)
 - (a) It controls the synthesis of protein
 - (b) It has always double stranded α -helix structure
 - (c) It usually does not replicate
 - (d) It is present in the nucleus of the cell
- 77. Among the following compounds, which one is found in RNA ? (JEE Main 2019)



ROUND II Mixed Bag

- **1.** Consider the following reactions :
 - I. Glucose + $ROH \xrightarrow{Dry HCl} Acetal$ $\xrightarrow{x \text{ eq. of}} Acetyl derivative$
 - II. Glucose $\xrightarrow{\text{Ni/H}_2} A \xrightarrow{y \text{ eq. of}} \text{Acetyl}$ derivative $\xrightarrow{\text{CH}_3\text{CO}_2\text{O}}$
 - III. Glucose $\xrightarrow{z \text{ eq. of}} \text{Acetyl derivative}$

'x', 'y' and 'z' in these reactions are respectively (JEE Main 2020)

(a) 5. 4 and 5	(b) 4, 5 and 5
(c) 5, 6 and 5	(d) 4, 6 and 5

- 2. An electric current is passed through an aqueous solution of a mixture of alanine (isoelectric point 6.0), glutamic acid (3.2) and arginine (10.7) buffered at pH 6. What is the fate of the three acids?
 - (a) Glutamic acid migrates to anode at pH 6. Arginine present as a cation and alanine to the cathode. Alanine in a dipolar ion remains uniformly distributed in solution
 - (b) Glutamic acid migrates to cathode and others remain uniformly distributed in solution
 - (c) All these remain uniformly distributed in solution
 - (d) All three move to cathode
- 3. The correct observation in the following reactions, is

 $\begin{array}{c} \text{Sucrose} & \xrightarrow[(\text{Hydrolysis})]{\text{Glycosidic bond}} A + B & \xrightarrow[(\text{reagent}]{\text{Seliwanoff s}} \\ & \xrightarrow[(\text{Hydrolysis})]{\text{Glex Main 2020}} \end{array}$

- (a) Formation of blue colour
- (b) Gives no colour
- (c) Formation of red colour
- (d) Formation of violet colour

4. Isoelectric point is a

- (a) specific temperature
- (b) suitable concentration of amino acid

- (c) hydrogen ion concentration that does not allow migration of amino acid under electric field
- (d) melting point of an amino acid under the influence of electric field
- **5.** From the following statements :
 - I. Albumin is a simple protein.
 - II. Amino acid alanine contains an acidic side chain.
 - III. Insulin is a hormone.
 - IV. Muscles contain the protein keratin.

Choose the wrong statements.

- (a) I, II (b) III, IV (c) I, III (d) II, IV
- **6.** The correct statement in respect of protein haemoglobin is that it
 - (a) acts as an oxygen carrier in the blood
 - (b) forms antibodies and offers resistance to diseases
 - (c) functions as a catalyst for biological reactions
 - (d) maintains blood sugar level
- 7. Glucose and galactose are having identical configuration in all the positions except position.
 (a) C-3
 (b) C-4
 (c) C-2
 (d) C-5
- **8.** The number of amino acids in insulin is (a) 21 (b) 574 (c) 51 (d) 5733
- **9.** Two monomers in maltose are (JEE Main 2020) (a) α -D-glucose and α -D-glucose
 - (b) α -D-glucose and α -D-galactose
 - (c) α -D-glucose and β -D-glucose
 - (d) α -D-glucose and α -D-fructose
- **10.** A chemist has 4 samples of artificial sweetener *A*, *B*, *C* and *D*. To identify these samples, he performed certain experiments and noted the following observations :
 - I. *A* and *D* both form blue-violet colour with ninhydrin.
 - II. Lass aigne extract of C gives positive ${\rm AgNO}_3$ test and negative ${\rm Fe}_4[{\rm Fe}({\rm CN})_6]_3$ test.

