Unit

14

Biomolecules

SYLLABUS

- **Unit XIV: *Biomolecules (Periods 12)***
- *Carbohydrates: Classification (aldoses and ketoses), monosaccharides (glucose and fructose),*
  oligosaccharides (sucrose, lactose, maltose),
  polysaccharides (starch, cellulose, glycogen); importance.
- *Proteins: Elementary idea of a - amino acids, peptide bond, polypeptides, proteins, primary* structure, secondary structure, tertiary structure and Quaternary structure (qualitative idea only), denaturation of proteins; enzymes.
- *Vitamins: Classification and functions.*
- *Nucleic Acids: DNA and RNA .*

- The pursuit of knowledge of what goes on chemically within a living system falls in the domain of ***biochemistry.***
- Living systems are made up of various complex biomolecules like carbohydrates, proteins, nucleic acids, lipids, etc.
- Proteins and carbohydrates are essential constituents of our food.
- These biomolecules interact with each other and constitute the molecular logic of life processes.
- In addition, some simple molecules like vitamins and mineral salts also play an important role in the functions of organisms.

Carbohydrates

- Carbohydrates are primarily produced by plants and form a very large group of naturally occurring organic compounds.
- Some common examples are cane sugar, glucose, starch, etc.
- Most of them have a general formula, $C_x(H_2O)_y$, and were considered as hydrates of carbon from where the name carbohydrate was derived..

CARBOHYDRATES ….

- *carbohydrates may be defined as optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis*
- Some of the carbohydrates, which are sweet in taste, are also called sugars.
- The most common sugar, used in our homes is named as sucrose whereas the sugar present in milk is known as lactose.
- Carbohydrates are also called saccharides (Greek: *sakcharon means sugar).*

CLASSIFICATION OF CARBOHYDRATES

- Carbohydrates are classified on the basis of their behaviour on hydrolysis. They have been broadly divided into following three groups.
- (i) *Monosaccharides:*
- (ii) *Oligosaccharides*:
- (iii) *Polysaccharides:*

- **(i) *Monosaccharides*: *A carbohydrate that cannot be hydrolysed further*** to give simpler unit of polyhydroxy aldehyde or ketone is called a monosaccharide.
- About 20 monosaccharides are known to occur in nature.
- Some common examples are glucose, fructose, ribose, etc.
- **(ii) *Oligosaccharides: Carbohydrates that yield two to ten*** monosaccharide units, on hydrolysis, are called oligosaccharides.
- They are further classified as disaccharides, trisaccharides, tetrasaccharides, etc., depending upon the number of monosaccharides, they provide on hydrolysis.

- (iii) ***Polysaccharides*****: *Carbohydrates which yield a large number of*** monosaccharide units on hydrolysis are called polysaccharides.

- Some common examples are starch, cellulose, glycogen, gums, etc.

- Polysaccharides are not sweet in taste, hence they are also called non-sugars.

- The carbohydrates may also be classified as either reducing or non-reducing sugars.

Reducing sugars

- All those carbohydrates which reduce Fehling's solution and Tollens' reagent are referred to as reducing sugars.
- All monosaccharides whether aldose or ketose are *reducing sugars.*

NON-REDUCING SUGARS

•In disaccharides, if the reducing groups of monosaccharides i.e., aldehydic or ketonic groups are bonded, these are non-reducing sugars e.g. sucrose.

•On the other hand, sugars in which these functional groups are free, are called reducing sugars, for example, maltose and lactose.

MONOSACCHARIDES

- Monosaccharides are further classified on the basis of number of carbon atoms and the functional group present in them.
- If a monosaccharide contains an aldehyde group, it is known as an aldose and if it contains a keto group, it is known as a ketose.
- Number of carbon atoms constituting the monosaccharide is also introduced in the name

Different Types of Monosaccharides

Carbon atoms	General term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

Preparation of Glucose

- *1.* ***From sucrose*** *(Cane sugar):*
- *If sucrose is boiled with dilute HCl or* H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equal amounts.

