



Biomolecules

Section (A) : Carbohydrates

1. Concept

Generally, carbohydrates are substances with the general formula $C_x(H_2O)_y$. They are called carbohydrates (hydrates of carbon) because they contain hydrogen and oxygen in the same proportion as in water. However, a number of compounds have been found, which are carbohydrates by chemical behaviour but do not confirm to the formula $C_x(H_2O)_y$. E.g : 2-deoxyribose.

- (i) carbohydrates are biopolymers of polyhydroxy aldehyde or polyhydroxy ketones.
- (ii) monomeric polyhydroxy aldehydes or ketones can also exist in hemiacetal and acetal forms in cyclic structures.
- (iii) Almost all of these compounds are chiral and optically active. An exception of this is 1,3-dihydroxypropanone.
- (iv) All natural carbohydrates have D-configuration.

2. Classification of Carbohydrates

(a) Classification on the basis of number of hydrolysed products

S.No.	Carbohydrate	No. of units (on hydrolysis)	Examples
1	Monosaccharides	1 or single unit (cannot be hydrolysed)	Glucose, Fructose, Galactose
2	Oligosaccharides	2 to 10 units	Sucrose, Maltose, Lactose
3	Polysaccharides	Many units	Starch, Cellulose, Gums, Resins etc

(b) Classification on the basis of functional groups

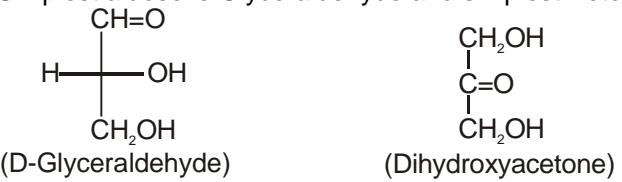
S.No.	Carbohydrate	No. of functional group	Examples
1	Aldose	Aldehyde $CH = O$ $(CHOH)_n$ CH_2OH	Glyceraldehyde, Erythrose, Threose, Ribose & 2-Deoxyribose, Glucose, Mannose, Allose.
2	Ketose	Ketone CH_2OH $C = O$ $(CHOH)_n$ CH_2OH	$n = 0$; Ketotriose, $n = 1$; Ketotetroses, $n = 2$; Ketopentoses, $n = 3$; Ketohexoses

(c) Classification of monosaccharides on basis of carbon atoms in hydrolysed product.

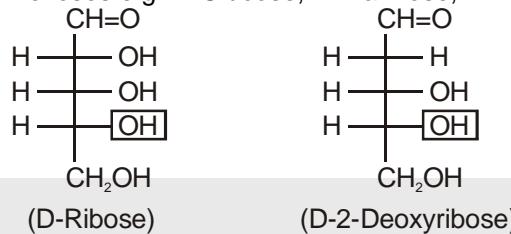
S.No.	Carbon atoms	General term	Aldehyde	Ketone
1	3	Triose	Aldotriose	Ketotriose
2	4	Tetrose	Aldotetrose	Ketotetrose
3	5	Pentose	Aldopentose	Ketopentose
4	6	Hexose	Aldohexose	Ketohexose
5	7	Heptose	Aldoheptose	Ketoheptose

Some facts :

- Number of carbons in monosaccharides are generally 3 to 7.
- Simplest aldose is Glyceraldehyde and simplest Ketose is Dihydroxyacetone.

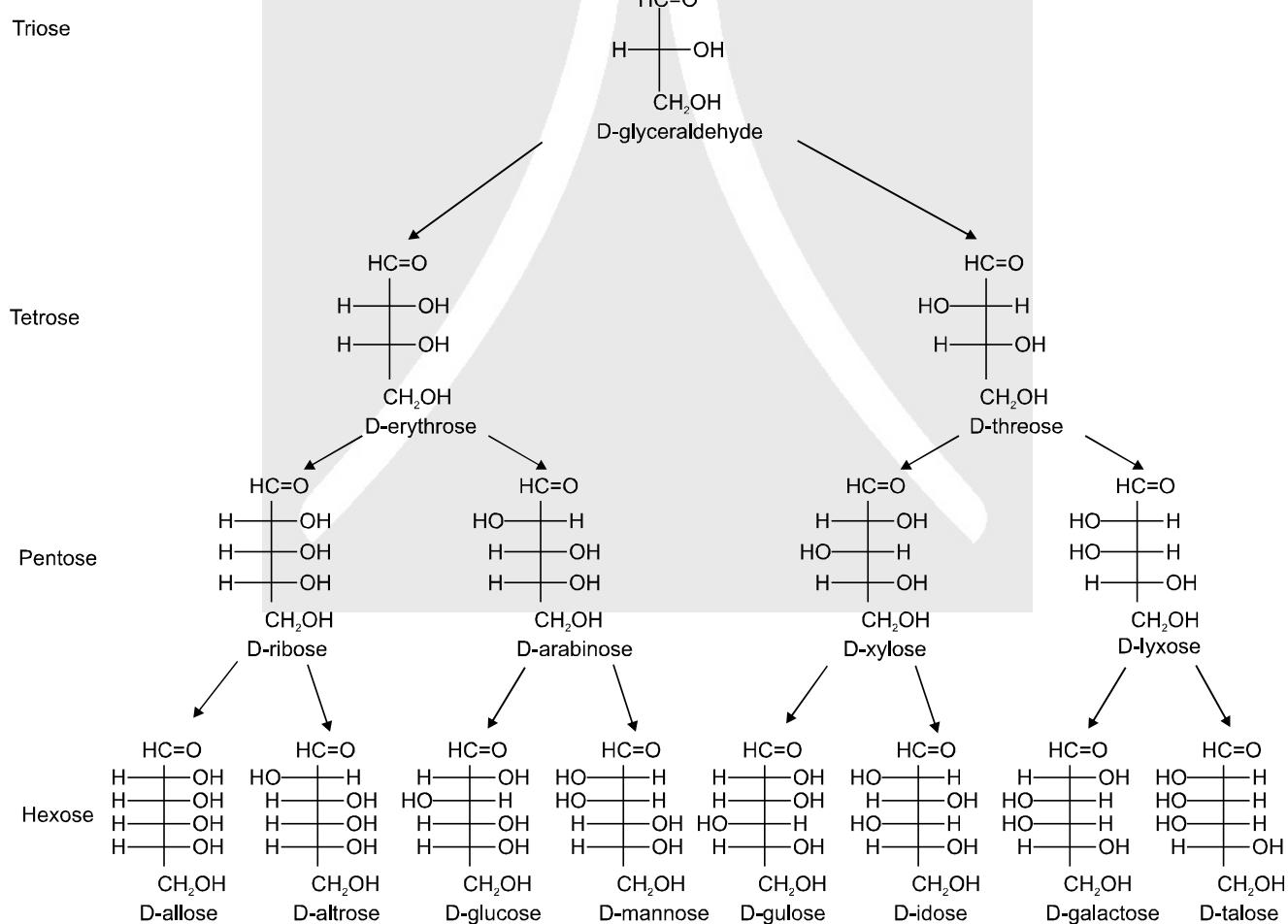


- Most naturally occurring monosaccharides are :
 - Pentoses e.g. D-Ribose (present in RNA) and 2-Deoxyribose (present in DNA)
 - Hexoses e.g. D-Glucose, D-Mannose, D-Allose, D-Galactose and D-Fructose



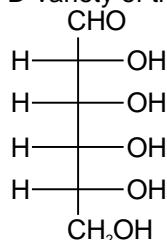
3. Stereochemistry of Aldoses :

The monosaccharides are chiral and may have D or L configuration. A simple illustration of all 'D' forms is given below.

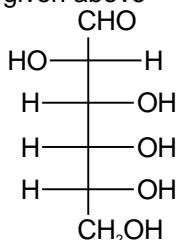


Optical isomers of Aldohexoses : Aldohexoses have four asymmetric carbon atoms, therefore they have sixteen optical isomers out of which 8 are D and 8 are L variety (overall Eight pairs of enantiomers).

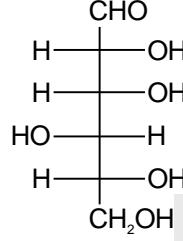
D-variety of them are given above



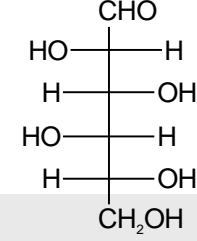
D(+) -allose
(I)



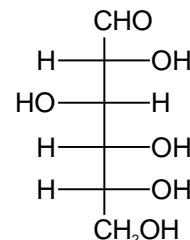
D(+) -altrose
(II)



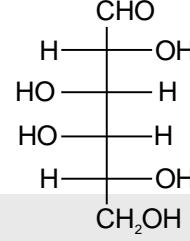
D(+) -gulose
(V)



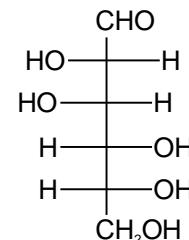
D(+) -idose
(VI)



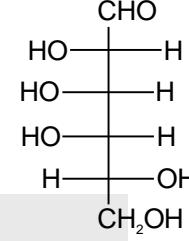
D(+) -glucose
(III)



D(+) -galactose
(VII)



D(+) -mannose
(IV)



D(+) -talose
(VIII)

Note : 1. D-aldohexoses shown above have diastereomeric relationship with each other
2. D-aldohexoses can be either dextro (+) or laevo (-).

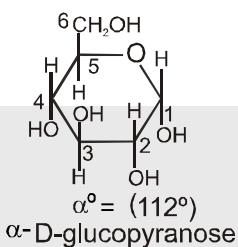
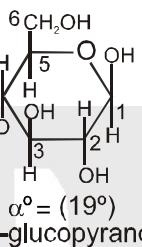
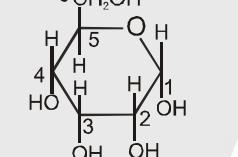
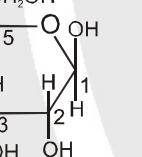
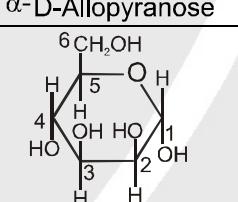
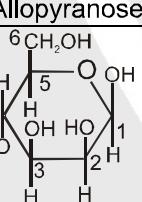
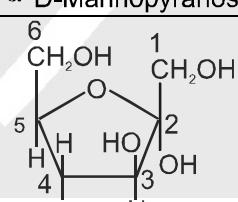
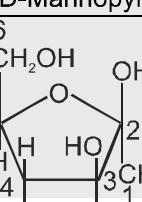
4. Structure of aldohexoses : All form of Aldose or ketose may exist in open chain form as well as in cyclic pyranose or furanose form.

(i) **Open chain structure of monosaccharides :**

Carbohydrate	Structure	Functional Group	Typical nature
D-Glucose	$ \begin{array}{c} \text{HC=O} \\ \\ \text{H} - \text{OH} \\ \\ \text{HO} - \text{H} \\ \\ \text{H} - \text{OH} \\ \\ \text{H} - \text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	Aldehyde	3rd (L)
D-Allose	$ \begin{array}{c} \text{HC=O} \\ \\ \text{H} - \text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	Aldehyde	No (L)
D-Mannose	$ \begin{array}{c} \text{HC=O} \\ \\ \text{HO} - \text{H} \\ \\ \text{HO} - \text{H} \\ \\ \text{H} - \text{OH} \\ \\ \text{H} - \text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	Aldehyde	2, 3 (L)
D-Galactose	$ \begin{array}{c} \text{HC=O} \\ \\ \text{H} - \text{OH} \\ \\ \text{HO} - \text{H} \\ \\ \text{HO} - \text{H} \\ \\ \text{H} - \text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	Aldehyde	3, 4 (L)

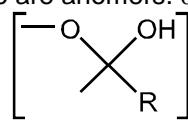
D-Fructose	$ \begin{array}{c} \text{CH}_2 - \text{OH} \\ \\ \text{C} = \text{O} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{CH}_2 - \text{OH} \end{array} $	Ketone	3 (L)
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(ii) Cyclic structure of monosaccharide

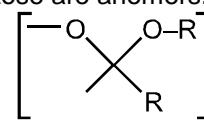
Carbohydrate	Cyclic structure	
Glucose	 <p>$\alpha^{\circ} = (112^{\circ})$ α-D-glucopyranose</p>	 <p>$\alpha^{\circ} = (19^{\circ})$ β-D-glucopyranose</p>
Allose	 <p>α-D-Allopyranose</p>	 <p>β-D-Allopyranose</p>
Mannose	 <p>α-D-Mannopyranose</p>	 <p>β-D-Mannopyranose</p>
Fructose	 <p>α-fructofuranose</p>	 <p>β-fructofuranose</p>

Anomers :

Anomers are diastereomers that differ in the configuration at the acetal or hemiacetal C atom of a sugar in its cyclic form (Anomeric carbon: A carbon bonded with two 'O' atoms). For example, α -D(+) and β -D(+) glucose are anomers. α -D(-) and β -D(-) fructose are anomers.