III. Lassaigne extract of B and D gives positive sodium nitroprusside test.

Based on these observations, which option is correct? (JEE Main 2020)

- (a) *A* : Alitame; *B* : Saccharin ; *C* : Aspartame; *D* : Sucralose
- (b) A : Saccharin; B : Alitame; C : Sucralose; D : Aspartame
- (c) A : Aspartame; B : Alitame; C : Saccharin; D : Sucralose
- (d) A : Aspartame; B : Saccharin; C : Sucralose; D : Alitame
- **11.** For the thiol group of cysteine at pH 8.2, of pK_a is
 - 8.3, the concentration ratio of RS^- vs RSH

$$\left| \begin{array}{c} \text{cysteine H}_2\text{N} - \begin{array}{c} \text{CH} - \text{COOH} \\ | \\ \text{CH}_2\text{SH} \end{array} \right| \text{ is } \\ \text{(a) } 0.8 \quad \text{(b) } 0.6 \quad \text{(c) } 0.9 \end{array} \right|$$

12. In cysteine at $pK_a = 8.3$, pH = 8.2. If total amounts of *R*SH and *R*S⁻ is equal to 100%, then the side-chain of cysteine will exist in the protonated thio form to the extent of (a) 26% (b) 36%

(d) 0.2

(JEE Main 2019)

(a)	2070	(0)	00/0
(c)	46%	(d)	56%

- 13. If pK_a of carboxyl (2.34) and ammonia (9.69) groups, for alanine, the pH would be
 (a) 12.03 (b) 7.35
 (c) 6.02 (d) 11.33
- **14.** Fructose and glucose can be distinguished by
 - (a) Fehling's test
 - (b) Barfoed's test
 - (c) Benedict's test
 - (d) Seliwanoff's test
- **15.** The peptide that gives positive ceric ammonium nitrate and carbylamine tests is (JEE Main 2019)
 - (a) Lys-Asp
 - (b) Ser-Lys
 - (c) Gln-Asp
 - (d) Asp-Gln
- 16. Which of the following statement is not true about sucrose? (JEE Main 2019)

(a) It is also named as invert sugar.

- (b) The glycosidic linkage is present between C_1 of $\alpha\mbox{-glucose}$ and C_2 of $\beta\mbox{-fructose}$
- (c) It is a non-reducing sugar
- (d) On hydrolysis, it produces glucose and fructose

17. The product of the reaction D-glyceraldehyde $\xrightarrow{\text{Me}_2\text{CO}}_{\text{HCl}} \xrightarrow{\text{H}_2\text{C}=\text{CHMgCl}} \xrightarrow{\text{O}_3} \xrightarrow{\text{O}_3}$



- 18. Glucose on prolonged heating with HI gives
 (a) n-hexane
 (b) 1-hexene (JEE Main 2018)
 (c) Hexanoic acid
 (d) 6-iodohexanal
- **19.** The predominant form of histamine present in human blood is $(pK_a, \text{Histidine} = 6.0)$ (*JEE Main 2018*)



20. Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution ? (JEE Main 2017)



- 21. Which of the following compounds can be detected by Molisch's test ? (AIEEE 2008)
 - (a) Nitro compounds (b) Sugar's
 - (c) Amines (d) Primary alcohols
- **22.** Which one of the following statements is correct? (AIEEE 2012)
 - (a) All amino acids except lysine are optically active.
 - (b) All amino acids are optically active.
 - (c) All amino acids except glycine are optically active.
 - (d) All amino acids except glutamic acids are optically active.

23. The correct match between Column I and Column II is

	Column I		Column II
А.	Ester test	Ρ.	Tyr
В.	Carbylamine test	Q.	Asp
С.	Phthalein dye test	R.	Ser
		S.	Lvs

Codes	(JEE Main 2019)
(a) $A \rightarrow Q; B \rightarrow S; C \rightarrow R$	(b) $A \rightarrow R, B \rightarrow Q; C \rightarrow P$
(c) $A \rightarrow R; B \rightarrow S; C \rightarrow Q$	(d) $A \rightarrow Q; B \rightarrow S; C \rightarrow P$

- **24.** Sucrose (cane sugar) is a disaccharide. One molecule of sucrose on hydrolysis gives
 - (a) 2 molecules of glucose [NCERT Exemplar]
 - (b) 2 molecules of glucose + 1 molecule of fructose
 - (c) 1 molecule of glucose + 1 molecule of fructose
 - (d) 2 molecules of fructose
- **25.** An organic compound consumes 4 moles of periodic acid to form following compounds, per mole of the starting compounds HCHO, 3HCOOH and CH₂COOH. The organic compound is