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

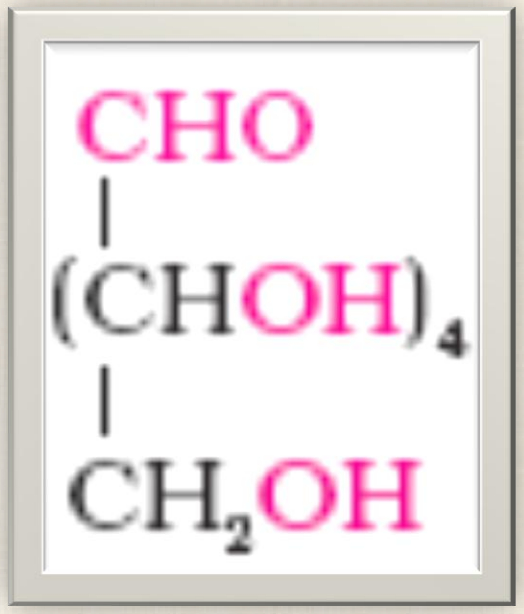
2. From starch:

Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute H_2SO_4 at 393 K under pressure.

$$\underset{\text{Starch or cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[393\text{ K};\ 2\text{-}3\text{ atm}]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

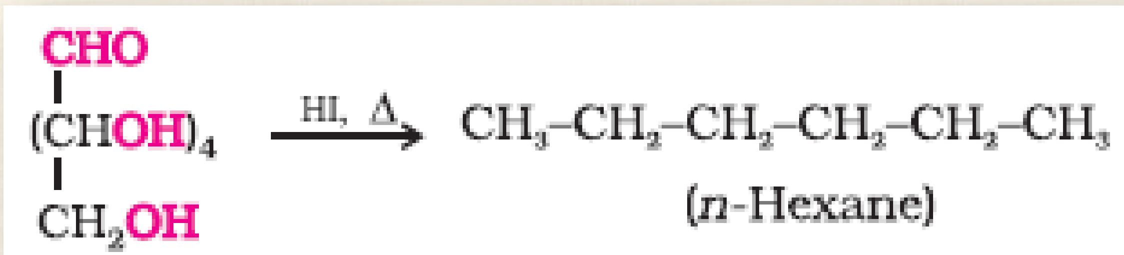
Structure of Glucose

- Glucose is an aldohexose and is also known as dextrose.
- It is the monomer of many of the larger carbohydrates, namely starch, cellulose
- It was assigned the structure given below on the basis of the following evidences:

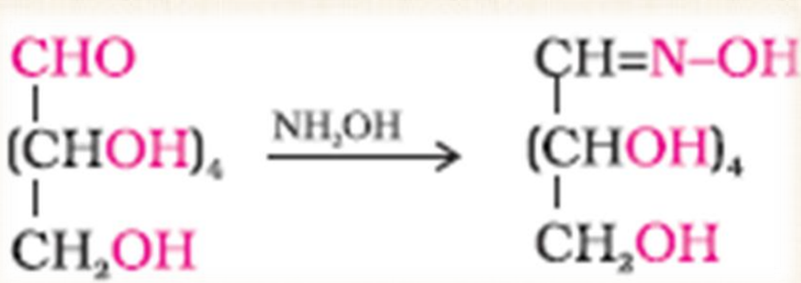


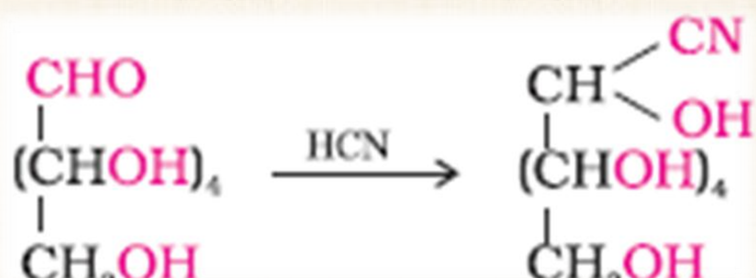
STRUCTURE OF GLUCOSE

- 1. Its molecular formula was found to be $C_6H_{12}O_6$.
- 2. On prolonged heating with HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.

