BIOMOLECULES

CHAPTER 14

INTRODUCTION

Carbohydrates are defined as polyhydroxy aldehydes or polyhydroxy ketones or substances which give these on hydrolysis and contain at least one chiral carbon atom. It may be noted here that aldehydic and ketonic groups in carbohydrates are not present as such but usually exist in combination with one of the hydroxyl groups of the molecule in the form of hemiacetals and hemiketals respectively.

Classification

The carbohydrates are divided into three major classes depending upon whether or not they undergo hydrolysis, and if they do, on the number of products formed.

(i) **Monosaccharides:** The monosaccharides are polyhydroxy aldehydes or polyhydroxy ketones which cannot be decomposed by hydrolysis to give simpler carbohydrates. Examples are glucose and fructose, both of which have molecular formula, $C_6H_{12}O_6$.

$$\underset{\text{glucose or fructose}}{C_6H_{12}O_6} + H_2O \xrightarrow{H^+} \text{No reaction}$$

(ii) **Oligosaccharides:** The oligosaccharides (Greek, oligo, few) are carbohydrates which yield a definite number (2-9) of monosaccharide molecules on hydrolysis. They include,

(a) Disaccharides, which yield two monosaccharide molecules on hydrolysis. Examples are sucrose and maltose, both of which have molecular formula, $C_{12}H_{22}O_{11}$.

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

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{2C_6H_{12}O_6}$$

(b) Trisaccharides, which yield three monosaccharide molecules on hydrolysis. Example is raffinose, which has molecular formula, $C_{18}H_{32}O_{16}$.

$$\underset{\text{raffinose}}{C_{18}H_{32}O_{16}} + 2H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} + \underset{\text{galactose}}{C_6H_{22}O_6}$$

(c) Tetrasaccharides, etc.

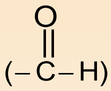
(iii) **Polysaccharides:** The polysaccahrides are carbohydrates of high molecular weight which yield many monosaccharide molecules on hydrolysis. Examples are starch and cellulose, both of which have molecular formula, $(C_6H_{10}O_5)_n$.

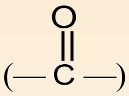
$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H^+} \underset{\text{glucose}}{nC_6H_{12}O_6}$$

In general, the monosaccharides and oligosaccharides are crystalline solids, soluble in water and sweet to taste. They are collectively known as sugars. The polysaccharides, on the other hand, are amorphous, insoluble in water and tasteless. They are called non-sugars. The carbohydrates may also be classified as either reducing or non-reducing sugars. All those carbohydrates which have the ability to reduce Fehling's solution and Tollen's reagent are referred to as reducing sugars, while others are non-reducing sugars. All monosaccharides and the disaccharides other than sucrose are reducing sugars.

MONOSACCHARIDES

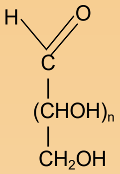
The monosaccharides are the basis of carbohydrate chemistry since all carbohydrates are either monosaccharides or are converted into monosaccharides on hydrolysis. The monosaccharides are polyhydroxy aldehydes or polyhydroxy ketones. There are, therefore, two main classes of monosaccharides.

1. The Aldoses, which contain an aldehyde group 
$(-\overset{\overset{\displaystyle O}{\|}}{C}-H)$

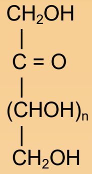
2. The Ketoses, which contain a ketone group 
$(-\overset{\overset{\displaystyle O}{\|}}{C}-)$

The aldoses and ketoses are further divided into sub-groups on the basis of the number of carbon atoms in their molecules, as trioses, tetroses, pentoses, hexoses, etc. To classify a monosaccharide completely, it is necessary to specify both, the type of the carbonyl group and the number of carbon atoms present in the molecule. Thus monosaccharides are generally referred to as Aldo trioses, aldosterone's, aldopentose's, aldohexoses, ketohexoses, etc.

The aldoses and ketoses may be represented by the following general formulas.



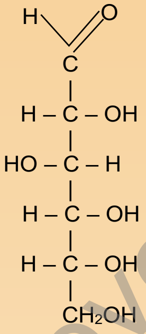
Aldoses
(n = 1, 2, 3, 4, 5)



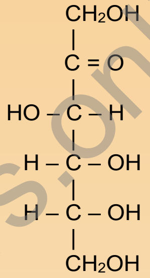
$$\begin{array}{c} CH_2OH \\ | \\ C=O \\ | \\ (CHOH)_n \\ | \\ CH_2OH \end{array}$$

Ketoses
(n = 0, 1, 2, 3, 4)

Glucose and fructose are specific examples of an aldose and a ketose.



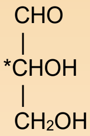
Glucose (an aldohexose)



fructose
(a ketohexose)

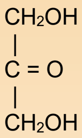
Trioses

D and L Terminology: The simplest of all carbohydrates that fit the definition we have given for carbohydrates are the trioses, glyceraldehyde and dihydroxyacetone. Glyceraldehyde is aldotriose, and dihydroxyacetone is a ketotriose.



$$\begin{array}{c} CHO \\ | \\ {}^*CHOH \\ | \\ CH_2OH \end{array}$$

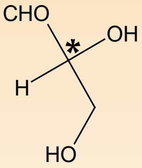
Glyceraldehyde
(an aldotriose)



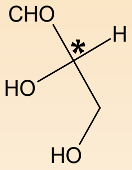
$$\begin{array}{c} CH_2OH \\ | \\ C=O \\ | \\ CH_2OH \end{array}$$

Dihydroxyacetone
(a ketotriose)

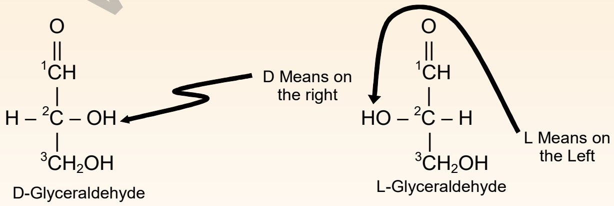
Glyceraldehyde contains one asymmetric carbon atom (marked by an asterisk) and can thus exist in two optically active forms, called the D-form and the L-form. Clearly, *the two forms are mirror images that cannot be superimposed,* that is they are ***enantiomers***.



D-Glyceraldehyde



L-Glyceraldehyde



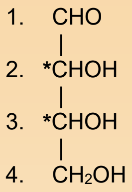
The two forms of glyceraldehyde are especially important because the more complex monosaccharides may be considered to be derived from them. They serve as a reference point for designating and drawing all other monosaccharides. In carbohydrate chemistry, the Fischer projection formulas are always written with the aldehyde or ketone groups at the top of the structure. By definition, if the hydroxyl group on the asymmetric carbon atom farthest from aldehyde or ketone group projects to the right, the compound is a member of the D-family. If the hydroxyl group on the farthest asymmetric carbon projects to the left, the compound is a member of the L-family. The maximum number of optical isomers of a sugar is related to the number of asymmetric carbon atoms in the molecule and may be calculated by the following simple equation.

Maximum Number of Optical Isomers = 2^{n}, where n = the number of asymmetric carbon atoms. Since glyceraldehyde contains only one asymmetric carbon atom, the number of optical isomers is 2^1. We know that 2^1 is = 2, and we have seen that there indeed two different glyceraldehyde's.

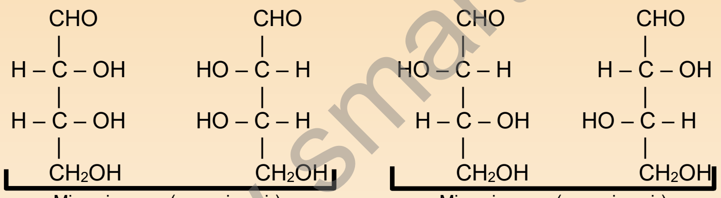
Aldotetroses

If we examine the general formula of an aldotetrose, we see that they contain two asymmetric carbon atoms (marked by asterisks).

This means that 2^2 or 4 optical isomers are possible. They may be represented as the following two pairs:



an aldotetrose



Mirror images (recemic pair)

D (–)-erythrose L (+)-erythrose

Mirror images (recemic pair)

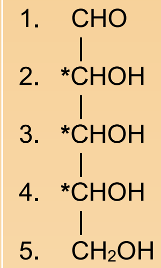
D (–)-threose L (+)-threose

All four isomers have been prepared synthetically. The D- and L-erythrose are mirror images, that is, they are enantiomers. They have exactly the same degree of rotation but in opposite directions. Equal amounts of the two would constitute a racemic mixture, that is, a mixture that would allow a plane-polarised light to pass through the solution unchanged but could be separated into dextrorotatory and levorotatory isomers. The same comments hold for D- and L-threose. However, D-erythrose and L-threose are not images, that is, they are diastereomers *(optical isomers that are not mirror images are called diastereomers),* and the degree of rotation of each would probably differ.

Aldopentoses

If we examine the general formula of an aldopentose, we see that they contain three asymmetric carbon atoms.

This means that 2^3 or 8 optical isomers are possible. These are: - D(–) xylose, L(+)-xylose, D(–) xylose, L(–)xylose, D(–) arabinose, L(+)-arabinose, D(–)-ribose, L(+)-ribose

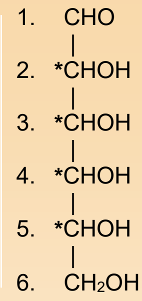


an aldopentose

Aldohexoses

If we examine the general formula of aldohexose, we see that it contains four asymmetric carbon atoms. This means that 2^4 or 16 optical isomers are possible. D and L forms of altrose, talose glucose, mannose, galactose, talose, arabinose and idose

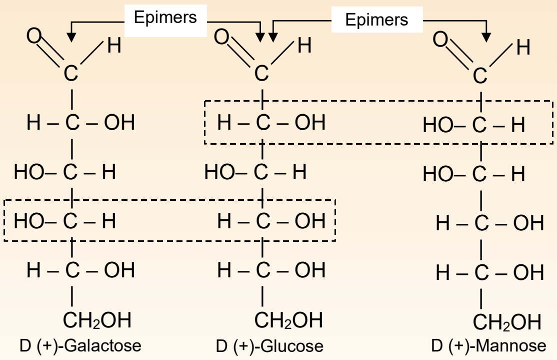
Only three of the sixteen possible aldohexoses are found in nature (all sixteen isomers have been prepared synthetically). They are D-glucose, D- mannose, and D-galactose. No one of these three optical iosmers is a mirror image of any of the others, so all three are diastereomers of each other.



an aldohexose

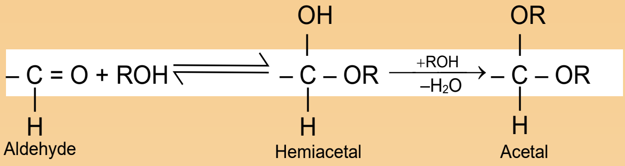
Epimers

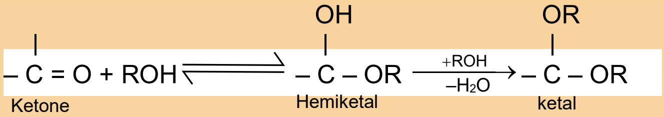
A pair of diastereomers that differ only in the configuration about of a single carbon atom are said to be epimers. e.g D(+)- glucose is epimeric with D(+) -mannose and D(+) -galactose as shown below:



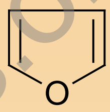
Cyclic structure of Monosaccharides

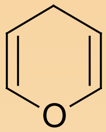
We know that aldoses (and ketoses) react with alcohols to give first hemiacetals (and hemiketals) and then acetals (and ketals), i.e.


$$-\underset{H}{C}=O + ROH \rightleftharpoons -\overset{OH}{\underset{H}{C}}-OR \xrightarrow[-H_2O]{+ROH} -\overset{OR}{\underset{H}{C}}-OR$$


$$-\overset{|}{C}=O + ROH \rightleftharpoons -\overset{OH}{C}-OR \xrightarrow[-H_2O]{+ROH} -\overset{OR}{C}-OR$$

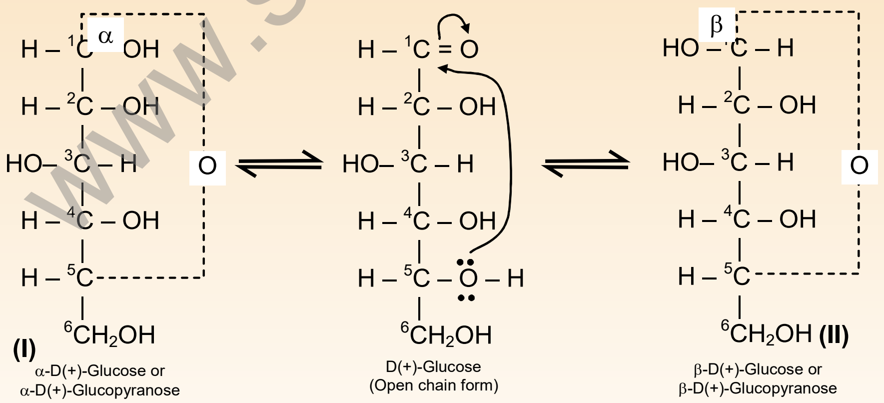
Since monosaccharides contain a number of hydroxyl groups and an aldehyde or a keto group, therefore, any one of the –OH groups (usually C_4 or C_5 in aldohexoses and C_5 or C_6 in ketohexoses) may combine with the aldehyde or the keto group to form intramolecular hemiacetal or hemiketal.


furan


pyran

As a result, the open chain formulae do not represent the actual structures of the monosaccharides. Their actual structures are cyclic involving five or six membered rings containing an oxygen atom. The five membered ring containing one oxygen atom because of its similarity with furan is called the furanose form and the six membered ring containing one oxygen atom because of its resemblance with pyran is called the pyranose form. In nut shell, all the monosaccharides (pentoses and hexoses) in the free state always exist in the pyranose form. However, in the combined state some monosaccharides such as ribose, 2-deoxyribose, fructose etc., usually exist in the furanose form.