(a) glucose	(b) fructose
(c) gluconic acid	(d) sorbitol

- **26.** An optically active compound *A*, gave an $[\alpha]_D^{25} = 30^\circ$, while a mixture of *A* and its enantiomer *B*, gave $[\alpha]_D^{25} = +15^\circ$. The ratio of *A* to *B* in the mixture is (a) 1 to 3 (b) 3 to 1 (c) 1 to 2 (d) 2 to 1
- **27.** Which of the following statement(s) is/are true?
 - I. All amino acids contain one chiral centre.
 - II. Some amino acids contain one, while some contain more chiral centre or even no chiral centre.
 - III. All amino acids found in protein have L-configuration.
 - IV. All amino acids found in proteins have 1° amino group.
 - (a) II, III and IV(b) II and III(c) I, III and IV(d) I and IV
- **28.** Histidine, a heterocyclic amino acid has following structure at pH < 1.82



At pH > 1.82, it should have which structure ?



29. A, B and C are three biomolecules. The results of the tests performed on them are given below: (JEE Main 2020)

	Molisch's test	Barfoed test	Biuret test
1	Positive	Negative	Negative
	D	D	37

B	Positive	Positive	Negative
C	Negative	Negative	Positive

A, B and C are respectively:

- (a) A = Lactose, B = Glucose, C = Alanine
- (b) A = Glucose, B = Fructose, C = Albumin
- (c) A = Lactose, B = Glucose, C = Albumin
- (d) A = Lactose, B = Fructose, C = Alanine
- **30.** Maltose on treatment with dilute HCl gives
 - (a) D-glucose and D-fructose (JEE Main 2019)
 - (b) D-fructose
 - (c) D-galactose
 - (d) D-glucose

Numeric Value Questions

- 31. The number of chiral carbon(s) present in peptide, Ile-Arg-Pro, is (JEE Main 2020)

Answers

Round I									
1. (d)	2. (d)	3. (a)	4. (b)	5. (c)	6. (a)	7. (a)	8. (d)	9. (d)	10. (c)
11. (c)	12. (c)	13. (b)	14. (c)	15. (c)	16. (a)	17. (b)	18. (d)	19. (d)	20. (a)
21. (b)	22. (d)	23. (b)	24. (b)	25. (a)	26. (a)	27. (a)	28. (d)	29. (a)	30. (d)
31. (c)	32. (d)	33. (a)	34. (b)	35. (c)	36. (d)	37. (d)	38. (d)	39. (c)	40. (c)
41. (d)	42. (d)	43. (d)	44. (a)	45. (d)	46. (c)	47. (c)	48. (b)	49. (c)	50. (d)
51. (c)	52. (d)	53. (b)	54. (a)	55. (b)	56. (d)	57. (d)	58. (d)	59. (b)	60. (a)
61. (a)	62. (c)	63. (a)	64. (c)	65. (c)	66. (c)	67. (c)	68. (b)	69. (b)	70. (a)
71. (a)	72. (a)	73. (d)	74. (b)	75. (a)	76. (b)	77. (a)			
Round II									
1. (d)	2. (d)	3. (c)	4. (c)	5. (d)	6. (a)	7. (b)	8. (c)	9. (a)	10. (d)
11. (a)	12. (d)	13. (c)	14. (d)	15. (b)	16. (b)	17. (a)	18. (a)	19. (d)	20. (a)
21. (b)	22. (c)	23. (d)	24. (c)	25. (c)	26. (b)	27. (b)	28. (a)	29. (c)	30. (d)
31. (4)	32. (9)	33. (3)							

Solutions

Round I

- **1.** Carbohydrate are optically active polyhydroxy aldehyde or polyhydroxy ketones.
 - > C = 0,— OH are functional groups of typical ketose.
 - -CHO, -OH functional groups of typical aldose.



- **4.** α-D-(+)-glucopyranose and β-D-(+)-glucopyranose are anomers (a pair of stereoisomers which differ in configuration only around first carbon atom).
- **7.** Chiral centre is also called stereo-centre or stereogenic center.

