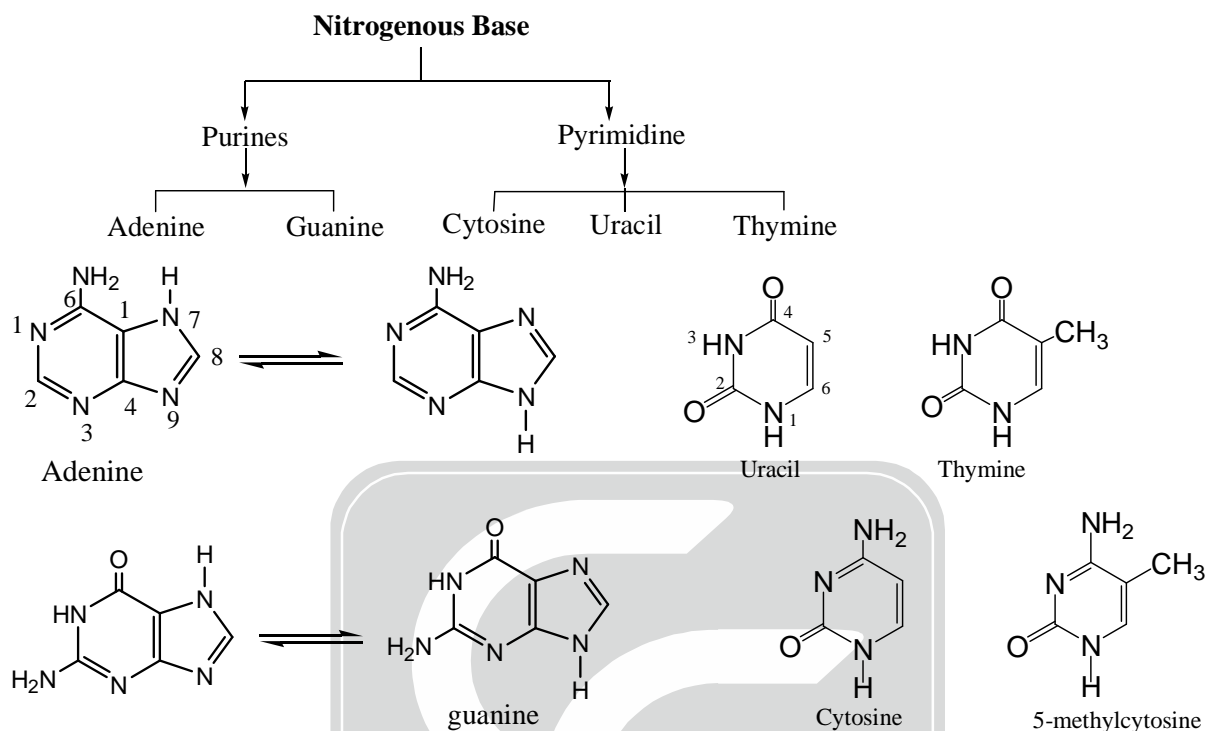


3.3. Nucleic Acid :

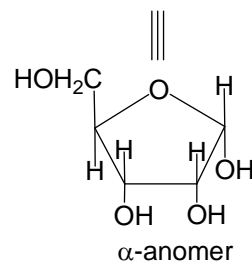
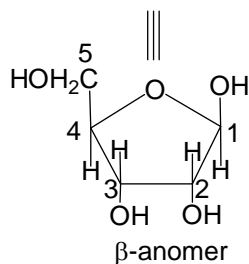
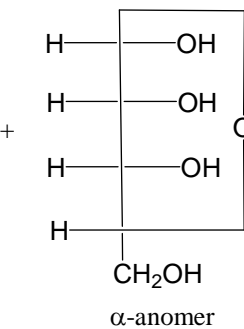
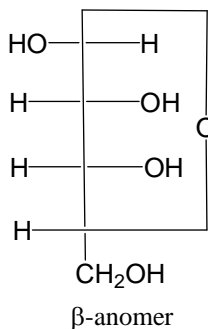
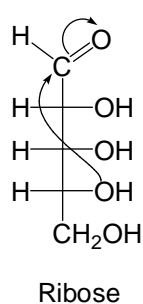
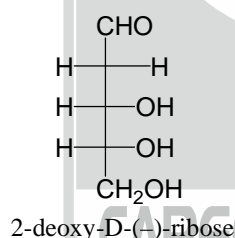
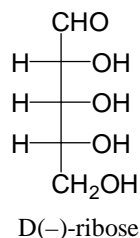
Nucleic acids are colourless solids which contain: Carbon, hydrogen, oxygen, nitrogen and phosphorus. There are three components of the nucleic acid such as

(1) Nitrogenous Base (2) Sugar/Carbohydrate (3) Phosphate group PO_4^{3-} (H_3PO_4).

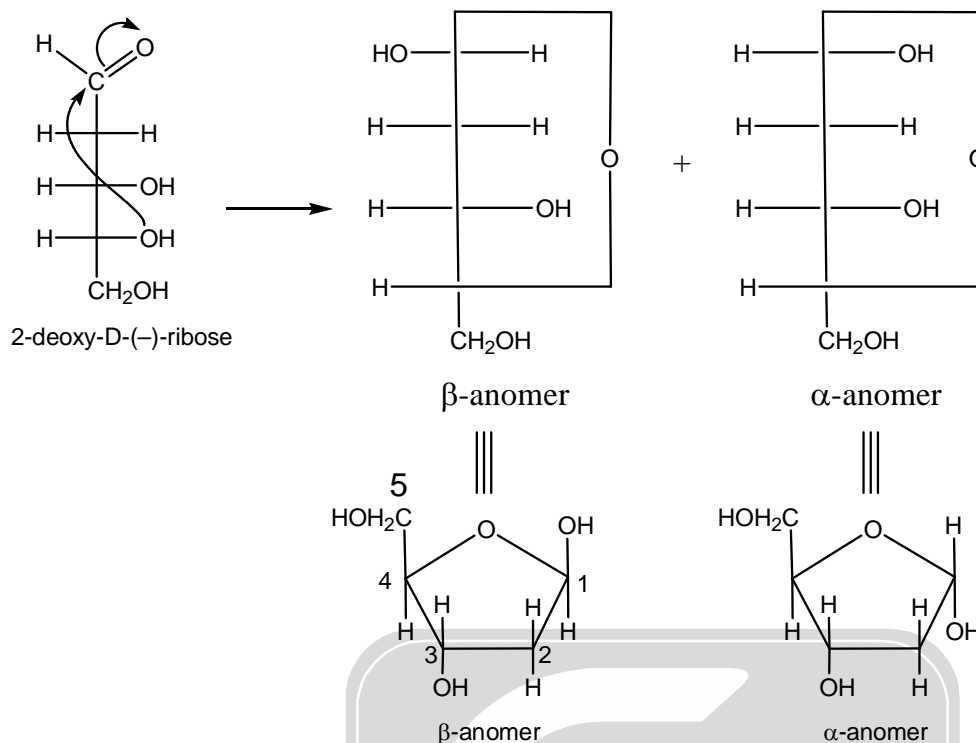
1. There are two types of bases which occurs in nucleic acids: purines and pyrimidines. The most common purine bases are adenine and guanine whereas the most common pyrimidine bases are uracil, thymine and cytosine.



2. **Sugars:** The sugar present in the nucleic acids are pentoses: D(-)-ribose and 2-deoxy-D(-)-ribose.

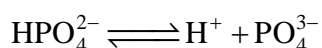
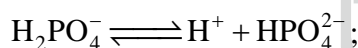
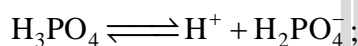
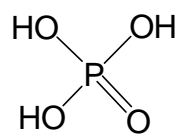


3. Deoxy Ribose:

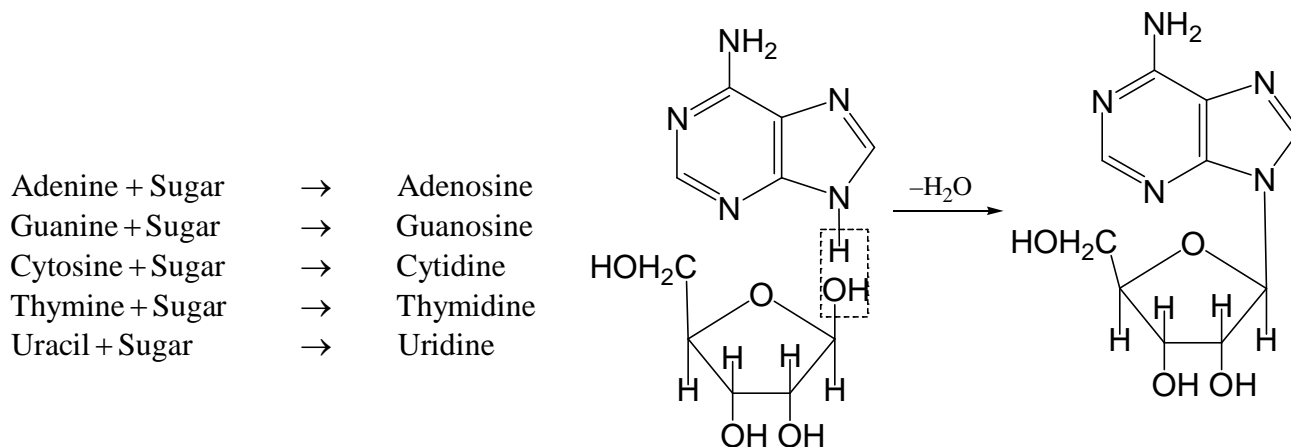


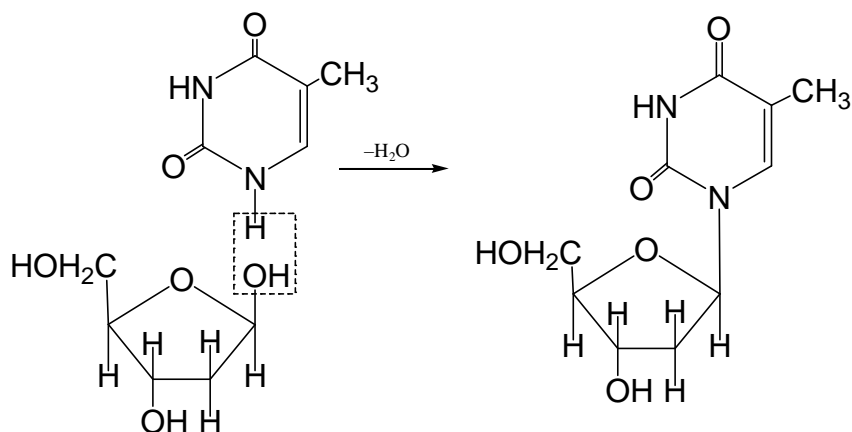
Remark: In nucleic acid sugars are in β -anomeric, furanose form and it is hemiacetal.