Hemiacetal functional group



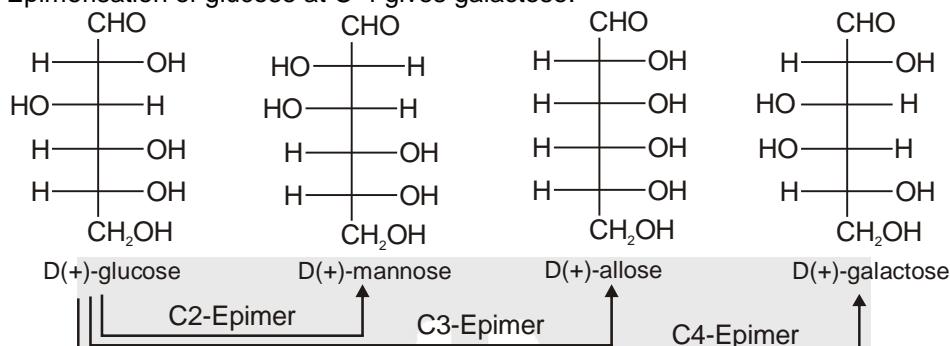
Acetal functional group



Epimers : Diastereomers with more than one stereocentre that differ in the configuration about only one stereocentre (other than anomeric carbon) are called epimers.

Stereoisomers (other than anomers) are called epimers.

- i. D-Erythroose and L-threose are epimers.
- ii. D-glucose and D-galactose are C-4 epimers and
- iii. D-idose and D-talose are C-3 epimers.
- iv. D-glucose and D-mannose are C-2 epimers.
- v. Epimerisation of glucose at C-2 gives mannose.
- vi. Epimerisation of glucose at C-3 gives allose.
- vii. Epimerisation of glucose at C-4 gives galactose.



Reducing and non Reducing properties of (Sugars) :

	(I) Reducing sugars	(II) Non Reducing sugars
1.	Reduces Tollen's reagent, Fehling's solution & Benedict's solution.	Don't reduce Tollen's, Fehling's & Benedict's solution.
2.	Should have atleast one hemiacetal or hemiketal functional group. Ex. All Mono and Oligosaccharides except Sucrose	Should have acetal linkage. Ex. All Polysaccharides and few Oligosaccharides (Ex. Sucrose)

MONOSACCHARIDES

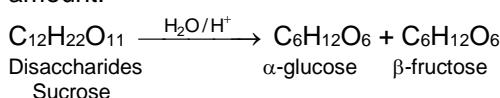
GLUCOSE

Glucose is the most common monosaccharide. It is known as Dextrose because it occurs in nature principally as the optically active dextrorotatory isomers. It acts as a reducing agent (reduces both Fehling's solution and ammonical silver nitrate solution ; **Tollen's reagent**). It is known as **dextrose** and found as grapes, honey, cane sugar, starch and cellulose.

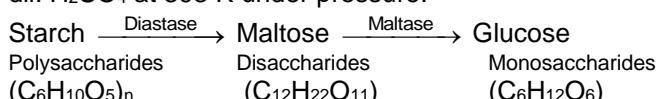
Preparation :

(i) By acid hydrolysis of cane sugar (a disaccharide) :

If sucrose is boiled with dil. HCl or H_2SO_4 in alcoholic solution. Glucose & fructose are obtained in equal amount.



(ii) By enzymatic action over starch : Glucose is obtained by hydrolysis of starch by boiling it with dil. H_2SO_4 at 393 K under pressure.



Structure of Glucose :

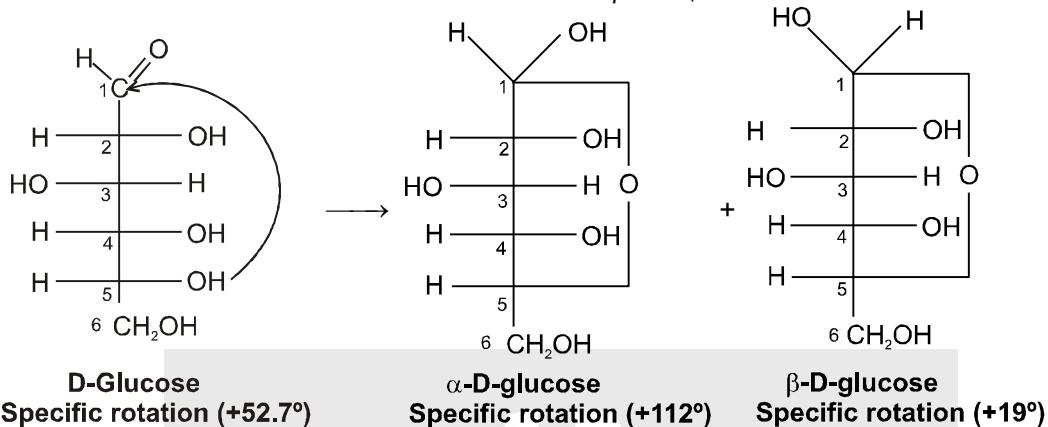
Open chain structure (Fisher projection) and Cyclic structure (Haworth projection) :

(1) Despite having aldehyde group, glucose does not give Schiff's test & it does not form the hydrogen sulphite (bisulphite) addition product with NaHSO_3 .

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

This behaviour could not be explained by open chain structure. It was proposed that one of –OH group add to CHO group, forms a cyclic structure.

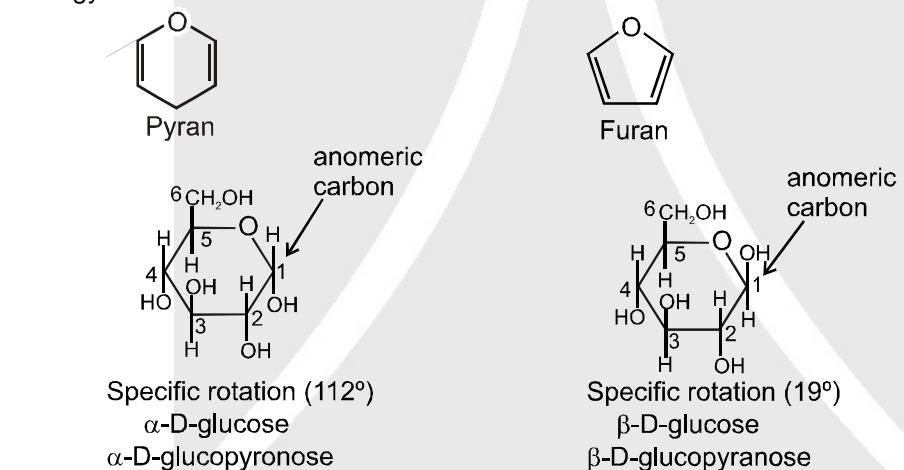
These two cyclic hemiacetal form of glucose differs only in configuration of the hydroxyl group at C1, called anomeric carbon. Such isomers i.e. α -form & β -form, are called anomers.



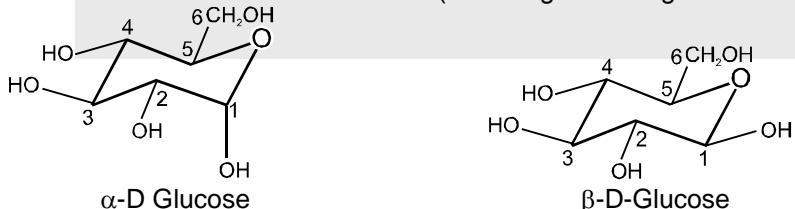
Note : β -form of D-glucose is more stable than α -D-Glucose.

Haworth projection

The six membered cyclic structure of glucose is called pyranose structure (α - or β -), in analogy with pyran and five membered cyclic structure of monosaccharides is called furanose structure (α or β) in analogy with furan



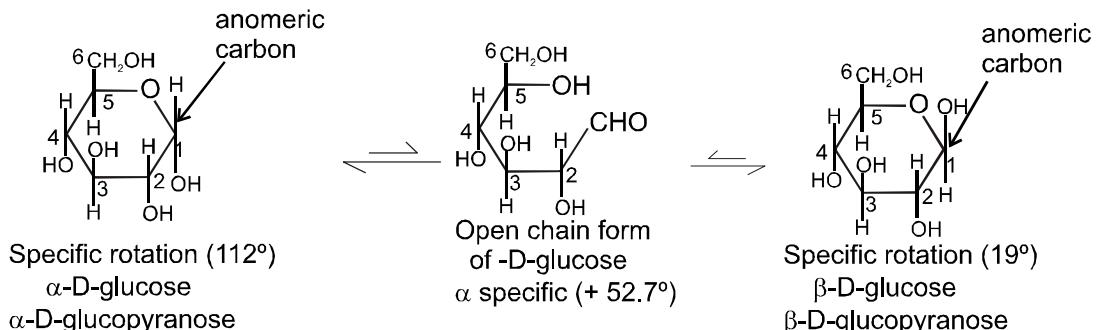
α and β -Glucose are anomers of each other (i.e change in configuration of 1st carbon atom only)



Properties of Anomers : Mutarotation

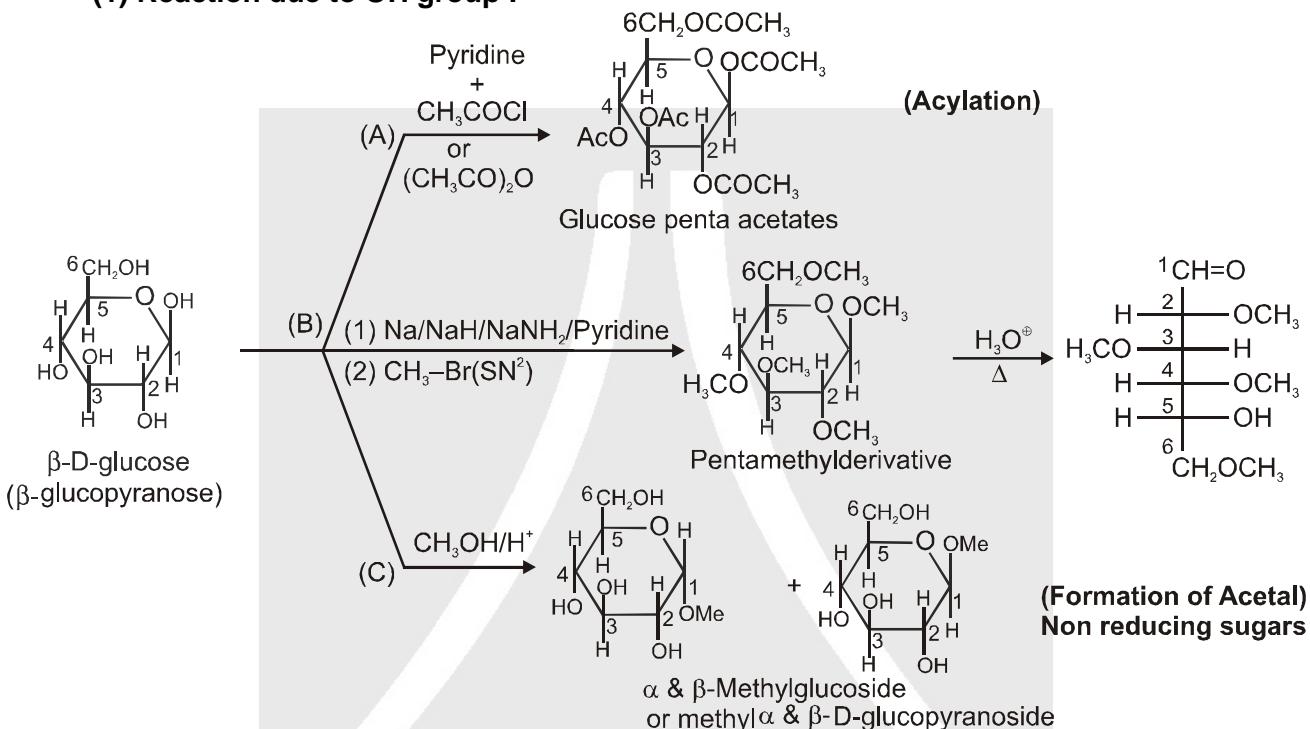
When one of the pure glucose anomers dissolve in water, an interesting change in the specific rotation is observed. When the α -anomer dissolves, its specific rotation gradually decreases from an initial value of +112° to +52.7°. When the pure β anomer dissolves, its specific rotation gradually increases from +19° to the same value of +52.7°. **This change (mutation) in the specific rotation is called mutarotation.** What is happening to each solution ?

Initially solution with only one anomeric form, undergoes equilibrium to the same mixture of α -and β -forms. The open chain form is in intermediate in the process of equilibrium. For mutarotation atleast one hemiacetal group must be present in the sugar therefore **all reducing sugars will mutarotate**.