Linear structure of glucose is as follows



Fischer formula

Number of stereo-centre (C^*) = 4.

Cyclic structure of glucose are as follows:



Haworth formula Number of stereo-centre (C^*) in each anomer = 5.

- When glucose reacts with Br₂ water, gluconic acid is obtained as main product.
- 9. The correct chemical equations are given as follows



Therefore,

(i) Saccharic acid not gluconic acid is obtained by the oxidation of glucose with HNO_3 . Thus, it is incorrect statement.

- (ii) Gluconic acid is a monocarboxylic acid and not a dicarboxylic acid. Thus, it is incorrect statement.
- (iii) Glucose exists predominantly in the cyclic structure than the open chain structure :



But gluconic acid can not exist in cyclic structure. (Stereochemical configurations are not specified in the structures given above, for simplicity). Thus, it is incorrect.

- (iv) Gluconic acid is a partial oxidation product of glucose. Hence, it is correct statement.
- **10.** Cyclic hemiacetal forms of monosaccharides which differ only in the configuration of the hydroxyl group at C_1 are anomers.
- **11.** The correct statements can be explained as follows
 - (a) **Penta-acetate** of glucose does not react with hydroxylamine to give oxime. Because, the cyclic form (pyranose) of glucose after pentaacetate formation does not have free —CHO or C = O group.
 - (b) Cyclic form of glucose has two diastereomeric forms which are named as α and β form. Each form its own crystal.

(d) Glucose reacts with hydroxylamine to form oxime. The incorrect statement is (c). It can be corrected as follows :

Glucose does not give Schiff's test due to absence of free — CHO in cyclic form.

- **12.** Fructose is oxidised by ammonical AgNO₃.
- 13. Aldehydes and α-hydroxy ketones give positive Tollen's test. Glucose is a polyhydroxy aldehyde and fructose is an α-hydroxy ketone.
- 14. The sweeter form of D-fructose is fructopyranose. The high temperature causes a shift in the pyranose ⇒ furanose equilibrium towards the less sweet furanose.
- **15.** The specific rotation of invert sugar is one half of the sum of those of individual monosaccharides.
 - \therefore Specific rotation of invert sugar

$$=\frac{1}{2} [+52.7^{\circ} + (-92.4^{\circ})] = -19.9^{\circ}$$

16. Lactose contains α -glycosidic linkage between C_1 of galactose an C_4 of glucose.



19. Amylopectin is the water-soluble component of starch. It is a branched-chain polymer of α -D-glucose. The main chain consists of an α -1, 4'- glycosidic linkages between α -D-glucose units and the branches are connected to the main chain by α -1, 6'-glycosidic linkages.

Its structure can be represented as,



20. Glycogen is not a straight chain polymer similar to amylose. It is highly branched structure similar to amylopectin.

It is known to be the storage material of animals. It is found in liver, muscles and brain. It breaks down to glucose by the action of enzymes when body needs a glucose. It is also found in yeast and fungi. Statement (a) is incorrect.

22. Protein gives blue-violet colour with ninhydrin while carbohydrate give negative test with ninhydrin. Carbohydrates give brown red ppt. with Benedict's solution. Hence, compound is a monosaccharide.



27. Cations move towards cathode and when pH < pI, thus cationic form dominates.

28. ∵ Here, pH = 10.5 and pI = 9.6 pH > pI ∴ Anionic form dominates, COO⁻ i.e. H₂N — H is present in solution. (CH₂)₄ NH₂

29. $H_3 \overset{+}{N}CH - COOH \xrightarrow[First ionisation]{On neutralisation}} H_3 \overset{+}{N}CH - COO^-$ CH₂CH₂COOH Cationic form

$$\begin{array}{ccc} H_{3}\overset{+}{N}CH-COO^{-} \xrightarrow{\text{Second ionisation}} & H_{3}\overset{+}{N}CH-COO^{-} \\ & & \\ CH_{2}CH_{2}COOH & & \\ & CH_{2}CH_{2}COO^{-} \end{array}$$