4. Phosphate Group :

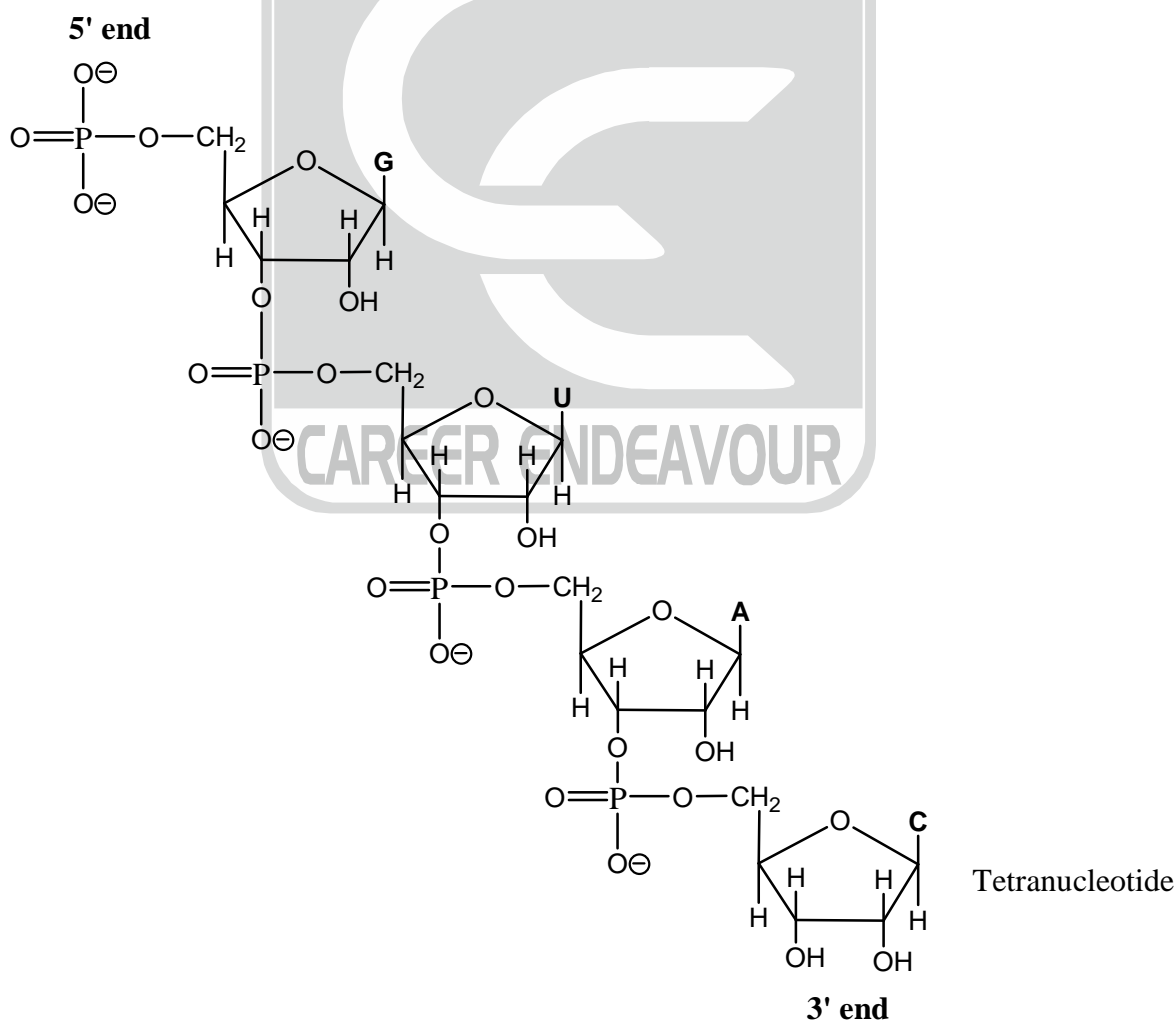


Nucleoside: The combination of a base (either a purine or pyrimidine with a sugar(ribose or deoxyribose) are called nucleosides. For example



**Ribonucleic Acids(RNA):**

- RNA is a polymer of ribonucleotides.
- The individual ribonucleotides are linked together by phosphodiester bonds.
- The attachment of the phosphate is at the 3'- position in the ribose molecules.
- The common bases in RNAs are adenine, guanine, uracil and cytosine.
- According to the source of nucleic acid there are three types of nucleic acid: Ribosomal RNA (r-RNA), Transfer RNA (t-RNA) and Messenger RNA (m-RNA).

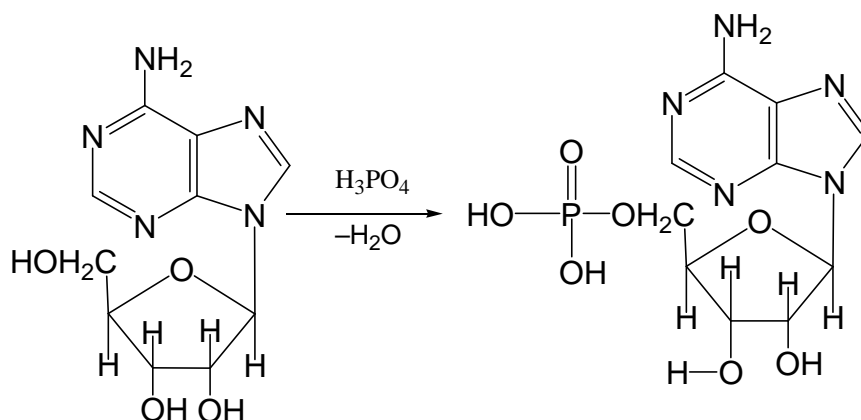
Primary Structure of RNA:

The secondary structure of RNA has been investigated and it appears that RNAs exist as a single strands which contain helical segments established by hydrogen bond.

Nucleotide:

Nucleotides are the combination of a nucleoside and phosphoric acid i.e. nucleotides are nucleosides phosphate. For example

Adenosine	+	phosphate	→	Adenylic acids
Guanosine	+	phosphate	→	Guanylic acids
Cytidine	+	phosphate	→	Cytidylic acids
Uridine	+	phosphate	→	Uridylic acids

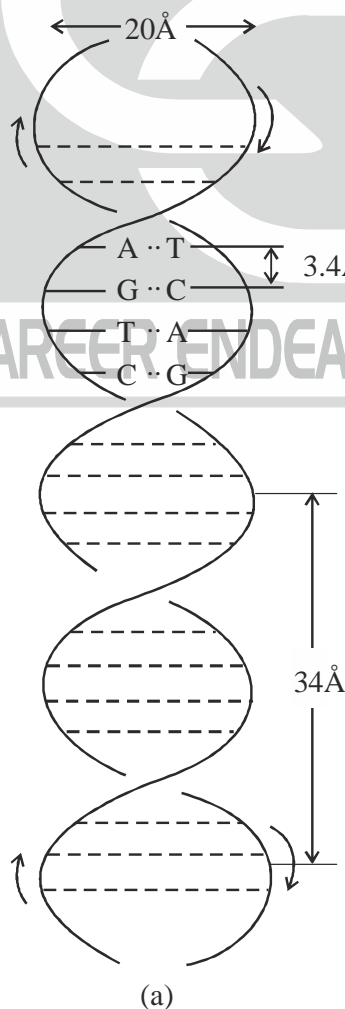


On the basis of sugar present in the nucleic acid, it can be classified into two parts: Ribonucleic acids (RNA) and the deoxyribonucleic acid (DNA).

Deoxyribonucleic acid:

- DNA are polymers of the deoxyribonucleotides and hydrolysis by certain enzymes result in a mixture of monomers.
- The common bases DNAs are Adenine(A), Guanine (G), Thymine (T) and Cytosine (C).

Secondary Structure of DNA: (Double helix model by Watson & Crick):



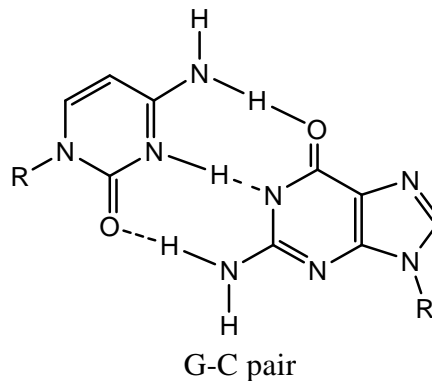
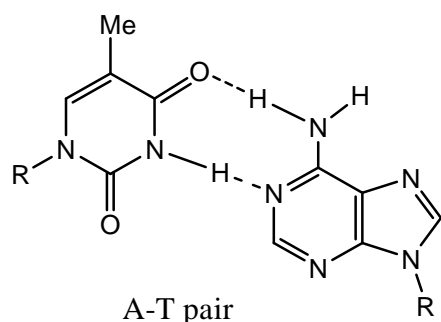
- Two strands are antiparallel.