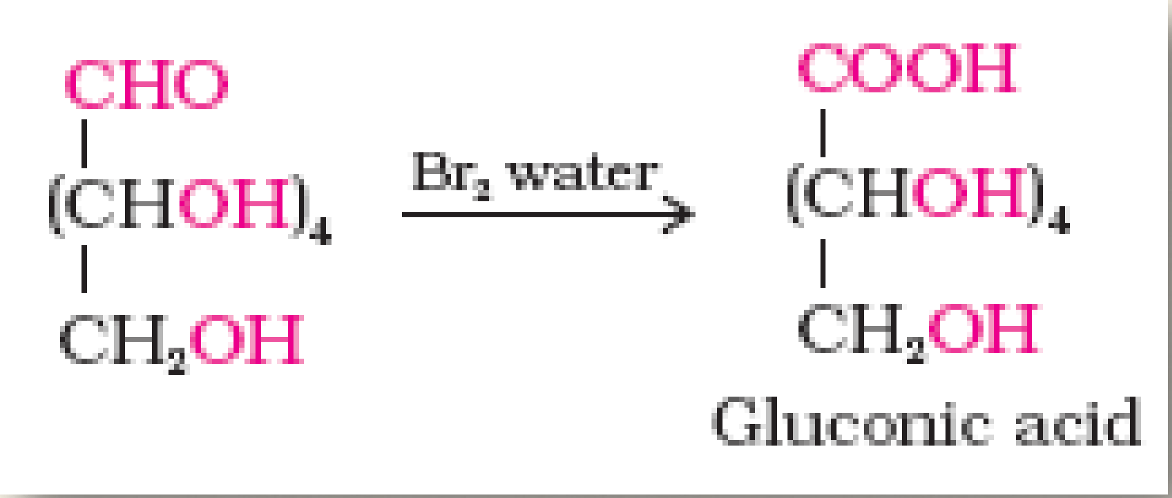


- 3. Glucose reacts with hydroxylamine to form an oxime and adds a molecule of hydrogen cyanide to give cyanohydrin. These reactions confirm the presence of a carbonyl group (>C = 0) in glucose.