So,
$$\mathbf{pI} = \frac{\mathbf{p}K_{a_1} + \mathbf{p}K_{a_3}}{2} = \frac{2.2 + 4.3}{2} = 3.25$$

- **30.** Proline has a 2° amino group. Hence, it is not estimated by this method.
- 31. The most basic amino acid is lysine. There are only two basic amino acids (amino acids with two basic nitrogen containing groups). These are lysine and arginine. Lysine have an ε-amino group. At physiological pH, the groups are protonated as follows

$$\begin{array}{c} \stackrel{\bullet}{\overset{\bullet}{\operatorname{H}_3}} \stackrel{\circ}{\underset{\scriptstyle H_3}{\overset{\bullet}{\operatorname{N}}}} \stackrel{\circ}{\underset{\scriptstyle H_2}{\overset{\circ}{\operatorname{CH}_2}}} \stackrel{\circ}{\underset{\scriptstyle H_2}{\overset{\scriptscriptstyle H}{\operatorname{CH}_2}} \stackrel{\circ}{\underset{\scriptstyle H_2}{\overset{\scriptscriptstyle H}{\operatorname{CH}_2}}} \stackrel{\circ}{\underset{\scriptstyle H_2}{\overset{\scriptscriptstyle H}{\operatorname{CH}_2}} \stackrel{\circ}{\underset{\scriptstyle H_2}{\overset{\scriptscriptstyle H}{\underset{\scriptstyle H_2}{\overset{\scriptscriptstyle H}{\operatorname{CH}_2}}} \stackrel{\circ}{\underset{\scriptstyle H_2}{\overset{\scriptscriptstyle H}{\operatorname{CH}_2}} \stackrel{\circ}{\underset{\scriptstyle H_2}{\overset{\scriptscriptstyle H}{\operatorname{CH}_2}} \stackrel{\circ}{\underset{\scriptstyle H_2}{\overset{\scriptscriptstyle H}{\operatorname{CH}_2}}} \stackrel{\circ}{\underset{\scriptstyle H_2}{\overset{\scriptscriptstyle H}{\operatorname{CH}_2}} \stackrel{\circ}{\underset{\scriptstyle H_2}{\overset{\scriptscriptstyle H}{\operatorname{CH}_2}} \stackrel{\circ}{\underset{\scriptstyle H_2}{\overset{\scriptscriptstyle H}{\operatorname{CH}_2}}} \stackrel{\circ}{\underset{\scriptstyle H_2}{\overset{\scriptscriptstyle H}{\operatorname{CH}_2}} \stackrel{\circ}{\underset{\scriptstyle H_2}{\overset{\scriptscriptstyle H}{\operatorname{CH}_2}}} \stackrel{\circ}{\underset{\scriptstyle H_2}{\overset{\scriptstyle H}{\operatorname{CH}_2}}} \stackrel{\scriptstyle H_2}{\underset{\scriptstyle H_2}{\overset{\scriptstyle H}{\operatorname{CH}_2}}} \stackrel{\scriptstyle H_2}{\underset{\scriptstyle H_2}} \stackrel{\scriptstyle H_2}{\underset{\scriptstyle H_2}{\overset{\scriptstyle H}{\operatorname{CH}_2}}} \stackrel{\scriptstyle H_2}{\underset{\scriptstyle H_2}} \stackrel{\scriptstyle H_2}{\underset{\scriptstyle H_2}}} \stackrel{\scriptstyle H_2}{\underset{\scriptstyle H_2}} \stackrel{\scriptstyle H_2}{\underset{\scriptstyle H_2}}} \stackrel{\scriptstyle H_2}{\underset{\scriptstyle H_2}}} \stackrel{\scriptstyle H_2}{\underset{\scriptstyle H_2}} \stackrel{\scriptstyle H_2}{\underset{\scriptstyle H_2}} \stackrel{\scriptstyle H_2}{\underset{\scriptstyle H_2}} \stackrel{\scriptstyle H_2}{\underset{\scriptstyle H_2}} \stackrel{\scriptstyle H_2}} \stackrel{\scriptstyle H_2}{\underset{\scriptstyle H_2}} \stackrel{\scriptstyle H_2}} \stackrel{\scriptstyle H_2}} \stackrel{\scriptstyle H_2} \stackrel{\scriptstyle H_2}} \stackrel{\scriptstyle H_2} \stackrel\scriptstyle H_2} \stackrel\scriptstyle H_2} \stackrel\scriptstyle H_2} \stackrel{\scriptstyle H_2} \stackrel\scriptstyle H_2} \stackrel\scriptstyle$$

Asparagine is an acidic amino acid. It is the amide of aspartate.