Chemical Reactions of Anomers (Glucose)

(1) Reaction due to OH group :

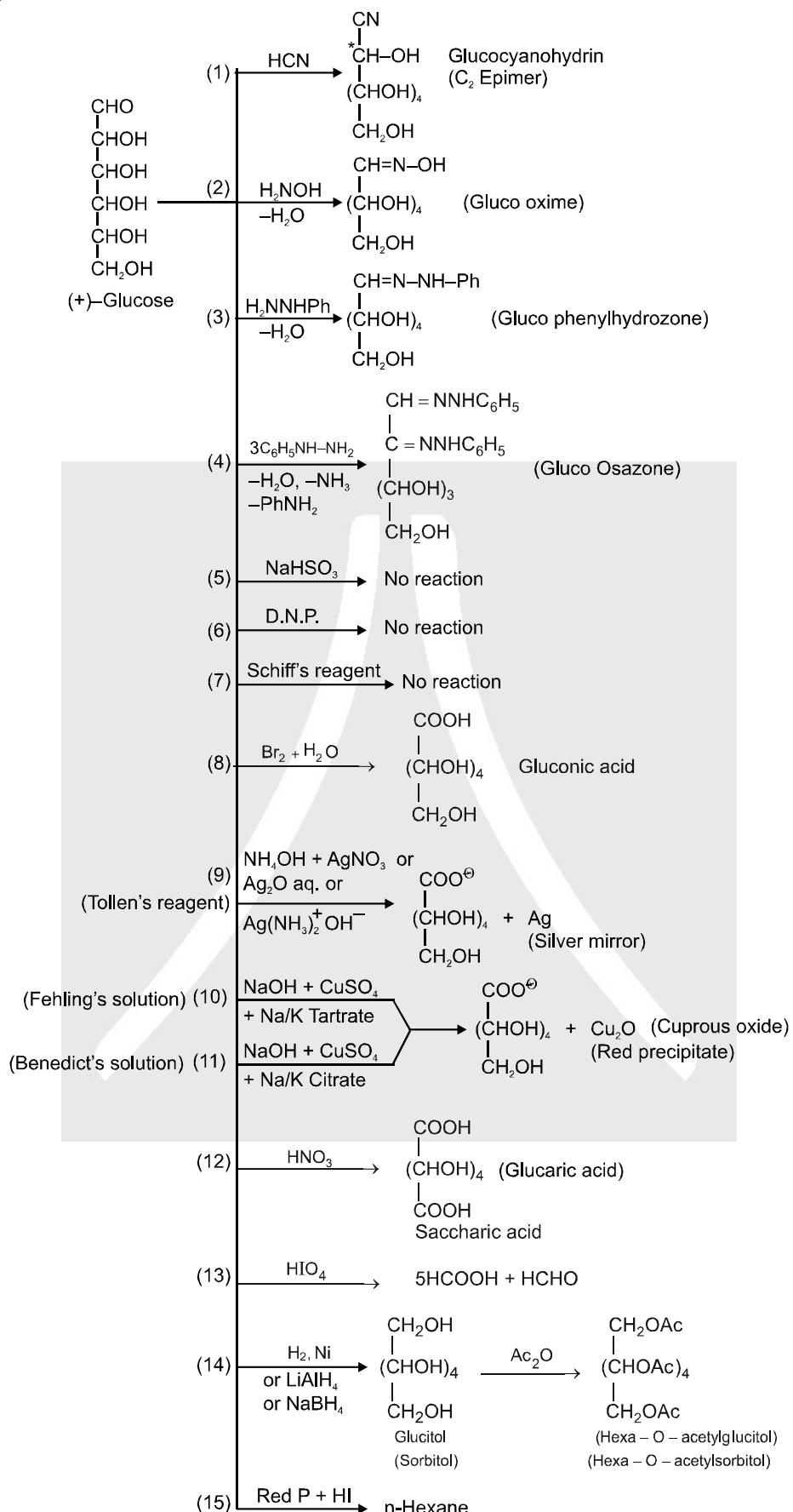


Note :

- (A) Acylation with acid halide or acetic anhydride gives pentaacetates which confirms the presence of five $-\text{OH}$ groups.
- (B) After Hydrolysis product of pentamethyl derivatives, aldehyde group and hydroxy of C_5 regenerated hence hydroxy of C_5 is involved in the hemiacetal formation.
- (C)
 - (i) Sugars in the form of **acetals** are called **glycosides**. ($\text{glucose} \rightarrow \text{glucoside}$, $\text{mannose} \rightarrow \text{mannoside}$, $\text{ribose} \rightarrow \text{riboside}$, $\text{fructose} \rightarrow \text{fructoside}$ etc).
 - (ii) In the formation of glycosides only one mole of alcohol is required so monosaccharides are already present in the hemiacetal form with one of the hydroxyl group and carbonyl group.
 - (iii) Glycosides are non-reducing and will not show mutarotation because in neutral and basic condition glycosides are stable (cyclic form cannot open to the free carbonyl compound).
 - (iv) After acidic hydrolysis of glycosides, product form will have reducing property and also show mutarotation.

(2) Reaction due to aldehyde :

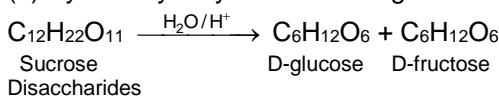
In aqueous solution, α -Anomer or β -Anomer remains in the equilibrium with each other by small amount of open chain forms (0.02%), in which carbonyl group is regenerated and gives various reactions.



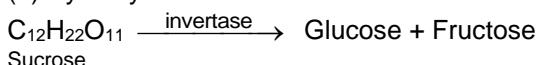
FRUCTOSE

Fructose preparation :

(1) By acid hydrolysis of cane sugar.



(2) By enzymatic action of sucrose.

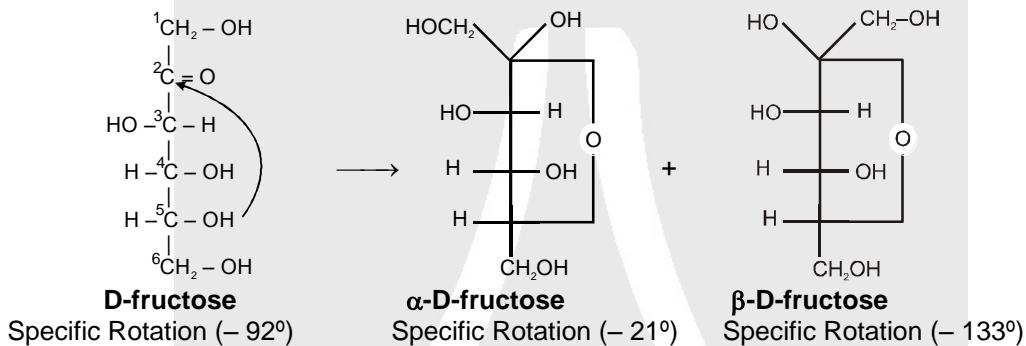


Note : (i) Glucose & fructose obtained by acid hydrolysis of sucrose can be separated by treating with $\text{Ca}(\text{OH})_2$ which forms calcium glucosate & calcium fructosate. Calcium fructosate, being water insoluble, is separated out easily.

(ii) Fructose is the sweetest monosaccharide.

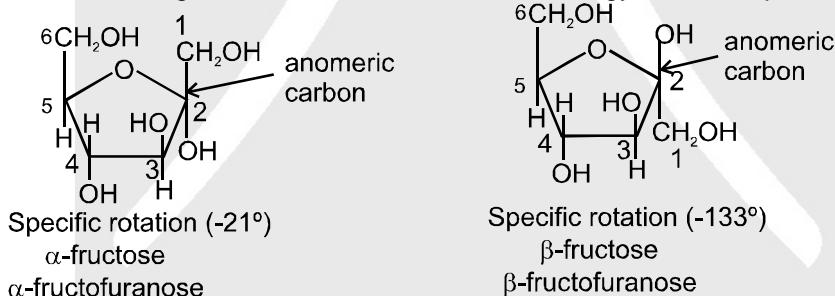
Structure of fructose :

It also exists in two cyclic forms which are obtained by the addition of $-\text{OH}$ at C5 to the ($\text{C}=\text{O}$) group.



Haworth projection : Fructofuranose

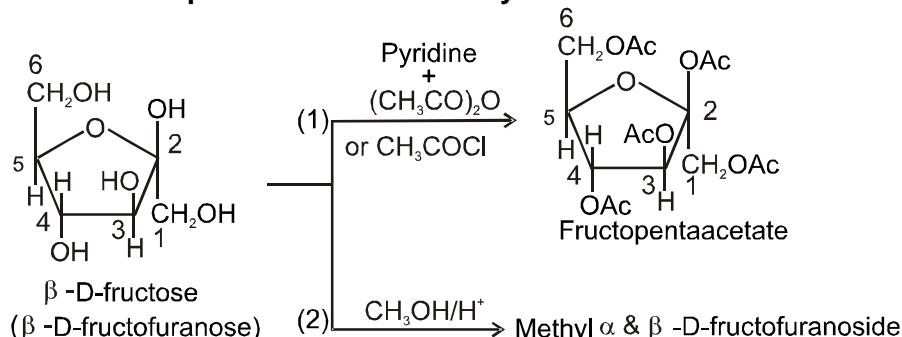
The five membered ring δ is named as furanose with analogy to the compound furan.



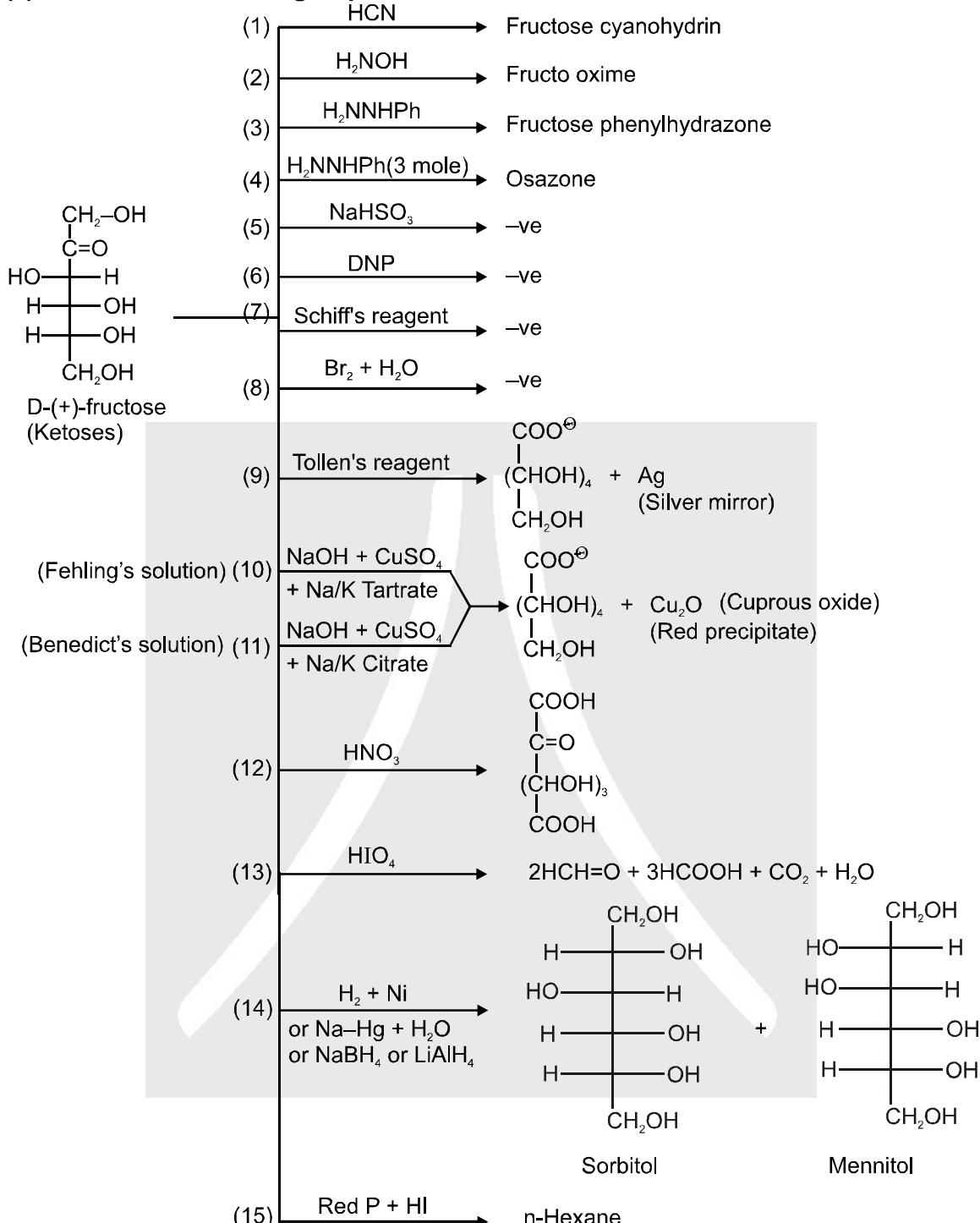
Chemical Reactions of Fructose :

Reaction due to -OH group at 2nd carbon :

(1) It forms fructose pentaacetate with acetyl chloride :