- The X-ray studies have shown that the pairs are planar and that the hydrogen bonds are almost collinear, their lengths lying between 2.8 and 2.9 Å.
- Each turn of the helix contains ten nucleotide pairs and the diameter of the helix is about 20 Å.
- The spacing between adjacent pair is 3.4 Å.

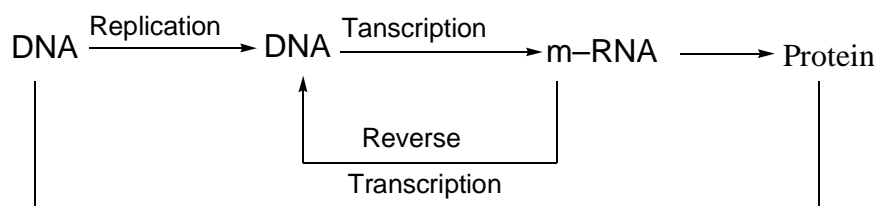
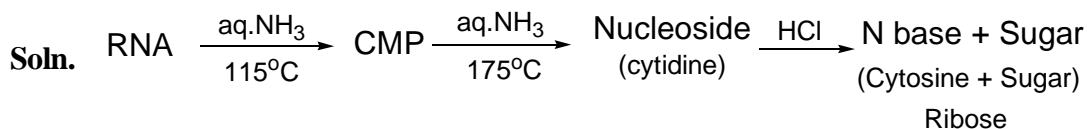
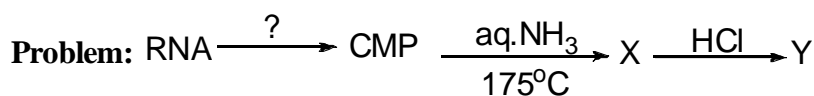
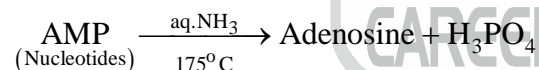
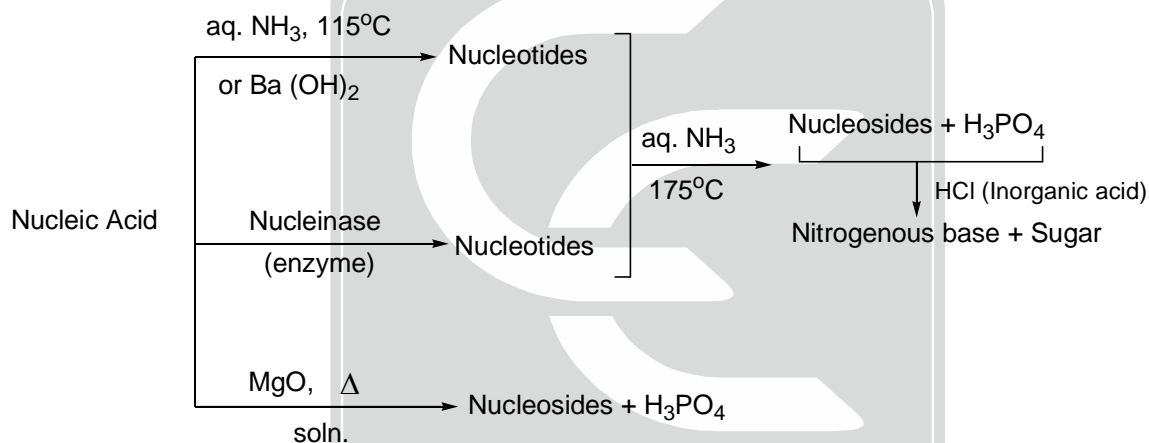
Base pairing in DNA.

Adenine always paired with thymine by double H-bonds.

Guanine always paired with cytosine by triple H-bonds.



Hydrolysis of Nucleic Acid :

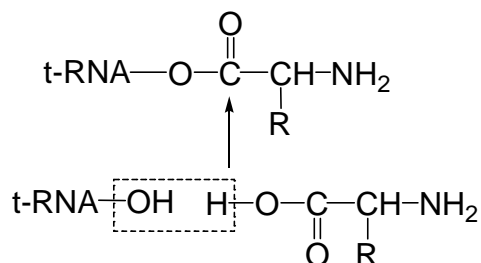


The whole process is known as central Dogma (flow of genetic information)

Site of protein synthesis in cell : Ribosomes r - RNA provide a template / base or the site where protein synthesis occur.

r-RNA : It provide a template / base or support on which protein synthesis takes place in Ribosome. It consist Protein & RNA.

t-RNA : They bring the amino acid to the site where protein synthesis occurs each amino acid has its own specific t-RNA and the bonding with t-RNA accurs line.



m-RNA :

It brings the information regarding the sequence of amino acid to the ribosomes. The four base in m-RNA exist in form triplet called as CODON with code for one specific amino acid. (an amino acid can have more than one codon).

eg. : UCU → serine → GCA + AGC (more than 1 codon is used for 1 amino acid)

3.4. Proteins :

- Proteins are nitrogenous substances which occurs in protoplasm of all animal and plants cells. Their composition varies with the source: carbon, 46-55%; hydrogen, 6-9%; oxygen, 12-30%; nitrogen, 10-32%; sulphur, 0.2-0.3%. Other elements may also be present, for example phosphorus (nucleoproteins), iron(homeoglobin).
- Proteins can be broken down into smaller and smaller fragments until, the final products are amino acids.
Protein → polypeptides → peptides → amino acids.
- There are no sharp dividing lines between peptides, polypeptides and proteins. Generally–
If the molecular weight above ~ 10, 000 = Proteins.
If the molecular weight below ~ 10, 000 = Peptide and polypeptide.
- The physical and chemical properties of proteins and peptides are different.
- Proteins are amphoteric in nature.
- All proteins are optically active, and may be coagulated and precipitated from aqueous solution by heat, the addition of acids, alkalis, salts, organic solvents miscible with water.
- Proteins in precipitated state are called denatured and the process of reaching this state, denaturation occurs most readily near the isoelectric point.
- Denaturation is generally irreversible, but in many cases the process has been reversed this reversal of denaturation is called renaturation.

Classification of proteins:

(A) Simple Proteins

(B) Conjugated Proteins

(A) Kind of simple proteins:

- Albumins:** These are soluble in water, acids and alkalis. It is coagulated by heat.
- Globulins:** These are insoluble in water, but are soluble in dilute salt solution and in dilute solutions of strong inorganic acids and alkali.
- Prolamins:** These are insoluble in water or salt solution but are soluble in dilute acids and alkalis.
- Glutelins:** These are insoluble in water or dilute salt solution, but are soluble in dilute acids alkalis. They are coagulated by heat, glutelins are rich in arginine, proline and glutamic acids.
- Scleroproteins:** These are insoluble in water or salt solution, but are soluble in concentrated acid. For example: keratin(from hair, hoof), fibroin (from silk).
- Basic Proteins:** These are strongly basic, and are of the two kinds: (a) Histones (b) Protamines

(B) Conjugated proteins: These are proteins which contains a non-protein group (i.e. a compound not containing amino acid residues) attached to the protein part. The non protein group is known as prosthetic group and it may be separated from the protein part by careful hydrolysis.

Kinds of conjugated proteins.

(i) Nucleoproteins: In nucleoproteins the prosthetic group is a nucleic acid.

(ii) Chromoproteins: Their prosthetic group are coloured. For example, chlorophyll and haemoglobin.

(iii) Glycoproteins: In glycoproteins the prosthetic group contains a carbohydrates or a derivative of carbohydrate. It is also known as mucoproteins.

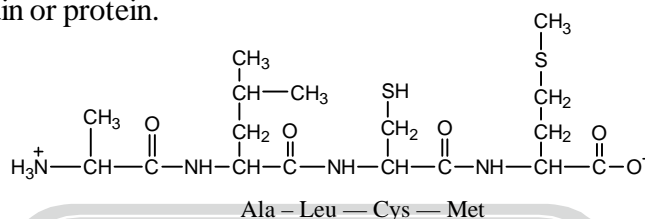
(iv) Phosphoproteins: In phosphoproteins the prosthetic group contains phosphoric acids.

(v) Lipoproteins: In lipoproteins the prosthetic group is lecithin, kephalin etc.

(vi) Metalloproteins: The metalloproteins contain metal which is an integral part of the structure.