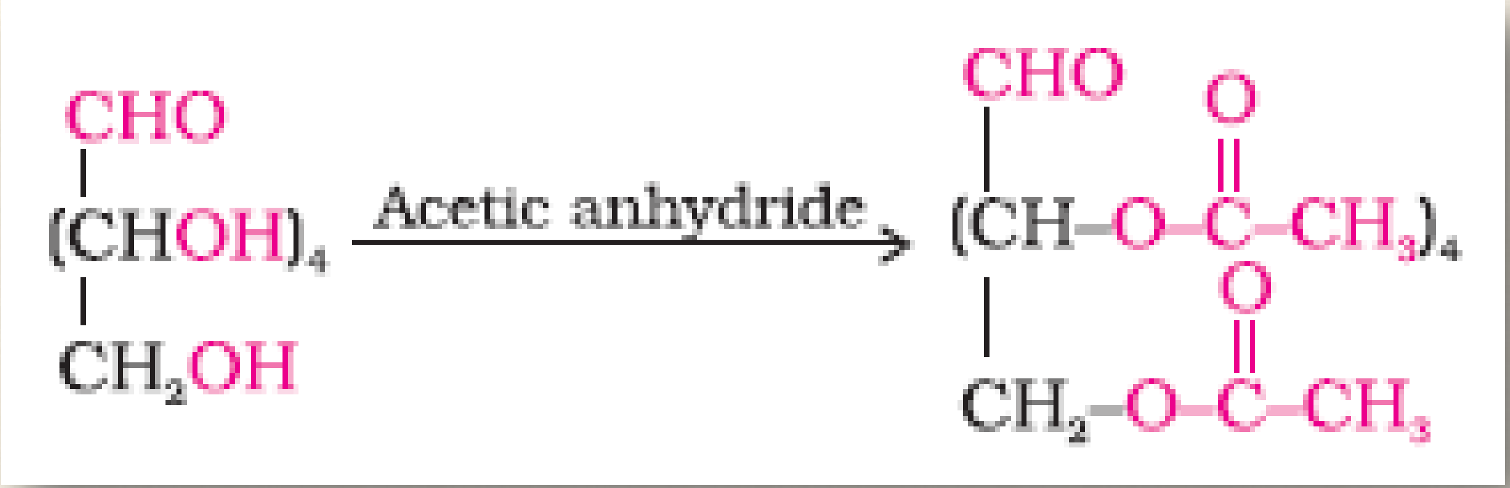




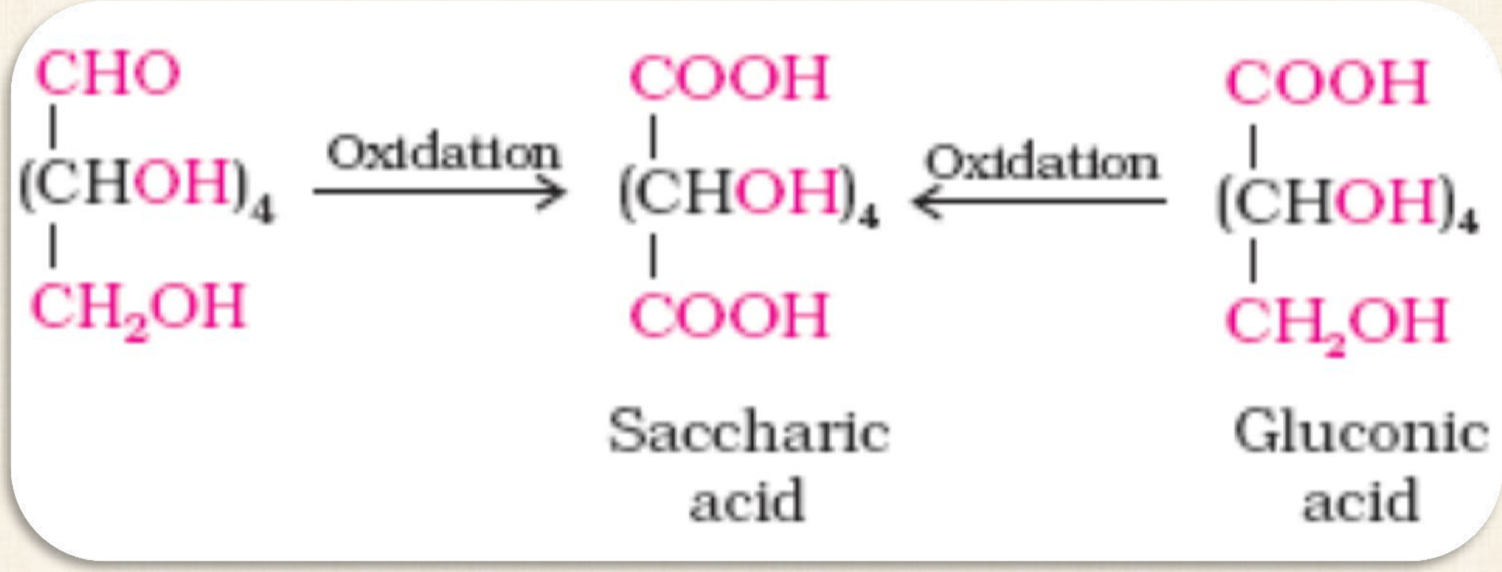
- 4. Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water.
- This indicates that the carbonyl group is present as an aldehydic group.