Histidine is an imidazole substituted alanine.

Serine contain alcohol group and is an —OH substituted alanine.

32. Histidine has following structure is



At highly acidic pH, i.e. 2 both the nitrogens with lone pairs will accept one H^+ each and -C - OH will not

loose its $H^{\scriptscriptstyle +}.$ Thus, the final structure of histidine at $pH=\ 2$ will be



33. (i) Barfoed test is used for detecting the presence of monosaccharides like glucose, fructose etc. Barfoed reagents is Cu (II) acetate solution.





- **37.** The first codon of *m*-RNA will be always **AUG**. This codon specifies the amino acid methionine. So, the first amino acid in a polypeptide chain will be always methionine.
- **39.** The secondary structure of protein includes two types: α -helix and β -pleated sheet. In α -helix structure, the polypeptide chain is coil around due to presence of intramolecular H-bonding.
- 40. Six isomeric tripeptide may exist as,

Val. Uyr. Ala, Tyr. Ala. Val Val. Ala. Tyr, Ala. Tyr. Val Tyr. Val. Ala, Ala. Val. Tyr

- **44.** Val-Gly-Phe-val-Ala-Val Random hydrolysis gives Ala-Val dipeptide fragment which indicates the connected presence of Ala and Val.
- **45.** Amino acid molecules can be represented as,

$$R$$
—CH $<_{\rm NH_2}^{\rm COOH}$

Nature of the 'R' group will determine the basicity (hence, pK_a) of an amino acid.

	<i>'R'</i> in the amino group	Nature of <i>R</i>	Nature of the amino acids
1.	$-(CH_2)_{3}-NH-C \bigvee_{NH_2}^{\uparrow} HH_2$ (Arginine : Arg)	Basic	More basic (due to the presence of acetamidine group)
2.	-CH2-C	Acidic	Acidic
	(Aspartic acid: Asp)		
3.	—H (Glycine) : Gly	Neutral	Neutral
4.	$-(CH_2)_4$ $-NH_3$ (Lysine : Lys)	Basic	Basic

Acetamidine group present in arginine is

Its self-protonation/deprotonation makes its conjugate acid very stable.

The resonating structure of acetamidine group is

The basicity order of given amino acids in aqueous solution is as follows:

Asp < Gly < Lys < Arg

Thus, order of pK_a values is also,

$$\label{eq:approx} \begin{split} & {\rm Asp} < {\rm Gly} < \ {\rm Lys} \ < \ {\rm Arg} \\ & {\rm p}K_{a} \ {\rm value}: \ (3) \ (6) \ (9.8) \ (10.8) \end{split}$$

 ${\bf 46.}\,$ Formation of the tripeptide (Val-Ser-Thr) can be shown



- **47.** Albumin and insulin are common examples of globular proteins. In this structure, chains of polypeptides coil around to give a spherical shape.
- **48.** In fibrous proteins, polypeptide chains are held together by hydrogen and disulphide bonds.
- **49.** The internal rearrangement of 3-phosphoglyceric acid into 2-phosphoglyceric acid takes place in the presence of enzyme phosphoglycero mutase.
- **55.** Pepsin, ptyalin and lipase are enzyme while cellulose is not the enzyme. It is a polysaccharide.
- **57.** Almost all enzymes are globular proteins. These are biocatalysts because they speed up the reactions in biosystems.
- 65. Ascorbic acid is vitamin C. Its structure is



74. Oxytocin is a hormone.



75. Adenine and lysine react with CHCl₃ and alc. KOH. This type of reagent show carbylamine reaction. Carbylamine reaction is given by only primary amine.