Cyclic Structure of Glucose – Anomers


(I) α-D(+)-Glucose or α-D(+)-Glucopyranose

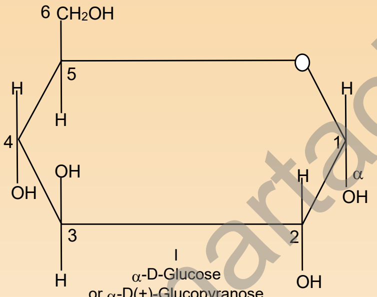
D(+)-Glucose (Open chain form)

(II) β-D(+)-Glucose or β-D(+)-Glucopyranose

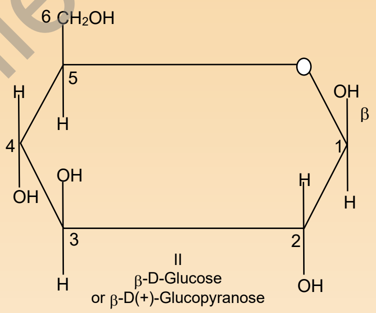
We have discussed above that monosaccharides have cyclic hemiacetal or hemiketal structures. To illustrate, let us first consider the example of D-glucose. During hemiacetal formation C_5 – OH of glucose combines with the C_1 – aldehydic group. As a result, C_1 becomes chiral or asymmetric and thus has two possible arrangements of H and OH groups around it. In other words, D-glucose exists in two stereoisomeric forms, i.e., α-D-glucose and β-D-glucose as shown below:

In α-D-glucose, the OH group at C_1 is towards right while in β-D-glucose, the OH group at C_1 is towards left. *Such a pair of stereoisomers which differ in configuration only around C_1 are called **anomers*** and the C_1 carbon is called Anomeric carbon (or glycosidic carbon. The cyclic structures of monosaccharides can be better represented by *Haworth Projection formulae*. To get such a formula for any monosaccharide (say α-and β-D-glucose), draw a hexagon with its oxygen atom at the upper right-hand corner. Place all the groups (on C_1, C_2, C_3 and C_4) which are present on left hand side in structures I and II, above the plane of the ring and all those groups on thright-hand side below the plane of the ring.

The terminal – CH_2OH group is always placed above the plane of the hexagon ring (in D-series). Following the above procedure, Haworth Projection Formulae for α-D-glucose (I) and β-D-glucose (II) are obtained as shown below:



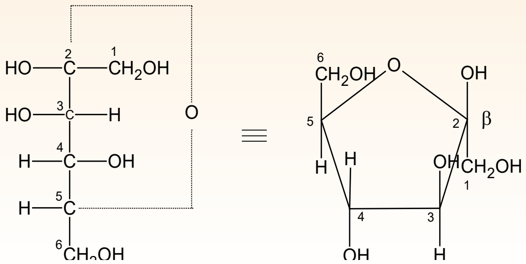
I
α-D-Glucose
or α-D(+)-Glucopyranose



II
β-D-Glucose
or β-D(+)-Glucopyranose

Cyclic structure of Fructose

Like glucose, fructose also has a cyclic structure. Since fructose contains a keto group, it forms an intramolecular hemiketal. In the hemiketal formation, C_5– OH of the fructose combines with C_2-keto group. As a result, C_2 becomes chiral and thus has two possible arrangements of CH_2OH and OH group around it. Thus, D-fructose exists in two stereoisomeric forms, i.e., α-D-fructopyranose and β-D fructopyranase. However, in the combined state (such as sucrose), fructose exists in furanose form as shown below:



MUTAROTATION

The two stereoisomeric forms of glucose, i.e., α-D-glucose and β-D-glucose exist in separate crystalline forms and thus have different melting points and specific rotations. For example, α-D-glucose has a m.p. of 419 K with a specific rotation of +112° while β-D-glucose has a m.p. of 424 K and has a specific rotation of +19°. However, when either of these two forms is dissolved in water and allowed to stand, it gets converted into an equilibrium mixture of α-and β-forms through a small amount of the open chain form.

$$\underset{(36\%)}{\alpha\text{-D-Glucose}} \rightleftharpoons \underset{(0.02\%)}{\text{Open chain form}} \rightleftharpoons \underset{(64\%)}{\beta\text{-D-Glucose}}$$

As a result of this equilibrium, the specific rotation of a freshly prepared solution of α-D-glucose gradually decreases from of +112° to +52.7° and that of β-D-glucose gradually increases from +19° to +52.7°.

$$\underset{[\alpha]_D = +112^\circ}{\alpha\text{-D-Glucose}} \rightleftharpoons \underset{[\alpha]_D = +52.7^\circ}{\text{Equilibrium mixture}} \rightleftharpoons \underset{[\alpha]_D = +19^\circ}{\beta\text{-D-Glucose}}$$

Where $[\alpha]_D$ = specific rotation

This change in specific rotation of an optically active compound in solution with time, to an equilibrium value, is called ***mutarotation***. During mutarotation, the ring opens and then recloses either in the inverted position or in the original position giving a mixture of α-and-β-forms. All reducing carbohydrates, i.e., monosaccharides and disaccharides (maltose, lactose etc.) undergo mutarotation in aqueous solution.

REACTIONS OF GLUCOSE

(a) With HI/P: It undergoes reduction to form n-hexane while with sodium amalgam it forms sorbitol.

$$\text{Glucose} \xrightarrow{HI/P} CH_3-(CH_2)_4-CH_3$$

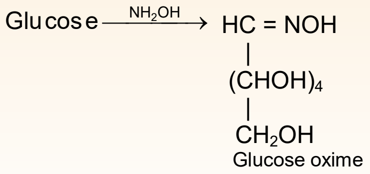
n-hexane

$$\text{Glucose} \xrightarrow{Na/Hg} CH_2OH-(CHOH)_4-CH_2OH$$

sorbitol

(b) With H_2O: It forms neutral solution

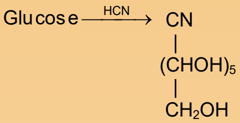
(c) With Hydroxylamine (NH_2OH)



$$\text{Glucose} \xrightarrow{NH_2OH} \begin{array}{l} HC=NOH \\ \;| \\ (CHOH)_4 \\ \;| \\ CH_2OH \end{array}$$

Glucose oxime

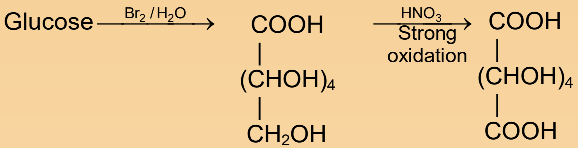
(d) With HCN: It forms addition product cyanohydrin



$$\text{Glucose} \xrightarrow{HCN} \begin{array}{l} CN \\ | \\ (CHOH)_5 \\ | \\ CH_2OH \end{array}$$

Glucose cyanohydrin

(e) Oxidation: Glucose on oxidation with Br_2 gives gluconic acid which on further oxidation with HNO_3 gives glucaric acid

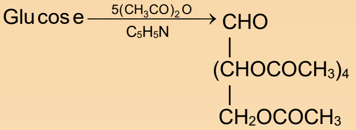


$$\text{Glucose} \xrightarrow{Br_2/H_2O} \begin{array}{l} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow[\text{Strong oxidation}]{HNO_3} \begin{array}{l} COOH \\ | \\ (CHOH)_4 \\ | \\ COOH \end{array}$$

Gluconic acid Glucaric acid

(f) With Tollen reagent and Fehling solution. Glucose forms silver mirror and red ppt. of Cu_2O respectively.

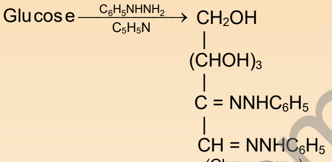
(g) With acetic anhydride. In presence of pyridine glucose forms pentaacetate.



$$\text{Glucose} \xrightarrow[C_5H_5N]{5(CH_3CO)_2O} \begin{array}{l} CHO \\ | \\ (CHOCOCH_3)_4 \\ | \\ CH_2OCOCH_3 \end{array}$$

Glucose pentaacetate

(h) With phenylhydrazine: it forms glucosazone



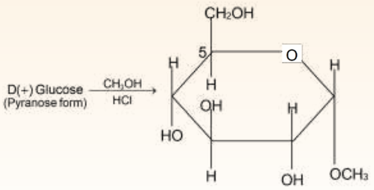
$$\text{Glucose} \xrightarrow[C_5H_5N]{C_6H_5NHNH_2} \begin{array}{l} CH_2OH \\ | \\ (CHOH)_3 \\ | \\ C = NNHC_6H_5 \\ | \\ CH = NNHC_6H_5 \end{array}$$

(Glucosazone)

(i) With conc. HCl acid: Glucose gives laevulinic acid

$$\text{Glucose} \xrightarrow{\text{Conc. HCl}} \underset{\text{Laevulinic acid}}{CH_3CO \cdot CH_2CH_2 \cdot COOH} + HCOOH + H_2O$$

(j) Glycoside formation: When a small amount of gaseous HCl is passed into a solution of D (+) glucose in methanol , a reaction takes place that results in the formation of anomeric methyl acetals.



Methyl α-D-glucopyranoside
+
Methyl β-D-glucopyranoside

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

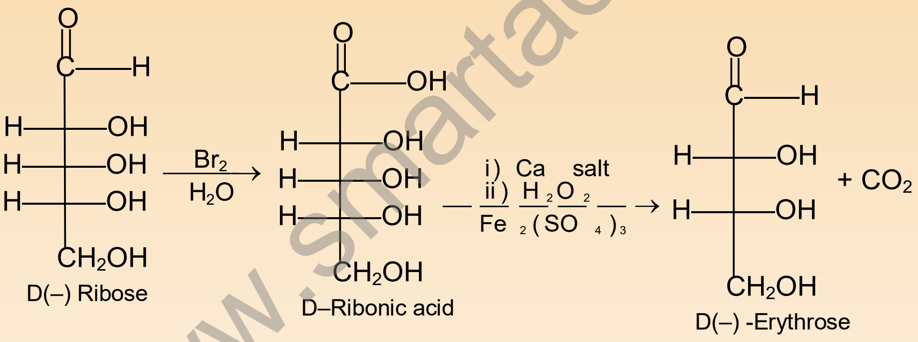
Other reactions

(a) *Kiliani - Fischer Synthesis*: - This is a method of lengthening the carbon chain of an aldose. To illustrate, we take synthesis of D-threose and D-erythrose (Aldotetroses) from D-glyceraldehyde (an Aldo triose).

Addition of HCN to glyceraldehyde produces two epimoric cyanohydrins because reaction creates a new stereocenter. The cyanohydrins can be separated easily (since they are diastereomers) and each can be converted to an aldose through hydrolysis, acidification and lactonisation, and reduction with Na—Hg in presence of H_2SO_4. One cyanohydrin ultimately yields D-erythrose and D-threose.

Here we can see that both sugars are D-sugars because starting compound is D-glyceraldehyde and its stereocenter is unaffected by its synthesis.

(b) *Ruff Degradation:* It is opposite to Kiliani Fischer synthesis that can be used to shorten the chain by a similar unit. The ruff degradation involves (i) Oxidation of the aldose to an adonic acid using Bromine water. (ii)Oxidative decarboxylation of the adonic acid to the next lower aldose using H_2O_2 and $Fe_2(SO_4)_3$. D-ribose for example can be reduced to D-erythrose.