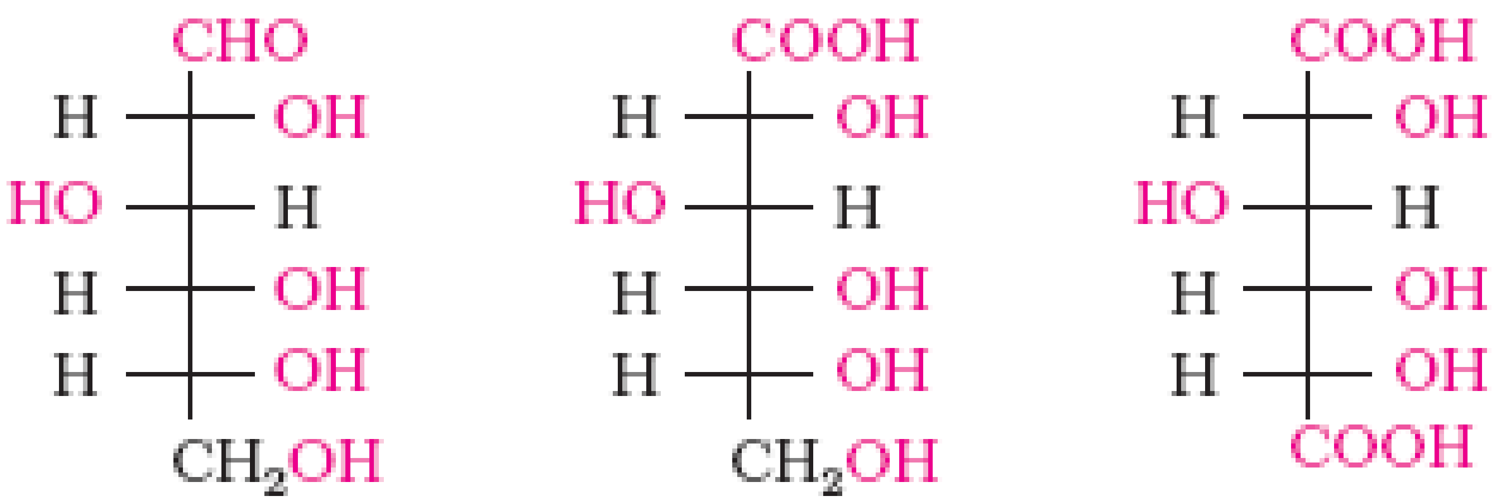
- 5. Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five –OH groups.
- Since it exists as a stable compound, five –OH groups should be attached to different carbon atoms.



- 6. On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid.
- This indicates the presence of a primary alcoholic (–OH) group in glucose.

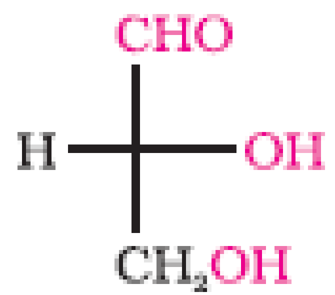


- The exact spatial arrangement of different —OH groups was given by Fischer after studying many other properties.
- Its configuration is correctly represented as **I.**
- **So gluconic acid is represented as II and saccharic acid as III.**

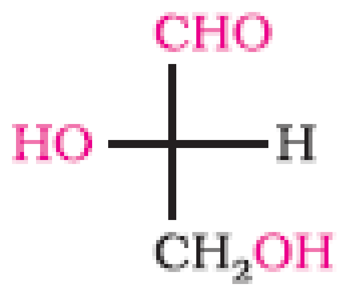


I II III

- **Glucose is correctly named as D(+)-glucose**.
- Glyceraldehyde contains one asymmetric carbon atom and exists in two enantiomeric forms as shown below.