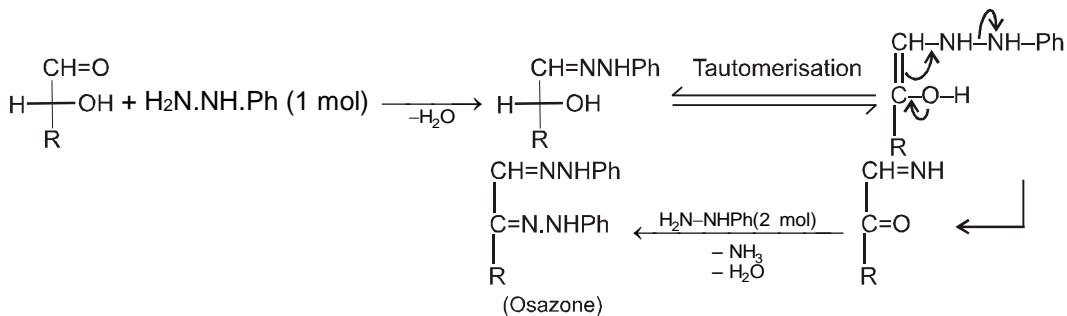


(2) Reaction due to keto group :

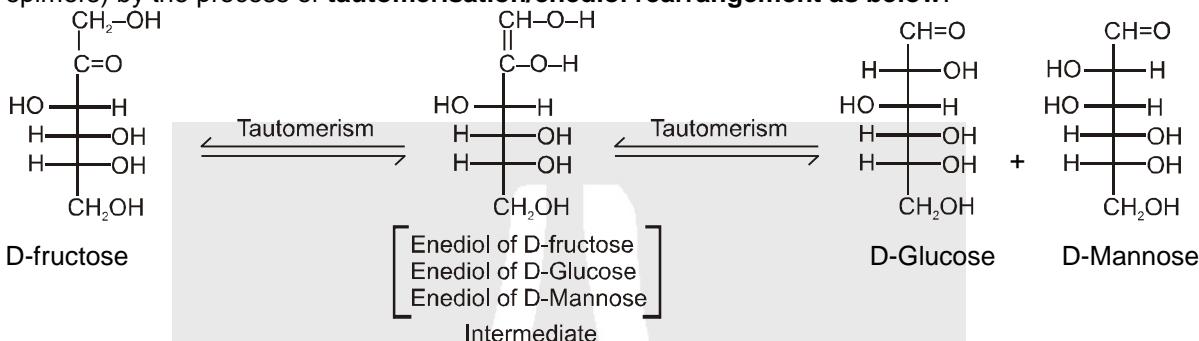


Some Highlights :

1. Since glucose & fructose (Aldoses/Ketoses) reacts with HCN, H_2NOH , H_2NNHPh which indicates the presence of carbonyl group but they don't react with DNP, NaHSO_3 & Schiff's reagent (weak reagents) therefore we can conclude that carbonyl group is not free, but remains in the form of cyclic structures.
2. In the formation of osazone, C₁ & C₂ are only involved so glucose, fructose and C-2 epimers (Glucose & Mannose), (Threose and Erythrose) give same osazone.
Osazone are crystalline solid having sharp melting point so used for identifying the carbohydrates. In the osazone formation three molecules of NH_2NHPH is overall consumed out of which two molecule react with nucleophilic addition/elimination reaction forming hydrazone whereas one molecule undergoes redox reaction.



3. Both glucose and fructose gives test with Tollen's reagent, Fehling's solution and Benedict's solution because in basic medium, ketoses remains in the form of dynamic equilibrium with Aldoses (C-2 epimers) by the process of **tautomerisation/enediol rearrangement as below.**



4. Only $\text{Br}_2/\text{H}_2\text{O}$ is used for the identification of Aldoses & Ketoses. (Mild oxidising agent like bromine water (Neutral) Oxidises only aldehydic group).

5. Oxidation with HNO_3 , gives information that one primary alcohol is present in aldoses and two primary alcohols are present in ketoses.

6. Reduction product with Na/Hg and H_2O gives only one alcohol with aldoses and two alcohols with ketoses (C-2 epimers)

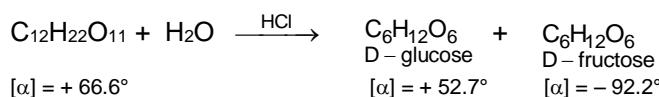
7. Reduction product with Red P & HI, gives n-Hexane which indicates that all the six carbon atoms are linearly arranged.

Disaccharides

Condensation of two monosaccharides after loss of water molecule (Glycosidic bond), gives disaccharides. Common examples are sucrose, maltose, lactose, cellulose.

(a) Sucrose : (Cane sugar)

- (i) Sucrose is a white crystalline solid, soluble in water.
- (ii) When heated above its melting point, it forms a brown substance known as caramel.
- (iii) Sucrose is dextrorotatory, its specific rotation being $+ 66.5^\circ$.
- (iv) On hydrolysis with dilute acids sucrose yields an equimolar mixture of D(+)-glucose and D(-)-fructose :



Since D(-)-fructose has a greater specific rotation than D(+)-glucose, the resulting mixture is laevorotatory.

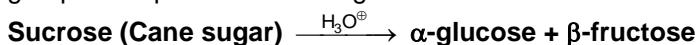
Since the hydrolysis of cane-sugar (sucrose) gives laevorotatory solution in place of original dextrorotatory solution therefore hydrolysis of cane-sugar is also known as the **inversion of cane-sugar or Inversion of sucrose** and the mixture of sugars are known as **invert sugar**.

Ex. D-Glucose & D-Fructose.

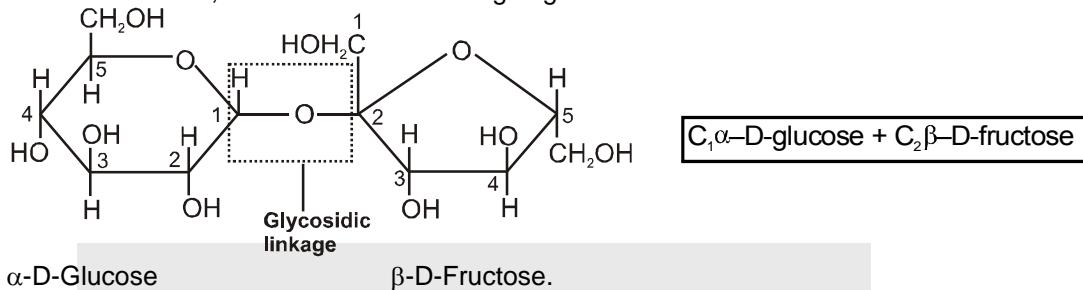
The inversion (i.e., hydrolysis) of cane-sugar may also be effected by the enzyme invertase which is found in yeast.



(v) Sucrose is not a reducing sugar, e.g., it will not reduce Fehling's solution or Tollen's reagent. It does not form an oxime or an osazone, and does not undergo mutarotation. This indicates that hemiacetal group is not present in the rings.

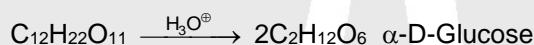


In sucrose two monosaccharides are joined together by an oxide linkage formed by loss of water molecule. Such linkage through oxygen atom is called glycosidic linkage. In sucrose linkage is between C1 of α -glucose and C2 of β -fructose. Since the reducing group of glucose & fructose are involved in glycosidic bond formation, sucrose is non reducing sugar.



(b) Maltose : (Malt sugar)

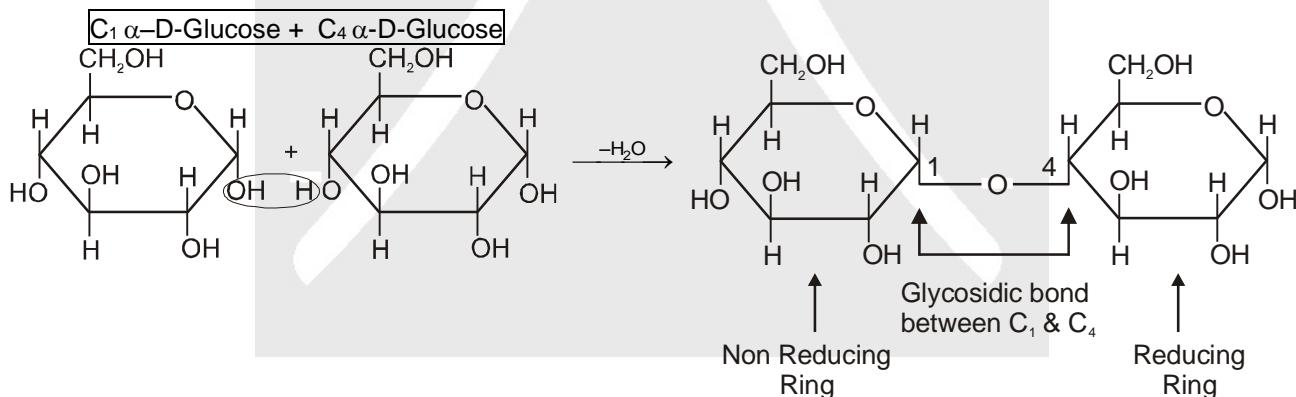
Maltose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is produced by the action of malt (which contains the enzyme diastase) on starch:



When it is hydrolysed with dilute acids or by the enzyme maltase, maltose yields two molecules of D (+)-glucose. Maltose is a reducing sugar, e.g., it reduces Fehling's solution or Tollen's reagent; it forms an oxime and an osazone, and undergoes mutarotation. This indicates that at least one hemiacetal group (of the two glucose molecules) is free in maltose.

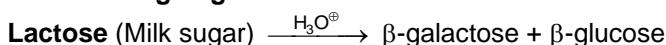


Formation of Maltose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$)

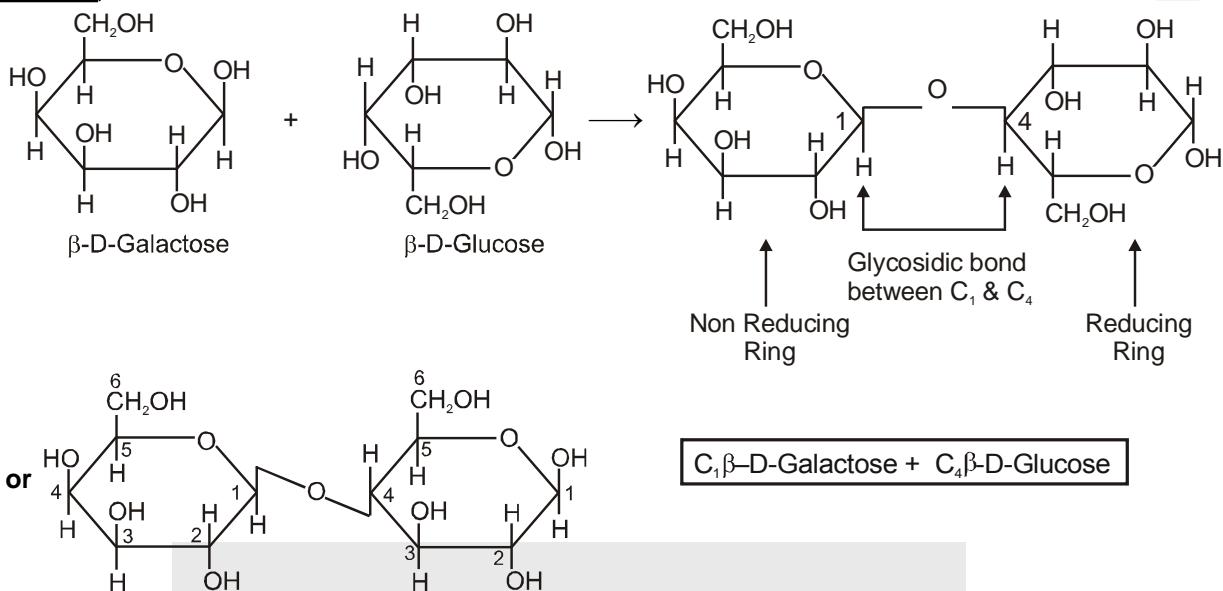


(c) Lactose : (Milk Sugar)

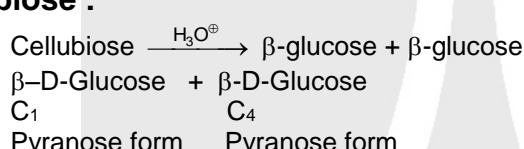
Lactose occurs in the milk of all animals and is dextrorotatory. It is hydrolysed by dilute acids or by the enzyme lactase, to an equimolecular mixture of D(+)-glucose and D(+)-galactose. Lactose is a reducing sugar.