DISACCHARIDES

Carbohydrates which upon hydrolysis give two molecules of the same or different monosaccharides are called disaccharides. Their general formula is $C_{12}H_{22}O_{11}$. The three most important disaccharides are sucrose, maltose, and lactose. Each one of these on hydrolysis with either an acid or an enzyme gives two molecules of the same or different monosaccharides as shown below:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or Invertase}]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

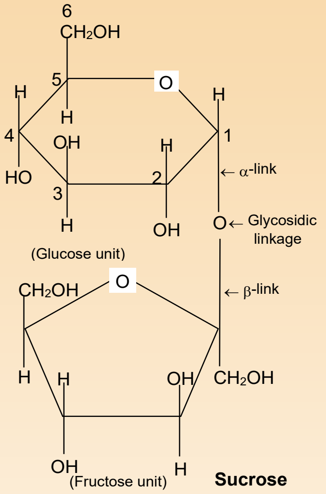
$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or Maltase}]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or Lactase}]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$

Disaccharides may also be considered to be formed by a condensation reaction between two molecules of the same or different monosaccharides with the eliminatioin of a molecule of water. This reaction involves the formation of an acetal from a hemiacetal and an alcohol – in which one of the monosaccharides acts as the hemiacetal while the other acts as the alcohol.

Sucrose

It is formed by condensation of one molecule of glucose and one molecule of fructose. Unlike maltose and lactose, it is non-reducing sugar since both glucose (C_1 - α) and fructose (C_2 - β) are connected to each other through their reducing centers. Its structure is shown below:



Sucrose

Hydrolysis: (Invert Sugar or Invertase). Hydrolysis of sucrose with hot dilute acid yields D-glucose and D-fructose.

$$\underset{\substack{\text{Sucrose}\\ [\alpha]_D\ =\ +66.5^\circ}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underbrace{\underset{\substack{\text{D-glucose}\\ [\alpha]_D\ =\ +53^\circ}}{C_6H_{12}O_6} + \underset{\substack{\text{D-fructose}\\ [\alpha]_D\ =\ -92^\circ}}{C_6H_{12}O_6}}_{\text{Invert Sugar}}$$

$$[\alpha]_D = (+53^\circ) - (-92^\circ) = -39^\circ$$

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

POLYSACCHARIDES

Polysaccharides are formed when a large number (hundreds to even thousands) of monosaccharide molecules join together with the elimination of water molecule. Thus, polysaccharides may be regarded as condensation polymers in which the monosaccharides are joined together by glycosidic linkages. Some important polysaccharides are:

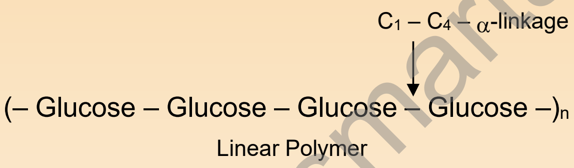
1. Cellulose
2. Starch
3. Glycogen
4. Gums and
5. Pectin

Starch

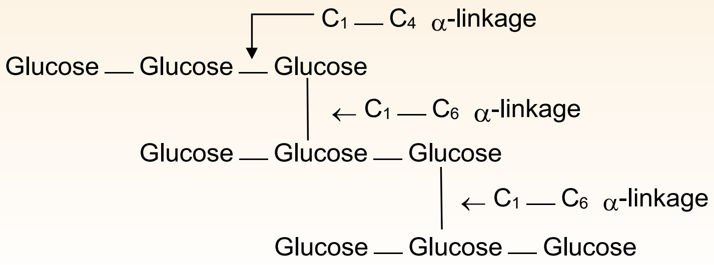
It is a polymer of glucose. Its molecular formula is $(C_6H_{10}O_5)_n$ where the value of n (200 – 1000) varies from source to source. It is the chief food reserve material or storage polysaccharide of plants and is found mainly in seeds, roots, tubers, etc. Wheat, rice, potatoes, corn, bananas etc., are rich sources of starch.

Starch is not a single compound but is a mixture of two components – amylose (10 to 20%) and amylopectin (20 to 80%). Both amylose and amylopectin are polymers of α-D-glucose.

Amylose is a linear polymer of α-D-glucose. It contains about 200 glucose units which are linked to one another through α-linkage involving C_1 of one glucose unit with C_4 of the other as shown below:



Amylopectin, on the other hand, is a highly branched polymer. It consists of a large number (several branches) of short chains each containing 20-25 glucose units which are joined together through α-linkages involving C_1 of one glucose unit with C_4 of the other. The C_1 of terminal glucose unit in each chain is further linked to C_6 of the other glucose unit in the next chain through C_1 – C_6 α-linkage. This gives amylopectin a highly branched structure as shown below.-



Hydrolysis: Hydrolysis of starch with hot dilute acids or by enzymes gives dextrin's of varying complexity, maltose and finally D-glucose. Starch does not reduce Tollen's reagent and Fehling's solution.

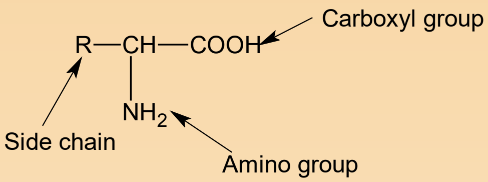
Uses: It is used as a food. It is encountered daily in the form of potatoes, bread, cakes, rice etc. It is used in coating and sizing paper to improve the writing qualities. Starch is used to treat textile fibers before they are woven into cloth so that they can be woven without breaking. It is used in manufacture of dextrin's, glucose and ethyl alcohol. Starch is also used in manufacture of starch nitrate, which is used as an explosive.

AMINO ACIDS

Introduction

(i) Amino acids are organic compounds of both, an amino group & carboxylic group.

(ii) They are represented by general formula:



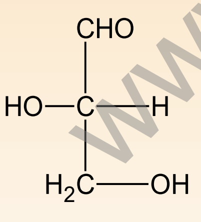
$R-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$

(iii) These amino acids are very important because they are the building blocks of protein.

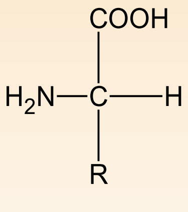
(iv) Protein is the natural polymer moving α - amino acids as monomer.

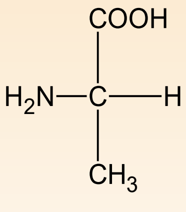
(v) With the exceptions of glycine. All the other amino acids have chiral carbon & have two optically active isomers.

(vi) All naturally occurring amino acids are in L – series in which $-NH_2$ group on the left and $-OH$ group in the right as L – glyceraldehyde's.



L - Glyceraldehyde



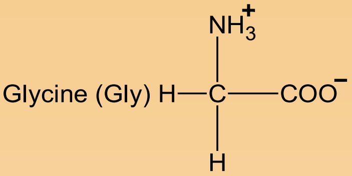


L - Alanine

Classification

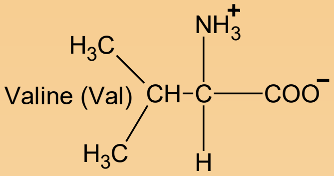
Amino acid with non – polar side chain

(i)

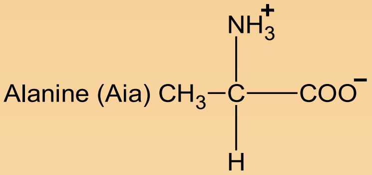


$H-\overset{NH_3^+}{\underset{H}{C}}-COO^-$

(ii)

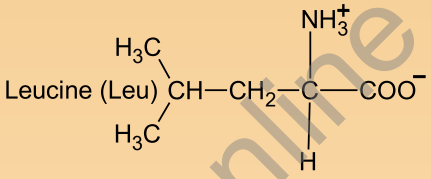


(iii)

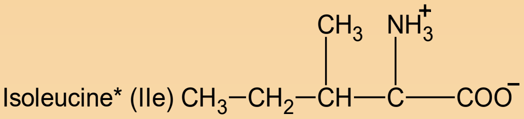


$CH_3-\overset{NH_3^+}{\underset{H}{C}}-COO^-$

(iv)

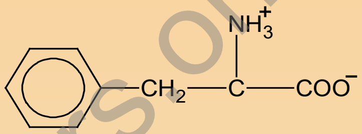


(v)

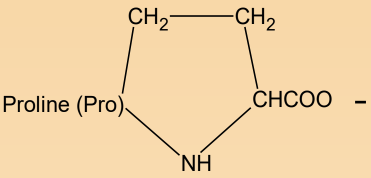


$CH_3-CH_2-\overset{CH_3}{CH}-\overset{NH_3^+}{C}-COO^-$

(vi)



(vii)



Essential amino acids

(a) These must be supplied to our diet as are not synthesized in body.

(b) Some of them are

(1) Valine (2) Leucine (3) Isoleucine (4) Phenylalanine (5) Arginine (5) Threonine

(6) Tryptophan (7) Methionine (8) Lysine (9) Arginine (10) Histidine

Note: Histidine and arginine are essential i.e., can be synthesized but not in quantities sufficient to permit normal growth.

Non – Essential Amino acids

These amino acids are synthesized in body.

Some of them are

These are as follows:

(1) Glycine (2) Alanine (3) Tyrosine (4) Serine (5) Cystine (6) Proline (7) Hydroxyproline

(8) Cysteine (9) Aspartic acid (10) Glutamic acid

Synthesis of α - amino acids

Protein can be hydrolyzed by refluxing with dilute hydrochloric acid to give a mixture of α - amino acids. The resulting mixture can be separated by

(a) fractional crystallization.

(b) Fractional distillation of their ester followed by hydrolysis (Fischer's method)

(c) Selective precipitation as salt with phosphotungstic and picric acid.

(d) Distribution of amino acid between n – butanol saturated with water (Dakin's method).

(e) Column, paper and gas chromatography.

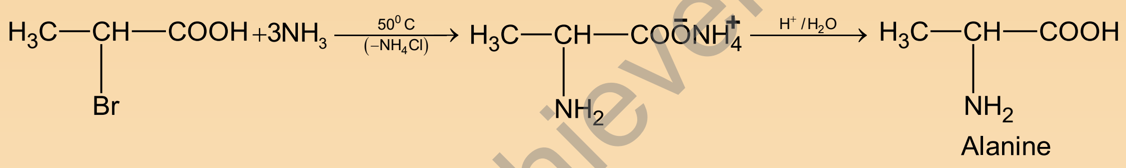
(f) Electrophoresis.

By amination of α - halo acid

(i)

$$\underset{\text{Chloro acetic acid}}{Cl-CH_2-COOH} + \underset{\text{(excess)}}{3NH_3} \xrightarrow[(-NH_4Cl)]{50^0\,C} H_2N-CH_2-COO^-NH_4^+ \xrightarrow{H^+/H_2O} \underset{\text{Glycine}}{H_2N-CH_2-COOH}$$

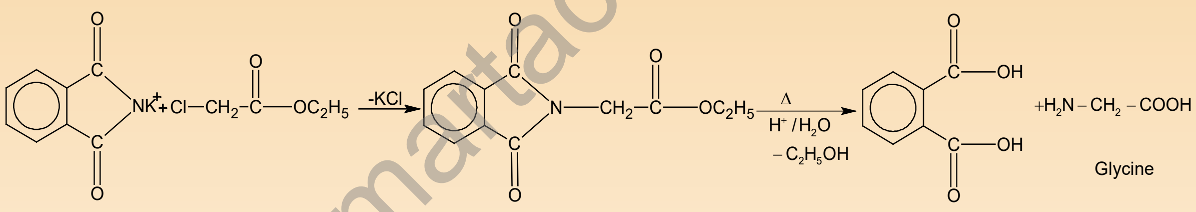
(ii)



$$H_3C-\underset{\underset{Br}{|}}{CH}-COOH + 3NH_3 \xrightarrow[(-NH_4Cl)]{50^0\,C} H_3C-\underset{\underset{NH_2}{|}}{CH}-CO\bar{O}N\overset{+}{H_4} \xrightarrow{H^+/H_2O} H_3C-\underset{\underset{NH_2}{|}}{CH}-COOH$$

Alanine

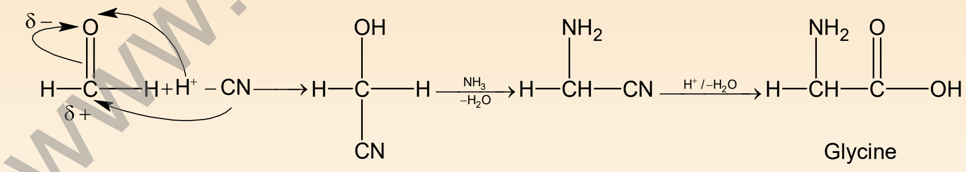
By Gabriel synthesis



Potassium phthalimide Ethyl chloroacetate Phthalic acid Glycine

By Strecker Synthesis

(i)

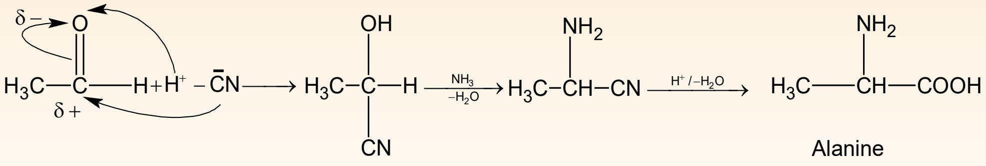


$$H-\overset{\overset{\delta-}{O}}{\overset{||}{\underset{\delta+}{C}}}-H + H^+ - CN \longrightarrow H-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-H \xrightarrow[-H_2O]{NH_3} H-\overset{\overset{NH_2}{|}}{CH}-CN \xrightarrow{H^+/-H_2O} H-\overset{\overset{NH_2}{|}}{CH}-\overset{\overset{O}{||}}{C}-OH$$

Glycine

Formaldehyde Cyanohydrin

(ii)



$$H_3C-\overset{\overset{\delta-}{O}}{\overset{||}{\underset{\delta+}{C}}}-H + H^+ - \bar{C}N \longrightarrow H_3C-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-H \xrightarrow[-H_2O]{NH_3} H_3C-\overset{\overset{NH_2}{|}}{CH}-CN \xrightarrow{H^+/-H_2O} H_3C-\overset{\overset{NH_2}{|}}{CH}-COOH$$

Alanine

Acetaldehyde Cyanohydrin

Note: Generally the aldehyde is treated with a mixture of ammonium chloride and potassium cyanide in aqueous solution.