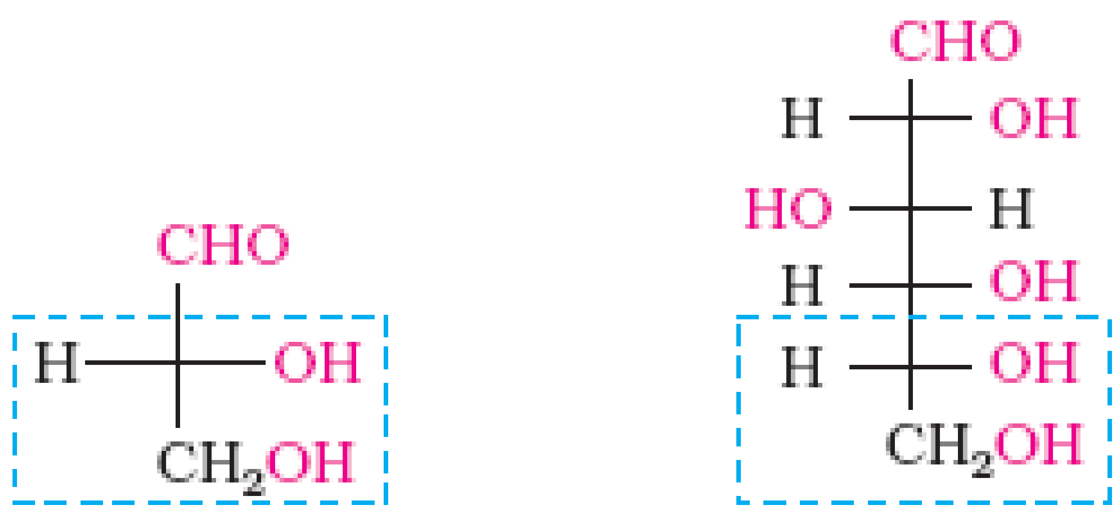
(+) – Glyceraldehyde



(–) – Glyceraldehyde

All those compounds which can be chemically correlated to (+) isomer of glyceraldehyde are said to have **D-configuration** whereas those which can be correlated to (–) isomer of glyceraldehyde are said to have **L—configuration.**

- For assigning the configuration of monosaccharides, it is the lowest asymmetric carbon atom (as shown below) which is compared. As in (+) glucose, —OH on the lowest asymmetric carbon is on the right side which is comparable to (+) glyceraldehyde, so it is assigned D-configuration.
- For this comparison, the structure is written in a way that most oxidised carbon is at the top.



D– (+) – Glyceraldehyde   D–(+) – Glucose

CYCLIC STRUCTURE OF GLUCOSE

- The structure **(I) of glucose explained most of its properties but the** following reactions and facts could not be explained by this structure.

- 1. Despite having the aldehyde group, glucose does not give 2,4-DNP test, Schiff's test and it does not form the hydrogensulphite addition product with $NaHSO_3$.