Formation of Lactose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$)



(d) Cellubiose :



DISACCHARIDE

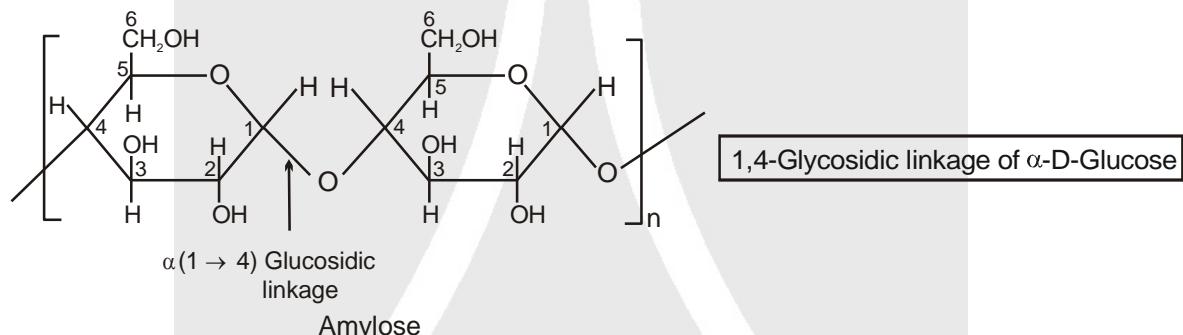
Disaccharide	Structure	Monomeric unit linkage	Properties
Maltose	 Maltose (α -1,4-glycosidic linkage)	α -D (+) Glucose + α -D (+) Glucose (α -1, 4-glycosidic linkage)	Produced by action of malt on starch. Undergoes mutarotation.
Sucrose	 Glycosidic linkage	α -D-glucose + β -D-fructose (α -1, β -2 glycosidic linkage)	White crystalline solid, soluble in water. dextrorotatory specific rotation + 66.5°
Lactose	 Lactose (β -1,4-glycosidic linkage)	β -D (+) Glucose + β -D (+) galactose (β -1, 4- glycosidic linkage)	dextrorotatory

POLYSACCHARIDES

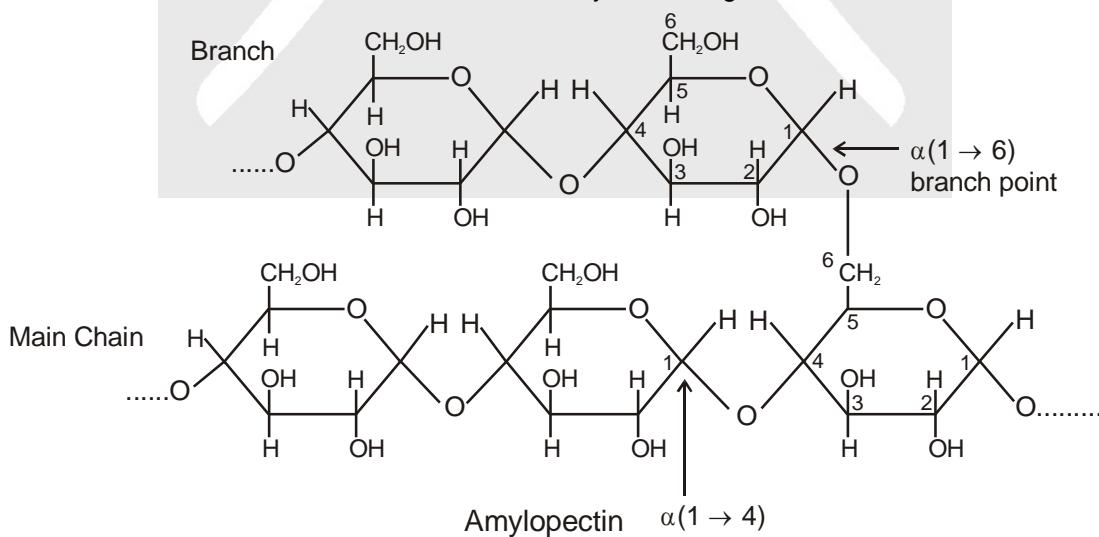
Polysaccharides : It contains large number of monosaccharide units joined together by glycosidic linkage (acetal bond). They are food storage or structural material.

(i) Starch, $(C_6H_{10}O_5)_n$

- (i) Starch is the main contributor of carbohydrates in our diet. It exists exclusively in plants, stored in the seeds, roots, and fibres as food reserve. Example rice, potato.
- (ii) Starch is actually a mixture of two structurally different polysaccharides, Amylose (15-20%) and Amylopectin (80-85%).
- (iii) When starch is heated with hot water, it can be separated into its components. The part that is soluble in water is amylose and remaining fraction is amylopectin.
- (iv) Both amylose and amylopectin are composed of D-glucose units.
- (v) The **amylose** molecule is made up of D-glucose unit joined by α -glycosidic linkages between C-1 of one glucose unit and C-4 of the next glucose unit. The number of D-glucose units in amylose range from 60-300.



- (vi) **Amylopectin** has a branched-chain structure. It is composed of chains of 25 to 30 D-glucose units joined by α -glycosidic linkages between C-1 to one glucose unit and C-4 of the next glucose unit. These chains are in turn connected to each other by 1, 6-linkages.



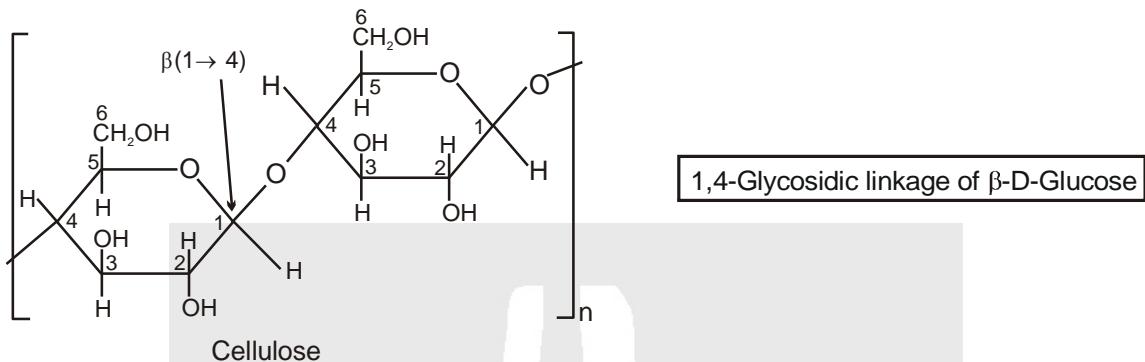


α -amylose soluble in water, and the solution gives a blue colour with iodine. Amylopectin is insoluble in water, is stable in contact with water, and gives a violet colour with iodine.

(ii) Glycogen (Animal Storage)

It is also like amylopectin but branching will take place after every 5 to 6 glucose unit. (highly branched)

(iii) Cellulose, $(C_6H_{10}O_5)_n$



1. Cellulose is linear chain natural polymers of β -D glucose units joined by 1, 4-glycosidic linkage (Natural linear polymers).
2. Cellulose is the main structural material of tree and other plants. Wood is 50% cellulose, while cotton wool is almost pure cellulose.
3. Artificial silk, rayon, is used collectively to cover all synthetic or manufactured fibres from cellulose.
4. The nitrates are prepared by the reaction of cellulose with a mixture of nitric and sulphuric acids, and the degree of 'nitration' depends on the concentrations of the acids and the time of the reaction. Cellulose trinitrate (12.2 – 13.2%N) is known as **gun-cotton** and is used in the manufacture of blasting explosives and smokeless powders.

Starch : (Plant Storage, Polymer of α -D-glucose),

Glycogen : (Animal Storage, Polymer of α -D-glucose),

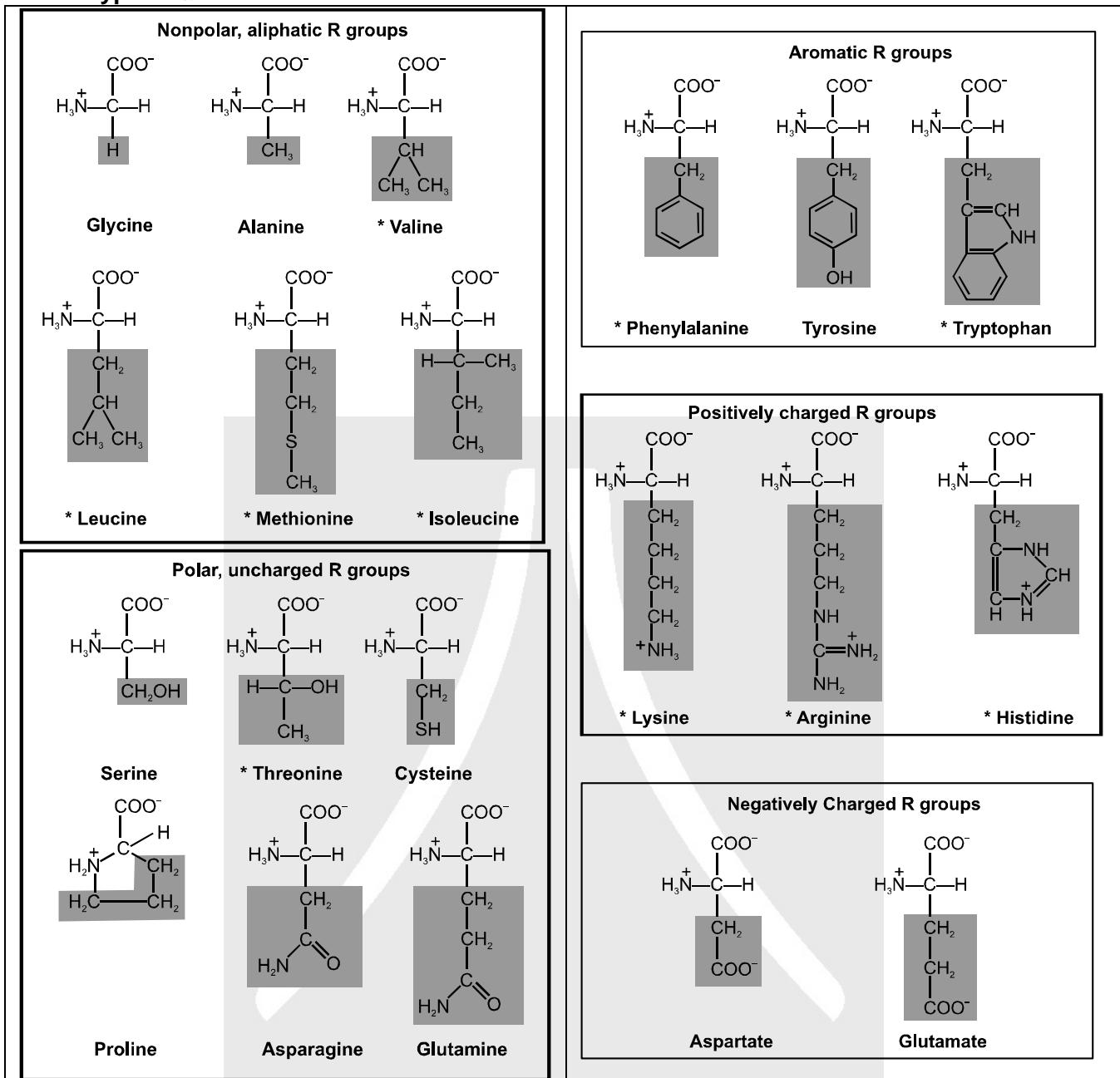
Cellulose : (Plant Skeleton, Polymer of β -D-glucose)

Section (B) : Amino Acids & Proteins

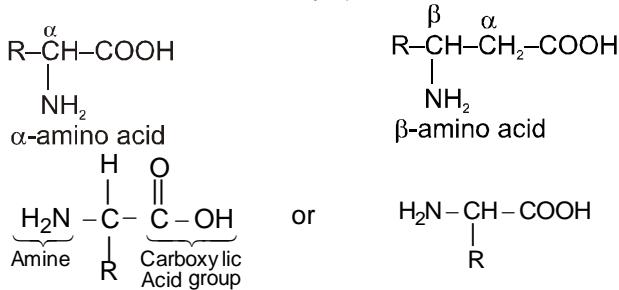
Proteins : Proteins are the most abundant-biomolecules of the living beings. The chief sources of proteins are milk, cheese, pulses, peanuts, fish, meat etc. These are high molecular mass complex, biopolymers of amino acids.

Amino Acids : Each living cell is made up of thousands of different proteins. All natural proteins are polymers of α -(L) amino acids and on partial hydrolysis give peptides of varying molecular masses which upon complete hydrolysis give α -amino acids.