Note: Generally the aldehyde is treated with a mixture of ammonium chloride and potassium cyanide in aqueous solution.

$$NH_4Cl + KCN \xrightarrow{\text{Aqueous}} NH_4CN + KCl$$

$$NH_4CN \xrightarrow{\text{Aqueous}} NH_3 + HCN$$

Physical properties of amino acid

(i) Amino acids are generally, crystalline substance having sweet taste.

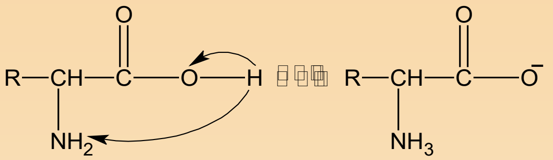
(ii) They melt with decomposition at higher temperature (more than 200°C).

(iii)They are soluble in water but insoluble in organic solvents.

ZWITTER ION

(i) Amino acids contain both acidic carboxyl group (–COOH) and basic amino group in the same molecules.

(ii) In aqueous solution, the acidic carboxyl group can lose a proton and basic amino group can gain a proton in a kind of internal acid – base reaction.



$$R-\underset{NH_2}{CH}-\overset{O}{\overset{\|}{C}}-O-H \qquad R-\underset{NH_3}{CH}-\overset{O}{\overset{\|}{C}}-O^-$$

Dipolar ion or Zwitter ion

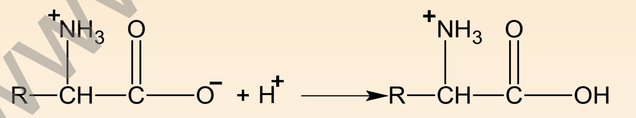
(iii)The product of this internal reaction is called a Dipolar or a Zwitter ion.

(iv)The Zwitter ion is dipolar, changed but overall, electrically neutral and contain both a positive and negative charge.

(v) Amino acid in the dipolar ion form is amphoteric in nature.

(vi)Depending upon the pH of the solution, the amino acid can donate or accept proton.

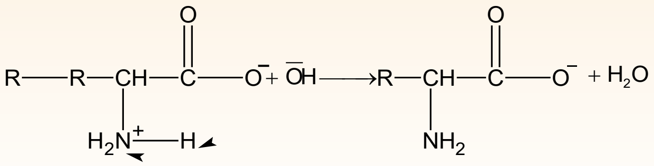
(A)



$$R-\overset{\overset{+}{N}H_3}{CH}-\overset{O}{\overset{\|}{C}}-O^- + H^+ \longrightarrow R-\overset{\overset{+}{N}H_3}{CH}-\overset{O}{\overset{\|}{C}}-OH$$

Positive ion (cation)

(B) An amino acid in basic solution



$$R-R-\underset{H_2\overset{+}{N}-H}{CH}-\overset{O}{\overset{\|}{C}}-O^- + \overset{-}{O}H \longrightarrow R-\underset{NH_2}{CH}-\overset{O}{\overset{\|}{C}}-O^- + H_2O$$

Negative ion (Anion)

ISOELECTRIC POINT

(i) When ionized form of amino acid is placed in an electric field it will migrate towards the opposite electrode.

(ii) Depending upon the pH of the medium following three thing may happen.

- (a) In acidic medium, the cation moves towards cathode.
- (b) In basic medium, the anion move towards anode.
- (c) The Zwitter ion does not move towards any of the electrodes.

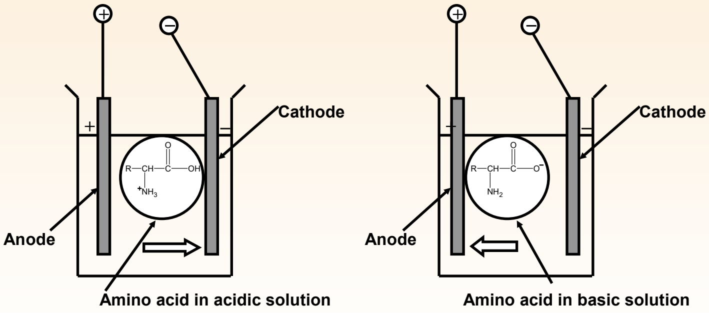
(iii) At a certain pH (i.e., H^+ concentration), the amino acid molecules show no tendency to migrate towards any of the electrodes and exists as a neutral dipolar ion, when placed in electric field is known as isoelectric point.

(iv) All amino acids do not have the same isoelectric point & it depends upon the nature of R – linked to α- carbon atom.

Isoelectric point of some amino acid

Amino acid	**Isoelectric point**
Neutral amino acids	**(pH 5.5 to 6.3)**
Glycine	5.7
Alanine	6.1
Valine	6.0
Serine	5.7
Threonine	5.6
Acidic amino acids	**($pH \approx 3$)**
Aspartic acid	2.8
Glutamic acid	3.2
Basic amino acids	**($pH \approx 10$)**
Lysine	9.7
Arginine	10.8

(v) Amino acids have minimum aqueous solubility at isoelectric point.



Effect of electric field on an amino acid ion Acidic and Basic solution

Chemical Properties

Amino acids show the following characteristic reactions.

1.Reaction of the carboxyl group.

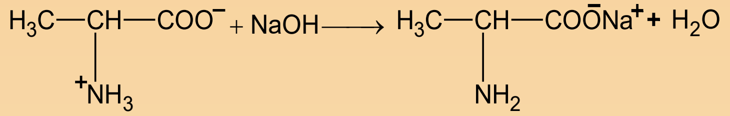
2.Reaction of the amino group.

3.Reaction involving both the carboxyl and the amino group.

Reaction of the carboxyl group

Reaction with base

(i) $\underset{\text{Glycine}}{H_3N^+ - CH_2 - COO^-} + NaOH \longrightarrow \underset{\text{Sodium amino acetate}}{H_2N - CH_2 - COO^-Na^+} + H_2O$

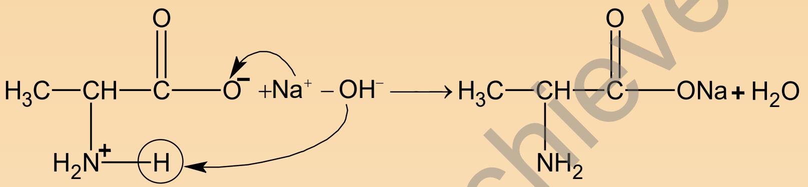
(ii) 

$$H_3C-\underset{\underset{^+NH_3}{|}}{CH}-COO^- + NaOH \longrightarrow H_3C-\underset{\underset{NH_2}{|}}{CH}-CO\bar{O}Na^+ + H_2O$$

Alanine

Sodium, α – amino propionate

Mechanism:



Alanine

Sodium, α – amino propionate

Esterification

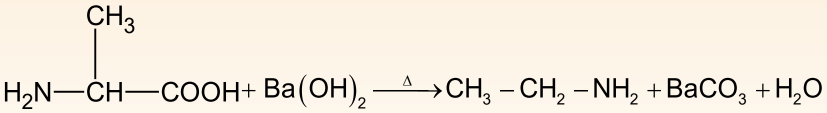
$$\underset{\text{Glycine}}{H_3N^+ - CH_2 - COO^-} \xrightarrow{HCl} Cl^- H_3N^+ - CH_2 - COOH \xrightarrow{C_2H_5OH} Cl^- H_3N^+ - CH_2 - COOC_2H_5$$

$$\xrightarrow{AgOH} \underset{\text{Ethyl}-\alpha-\text{amino acetate}}{H_2N - CH_2 - COOC_2H_5} + AgCl + H_2O$$

Note: HCl first converts the dipolar ion into an acid which is subsequently esterified.

Decarboxylation

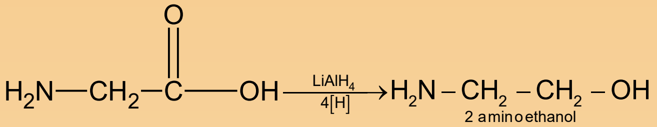
$$\underset{\text{Glycine}}{H_2N - CH_2 - COOH} + Ba(OH)_2 \xrightarrow{\Delta} \underset{\text{Methyl amine}}{CH_3 - NH_2} + BaCO_3 + H_2O$$



$$H_2N-\overset{\overset{CH_3}{|}}{CH}-COOH + Ba(OH)_2 \xrightarrow{\Delta} CH_3 - CH_2 - NH_2 + BaCO_3 + H_2O$$

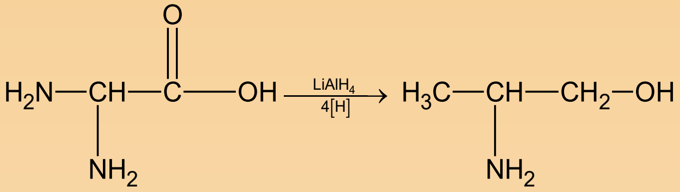
Alanine

Reduction



$$H_2N-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[4[H]]{LiAlH_4} H_2N-CH_2-CH_2-OH$$

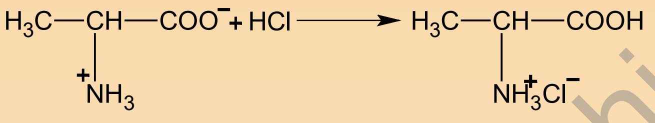
Glycine 2 aminoethanol



$$H_2N-\underset{NH_2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[4[H]]{LiAlH_4} H_3C-\underset{NH_2}{\underset{|}{CH}}-CH_2-OH$$

Reaction with strong acid

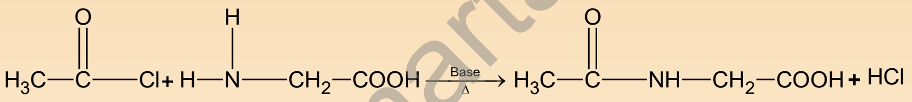
$$\underset{\text{Glycine}}{H_3N^+-CH_2-COO^-}+HCl \longrightarrow \underset{\text{Glycine hydrochloride}}{Cl^-H_3N^+-CH_2-COOH}$$



$$H_3C-\underset{\overset{+}{N}H_3}{\underset{|}{CH}}-COO^- + HCl \longrightarrow H_3C-\underset{\overset{+}{N}H_3Cl^-}{\underset{|}{CH}}-COOH$$

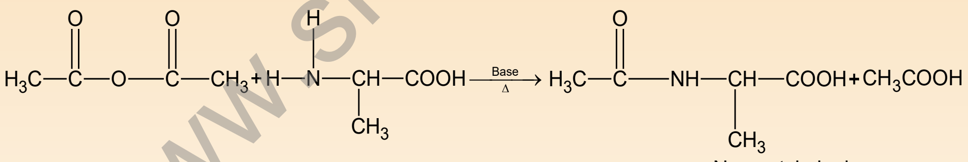
Alanine Alanine hydrochloride

Acetylation



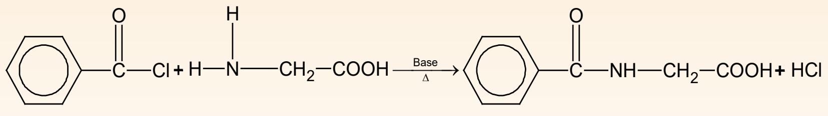
$$H_3C-\overset{O}{\overset{\|}{C}}-Cl + H-\overset{H}{\overset{|}{N}}-CH_2-COOH \xrightarrow[\Delta]{Base} H_3C-\overset{O}{\overset{\|}{C}}-NH-CH_2-COOH + HCl$$

Acetyl chloride Glycine N - acetylglycine



$$H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + H-\overset{H}{\overset{|}{N}}-\underset{CH_3}{\underset{|}{CH}}-COOH \xrightarrow[\Delta]{Base} H_3C-\overset{O}{\overset{\|}{C}}-NH-\underset{CH_3}{\underset{|}{CH}}-COOH + CH_3COOH$$

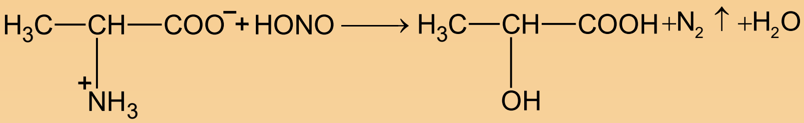
Acetic anhydride Alanine N - acetyl alanine



Benzylchloride Benzoylglyxcine (hippuric acid)

Reaction with Nitrous acid

$$\underset{\text{Glycine}}{H_3N^+ - CH_2 - COO^-} + \underset{\text{Nitrous acid}}{HONO} \longrightarrow \underset{\text{Glycollic acid}}{HO - CH_2 - COOH} + N_2\uparrow + H_2O$$



$$H_3C-\underset{\overset{+}{N}H_3}{CH}-COO^- + HONO \longrightarrow H_3C-\underset{OH}{CH}-COOH + N_2\uparrow + H_2O$$

Aniline Nitrous acid Lactic acid

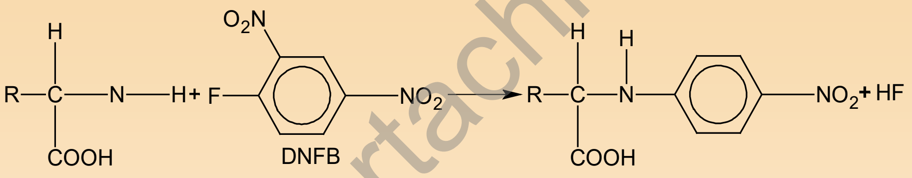
Note: (i) This reaction forms the basis of the "van slyke method" for the estimation of amino acids.