General reaction is as follows :

$$\begin{array}{c} R \longrightarrow \mathrm{NH}_2 + \mathrm{CHCl}_3 + 3\mathrm{KOH} \longrightarrow \\ ^{1^{\circ} \text{ amine}} \qquad \qquad R \longrightarrow \mathrm{R} \longrightarrow \mathrm{R} = \mathrm{C} + 3\mathrm{KCl} + 3\mathrm{H}_2\mathrm{O} \\ \mathrm{Isocyanide} \end{array}$$

Adenine and lysine both have primary amine.

(a) Adenine



In this structure, primary amine is present. Thus, it shows carbylamine reaction.

Lysine



Here, 2 primary amine are present, thus it show carbylamine reaction.



CH₃ N H

Here, secondary amine (2°) are present, thus it doesn't show carbylamine reaction.

Proline Cyclic amino acid



Here, secondary amine (2°) are present, thus it doesn't show carbylamine reaction.

- (c) **Adenine** show this reaction but **thymine** does not show this reaction with carbylamine reaction.
- (d) **Adenine** It show the reaction with carbylamine reaction but **proline** does not show reaction.
- **76.** RNA does not have double stranded α -helix structure. Helixes present in RNA are single-stranded but sometimes they fold back on themselves to form a double helix structure.

RNA usually does not replicate. It is present in the nucleus of the cell. It controls the synthesis of protein.

RNA molecules are of three types, i.e. messenger's RNA (*m*-RNA), ribosomal RNA (*r*RNA), transfer RNA (*t*-RNA).

Hence, correct answer is (b).

77. RNA contains, adenine (A), guanine (G), cytosine (C) and uracil (U). In the given options



is not a pyrimidine base but a derivative of uracil.

Round II

Ńе

 Glucose is a polyhydroxy aldohexose. Its number of free — OH groups can be calculated by acetylation process which is done by using (CH₃CO)₂O/Py or CH₃COCl/Py as :



Or
$$R(OH)_n + n(CH_3CO)_2O \xrightarrow[Py]{-nCH_3COOH} R(OCOCH_3)_n$$



So, *x*, *y* and *z* in these reactions are 4, 6 and 5 respectively.

2. At pH = 6, glutamic acid exists as a dianionic species and migrates to anode while arginine exists as cationic species and moves to cathode. Alanine does not migrate to any electrode at its isoelectric point.

3.
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Glycosidic bond}$$

Sucrose $C_6H_{12}O_6 + C_6H_{12}O_6$
 $\xrightarrow{Glucose} A(say)$ $\xrightarrow{Fructose} B$
 $\xrightarrow{A(say)}$ Red colouration

Seliwanoff's reagent test is given by ketohexoses (here, *B*) and sucrose only but not by any aldohexose (here, *A*), lactose and maltose.

- **4.** Isoelectric point is a pH at which Zwitter ions do not migrate towards any of the electrode. Amino acids are also Zwitter ions hence, they do not migrate under electric field at isoelectric point.
- **5.** Amino acid, alanine contains side chain of methyl group, i.e.

$$CH_3 - CH < NH_2 COOH$$

Muscles contain myoglobin protein.

 Haemoglobin act as an oxygen carrier in the blood because four Fe²⁺ ions of haemoglobin can bind with 4 molecules of O₂ and form oxyhaemoglobin.

 $Hb + O_2 \longrightarrow Oxyhaemoglobin$

7. Glucose and galactose are having identical configuration at all the positions except at C-4 position.

Both of them are diastereomers that differ in configuration at only one chirality center. Hence, these are called **epimers**. Structures of glucose and galactose are as follows



- **8.** Insulin is an important peptide hormone. Its structure was determined by Sangar. It has two polypeptide chains with 21 and 30 amino acids. Hence, total amino acids are 51.
- Maltose is a disaccharide formed from monosaccharides α-D- glucose and α-D-glucose *via* C₁—C₄ glycosidic linkage.





Fehling's solution CuSO₄ + Na, K-tartrate (Rochelle salt)

Barfoed's reagent

$$(CH_{3}COO)_{2}Cu + CH_{3}COOH + H_{2}O_{(1\%)} + H_{2}O_{(92\%)}$$

Benedict's solution $CuSO_4$ + Na-citrate + Na₂CO₃ **Seliwanoff's test** is used to differentiate between ketose and aldose. The reagent is a solution of resorcinol in concentrated HCl.