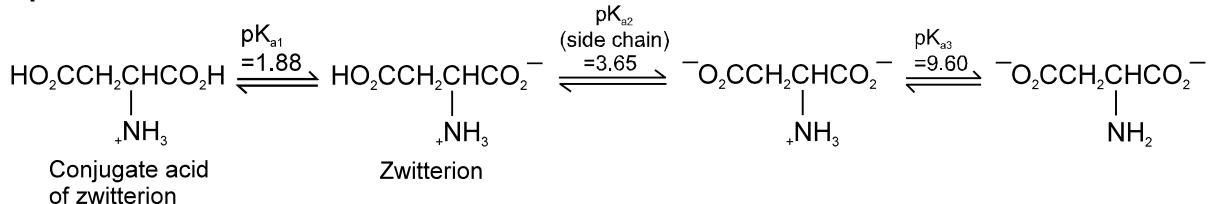
Type of α -amino acids :

The amino acids contain amino as well as carboxylic acid group. On the basis of position of amino group in the chain, these are named as α , β , γ etc. amino acid.



where, $R = \text{alkyl, aryl, or any other group, but never contain unstable, strained cycles or functional groups.}$

Aspartic acid :

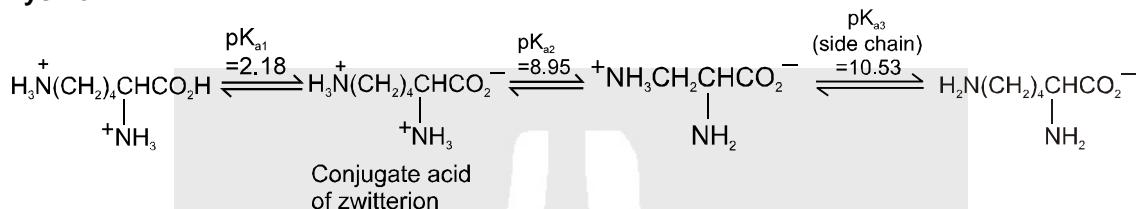


PI for acidic amino acid is calculated as $\frac{pK_{a_1} + pK_{a_2}}{2}$

The pI of aspartic acid is the average of pK_{a1} (1.88) and the pK_{a2} of the side chain (3.65) or 2.77.

(iii) For basic amino acid : where there are two NH₂ groups and one COOH group then isoelectric point varies between 7.6 to 10.8. e.g. Lysine (9.8)

Lysine:

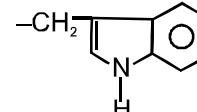


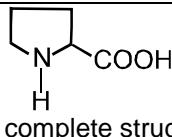
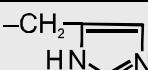
PI for basic amino acid is calculated as $\frac{pK_{a_2} + pK_{a_3}}{2}$

The PI of Lysine is the average of pK_{a2} (8.95) and the pK_a of the side chain (10.53) or 9.74.

Note : Amino acid has minimum aqueous solubilities at their isoelectric points.

Amino acids, their symbols and Isoelectric point :

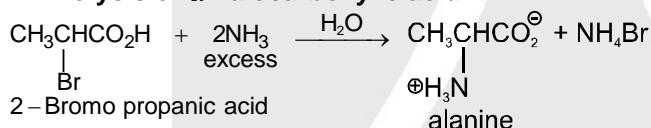
Amino acids, their symbols and isoelectric point					
S.No.	Name of the Amino acid	Three letter Symbol	One letter Code	Side chain (R)	Isoelectric point
		Neutral amino acids			
1	Glycine	Gly	G	– H	6.0
2	Alanine	Ala	A	– CH ₃	6.0
3	Valine*	Val	V	– CH–(CH ₃) ₂	6.0
4	Leucine*	Leu	L	– CH ₂ –CH–(CH ₃) ₂	6.0
5	Isoleucine*	I leu	I	– CH – C ₂ H ₅ CH ₃	6.1
6	Phenylalanine*	Phe	F	– CH ₂ –C ₆ H ₅ or CH ₂ Ph	5.5
7	Cysteine	Cys	C	– CH ₂ –SH	5.1
8	Methionine*	Met	M	– CH ₂ –CH ₂ –S–CH ₃	5.8
9	Tryptophan*	Trp	W		5.9
10	Serine	Ser	S	– CH ₂ –OH	5.7
11	Asparagine	Asn	N	– CH ₂ –CO.NH ₂	5.4
12	Glutamine	Gln	Q	– CH ₂ –CH ₂ –CO–NH ₂	5.7
13	Threonine*	Thr	T	– CH–CH ₃	6.5

14	Tyrosine	Tyr	Y		5.7
15	Proline	Pro	P	 (It is complete structure)	6.3
		Acidic amino acids			
16	Aspartic acid	Asp	D	$-\text{CH}_2\text{--COOH}$	3.0
17	Glutamic acid	Glu	E	$-\text{CH}_2\text{--CH}_2\text{--COOH}$	3.2
		Basic amino acids			
18	Lysine*	Lys	K	$-\text{CH}_2\text{--}(\text{CH}_2)_3\text{--NH}_2$	9.8
19	Arginine*	Arg	R	$-\text{CH}_2\text{--}(\text{CH}_2)_2\text{--NH--C}(\text{NH})\text{--NH}_2$	10.8
20	Histidine*	His	H		7.6

* Essential α -amino acids

(a) General methods of preparation

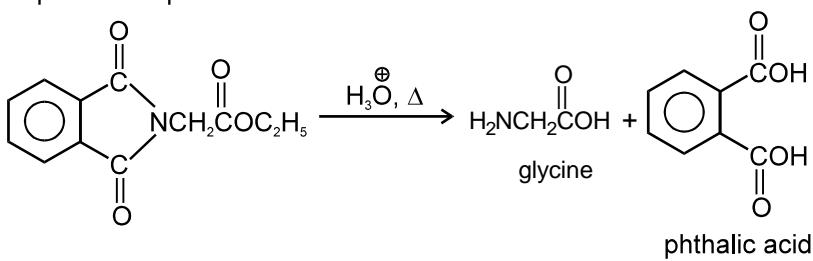
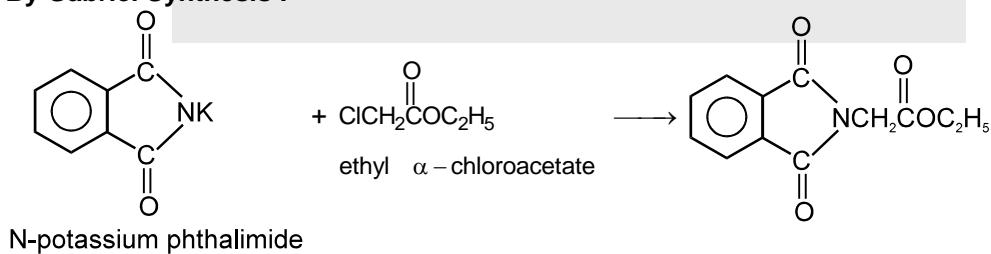
1. Aminolysis of α -halocarboxylic acid



2. **By strecker synthesis :** Aldehyde reacts with a mixture of NH_4Cl and NaCN to form α -aminonitrile (as an intermediate) which on hydrolysis gives an amino carboxylic acid.

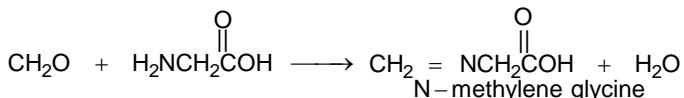


3. By Gabriel Synthesis :

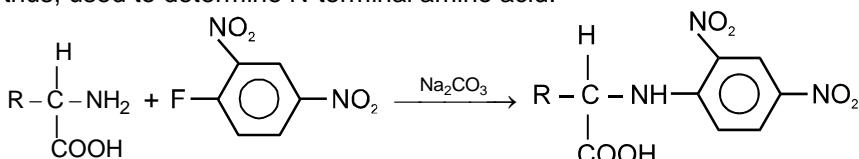


(b) Chemical reactions :

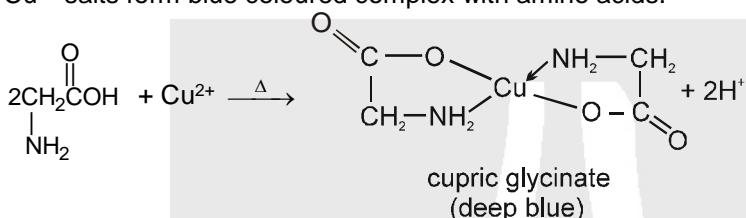
1. Formaldehyde reacts with amino acids to form N-methylene amino acids. In this reaction basic character is lost and thus, free acid can be determined by titration - Sorenson titration method for amino acids.



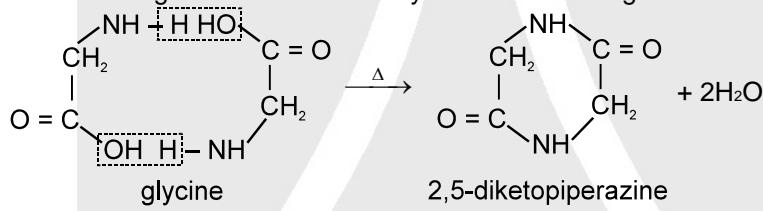
2. DNFB (**2, 4-dinitrofluorobenzene**) also called **Sanger's reagent** reacts with the free amino group of terminal amino acid in a peptide or protein to form yellow coloured dinitro phenyl amino acid. This is thus, used to determine N-terminal amino acid.



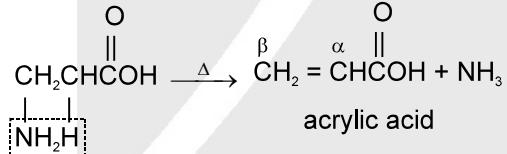
3. Cu^{2+} salts form blue coloured complex with amino acids.

**Effect of Heat :**

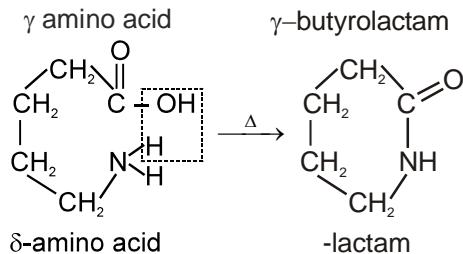
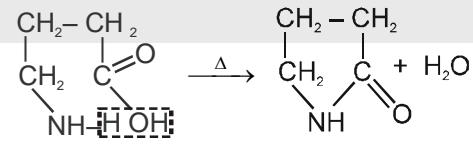
α -amino acids undergo intermolecular dehydration on heating at about 200°C to give diketopiperazines.



β -amino acids undergo intramolecular deamination on heating to form α, β -unsaturated acids.

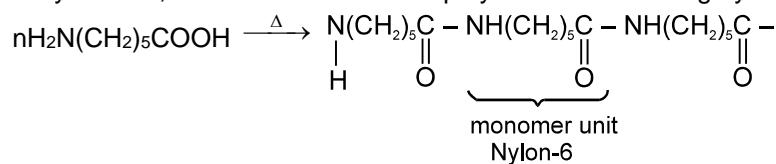


γ -amino acids and δ -amino acid undergo intramolecular dehydration to form cyclic amides called **Lactams**.

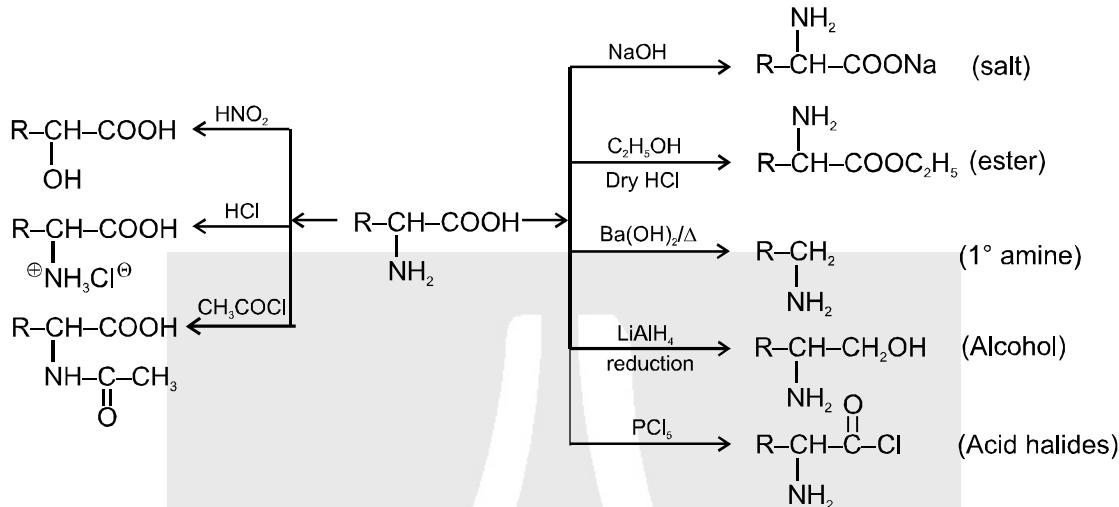




In case of ϵ -amino acid, intramolecular cyclisation would give a seven-membered ring, which is formed with difficulty. Hence, there is intermolecular polymerisation forming nylon-6.