(ii) The nitrogen is evolved (one half comes from the amino acid) quantitatively and its volume measured.

Reaction with Nitrosyl halide

$$\underset{\text{Glycine}}{H_2N - CH_2 - COOH} + NOCl \longrightarrow \underset{\text{Chloroacetic acid}}{Cl - CH_2 - COOH} + N_2\uparrow + H_2O$$

Reaction with 2, 4 – Dintrofluorobenzene (DNFB)



DNFB

(Sangar's reagent)

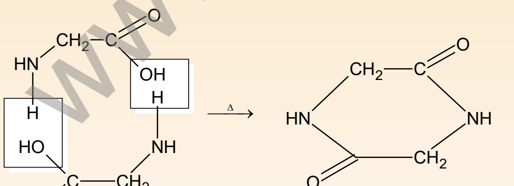
Dinitrophenyl amino acid

(DNP - amino acid)

Reaction involving both the carboxyl & the amino group

Effect of heat

α - amino acids undergo dehydration on heating (200°C) to give diketopiperazine.



Glycine (2 moles)

25 Diketopiperazine

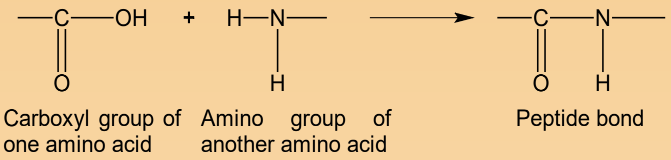
(A cyclic diamide)

PEPTIDES & PROTEINS

Introduction

(i) Proteins are formed by joining the carboxyl group of one amino to the α - amino group of another acid.

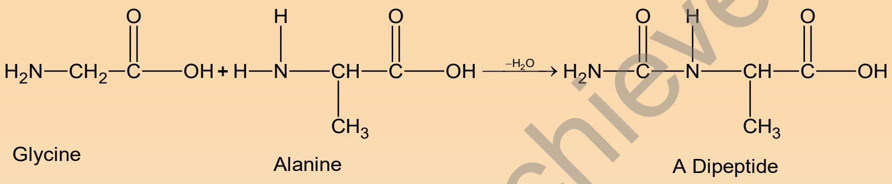
(ii) The bond formed between two amino acids by the elimination of water molecules is called peptide linkage.



$$-\underset{\underset{O}{\|}}{C}-OH + H-\underset{\underset{H}{|}}{N}- \longrightarrow -\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-$$

(iii)The product formed by linking amino acid molecules through peptide linkage —CO — NH — is called a peptide.

(iv)When two amino acids combined in this way the resulting product is called a dipeptide.

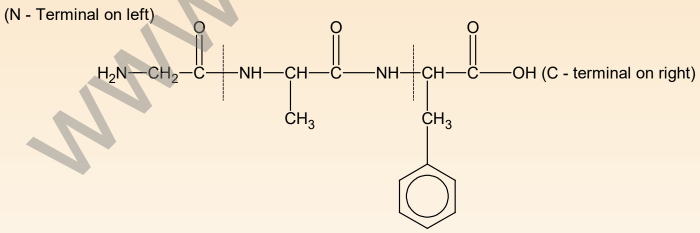


$$H_2N-CH_2-\overset{\overset{O}{\|}}{C}-OH + H-\overset{\overset{H}{|}}{N}-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{-H_2O} H_2N-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OH$$

(v) Peptide are further designated as tri, tetra or penta peptides accordingly as they contain three, four or five amino acid molecules, same or different.

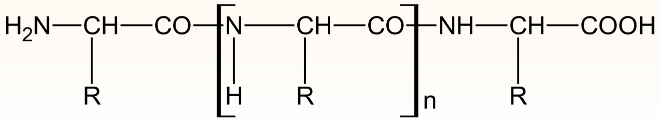
(vi)In a peptide the amino acid that contains the free amino group is called the N – terminal residue (written on L.H.S).

(vii) The amino acid that contains the free carboxyl group is called the C – terminal residue (written on R.H.S).



Glycylalanyphenylalanine (tripeptide) abbriviated as : Gly - Ala - phe

(viii) If a large number of α - amino acids (100 to 1000) are joined by peptide bonds the resulting polyamide is called polypeptide.



$$H_2N-\underset{\underset{R}{|}}{CH}-CO-\left[\underset{\underset{H}{|}}{N}-\underset{\underset{R}{|}}{CH}-CO\right]_n-NH-\underset{\underset{R}{|}}{CH}-COOH$$

(ix)By convention a peptide having molecular weight upto 10,000 is called polypeptide.

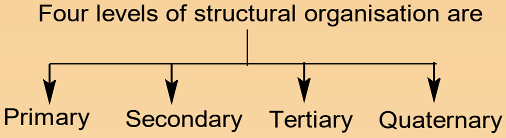
(x) While a peptide having a molecular mass more than 10,000 is called a protein. ‘

Structure of Proteins

(i) Proteins have three dimensional structures.

(ii) There are number of factors which determine the exact shape of proteins.

Structure of Proteins



Primary structure

(i) This type of structure was given by Friedrich Sanger in 1953 in Insulin.

(ii) Primary structure is confirmed by single polypeptide chain in a linear manner.

(iii) All amino acid is attached in a straight chain by peptide bond.

Secondary structure

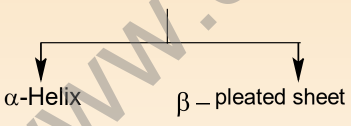
(i) The fixed configuration of polypeptide skeleton is referred to as the secondary structure of protein.

(ii) It gives information

(a) About the manner in which the protein chain is folded and bent.

(b) About the nature of the bond which stabilizes this structure.

(iii) This structure of protein is mainly of two types



(A) α-Helix

(a) The chain of α-amino acids coiled as a right-handed screw (called α-helix) because of the formation of hydrogen bond.

(b) The spiral is held together by H-bonds between N–H and C = O group vertically adjacent to one another.

(c) X-Ray studies have shown that there are approximately 3.6 amino acid unit for each turn in helix.

(d) Such proteins are elastic i.e.; they can be stretched.

(e) On stretching weak H-bonds break up and the peptide act like a spring.

(f) The hydrogen bonds are reformed on releasing the tension.

e.g., Myosin, Keratin, Tropomyosin.

(B) Beta-pleated sheet

(a) Polypeptide chains are arranged side by side.

(b) The chains are held together by a very large number of hydrogen bond between $C = O$ and NH of different chains.

(c) These sheets can slide over each other to form a three-dimensional structure called a beta pleated sheet.

e.g., Silk has a beta pleated structure.

Tertiary structure

(i) It refers to the arrangement and interrelationship of the twisted chain of protein into specific layer or fibers.

(ii) This tertiary structure is maintained by weak interatomic force such as, H-bonds hydrophobic bond, van der Waals' force and disulfide bonds (e.g., Insulin).

e.g., Protein of tobacco mosaic virus (TMV); Myoglobin; Hemoglobin

Quaternary structure

(i) When two or more polypeptide chain united by the force other than covalent bond i.e., peptide and disulphide bonds.

(ii) It refers to final three-dimensional shape that results from twisting bonding and folding of the protein helix.

(iii) It is most stable structure.

Classification of Proteins

There are two methods for classifying proteins.

(i) Classification according to Composition

(ii) Classification according to Functions

Classification according to Composition

Simple proteins

(i) Simple proteins are those which yield only α-amino acids upon hydrolysis.

(ii) Simple proteins are composed of chain of amino acid unit only joined by peptide linkage.

Examples are:

Egg (albumin); Serum (globulins); Wheat (Glutelin); Rice (Cryzenin)

Conjugated proteins

(i) Conjugated proteins are those which yield α - amino acids plus a non-protein material on hydrolysis.

(ii) The non protein material is called the prosthetic group.

Example:

Casein in milk (prosthetic group is phosphoric acid); Hemoglobin (prosthetic group is Nucleic acid); Cholesterol (prosthetic group – lipid).

According to molecular shape, proteins are further classified into two types.

(A) Fibrous protein

(a) These are made up of polypeptide chain that are parallel to the axis & are held together by strong hydrogen and disulfide bonds.

(b) They can be stretched & contracted like thread.

(c) They are usually insoluble in water.

Example:

Keratin (hair, wool, silk & nails); Myosin (muscle)

(B) Globular Proteins

(a) These have more or less spherical shape (compact structure).

(b) α - amino helix are tightly held bonding; H – bonds, disulphide bridges, ionic or salt bridges:

Examples:

Albumin (egg)

Classification According to functions

The functional classification includes following groups.

Structural proteins

These are the fibrous proteins such as collogen (skin, cartilage & bones) which hold living system together.

Blood proteins

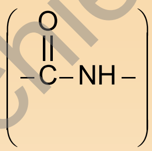
(i) The major proteins constituent of the blood is albumin hemoglobin & fibrinogen.

(ii) Their presence contributes to maintenance of osmotic pressure, oxygen transport system & blood coagulation respectively.

Tests of protein

Biuret test

(i) On adding a dilute of copper sulphatic to alkaline solution of protein, a violet color is developed.

(ii) This test is due to the presence of peptide  $\left(-\overset{O}{\overset{\|}{C}}-NH-\right)$ linkage.

Millon's test

(a) Millon's reagent consists of mercury dissolved in nitric acid (forming a mixture of mercuric & mercurous nitrates).

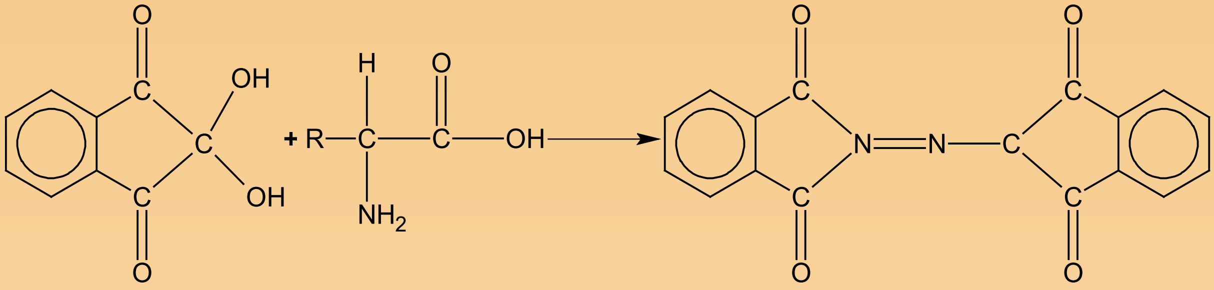
(b) When million's reagent is added to a protein, a white ppt is formed, which turn brick red on heating.

(c) This test is given by protein which yield tyrosine on hydrolysis (due to the presence of phenolic group).

Ninhydrin test

(i) This test is given by all proteins.

(ii) When protein is boiled with a dilute solution of ninhydrin, a violet colour is produced.



Uses of Proteins

(i) Protein constitutes as essential part of our food, meat, eggs, fish, cheese provide protein to human beings.

(ii) Casein (a milk protein) is used in the manufacture of artificial wool & silk.

(iii)Amino acid needed for medicinal use & feeding experiment, are prepared by hydrolysis of proteins.

(iv)Gelatin is used in desserts, salad’s, candies bakery goods etc.

(v) Leather is obtained by tanning the protein of animal hides.

(vi)Hemoglobin present in blood is responsible for carrying oxygen and CO_2.

(vii) Hormones control various process.

(viii) Enzymes are the proteins produces by living system & catalyze specific biological reaction.