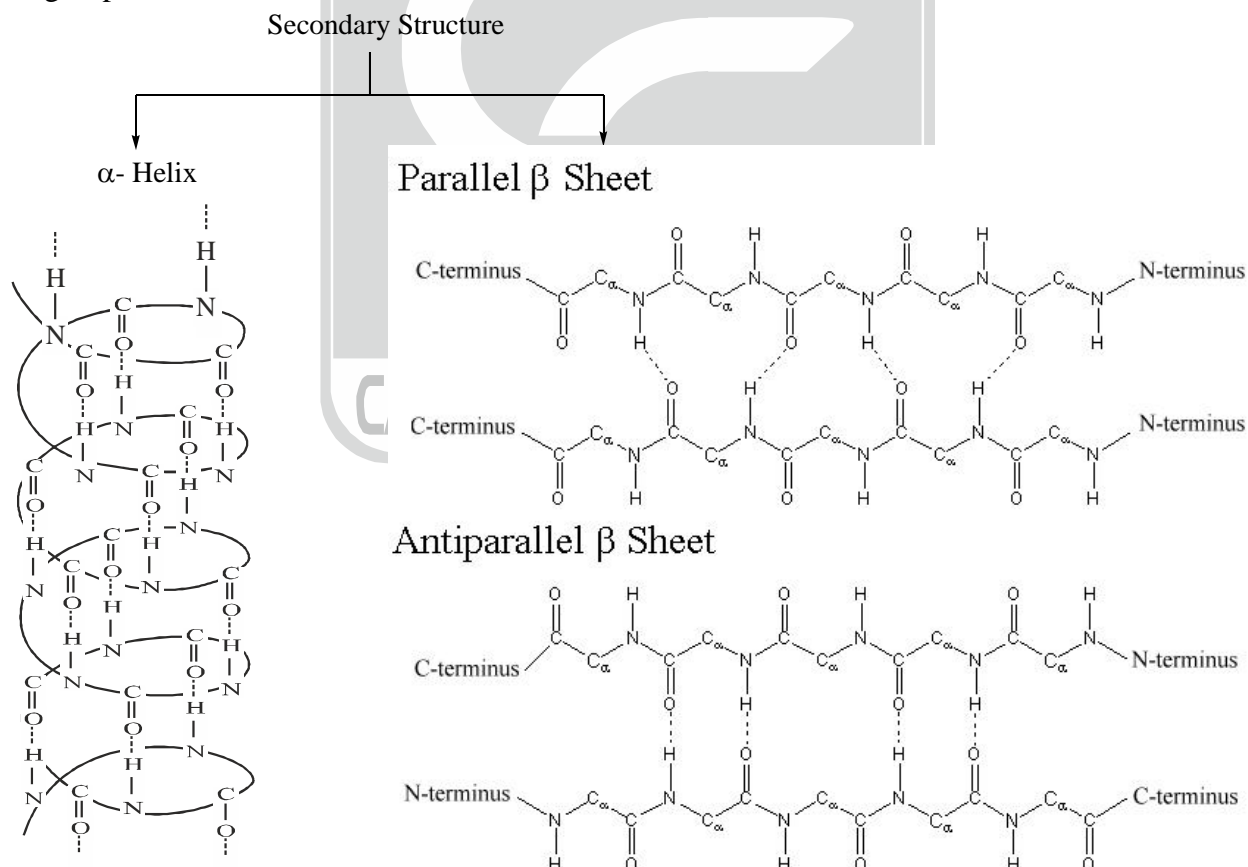
Structure of Proteins:

1. **Primary Structure:** The primary structure of proteins are the particular sequence of amino acids ,that is the backbone of a peptide chain or protein.



2. **Secondary structure:**

- In secondary structures polypeptide chains are arranged side by side.
- Hydrogen bonds form between chains.
- R groups of the amino acid extend above and below the sheet.



The α – helix model for the conformation of protein was proposed by Pauling and it suggest that:

- (i) The peptide group is planar

- (ii) Intramolecular hydrogen bonding stabilises the conformation and the strength of this bond is a maximum, when the atoms concerned ($C=O-H-N$) are collinear or, failing this ideal situation do not deviate by more than 30° .

The β – conformation, was proposed by Pauling. In this, the Pauli peptide chain is extended and chains are held together by inter molecular hydrogen bonds. There are two types of β -conformation(Pleated sheet): parallel and anti-parallel.

3. Tertiary Structure :

- The tertiary structure of protein deals with folding of entire molecule which involves hydrogen bonding, ionic, chemical and hydrophobic bonds.
- The tertiary structure that a protein assumes under the normal condition of temperature and pH will be its most stable arrangement. This has been referred to as the native conformation of that protein.
- There are two major molecular shapes of naturally occurring proteins: Globular and fibrous.
- Fibrous proteins have a large helical content and are essentially rigid molecules of rod-like shape.
- Globular proteins have a peptide chain which consist partly helical section and folded about the random coil section to give a spherical shape.
- In globular proteins most polar groups lies on the surface of the molecule and most hydrophobic side chain lies inside the molecules.
- The tertiary structure of protein have been elucidated by X-ray analysis, viscosity measurements, diffusion, light-scattering, ultracentrifuge methods and electromicroscopy.
- When a protein undergoes denaturation, the changes that occur involve changes in secondary and/or tertiary structure of proteins.

3.5. Carbohydrate :

Carbohydrates are polyhydroxy aldehydes, polyhydroxy ketones or compound that can be hydrolyzed to them. Carbohydrates are the ultimate source of most of the food.

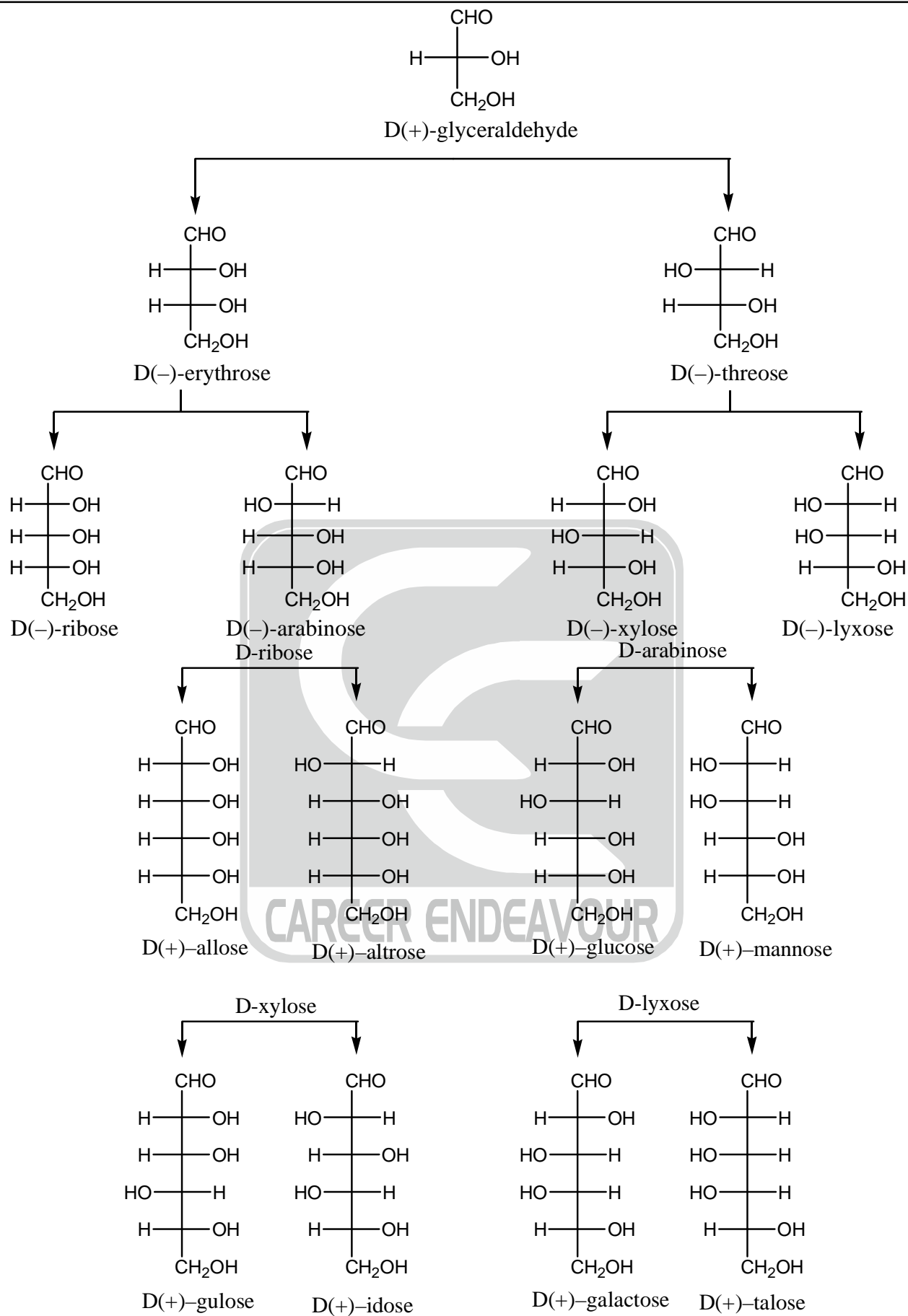
Classifications of Carbohydrate:

- (i) Monosaccharide (ii) Disaccharide (iii) Polysaccharide

- (i) Monosaccharide:** Carbohydrate that can not be hydrolyzed to simpler compounds is said to be monosaccharide. For example: Glucose, Fructose etc.
- (ii) Disaccharide:** A carbohydrate that can be hydrolyzed to two monosaccharide molecule is said to be disaccharide. For example: Lactose, Maltose, Sucrose, Cellobiose etc.
- (iii) Polysaccharide:** A carbohydrate that can be a hydrolyzed to many monosaccharide molecules is said to polysaccharide. For example: Starch, Amylose, Amylopectin, Cyclodextrine, Cellulose etc.

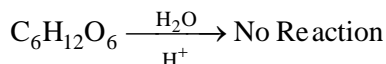
Monosaccharide may be further classified as aldoses, if it contain aldehyde and ketose, if contains ketonic group. On the basis of numbers of carbon atoms monosaccharides are also classified as: triose, tetrose, pentose, hexose and so on.

Reducing and Non-Reducing: Carbohydrate that reduce Fehling's solution (or Benedict's solutions) Tollen's are known as reducing sugar. All monosaccharide whether aldoses or ketose are reducing sugars. Most disaccharides are reducing sugars, for example lactose, maltose, cellobiose etc. except sucrose which is non-reducing sugar.