(c) Other Reactions of α -Amino Acid :



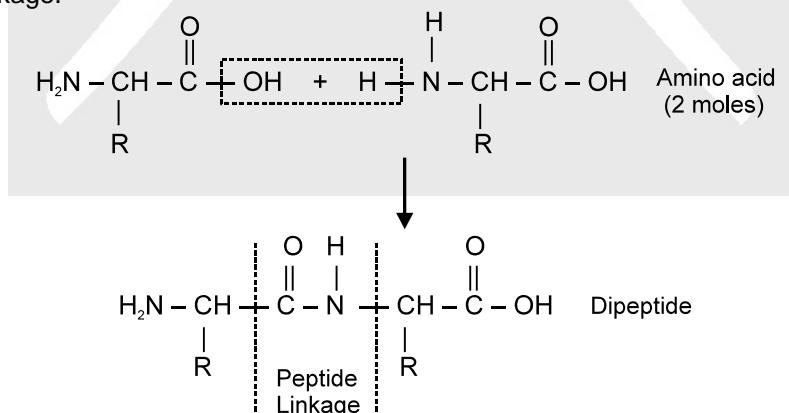
Peptides bonds and Proteins :

Peptides (Proteins) : Peptides are condensation polymers of α -amino acids formed by condensation of amino group of one α -amino acid with the carboxyl group of same or different α -amino acid by elimination of water. They are classified as di, tri, tetra, pentapeptides etc. according to two, three, four, five etc molecules of the same or different amino acid combining together. It determines their specific physiological functions in the living organism.

Structure of Proteins (Peptides)

Amino acids are bifunctional molecules with $-\text{NH}_2$ group at one end and $-\text{COOH}$ at the other. Therefore,

–COOH of one molecule and –NH₂ of another molecule interact by elimination of H₂O to form an amide-like linkage.



Peptide Linkage : The amino acid unit having free $-\text{NH}_2$ groups is called N-terminal end whereas the amino acid unit with free $-\text{COOH}$ group is called C-terminal end. The structure is written with N-terminal end to the left and C-terminal end to the right. At N-terminal or C-terminal further bond

formation take place and tri, tetra, pentapeptide are formed. $-\text{NH}-\text{CH}-\text{C}(\text{O})-\text{R}$ unit repeated in polypeptides.



Polypeptides : More than 10 amino acids join together is called polypeptides which is a linear chain natural polymer.

Naming of polypeptides : Naming of polypeptides starts from -N-terminal residue, and suffix -ine of amino acids is replaced by -yl for all except amino acid of C-terminal residue.

Example : Glycine → Glycyl, Alanine → Alanyl, Lysine → Lysyl

Alanylglycylphenylalanine means Ala-Gly-Phe or A-G-F.

Determining sequence of polypeptides by partial hydrolysis :

Q.1	Tripeptides	H_3O^+	Glycine, Alanine, Valine
		Partial Hydrolysis	Gly-Ala, Ala-Val

Write the structure of tripeptide?

Ans. Gly-Ala-Val.

Q.2	Tripeptides	H_3O^+	Glycine, Valine, Lysine
		Partial Hydrolysis	Valine-Lysin & Glycine-Valine

Write the structure of tripeptide?

Ans. Gly-Val-Lys.

PROTEINS

A polypeptide with more than 100 amino acid residues (mol. mass > 10,000) is called a protein but, a few polypeptide with lesser number of amino acid is also known.

Example : Insulin have 51 amino acids.

Classification of Proteins :

(I) On the basis of molecular structure : Proteins have been classified into two parts.

- (i) Fibrous proteins (ii) Globular proteins

(i) Fibrous Proteins : When polypeptide chain run parallel and fiber like structure then it is called fibrous protein. In Fibrous protein chain are held together by hydrogen and disulphide bond. These are insoluble in water.

Ex. Keratin, myosin.

(ii) Globular proteins : When polypeptide chain is folded to form spheroidal shape it is called globular protein. Such folding is because of a folding of polypeptides in such a way that lipophilic (fat soluble) part are pushed inward and hydrophilic part is pushed outward. These are soluble in water and sensitive to small change in temperature and pH.

Ex. Albumins in egg, enzyme and some hormones, etc.

(II) On the basis of chemical composition :

(i) Simple proteins : Simple proteins on hydrolysis give only α -amino acids. For example albumin in the white portion of eggs, glutenin in wheat, oxygenin in rice, keratin in hair, nails horns etc.

(ii) Conjugated Proteins : In conjugated proteins, protein part is combined with non-protein part. On hydrolysis these give a non protein part in addition to the α -amino acids. This non protein portion is called PROSTHETIC GROUP. Its function is to control the biological function of the protein.

Prosthetic groups may be carbohydrate, phosphate, lipids (ester of higher fatty acids) and so on.

Ex. Casein of milk, haemoglobin of blood are example of conjugated proteins.

(iii) Derived Proteins : Degradation products obtained by partial hydrolysis of simple or conjugated proteins with acids, alkalies or enzymes are called derived proteins. For example : proteoses, peptones, and polypeptides

Protein → Proteoses → Peptones → Polypeptides

Structure of Proteins :

Structure and shape of proteins can be studied at four different levels i.e. primary, secondary, tertiary and quaternary, each level being more complex than the previous one.

(i) Primary structure of Proteins :

Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of that protein. Any change in this primary structure i.e sequence of amino acids creates a different proteins.

Ex. Normal Haemoglobin : –Val – His – Leu – Thr – Pro – Glu – Lys –
Sickle cell anemia Haemoglobin : –Val – His – Leu – Thr – Pro – Val – Lys –

(ii) Secondary structure of Proteins :

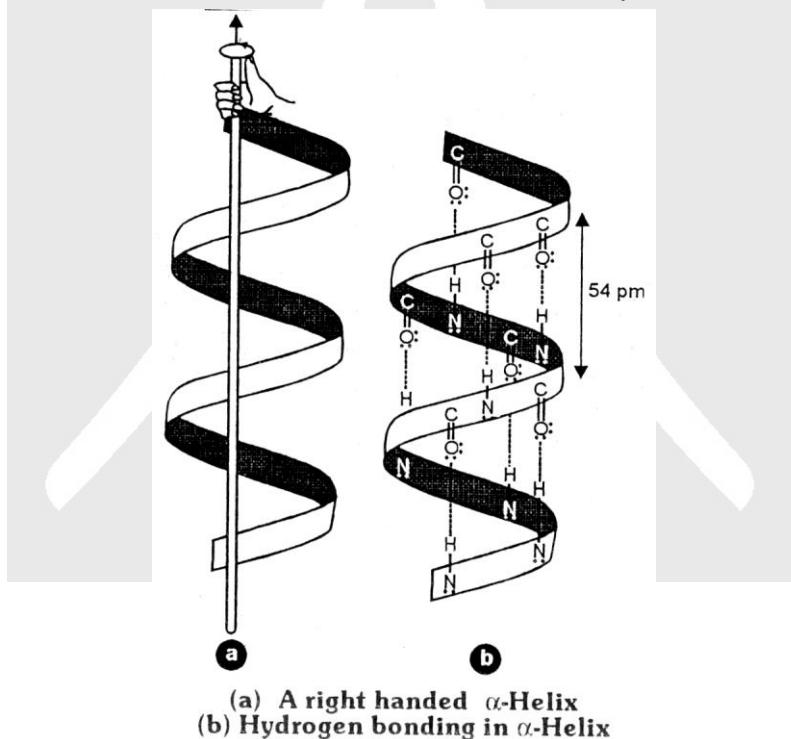
The shape in which a long polypeptide chain can exist is called secondary structure of proteins. The following two different secondary structure are possible.

(a) α -Helix structure

(b) β -pleated sheet structure

(a) α -Helix structure :

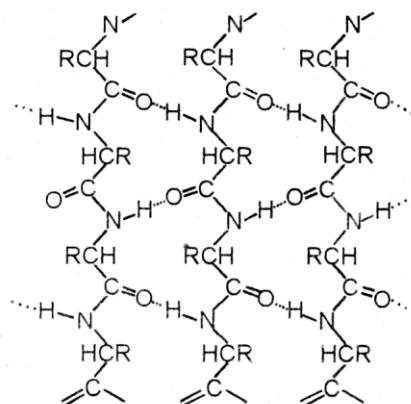
In α Helix a polypeptide chain forms all possible H-bonds by twisting into a right handed screw (helix) – NH group of each amino acid residue H-bond to the C=O of an adjacent turn of helix.



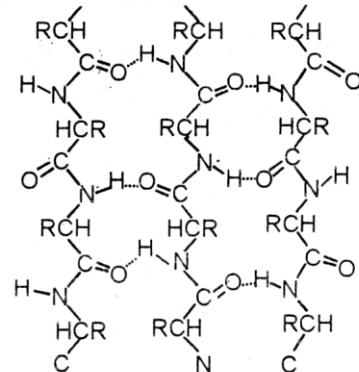
(b) β -pleated sheet structure or simply β -structure :

In β structure all peptide chains are stretched out to a nearly maximum extension and then laid side by side which are held together by inter molecular H– bond.

The poly peptide chains can link together in parallel and antiparallel sequence. These are represented as follows :-



(a) (PARALLEL)



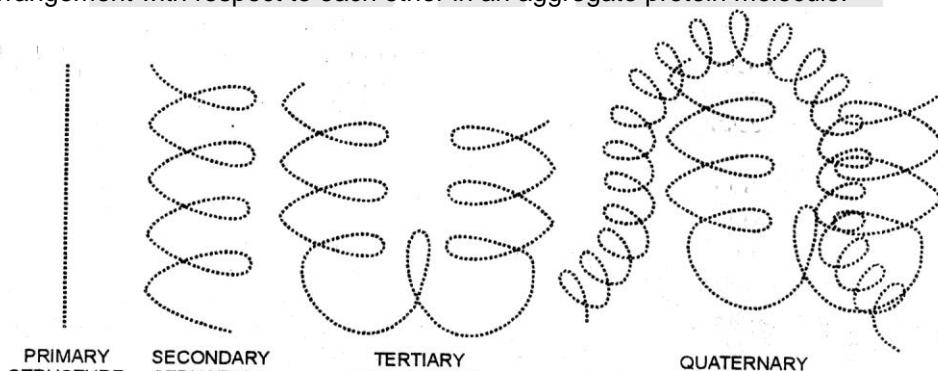
(b) (ANTIPARALLEL)

 β -Conformation of proteins (a) Parallel (b) Anti-parallel.**(iii) Tertiary structure of proteins :**

The tertiary structure of protein represent overall folding of the polypeptide chains i.e further folding of the secondary structure producing a 3D structure. It gives rise to two major molecular shapes fibrous and globular.

(iv) Quaternary structure of proteins :

There are certain proteins which are composed of two or more polypeptide chains referred to as sub-units or protomoss. The quaternary structure refers to the determination of the number of sub-units and their arrangement with respect to each other in an aggregate protein molecule.



Diagrammatic representation of four levels of protein structure (two subunits of two types in quaternary structure).

Denaturation of proteins :

When protein in native form is subjected to a physical change like temperature or pH, the H-bonds are disturbed. As a result globules get unfold and helices get uncoiled therefore proteins loses its activity. During denaturation 2° and 3° structures get destroyed but 1° structure remain the same.

Ex: Coagulation of egg while on boiling and curdling of milk caused by bacteria present in milk.

Renaturation of proteins :

Denaturation may be reversible or irreversible. Coagulation of egg on boiling and curdling of milk are example of irreversible protein denaturation. But in some cases it may be reversible and this process of reversibility is called renaturation. Hence, When the temperature and pH of a denatured protein are brought back 3° & 2° structures are restored.

Chemical Test :

(i) Biurate Test : $\text{CuSO}_4 + \text{alkaline solution} + \text{Protein} \rightarrow \text{Violet colour}$.

Biurate Test is for peptide linkage (Atleast two peptide linkage must be present; Dipeptide do not give this test).

(ii) Ninhydrin Test : Blue or violet colour with Ninhydrin.



Section (C) : Enzymes, Vitamins and Nucleic acids

Enzymes

Life is possible due to the coordination of various chemical reactions in living organisms. An example is the digestion of food, absorption of appropriate molecules and ultimately production of energy. This process involves a sequence of reactions and all these reactions occur in the body under very mild conditions. This occurs with the help of certain biocatalysts called **enzymes**. Almost all the enzymes are globular proteins. Enzymes are very specific for a particular reaction and for a particular substrate. The ending of the name of an enzyme is **-ase**.

Mechanism of Enzyme Action

Enzymes are needed only in small quantities for the progress of a reaction. Similar to the action of chemical catalysts, enzymes are said to reduce the magnitude of activation energy. For example, activation energy for acid hydrolysis of sucrose is 6.22 kJ mol⁻¹, while the activation energy is only 2.15 kJ mol⁻¹ when hydrolysed by the enzyme, sucrase.

Examples of few enzymes and their catalysed reaction.