Example:

Ureases (Urea $\rightarrow CO_2 + NH_2$)

Pepsin (Protein → Amino acid)

Trypsin (Protein → Amino acid)

Carbonic anhydride ($H_2CO_3 \rightarrow H_2O + CO_2$)

Nuclease (RNA, DNA → Nucleotides)

Isoelectric Point

What happens when a solution of an amino acid is placed in an electric field depends upon the acidity or basicity of solution. In quite alkaline solution.

$$\underset{\text{(II)}}{H_2N\text{-}CHRCOO^-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underset{\text{(I)}}{{}^+H_3N.CHRCOO^-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underset{\text{(III)}}{{}^+H_3N.CHRCOOH}$$

Anions (II) exceed cations (III), and there is a net migration of amino acid toward the anode. In quite acidic solution cations (III) are in excess, and there is a net migration of amino acid towards the cathode. If (II) and (III) are exactly balanced, there is no net migration; under such conditions any one molecule exists as a positive ion and as a negative ion for exactly the same amount of time and any small movement in the direction of one electrode is subsequently cancelled by an equal movement back towards the other electrode. The hydrogen ion concentration of the solution in which a particular amino acid does not migrate under the influence of an electric field is called the ***isoelectric point*** of that amino acid.

An amino acid shows its lowest solubility in a solution at the isoelectric point, since here there is the highest concentration of the dipolar ion. As the solution is made more alkaline or more acidic, the concentration of one of the more soluble ions, II or III increases.

If an amino acid has amino group and one carboxyl group, it has two pK values. The isoelectric point (PI) of this amino acid has the average value of the both pK values.
We take example of glycine.

$$\underset{\text{Conjugated acid (CA)}}{H_3{}^+N — CH_2 — COOH} \rightleftharpoons \underset{\text{Dipolar Ion (DI)}}{H_3N^+ — CH_2 — COO^-} + H^+ \qquad \ldots(1)$$

At equilibrium $K_1 = \frac{[DI][H^+]}{[CA]}$

$$\underset{\text{DI}}{H_3N^+ — CH_2 — COO^-} \rightleftharpoons \underset{\text{Conjugated Base (CB)}}{H_2N — CH_2 — COO^-} + H^+ \qquad \ldots(2)$$

At equilibrium $K_2 = \frac{[CB][H^+]}{[DI]}$

$[CA] = \frac{[DI][H^+]}{K_1}$

$[CB] = \frac{K_2[DI]}{[H^+]}$

At isoelectric point [CA] = [CB]

$$\frac{[DI][H_i^+]}{K_1} = \frac{K_2[DI]}{[H_i^+]}$$ Where $[H_i^+]$ = conc. of $[H^+]$ at isoelectric point.

or, $[H_i^+]^2 = K_1 K_2$

or, $2\log[H_i^+] = \log K_1 + \log K_2$

or $-2\log(H_i^+] = -\log k_1 - \log K_2$

or $2pH_i = pK_1 + pK_2$

or $pH_i = \frac{pK_1 + pK_2}{2}$

NUCLEIC ACIDS

Nucleic acids are biologically important polymers which are present in all living cells, also called as polynucleotides because repeating structural unit is nucleotide.

There are two types of nucleic acids

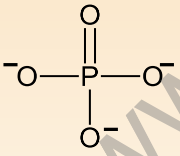
(i) DNA (deoxyribonucleic acid)

(ii) RNA (Ribonucleic acid)

Composition of nucleic acids

1. A phosphate groups
2. Sugar
3. Nitrogenous bases

1. Phosphate Group: Phosphate group in nucleic acid is:

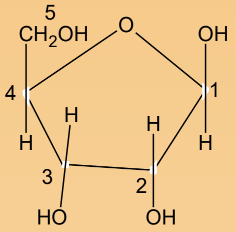


Phosphate group is bonded to a hydroxyl group of sugar.

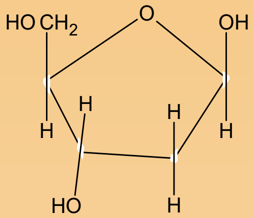
2. Sugar: Two types of sugars present in nucleic acids.

RNA (D – ribose)

DNA (D – deoxyribose)



D-ribose

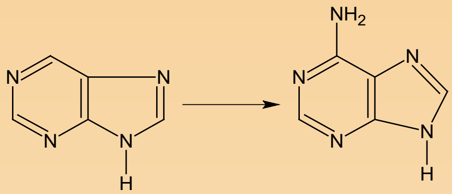


D-deoxyribose

3. Nitrogenous bases: Two types

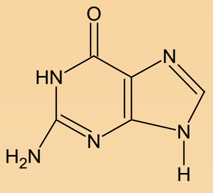
(i) Purines – Adenine (A) and Guanine (G)

(ii) Pyrimidines – Cytosine (C), thymine (T) and uracil (U)

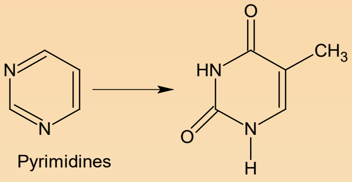


Purines

Adenine (A)

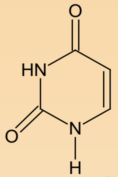


Guanine (G)

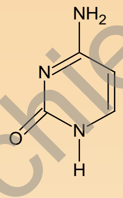


Pyrimidines

Thymine (T)



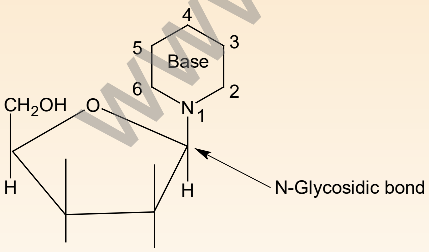
Uracil (U)



Cytosine (C)

NUCLEOSIDES AND NUCLEOTIDES

Nucleosides: Nucleoside contains only two basic components of nucleic acids (a pentose sugar and a nitrogenous base). During their formation, 1- position of pyrimidine or 9 – position of purine moiety is linked to C_1 of sugar (ribose or deoxyribose) by β - linkage.



General structure of a nucleoside

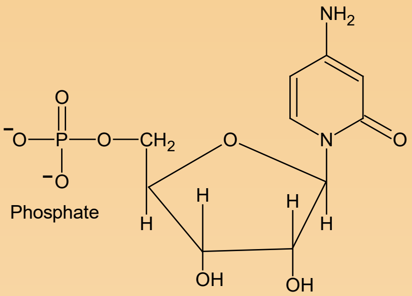
Depending upon the type of sugar present, nucleosides are of two types:

(i) Ribonucleosides and

(ii) Deoxyribonucleosides

Nucleotides: Nucleotides contains all the three basic components of nucleic acids. Nucleotides are nucleoside monophosphates.

They are of two types depending upon the type of sugar – Ribonucleotides and Deoxyribonucleotides. Nucleotide may be represented as follows.

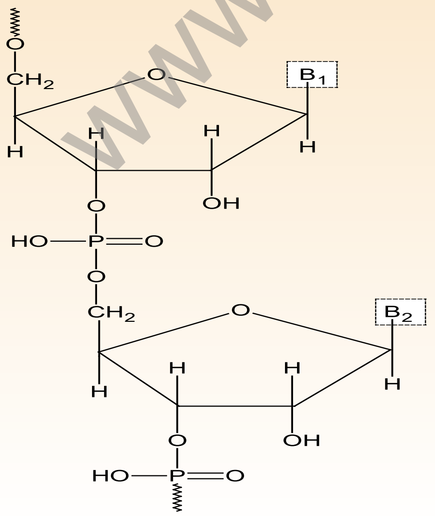


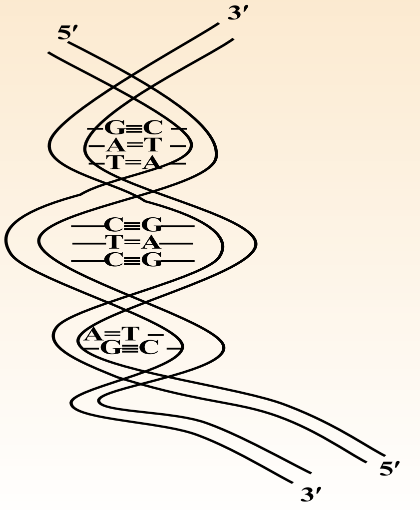
E.g: Structure of cytidine monophosphate

	DNA		RNA
1.	Sugar present in DNA is 2-deoxyribose.	1.	Sugar is D-ribose.
2.	It contains cytosine and thymine as pyrimidine.	2.	It contains cytosine and uracil as pyrimidine.
3.	It has double stranded α - helix structure.	3.	It has single stranded α - helix.
4.	DNA occurs in the nucleus of cell.	4.	RNA occurs in cytoplasm of the cell.
5.	Controls transmission of hereditary material.	5.	It control the synthesis of proteins.

Structure of DNA

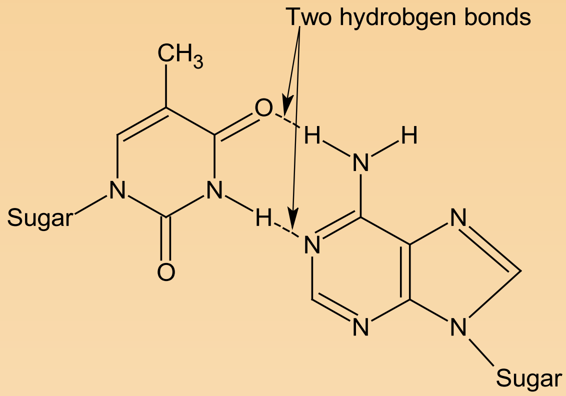
Primary structure and its double helix: Sequence in which four nitrogen bases are attached to the sugar phosphate backbone of a nucleotide chain is called primary structure.



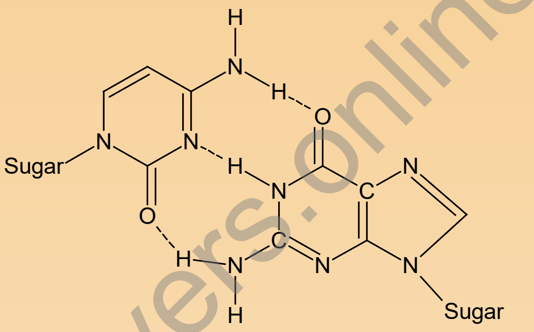


Watson and crick in 1953 proposed that DNA polymers form a duplex structure consisting of two strands of polynucleotide chain coiled around each other in the form of a double helix. Bases of one strand of DNA are paired with bases on the other strand by means of hydrogen bonding. According to Chargaff rule – Thymine and adenine can be joined by 2 hydrogen bonds (T = A) while cytosine and guanine can be joined by three hydrogen bonds.

hydrogen bonds (T = A) while cytosine and guanine can be joined by three hydrogen bonds.



(Thymine = Adenine)



Pairing of cytosine and guanine

$(C \equiv G)$

Structure of RNA is similar to DNA except that it is a single strand structure.

Biological functions of nucleic acids

Important functions are

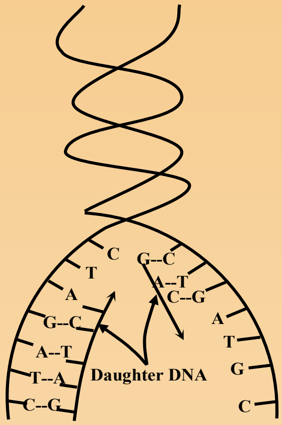
(1) Replication

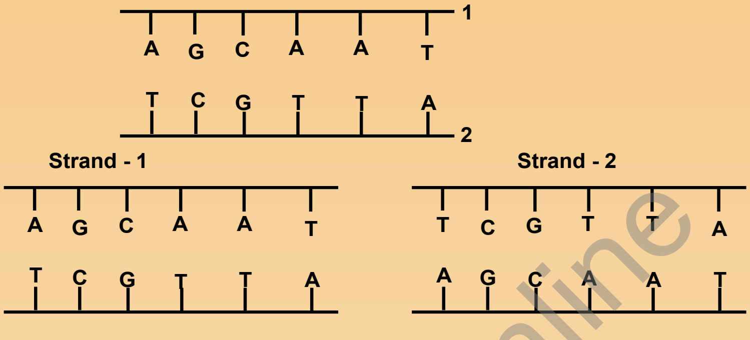
(2) Protein synthesis
  - Transcription
  - Translation

1. Replication

Process by which a single DNA molecule produces two identical copies of itself is called replication. Replication of DNA is an enzyme catalyzed process. In this process, two strands of DNA helix unwind and each strand serves as a template or pattern for the synthesis of a new strand. Newly synthesized complementary strand is an exact copy of the original DNA. In this way hereditary characteristics are transmitted from one cell to another.

another.