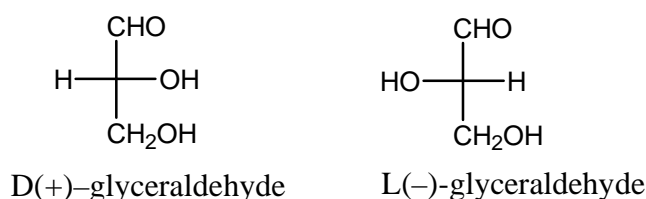


1. Mono Saccharides :

These are the sugars which can't be hydrolysed in to smaller molecules. $C_nH_{2n}O_n$ ($n = 2 - 6$)



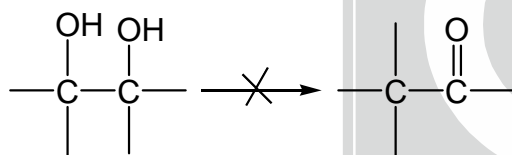
Configuration : In carbohydrates configurational differences are associated with different spatial arrangement of tetrahedrally disposed ligands attached to chiral carbon atoms. The presence of asymmetric carbon makes possible the formation of stereo isomers. Glyceraldehyde [CHO-CHOH-CH₂OH] is selected as the standard of reference to assign the configuration of carbohydrate because it is the simplest carbohydrate which is capable of optical isomerism. It is a aldotriose.



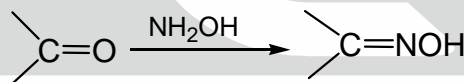
All natural sugars are D-sugars D(+)-glyceraldehyde taken as standard.

Structure elucidation of glucose :

1. Molecular Weight determination showed formula $C_6H_{12}O_6$
2. When glucose is treated with $(CH_3CO)_2O / Py \rightarrow$ Pentaacetate formed showing presence of five -OH group.
3. As glucose is not easily dehydrated, so -OH group are vicinal and not geminal



4. Glucose reacts with one mole of HCN to form cyanohydrin and with NH₂OH to form oxime. This indicates presence of a carbonyl group.



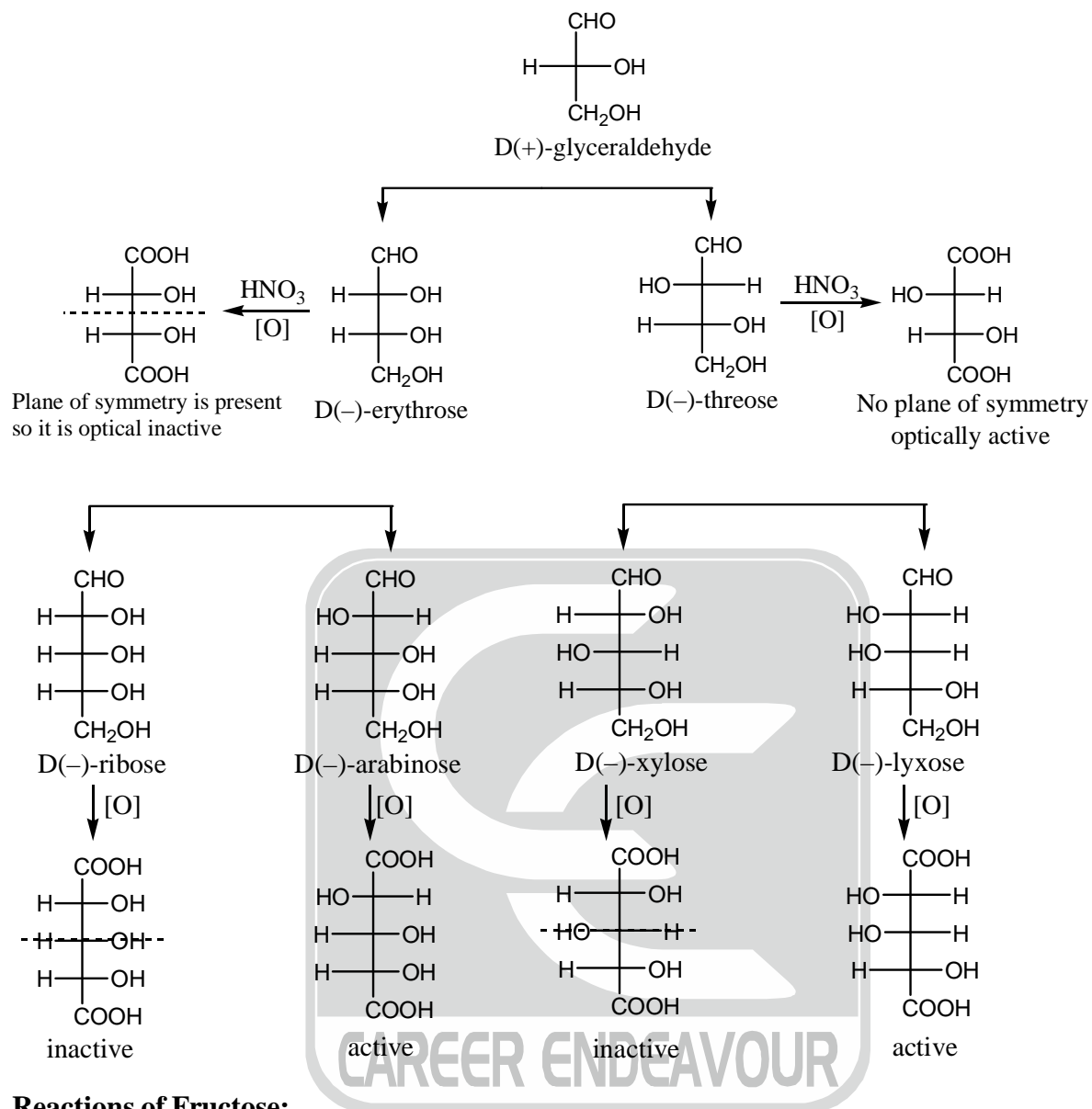
5. Oxidation of glucose with Br_2/H_2O give gluconic acid having same number of carbon atom as that of glucose. ($C_6H_{12}O_7$). This indicates that carbonyl group is on -CHO (aldehyde) group (keto group containing sugars give acid with less C-atoms).



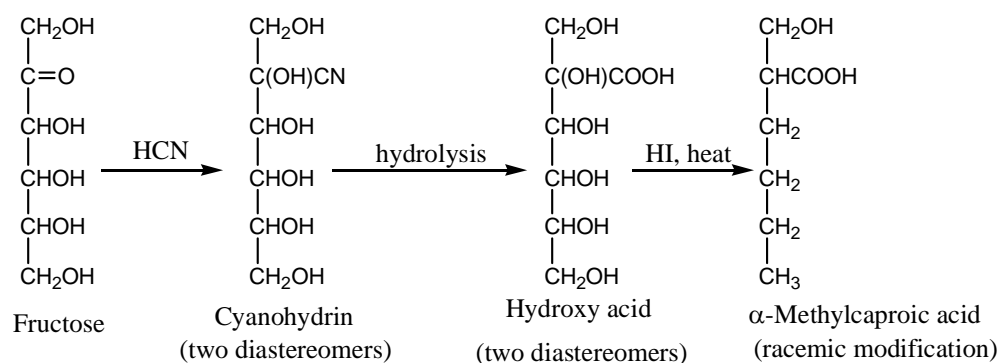
6. Oxidation of gluconic acid with HNO_3 produces a dicarboxylic acid (Glucaric acid) with molecular formula $C_6H_{10}O_8$. This indicates a presence of alcohol group (CH₂OH) and oxidation occurs with loss of 2Hs and gain of one oxygen atom.
7. Glucose dissolve in H₂O to produce a neutral solution shows that it don't contain -COOH.
8. Glucose on reduction with H_2/Ni , produces a hexa-hydric alcohol (Glucitol) (-CHO \rightarrow CH₂OH). This on reaction with HI/red P first yield 2-iodohexane at 100°C and then n-hexane on prolonged heating. It indicate that all six C atoms in glucose are in a straight chain.
9. Glucose on reaction with HCN, form cyanohydrin, which on hydrolysis and followed by reduction with HI/red phosphorus yields n-heptanoic acid which indicates the presence of six C atoms in straight chain.

10. Periodate or $\text{Pb}(\text{CH}_3\text{COO})_4$ oxidation of Glucose produces five molecule of HCOOH and HCHO group.

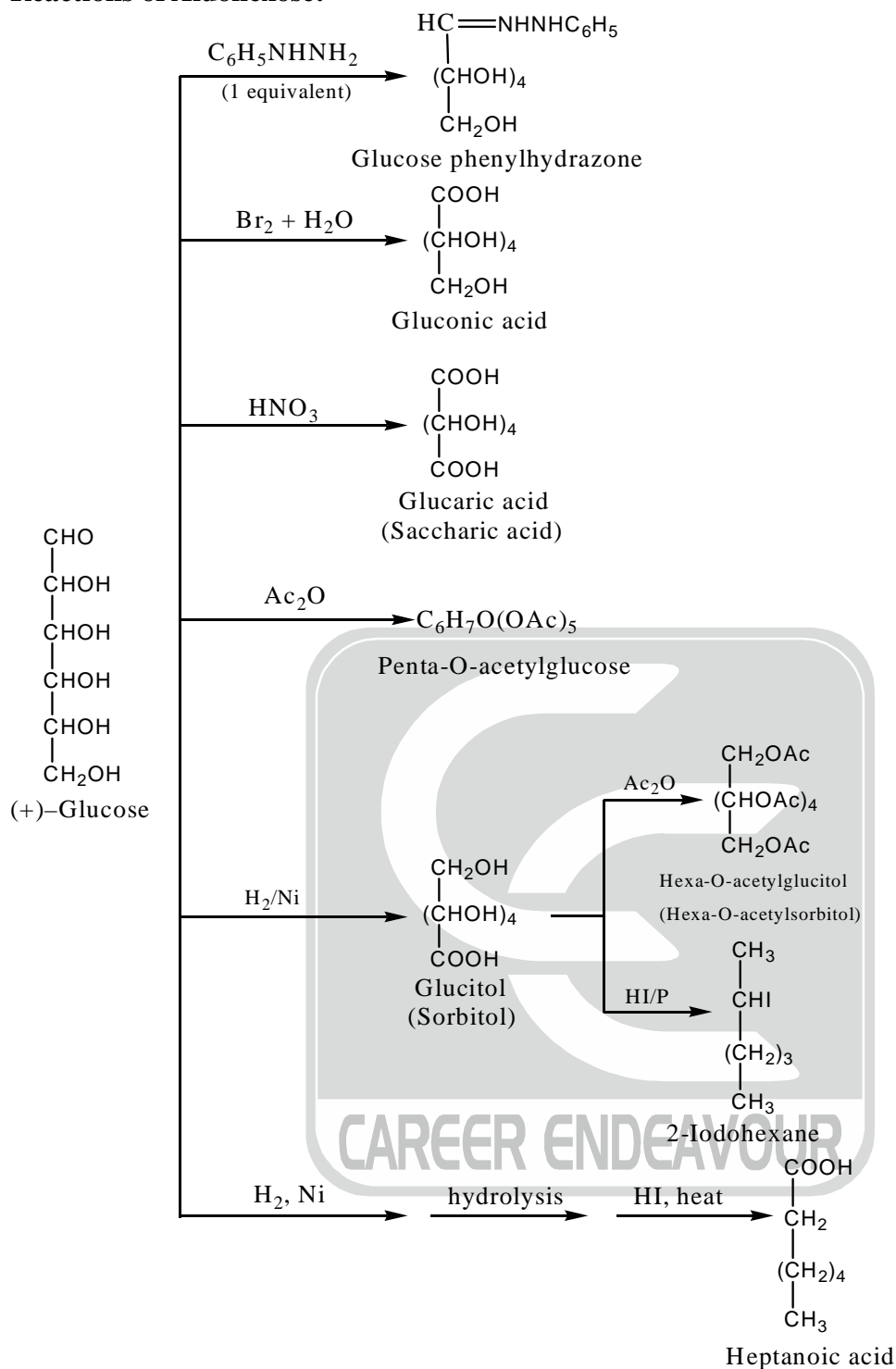
Optical activity in monosaccharide:



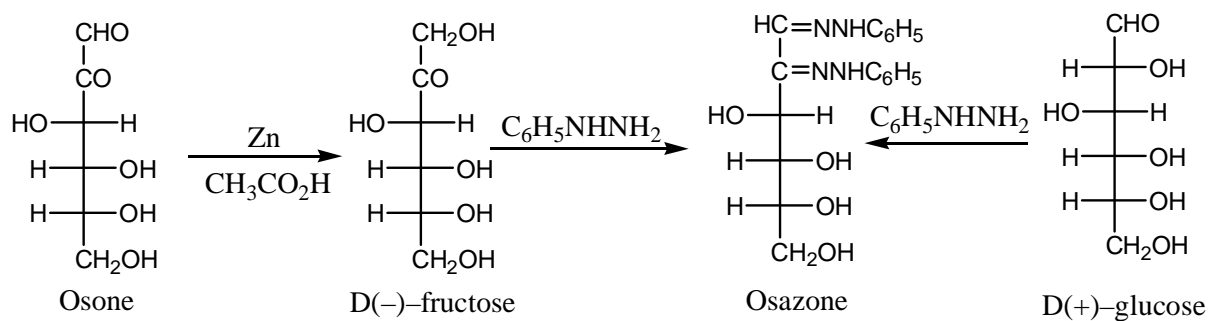
Reactions of Fructose:

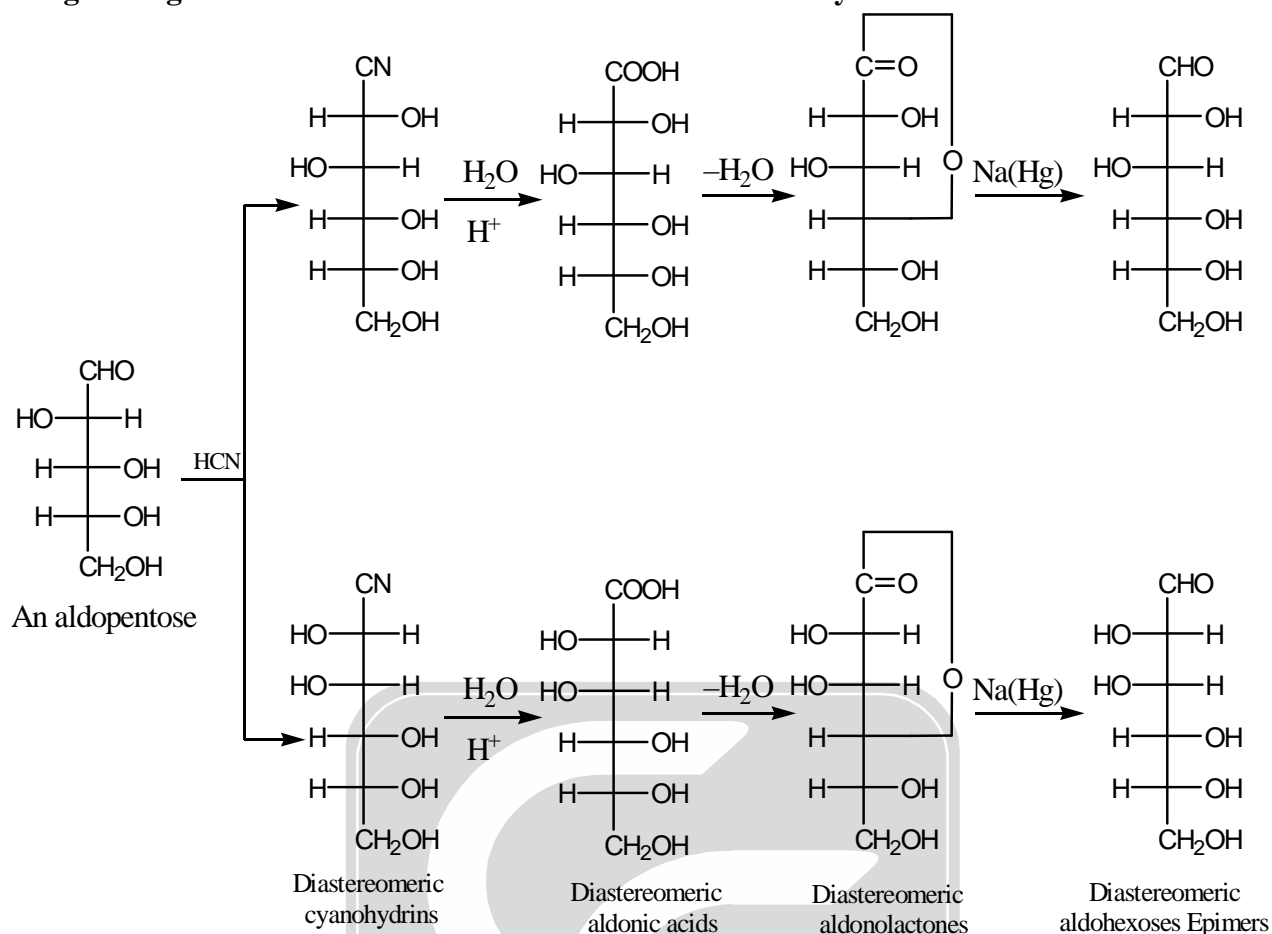
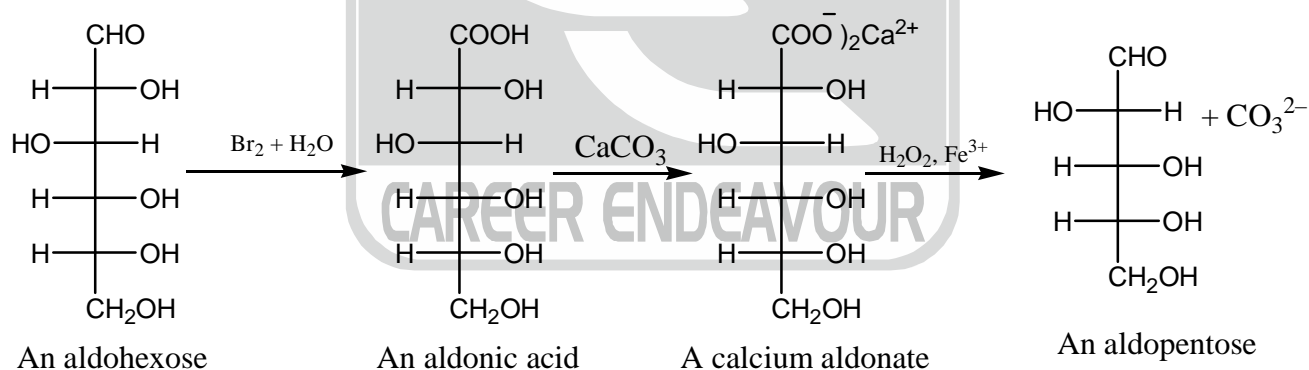


Reactions of Aldohexose:

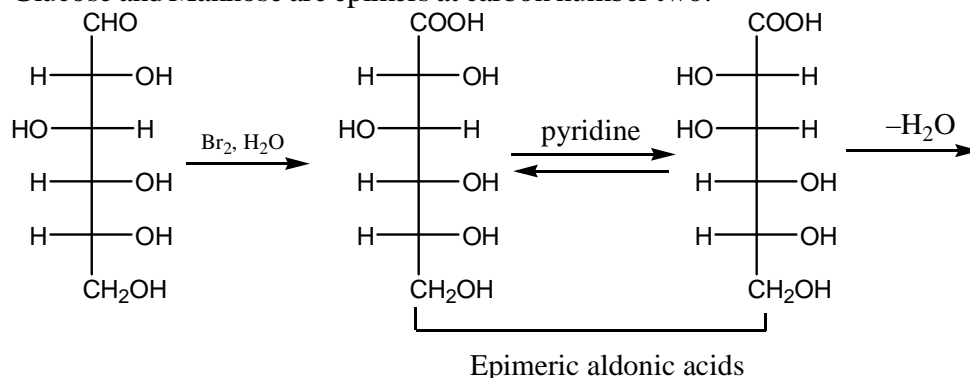


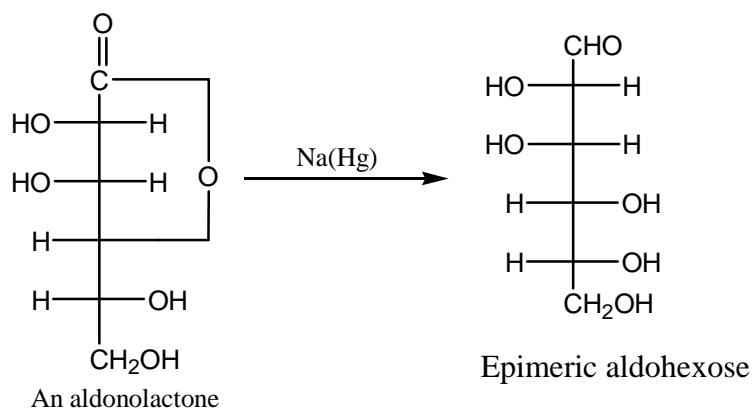
OSAZONE FORMATION OF KETOSE AND HEXOSE:



Lengthening the carbon chain of aldose. The Killiani-Fischer synthesis:**Shortening the carbon chain of Aldose: Ruff degradation:****Conversion of glucose into mannose:**

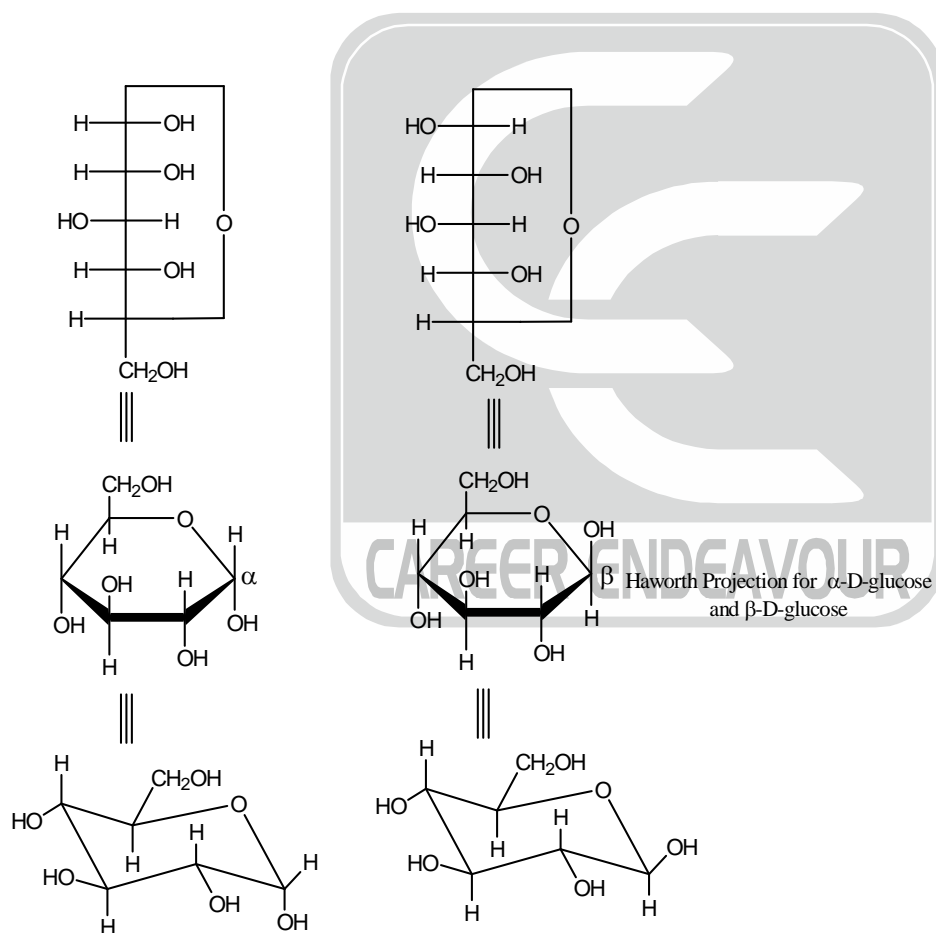
Glucose and Mannose are epimers at carbon number two.

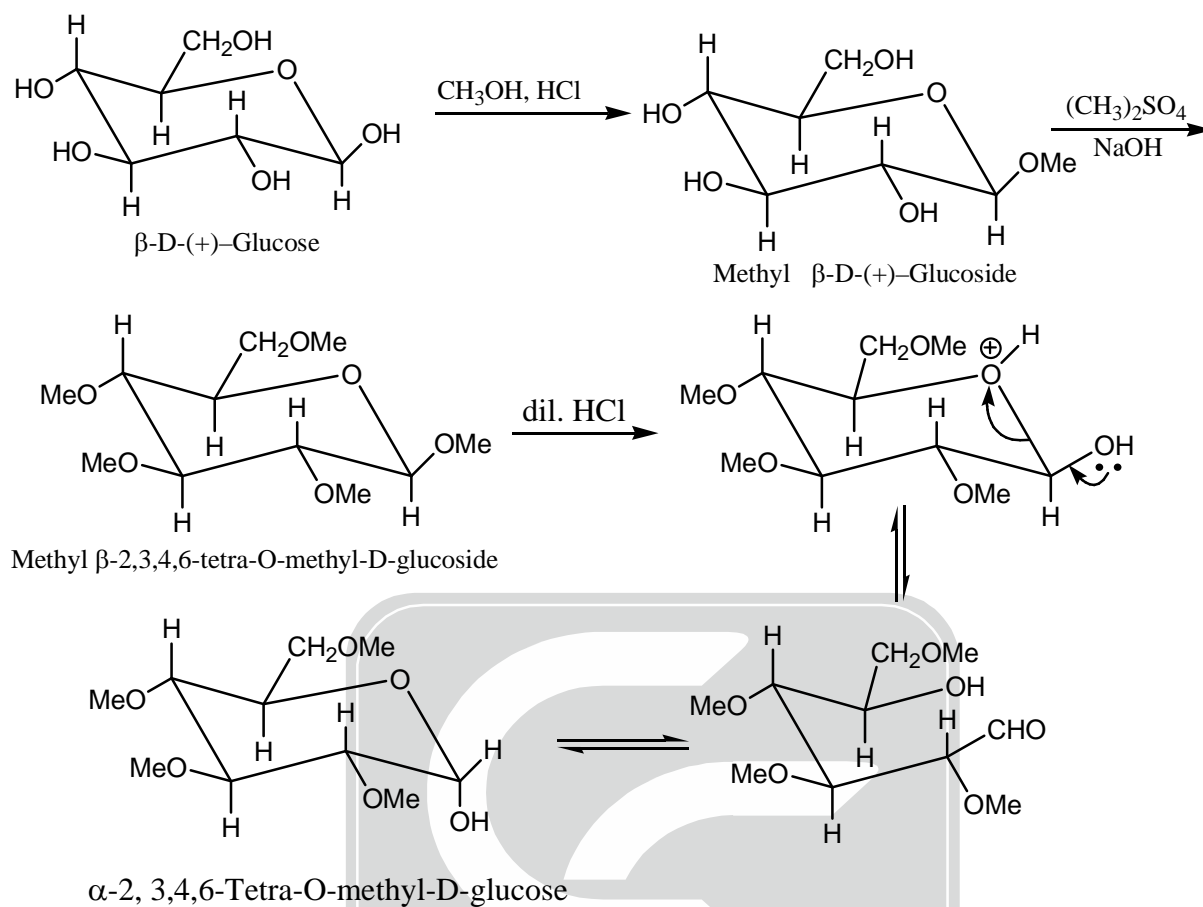




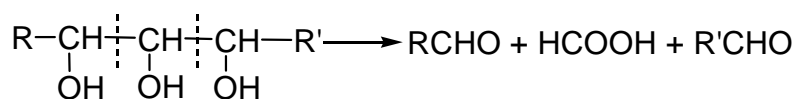
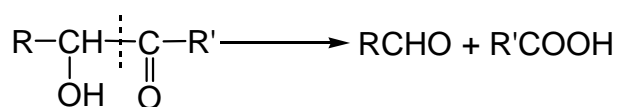
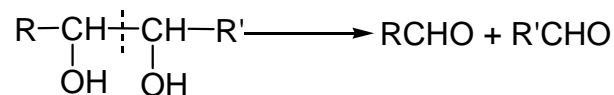
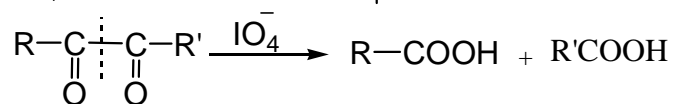
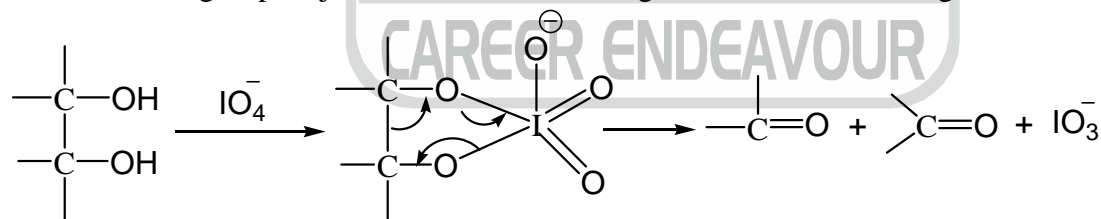
Cyclic structure of D(+)-glucose: Formation of glucosides:

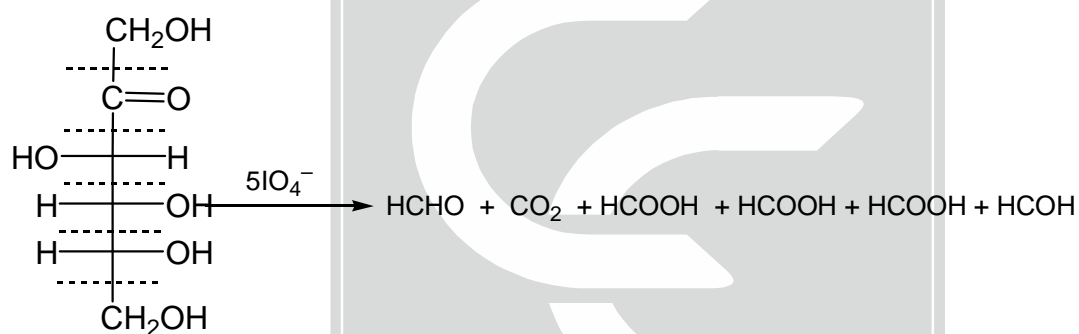
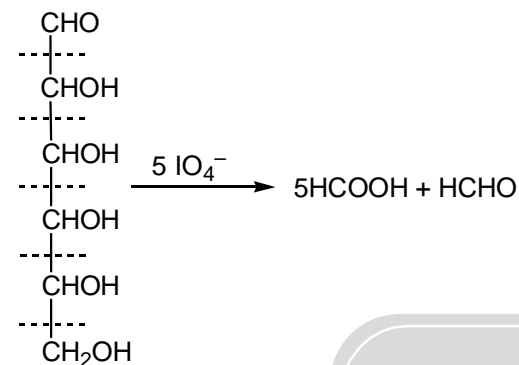
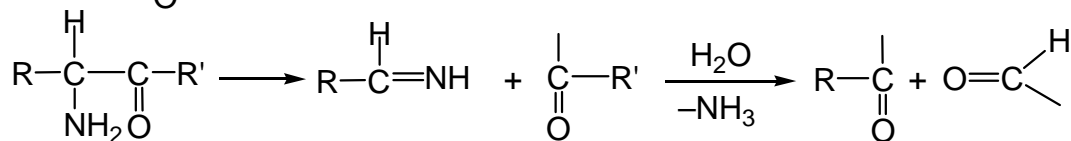
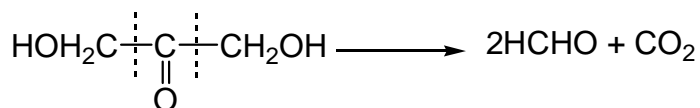
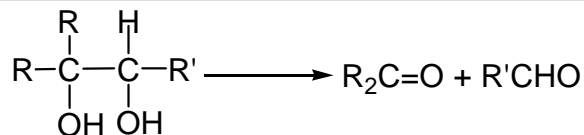
- D(+)-glucose fails to undergo certain reactions typical of aldehydes. For example it gives a negative Schiff test and does not form bisulfite addition product.
- D(+)-glucose exists in two isomeric forms which undergo mutarotations.
- D(+)-glucose forms two isomeric methyl D-glucosides.



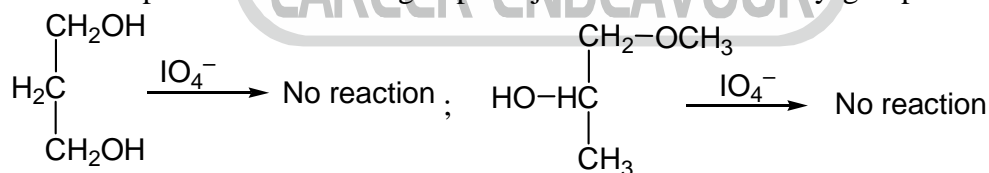
Problem:**HIO₄:**

On treatment with HIO₄ aqueous solution or Pb(OAc)₄ in organic solvent compounds containing two or more C=O or C–OH groups adjacent to each other undergo oxidation with cleavage of the C–C bond.

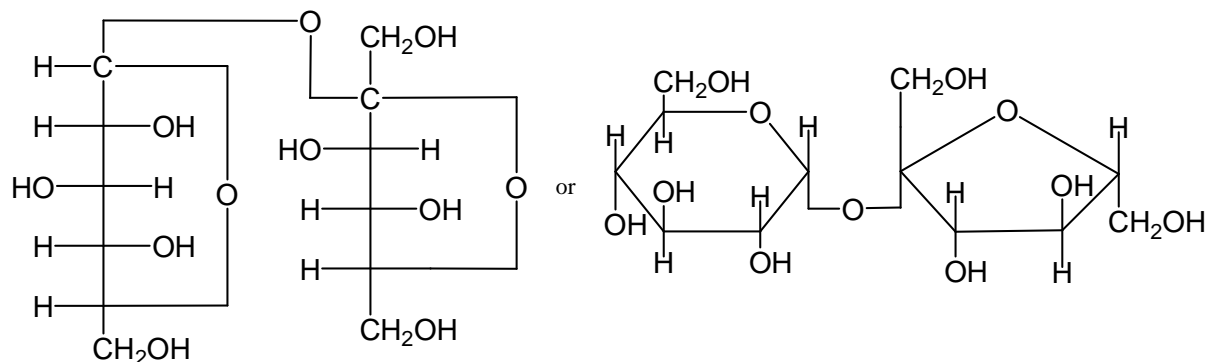


**Limitation:**

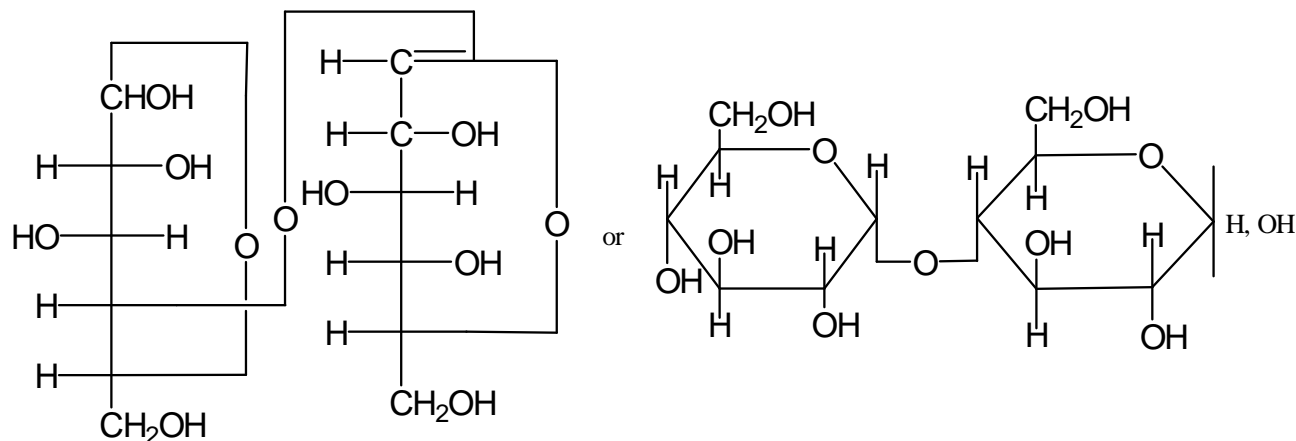
Periodate oxidation don't occur in which -OH group or C=O group are separated by a CH₂ group. It also do not cleave the compounds in which OH group is adjacent to a ether or acetyl group.

**Disaccharides:**

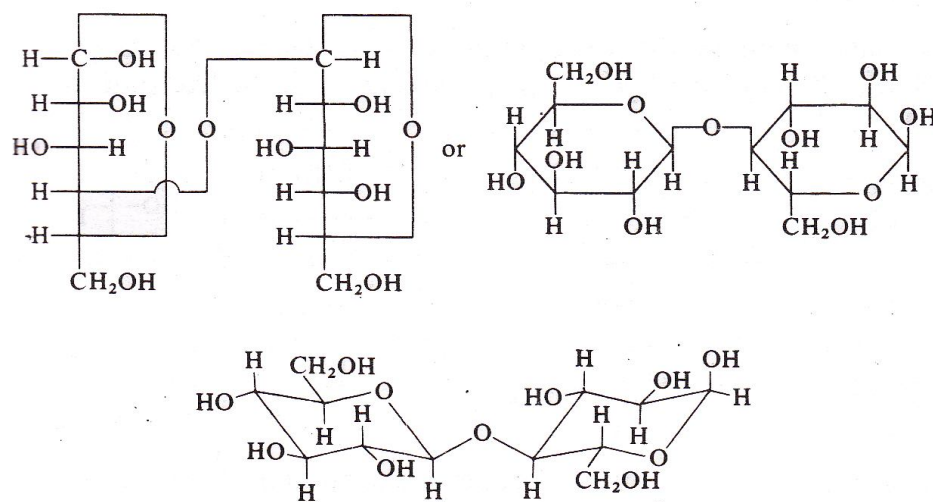
Sucrose: Sucrose is a non-reducing sugar. Upon hydrolysis with dilute acids or by enzyme invertase it gives an equimolar mixture of D-glucose and fructose.



Maltose: Maltose is 4-O- α -D-glucopyranosyl-D-glucopyranose. It is hydrolyzed by dilute acids and gives two molecules of D-glucose. Maltose is reducing sugar and it is hydrolyzed by enzyme maltase. The glycosidic link of the non-reducing half of the molecule is α -linkage.



Cellobiose: The Cellobiose is 4-O- β -D-glucopyranosyl-D-glucopyranose. Cellobiose upon hydrolysis with dilute acid gives two molecules of D-glucose. Since this hydrolysis is effected by emulsin, the glycosidic link must be beta. Cellobiose is reducing sugar.



Lactose: Lactose is 4-O- β -D-galactopyranosyl-D-glucopyranose. Lactose is reducing sugar and it is hydrolyzed by dilute acids and gives one molecules of D-glucose and another molecule of D-galactose. Since the lactose is also hydrolyzed by an enzyme lactase, it means that the glycosidic linkage is β .