S.No.	Enzyme	Source	Reaction
1.	Diastase	Malt	Conversion of starch into maltose $2(C_6H_{10}O_5)_{n(aq)} + nH_2O_{(l)} \xrightarrow{\text{Diastase}} nC_{12}H_{22}O_{11(aq)}$ Starch maltose
2.	Maltase	Malt.	Conversion of maltose into glucose $C_{12}H_{22}O_{11(aq)} + H_2O_{(l)} \xrightarrow{\text{Maltase}} 2C_6H_{12}O_{6(aq)}$ maltose glucose
3.	Invertase	Yeast	Inversion of cane sugar $C_{12}H_{22}O_{11(aq)} + H_2O_{(l)} \xrightarrow{\text{Invertase}} C_6H_{12}O_{6(aq)} + C_6H_{12}O_{6(aq)}$ Sucrose glucose Fructose
4.	Zymase	Yeast	Conversion of glucose into ethanol $C_6H_{12}O_{6(aq)} \xrightarrow{\text{Zymase}} 2C_2H_5OH_{(aq)} + 2CO_{2(g)}$ glucose ethanol
5.	Mycodermia aceti	old vinegar	Manufacture of acetic acid from ethyl alcohol. $CH_3CH_2OH_{(l)} + O_2 \xrightarrow{\text{mycodermia aceti}} CH_3COOH_{(l)} + H_2O_{(l)}$ Acetic acid
6.	Urease	soyabean	Decomposition of urea into NH ₃ +CO ₂ $NH_2CONH_{2(aq)} + H_2O_{(l)} \xrightarrow{\text{Urease}} 2NH_{3(g)} + CO_{2(g)}$
7.	Lactic bacilli	Curd	Conversion of milk into curd
8.	Pepsin	stomach	Conversion of proteins to peptides in the stomach.
9.	Trypsin	Intestines	conversion of protein into acids by hydrolysis in intestines.

Vitamins

It has been observed that certain organic compounds are required in small amounts in our diet but their deficiency causes specific diseases. These compounds are called **vitamins**. Most of the vitamins cannot be synthesised in our body but plants can synthesise almost all of them, so they are considered as essential food factors. However, the bacteria of the gut can produce some of the vitamins required by us. All the vitamins are generally available in our diet.

Different vitamins belong to various chemical classes and it is difficult to define them on the basis of structure. They are generally regarded as **organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism**. Vitamins are designated by alphabets A, B, C, D, etc. Some of them are further named as sub-groups e.g. B1, B2, B6, B12, etc. Excess of vitamins is also harmful and vitamin pills should not be taken without the advice of doctor.

The term "**Vitamine**" was coined from the word vital + amine since the earlier identified compounds had amino groups. Later work showed that most of them did not contain amino groups, so the letter 'e' was dropped and the term **vitamin** is used these days.



Classification of Vitamins

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

- Fat soluble vitamins:** Vitamins which are soluble in fat and oils but insoluble in water are kept in this group. These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.
- Water soluble vitamins:** B group vitamins and vitamin C are soluble in water so they are grouped together. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored (except vitamin B12) in our body.

Exception : Biotin (Vitamin H) : It is neither soluble in water nor in fats.

Some important Vitamins, their Sources and their Deficiency Diseases

S.No.	Vitamins	Characteristics	Sources	Deficiency disease
1	A (Retinal)	Soluble in oils and fats, stable to heat. Promote growth, vision and increases resistance to diseases.	Milk, Butter, eggs, fish, liveroil, rice kidney, green vegetables, angoes sweet potatoes, carrots, tomatoes etc.	Xerophthalmia (hardening of eye) cornea night blindness and xerosis (drying of skin)
2	B ₁ Thiamine	Soluble in water destroyed by heat above 313 K.	Pulses, nuts, cereals (rice, wheat), yeast, egg yolk, milk, green vegetables and fruits.	Beriberi (paralysis of legs and general weakness) loss of appetite
3	B ₂ (Riboflavin or lactoflavin)	Soluble in water sensitive to light but stable to heat.	Milk, yeast, green vegetables, meat, liver, kidney, egg white etc.	Retards growth general inflammation of tongue i.e darkened tongue dermatitis and cheilosis (racking at corners of mouth and lips).
4	B ₆ (Pyridoxin or adermin)	Soluble in water.	Rice bran, yeast, molasses, meat, fish, egg yolk etc.	Cause specific dermatitis and anaemia in man effects central nervous system.
5	B ₁₂ (cyanocobalamine)	Water soluble, stable to heat.	Milk, egg, liver of animals	Anemia (RBC deficient) inflammation of tongue and mouth
6	H (Biotin)	Neither soluble in water not in fats.	Yeast, liver, kidney and milk	Dermatitis, loss of hairs and paralysis
7	C (Ascorbic acid)	Soluble in water but destroyed by cooking.	Citrus fruits : Amla, tomatoes, green leafy vegetables. (Daily dosage 75 mg)	Cause scurvy (bleeding of gums pyorrhea bleeding of teeth)
8	D (Ergocalciferol)	Soluble in oil and fats, stable to heat and resists to oxidation to controls calcium and phosphorus metabolism.	Milk, butter, eggs, liver & meat. (Daily dosage 0.025 mg)	Rickets (deformation of bones) osteomalacia (soft bones and joint pain)
9	E (It is mixture of 4-vitamins a, b, g, d tocoferols)	Soluble in oils and fats, stable to heat and oxidation.	Vegetable oil, wheat germ oil, cotton seed oil, peanut oil, soyabean, eggs, milk, fish. (Daily dosage 5 mg)	Loss of sexual power of reproduction (sterility) increased muscular weakness.
10	K (phylloquinone mixture of two vitamins K ₁ & K ₂)	Soluble in oils and fats, stable to heat, sensible to light and alkali.	Vitamin K ₁ in alfalfa leaves vegetables. Vitamin K ₂ occurs mainly in bacteria.	Haemorrhage lengthens the time of blood clotting. Excessive bleeding in injury. Vitamin K ₁ & K ₂ and alkali bacteria.



Nucleic Acids

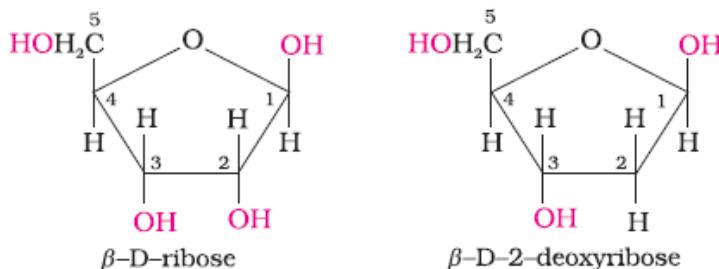
Every generation of each and every species resembles its ancestors in many ways. How are these characteristics transmitted from one generation to the next? It has been observed that nucleus of a living cell is responsible for this transmission of inherent characters, also called **heredity**. The particles in nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called **nucleic acids**.

These are mainly of two types, the **deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA)**. Since nucleic acids are long chain polymers of **nucleotides**, so they are also called polynucleotides.

Chemical Composition of Nucleic Acids

Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds (called bases).

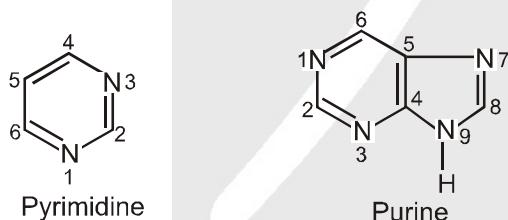
In DNA molecules, the sugar moiety is β -D-2-deoxyribose whereas in RNA molecule, it is β -D-ribose.



Nitrogenous bases have two categories

(a) Pyrimidine : It includes cytosine, thymine and uracil. Pyrimidine bases are made of only one ring of carbon and nitrogen.

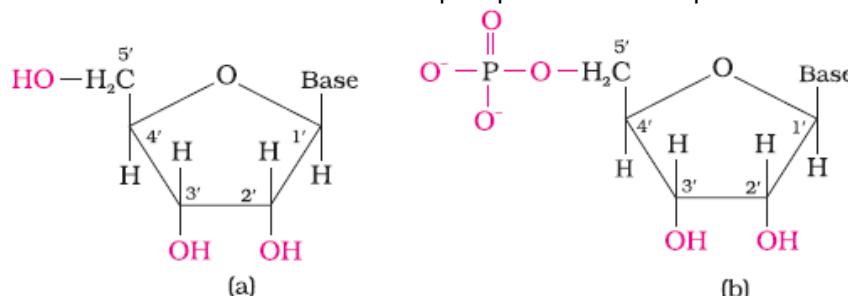
(b) Purine: It includes adenine and guanine. Purine bases are made of two ring of carbon and nitrogen. DNA contains four bases viz. adenine (A), guanine (G), cytosine (C) and thymine (T). RNA also contains four bases, the first three bases are same as in DNA but the fourth one is uracil (U).



Pyrimidines	Purines	
 Thymine (T)	 Uracil (U)	 Cytosine (C)

Structure of Nucleic Acids

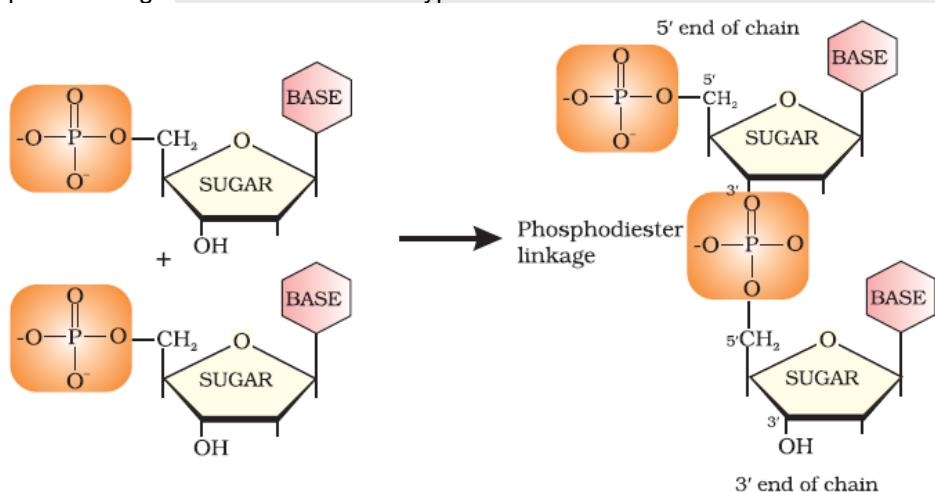
A unit formed by the attachment of a base to 1' position of sugar is known as **nucleoside**. In nucleosides, the sugar carbons are numbered as 1', 2', 3', etc. in order to distinguish these from the bases. When nucleoside is linked to phosphoric acid at 5'-position of sugar moiety, we get a nucleotide.



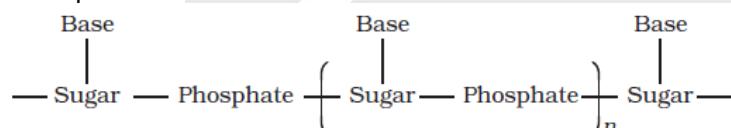
(a) a nucleoside

(b) a nucleotide

Nucleotides are joined together by phosphodiester linkage between 5' and 3' carbon atoms of the pentose sugar. The formation of a typical dinucleotide is shown below



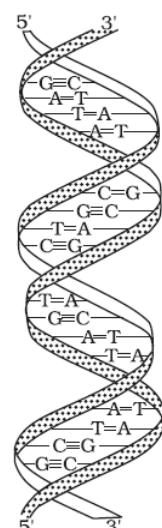
A simplified version of nucleic acid chain is as shown below.



Information regarding the sequence of nucleotides in the chain of a nucleic acid is called its primary structure. Nucleic acids have a secondary structure also. James Watson and Francis Crick gave a double strand helix structure for DNA. Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases.

Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.

In secondary structure of RNA, helices are present which are only single stranded. Sometimes they fold back on themselves to form a double helix structure. RNA molecules are of three types and they perform different functions. They are named as **messenger RNA (m-RNA)**, **ribosomal RNA (r-RNA)** and **transfer RNA (t-RNA)**.



Structure of DNA



DNA Fingerprinting

It is known that every individual has unique fingerprints. These occur at the tips of the fingers and have been used for identification for a long time but these can be altered by surgery. A sequence of bases on DNA is also 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.

Biological Functions of Nucleic Acids

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

Differences between DNA and RNA

	DNA		RNA
1	It usually occurs inside nucleus and some cell organelles.	1	Very little RNA occurs inside nucleus. Most of it is found in the cytoplasm.
2	DNA is the genetic material.	2	RNA is not the genetic material except in certain viruses, e.g. Reovirus.
3	It is double stranded with the exception of it some viruses (e.g. $\phi \times 174$).	3	RNA is single stranded except reovirus where is double stranded.
4	DNA contains over a million nucleotides.	4	Depending upon the type, RNA contains 70-1200 nucleotides.
5	DNA is of only two types; intra-nuclear and extra-nuclear.	5	There are at least three types of RNAs-mRNA, rRNA and tRNA.
6	It contains deoxyribose sugar.	6	It contains ribose sugar.
7	Nitrogen base thymine occurs in DNA alongwith three others-adenine, cytosine and guanine.	7	Thymine is replaced by uracil in RNA. The other three are similar-adenine, cytosine and guanine.
8	It replicates to form new DNA molecules.	8	It cannot normally replicate itself.
9	DNA transcribes genetic information to RNA.	9	RNA translates the transcribed message for forming polypeptides.
10	DNA controls metabolism and genetics Including variations.	10	It only controls metabolism under instruction from DNA.
11	Purine and pyrimidine bases are in equal number.	11	There is no proportionality between number of purines and pyrimidine bases.