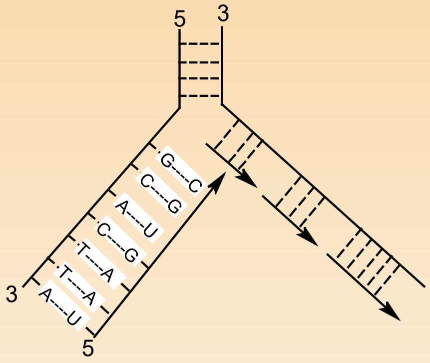


Replication of DNA

Protein Synthesis

$$\text{DNA} \xrightarrow[\text{(Transcription)}]{} \text{RNA} \xrightarrow[\text{(Translation)}]{} \text{Proteins}$$

(i) Transcription



It is the process of synthesis of RNA (mRNA) by using DNA as template. This process is similar to replication process. Differ in following ways.

In transcription, ribose nucleotide assemble along the uncoiled template instead of deoxyribose nucleotide and base uracil (U) is substituted for the base thymine (T).

Synthesis of RNA or DNA always takes place in 5′ - 3′ direction. Process is catalyzed by an enzyme RNA polymerase. In this way DNA transfers its genetic code to mRNA.

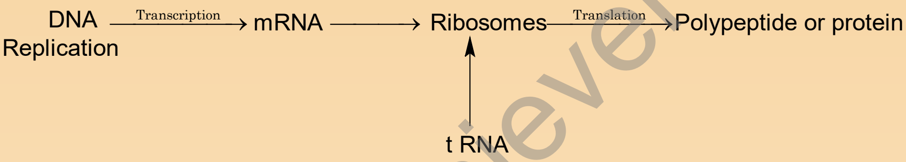
After synthesis, RNA detaches from DNA and moves from nucleus to the cytoplasm where it acts as template for protein synthesis. DNA returns to its double helix structure.

(ii) Translation

It is the process of synthesis of protein. This process is directed by mRNA in the cytoplasm of cell with the help of tRNA (transfer RNA) and ribosomal particles (RNA – protein complex).

The process occurs with the attachment of mRNA to ribosome particle mRNA then gives the message of the DNA and dictates the specific amino acid sequence for the synthesis of protein. 4 bases in mRNA act in the form of triplets and each triplet acts as a code for a particular amino acid. This triplet is called codon. There may be more than one codon for same amino acid. E.g., amino acid methionine has code AUG while glycine has 4 codons GGU, GGC, GGA, GGG.

These codon expressed in mRNA is read by tRNA carrying anticodon and is translated into an amino acid sequence. This process is repeated again and again thus proteins are synthesized. After completion, it is released from ribosome.



Protein synthesis is a fast process and about 20 amino acids are added in one second. It may be noted that translation is always unidirectional but transcription can sometimes be reversed. (RNA is copies into DNA) This is called reverse transcription (occurs in Retroviruses).

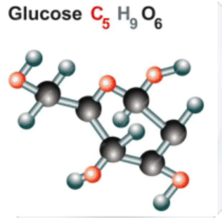
Genetic Code

Segment of DNA is called gene and each triplet of nucleotides is called a codon that specifies one amino acid. This relationship between nucleotide triplets and amino acids is called genetic code. E.g.

$$-\ \underbrace{A-U-G}_{\text{codon for methionine}}\ -\underbrace{C-C-U}_{\text{proline}}-\underbrace{G-C-U}_{\text{alanine}}-\text{a segment of mRNA}$$

Biomolecules

Glucose $C_5H_9O_6$



Carbohydrates

Optically active polyhydroxy aldehydes or ketones or compounds which produce units with specific functional groups on hydrolysis.

- **Classification :**

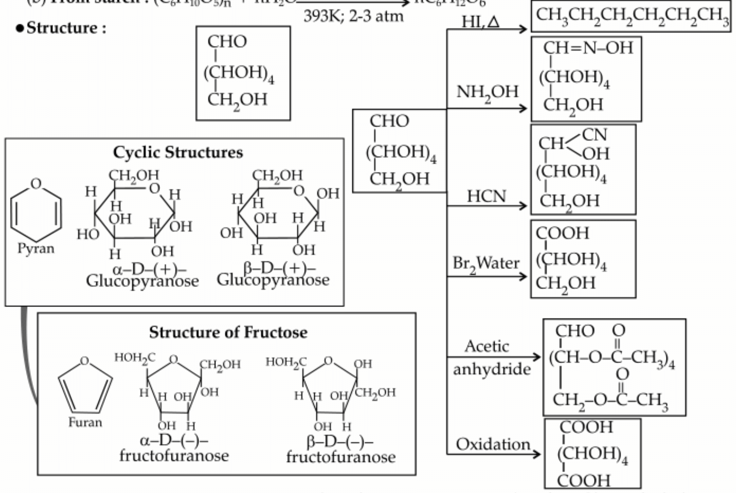
(I) **Monosaccharides :** (Aldehyde group – aldose, keto group –ketose)

Glucose : Preparation :

(a) **From sucrose :** $\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$

(b) **From starch :** $(C_6H_{10}O_5)_n + nH_2O \xrightarrow[393K;\ 2\text{-}3\ atm]{H^+} nC_6H_{12}O_6$

- **Structure :**



(II) **Disaccharides :** (Sucrose, maltose) Linkage between 2 monosaccharides– Glycosidic linkage

(III) **Polysaccharides :** Large number of monosaccharides units joined by glycosidic linkages. e.g.,

(a) Starch : Polymer of α–glucose with two components amylose and amylopectin

(b) Cellulose

(c) Glycogen

Importance :

- Form a major portion of food.
- As storage molecules.
- Cellulose forms cell wall of bacteria and plants.
- Raw materials for industries like textiles, paper, lacquers and breweries.

Proteins

-(Polymers of amino acids)

-Amino acids contain $-NH_2$ and –COOH group.

Classification :

- **On the basis of relative number of $-NH_2$ and –COOH group:**
  - (i) Neutral : Equal number of $-NH_2$ and –COOH group.
  - (ii) Basic : More number of $-NH_2$ than –COOH group.
  - (iii) Acidic : More number of –COOH than $-NH_2$ group.
- **On the basis of place of synthesis :**
  - (i) Essential – cannot be synthesized in the body.
  - (ii) Non-essential – synthesized in the body.
- **On the basis of shape :**
  - (I) Fibrous : Fibre-like structure
  - (ii) Globular : Spherical

Structure : $H_2N - CH_2 - \boxed{CO\text{–}NH} - \underset{CH_3}{CH}\text{–}COOH$ Peptide linkage

Denaturation of protein :

When a protein in its native form is subjected to physical change, globules unfold, helix get uncoiled and protein loses its biological activity.

Vitamin

Organic compounds required in diet in small amounts to perform specific biological functions for maintenance and growth.

Classification :

(i) **Fat soluble :** Soluble in fats and oils but insoluble in water. (Vitamins A,D,E and K)

(ii) **Water soluble :** B group and vitamin C are soluble in water.

Nucleic Acids

Chromosomes : Particles in nucleus responsible for heredity. Chromosomes are made up of proteins and nucleic acid.

Two types : Deoxyribonucleic acid (DNA), ribonucleic acid (RNA)

Composition : In DNA, sugar is β–D–2–deoxyribose whereas in RNA is β–D–ribose. DNA contains A,G,C,T whereas RNA has A,G,C,U.

Structure :

Nucleoside : Formed by attachment of a base to 1′ of sugar

Nucleotide : Formed by link to phosphoric acid at 5′ of sugar.

$-\underset{}{\overset{\text{Base}}{\text{Sugar}}}\text{–Phosphate–}\left[\overset{\text{Base}}{\text{Sugar}}\text{–Phosphate}\right]\text{–}\overset{\text{Base}}{\text{Sugar}}-$

Types of RNA : m–RNA, r–RNA, t–RNA

Biological Functions :

- Chemical basis of heredity.
- Responsible for identity of different species of organisms.
- Nucleic acids are responsible for protein synthesis in cell.

DNA Fingerprinting : Unique sequence of bases on DNA

A sequence of bases on DNA is unique for a person and information regarding this is called DNA fingerprinting. It is same for every cell and cannot be altered by any known treatment. DNA fingerprinting is now used

(i) in forensic laboratories for identification of criminals.

(ii) to determine paternity of an individual.

(iii) to identify the dead bodies in any accident by comparing the DNA's of parents or children.

(iv) to identify racial groups to rewrite biological evolution.

Enzymes

Globular proteins specific for particular reaction and for particular substrate. Mechanism : Reduces the magnitude of activation energy

Trace the Mind Map

‣ First Level ‣ Second Level ‣ Third Level

PRACTICE QUESTIONS

1. What is the term for a carbohydrate that cannot be further hydrolyzed into simpler units of polyhydroxy aldehyde or ketone?

(a) Monosaccharide
(b) Oligosaccharide
(c) Polysaccharide
(d) Sucrose

2. Which of the following is not considered a polysaccharide?

(a) Starch
(b) Cellulose
(c) Glycogen
(d) Maltose

3. What product is formed by the oxidation of glucose and gluconic acid with nitric acid?

(a) Rhamnose
(b) Saccharic acid
(c) Citric acid
(d) Oxalic acid

4. Which pair of substances can be considered epimers?

(a) Glucose and mannose
(b) Fructose and mannose
(c) Glucose and fructose
(d) Glucose and sucrose

5. In sucrose, how are the two monosaccharides linked together?

(a) C1 of a-D-glucose and C2 of b-D-fructose
(b) C2 of a-D-glucose and C1 of b-D-fructose
(c) C1 of b-D-glucose and C2 of b-D-fructose
(d) C1 of b-D-glucose and C2 of a-D-fructose

6. What is the composition of invert sugar?

(a) D-glucose + D-fructose
(b) L-glucose + D-fructose
(c) L-glucose + D-glucose
(d) L-glucose + L-glucose

7. Based on the provided structure, what is the name of the disaccharide?

(a) Sucrose (b) Maltose (c) Lactose (d) Talose

8. Which substance is commonly referred to as "animal starch"?

(a) Amylose (b) Amylopectin

(c) Glycogen (d) Cellulose

9. How many amino acids are required to form a protein in the human body?

(a) 25 (b) 100 (c) 20 (d) 10

10. Which of the following amino acids can the body synthesize?

(a) Valine (b) Leucine (c) Lysine (d) Glycine

11. What is the term for the structure of a protein where amino acids are linked together in a specific sequence within a polypeptide?

(a) Primary structure (b) Secondary structure

(c) Tertiary structure (d) Quaternary structure

12. What is the name for the spatial arrangement of two or more polypeptide chains in a protein?

(a) Primary structure (b) Secondary structure

(c) Tertiary structure (d) Quaternary structure

13. Which of the following is an example of protein denaturation?

(a) Coagulation of egg white (b) Clotting of blood

(c) Curdling of milk (d) Both (a) and (c)

14. What is the common name for an enzyme that catalyzes the oxidation of one substrate while simultaneously reducing another substrate?

(a) Reduction oxidase
(b) Oxidoreductase
(c) Oxidoreductase
(d) Reduce oxides

15. Which vitamin is classified as a fat-soluble vitamin?

(a) Vitamin A
(b) Vitamin B6
(c) Vitamin C
(d) Vitamin B2

16. Which vitamin is water-soluble?

(a) Vitamin C
(b) Vitamin D
(c) Vitamin E
(d) Vitamin K

17. What is another name for pyridoxine?

(a) Vitamin B2
(b) Vitamin B6
(c) Vitamin B12
(d) Vitamin B1

18. Which deficiency disease is caused by a lack of vitamin E?

(a) Beri-beri
(b) Rickets
(c) Scurvy
(d) Muscular weakness

19. What is the correct pairing between a nucleic acid and its respective sugar base?

(a) DNA -> b-D-3-deoxyribose
(b) DNA -> b-D-1-deoxyribose
(c) RNA -> b-D-ribose
(d) RNA -> b-D-3-deoxyribose

20. Identify the structures I and II and choose the correct option.

(a) I: b-D-ribose, II: b-D-2-deoxyribose

(b) I: a-D-ribose, II: b-D-3-deoxyribose

(c) I: b-D-deoxyribose, II: b-D-ribose

(d) I: b-D-deoxyribose, II: a-D-ribose

21. Which of the following components does not make up nucleic acid?

(a) Uracil
(b) Ribose sugar
(c) Phosphoric acid
(d) Guanidine

22. Which type of RNA is represented by m-RNA, t-RNA, and r-RNA?

(a) m-RNA
(b) t-RNA
(c) r-RNA
(d) All of these

23. Which of the following is not classified as a hormone?

(a) Insulin
(b) Endorphins
(c) Norepinephrine
(d) Thymine

24. What is the primary role of insulin?

(a) To decrease the glucose level in the human body

(b) To maintain blood glucose within a narrow range

(c) To regulate growth

(d) To transport minerals

25. A pair of diastereomers that differ only in the configuration about a single carbon atom (which is not a carbonyl group) are called

(A) Epimers
(B) Anomers
(C) Conformers
(D) Enantiomers

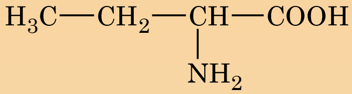
26. Carbohydrates which differ in configuration at the glycosidic carbon (i.e. C_1 in Aldose and C_2 in ketoses) are called

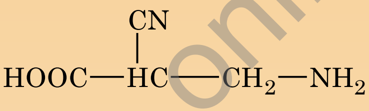
(A) Anomers
(B) Diastereomers
(C) Epimers
(D) Enantiomers

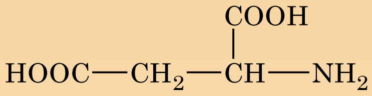
27. Glucose $\xrightarrow{Br_2+H_2O}$ [A], [A] is

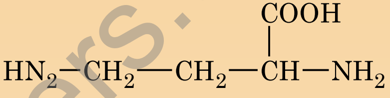
(A) Glucaric acid
(B) Gluconic acid
(C) Bromo hexane
(D) Hexanoic acid

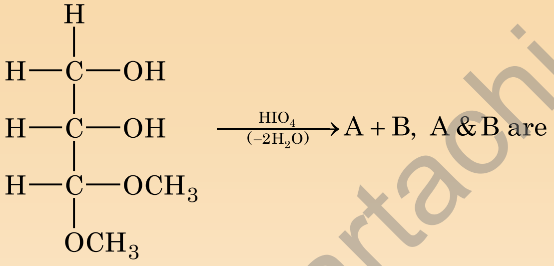
28. Which of the following is a basic amino acid?