 $\frac{[RSH]}{[RS^-] + [RSH]} \times 100 = 56\%$ **13.** pH = $\frac{2.34 + 9.69}{2} = 6.015$

...

or

 $8.2 = 8.3 + \log \frac{[RS^-]}{[RSH]}$

 $\frac{[RS^-]}{[RSH]} = 0.8$

12. From the above calculations, $\frac{[RSH]}{[RS^-]} = \frac{1}{0.8} = 1.25$

The reagent when heated along with a sugar will produce furfural or hydroxy- methylfurfural, which further reacts to give red colour. Ketose (fructose) reacts more quickly than aldose (glucose).

15. The peptide that gives positive cerric ammonium nitrate and carbylamine tests is ser-lys. The structures of serine and lysine are,

HO—CH₂—C H— COOH;
NH₂
Serine
$$H_2$$
 N—(CH₂)₄—C H— COOH
NH₂
Lysine

16. Sucrose is linked through a glycosidic linkage between C_1 of α -glucose and C_2 of β -fructose.

Since, the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non-reducing sugar.

Statement-(b) is not true for sucrose.



On hydrolysis with acids or enzyme, sucrose gives equimolar mixture of D-(+)-glucose and D-(-)-fructose.



18. HI is a strong reducing agent. It reduces both primary and secondary alcoholic groups of glucose along with the carbonyl group to produce *n*-hexane as



19. Our blood is slightly basic in nature with pH range from 7.35-7.4. The structure of histamine is given below



Basic nitrogen of imidazole ring

It is produced by decarboxylation of histidine having following structure.

It is clearly visible from the above structure that histamine has two basic centres namely aliphatic amino group and basic nitrogen of imidazole ring.

The aliphatic amino group has pK_a around 9.4.

In blood with pH around 7.4 the aliphatic amino group of histamine become protonated to give a single charged cation as shown below



20. Sugars have an aldehyde, a ketone, a hemiacetal or a hemiketal group is able to reduce an oxidising agent. These sugars are classified as reducing sugars.



Hemiacetal can be easily reduced by oxidising agent such as Tollen's reagent.



21. Molisch's test is used for the detection of carbohydrates. Add two drops of alcoholic solution of α -naphthol to the carbohydrate solution under study.

Add conc. H_2SO_4 slowly by the side of the test tube. A violet ring is formed at the junction of the two liquids, if carbohydrate is present.

Glycine
$$\operatorname{CH}_2^{\operatorname{NH}_2}$$
 is α -amino acetic acid with no

chiral carbon, thus optically inactive.

23.



- (A) Ester test confirms the presence of —COOH group.
- (B) Carbylamine test confirms the presence of $-NH_2$ group (1°).
- (C) Phthalein dye test confirms the presence of phenolic OH group.

The correct match is

$$A \to (Q); (B) \to (S) (C) \to (P)$$

Thus, the mixture is 50% optically pure. Hence, the amount of A = 50 + 25 = 75 $B = 0 + 25 = 25 \therefore A : B = 3 : 1$

- 28. On increasing the pH by adding an alkali; H⁺ will be lost from —COOH.
- **29.** Molisch's test is for all carbohydrates (except trioses and tetroses).

∴ Lactose, fructose and glucose give positive test.
Barfoed test is positive only for monosaccharides.
∴ It is given by glucose and fructose, not by lactose (because it is disaccharide).
Biuret test is for compounds with peptide linkages.
∴ Albumin (a protein) gives positive test. Alanine is an amino acid but have no peptide linkage.

 \therefore It does not give biuret test.

- So, A =lactose, B = glucose and C = albumin.
- 30. Maltose on treatment with dil. HCl gives D-glucose. Hydrolysis of maltose yields two moles of α- D-glucose.

Thus, it is composed of two α -D-glucose units in which C_1 of one glucose unit (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.



31. The amino acids present in the given tripeptide Ile-Arg-Pro are isolucine, arginine and proline.



Number of chiral carbons present in the given tripeptide is 4.



Total number of chiral carbon in sucrose = 9



These are three chiral centres shown by asterisk sign.