(A)

$H_3C-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$

(B)

$HOOC-\overset{\displaystyle CN}{\overset{|}{HC}}-CH_2-NH_2$

(C)

$HOOC-CH_2-\overset{\displaystyle COOH}{\overset{|}{CH}}-NH_2$

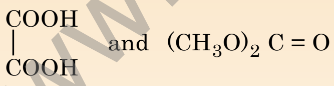
(D)

$HN_2-CH_2-CH_2-\overset{\displaystyle COOH}{\overset{|}{CH}}-NH_2$

29.


(A) HCHO & OHC.CH $(OCH_3)_2$

(B) HCHO & $(CH_3O)_2$ CH – COOH

(C) $(CH_3O)_2$ CHOCH & HCOOH

(D)

$\begin{matrix}COOH\\ |\\ COOH\end{matrix}$ and $(CH_3O)_2\ C = O$

30. Tertiary structure of protein contains which type of forces

(A) Electrostatic forces only

(B) Electrostatic as well as hydrogen bonds

(C) Electrostatic, hydrogen bonds and vander wall forces

(D) Electrostatic hydrogen bond, Vander wall forces, dipole-dipole attractions and disulphide cross-linkage

31. Primary structure of protein contains which type of bonds

(A) Only hydrogen
(B) Only covalent
(C) Only Vander wall
(D) All of these

32. Which of the following is optically inactive amino acid?

(A) Alanine
(B) Lysine
(C) Glycine
(D) Arginine

33. Deficiency of vitamin E causes

(A) Beri-Beri
(B) Scurvy
(C) Antifertility
(D) All of these

34. In the given reaction

Glucose +n phenyl hydrazine → osazone. Value of n

(A) Three
(B) Two
(C) One
(D) Four

35. Which of the following compounds will not show mutarotation?

(A) Methyl – α– D – glucopyranoside
(B) β – D (+) galactopyranose
(C) β – D (+) glucopyranose
(D) α– D (+) glucopyranose

36. The monomer of neoprene is

(A) chloroprene
(B) isoprene
(C) cebacic acid
(D) none of these

37. Which biomolecule act as catalyst?

(A) Carbohydrate
(B) Nucleic acid
(C) Protein
(D) Hormones

38. P – Cl – $C_6H_4NH_2$ and ph $NH_3^+Cl^-$ can be distinguished by

(A) NaOH

(B) $AgNo_3$

(C) Zn

(D) $LiAlH_4$

39. Write the sequence of bases on mRNA molecule synthesized on the following strand of DNA, TACAGTAAC

(A) ATGTCATTG

(B) UTGTCUTTG

(C) AUCACATTG

(D) AUGUCAUUG

40. Which of the following is not a monosaccharide?

(A) Fructose

(B) Ribose

(C) Glucose

(D) Pectins

41. Which of the following is vitamin – E?

(A) Retinol

(B) Calciferol

(C) Tocopherol

(D) Ascorbic acid

42. Most important energy carrier in all living cell is

(A) ADP

(B) ATP

(C) AMP

(D) UDP

43. Which of the following is sweetest?

(A) Sucrose

(B) Glucose

(C) Fructose

(D) Lactose

44. α – helix structure is

(A) Primary structure
(B) Secondary structure
(C) Tertiary structure
(D) Quaternary structure

45. Denaturation of protein takes place by

(A) Heating
(B) Addition of acid or base
(C) Addition of urea
(D) All of these

46. Maltose is made up of

(A) α – D – glucose
(B) D – fructose
(C) Glucose and fructose
(D) α – D – Glucose and β – D – glucose

47. Monomer units of starch are

(A) α – glucose
(B) β – glucose
(C) Galactose
(D) Pyranose

48. Which of the following is essential amino acid?

(A) Threonine
(B) Valine
(C) Lysine
(D) All of these

49. Which of the following is essential fatty acid?

(A) Oleic acid
(B) Linoleic Acid
(C) Linolenic Acid
(D) All of these

50. In a pentapeptide chain, how many peptide linkages are present?

(A) Five	(B) Four
(C) Six	(D) Three

51. Amino acids are derivatives of

(A) Tertiary amine	(B) Hydroxy acid
(C) Carboxylic acid	(D) Proteins

52. Lysine is which type of amino acid

(A) Basic	(B) Acidic
(C) β – amino acid	(D) Neutral

53. Which one of the following elements is not present in nucleic acid

(A) Carbon	(B) Oxygen
(C) Phosphorus	(D) Sulphur

54. Which is peptide hormone?

(A) Cytokinin	(B) Insulin
(C) Glucagon	(D) Progesterone

HINTS ANS SOLUTIONS

1. Answer: (a) Monosaccharide

Explanation: A carbohydrate that cannot be further hydrolyzed to simpler units is known as a monosaccharide, which is the simplest form of carbohydrate.

2. Answer: (d) Maltose

Explanation: Maltose is a disaccharide, not a polysaccharide. Polysaccharides are large carbohydrates composed of multiple monosaccharide units.

3. Answer: (b) Saccharic acid

Explanation: The oxidation of glucose and gluconic acid with nitric acid results in the formation of saccharic acid.

4. Answer: (c) Glucose and mannose

Explanation: Glucose and mannose are epimoric pairs because they only differ in the configuration of one chiral carbon atom.

5. Answer: (b) C2 of a-D-glucose and C1 of b-D-fructose

Explanation: In sucrose, a-D-glucose is linked to b-D-fructose through a glycosidic linkage between the C2 carbon of glucose and the C1 carbon of fructose.

6. Answer: (a) D-glucose + D-fructose

Explanation: Invert sugar is a mixture of D-glucose and D-fructose formed by the hydrolysis of sucrose.

7. Answer: (c) Lactose

Explanation: The provided structure represents lactose, a disaccharide composed of glucose and galactose.

8. Answer: (c) Glycogen

Explanation: Glycogen is often referred to as "animal starch" because it serves as the primary storage polysaccharide in animals.

9. Answer: (c) 20

Explanation: There are 20 different amino acids used to form proteins in the human body.

10. Answer: (c) Lysine

Explanation: Lysine is one of the amino acids that can be synthesized by the human body and is considered non-essential.

11. Answer: (a) Primary structure

Explanation: The primary structure of a protein refers to the specific sequence of amino acids in the polypeptide chain.

12. Answer: (d) Quaternary structure

Explanation: The quaternary structure of a protein describes the spatial arrangement of multiple polypeptide chains or subunits in a protein complex.

13. Answer: (d) Both (a) and (c)

Explanation: Coagulation of egg white (a) and curdling of milk (c) are both examples of protein denaturation.

14. Answer: (c) Oxidoreductase

Explanation: Oxidoreductases are enzymes that catalyze oxidation-reduction reactions involving the transfer of electrons.

15. Answer: (a) Vitamin A

Explanation: Vitamin A is classified as a fat-soluble vitamin.

16. Answer: (a) Vitamin C

Explanation: Vitamin C is a water-soluble vitamin.

17. Answer: (b) Vitamin B6

Explanation: Pyridoxine is another name for vitamin B6.

18. Answer: (d) Muscular weakness

Explanation: Vitamin E deficiency can lead to symptoms such as muscular weakness.

19. Answer: (a) DNA -> b-D-3-deoxyribose

Explanation: DNA contains b-D-3-deoxyribose sugar in its structure.

20. Answer: (a) I: b-D-ribose, II: b-D-2-deoxyribose

Explanation: Structure I is b-D-ribose, and structure II is b-D-2-deoxyribose.

21. Answer: (d) Guanidine

Explanation: Guanidine is not a component of nucleic acids.

22. Answer: (d) All of these

Explanation: m-RNA, t-RNA, and r-RNA are all types of RNA involved in various cellular processes.

23. Answer: (d) Thymine

Explanation: Thymine is a nitrogenous base found in DNA and RNA, not a hormone.

24. Answer: (b) To keep the blood glucose level within a narrow range

Explanation: Insulin's primary role is to regulate blood glucose levels and maintain them within a narrow and healthy range.

25. Answer: (A) Epimers

Explanation: Epimers are a type of diastereomers that differ in configuration around a single carbon atom (not a carbonyl group).

26. Answer: (A) Anomers

Explanation: Carbohydrates that differ in configuration at the glycosidic carbon (C1 in aldoses and C2 in ketoses) are called anomers.

27. Answer: (B) Gluconic acid

Explanation: [A] represents gluconic acid, which is a carboxylic acid derivative of glucose.

28. Answer: (A)

Explanation: The answer choices are incomplete. Please provide the complete options for a correct answer.

29. Answer: (B) HCHO & (CH3O)2 CH – COOH

Explanation: The given options are incomplete. Please provide complete options for a correct answer.

30. Answer: (D) Electrostatic, hydrogen bond, Vander Waal forces, dipole-dipole attractions, and disulfide cross-linkage

Explanation: Tertiary structure of proteins is stabilized by various forces, including electrostatic interactions, hydrogen bonds, Vander Waal forces, dipole-dipole attractions, and disulfide cross-linkages.

31. Answer: (B) Only covalent

Explanation: Primary structure of proteins is determined by the sequence of amino acids linked together by covalent peptide bonds.

32. Answer: (C) Glycine

Explanation: Glycine is an optically inactive amino acid due to its simple hydrogen side chain.

33. Answer: (C) Antifertility

Explanation: Deficiency of vitamin E does not cause beriberi or scurvy. It is not associated with any of the given options.

34. Answer: (D) Four

Explanation: In the given reaction, four molecules of phenyl hydrazine react with glucose to form osazone

35. Answer: (A) Methyl α-D-glucopyranoside

Explanation: Methyl α-D-glucopyranoside is a stable compound and does not show mutarotation, unlike other options.

36. Answer: (A) Chloroprene

Explanation: Neoprene is a synthetic rubber and its monomer is chloroprene.

37. Answer: (C) Protein

Explanation: Proteins act as catalysts and are known as enzymes.

38. Answer: (B) AgNO3

Explanation: P-Cl-C6H4NH2 will react with AgNO3 to form a white precipitate of AgCl, while ph NH3+Cl- will not react.

39. Answer: (A) ATGTCATTG

Explanation: This sequence represents the mRNA strand synthesized from the DNA strand TACAGTAAC.

40. Answer: (D) Pectin

Explanation: Pectin are not monosaccharides; they are a complex polysaccharide found in plant cell walls.

41. Answer: (C) Tocopherol

Explanation: Vitamin E is also known as tocopherol.

42. Answer: (B) ATP

Explanation: ATP (Adenosine triphosphate) is the primary energy carrier in living cells.

43. Answer: (C) Fructose

Explanation: Fructose is often considered the sweetest natural sugar among the options given.

44. Answer: (B) Secondary structure

Explanation: α-helix structure is a type of secondary structure in proteins.

45. Answer: (D) All of these

Explanation: Denaturation of proteins can occur through various processes, including heating, changes in pH (addition of acid or base), and the addition of chemicals like urea.

46. Answer: (C) Glucose and fructose

Explanation: Maltose is composed of two glucose molecules.

47. Answer: (A) α-glucose

Explanation: The monomer units of starch are α-glucose molecules.

48. Answer: (D) All of these

Explanation: Threonine, valine, and lysine are all essential amino acids.

49. Answer: (D) All of these

Explanation: Oleic acid, linoleic acid, and linolenic acid are all essential fatty acids.

50. Answer: (B) Four

Explanation: In a pentapeptide chain, there are four peptide linkages.

51. Answer: (C) Carboxylic acid

Explanation: Amino acids are derivatives of carboxylic acids.

52. Answer: (A) Basic

Explanation: Lysine is a basic amino acid due to its amino group.

53. Answer: (D) Sulfur

Explanation: Sulfur is not a primary element present in nucleic acids.

54. Answer: (B) Insulin

Explanation: Insulin is a peptide hormone produced by the pancreas.