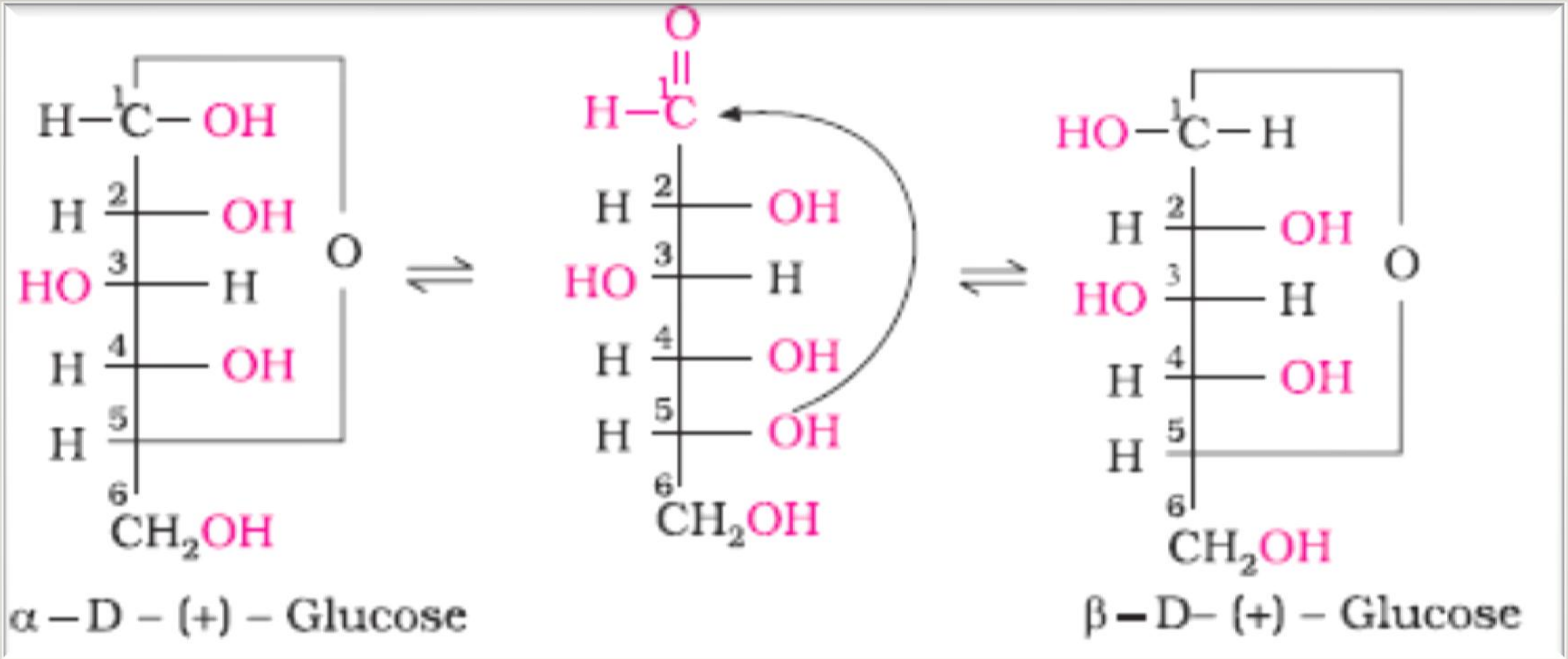
Cyclic Structure of Glucose

- 2. The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free —CHO group

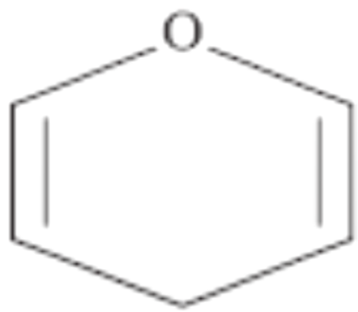
- 3. Glucose is found to exist in two different crystalline forms which are named as α and β. The α-form of glucose (m.p. 419 K) is obtained by crystallisation from concentrated solution of glucose at 303 K while the β-form (m.p. 423 K) is obtained by crystallisation from hot and saturated aqueous solution at 371 K.

- This behaviour could not be explained by the open chain structure **(I) for glucose.**
- **It was proposed that one of the —OH groups may add** to the —CHO group and form a cyclic hemiacetal structure.
- It was found that glucose forms a six-membered ring in which —OH at C-5 is involved in ring formation.
- This explains the absence of —CHO group and also existence of glucose in two forms as shown below.
- These two cyclic forms exist in equilibrium with open chain structure.

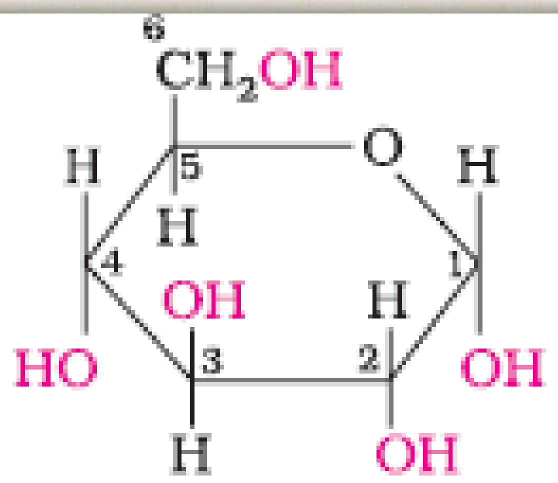
Cyclic Structure of Glucose



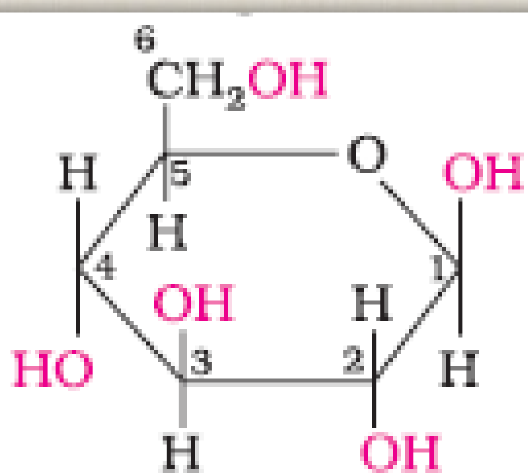
- The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called *anomeric carbon* (the aldehyde carbon before cyclisation).
- Such isomers, i.e., α-form and β-form, are called **anomers.**
- **The six membered cyclic structure** of glucose is called **pyranose structure (α– or β–), in analogy with** pyran.
- Pyran is a cyclic organic compound with one oxygen atom and five carbon atoms in the ring.
- The cyclic structure of glucose is more correctly represented by Haworth structure as given in thenext slide.



Pyran



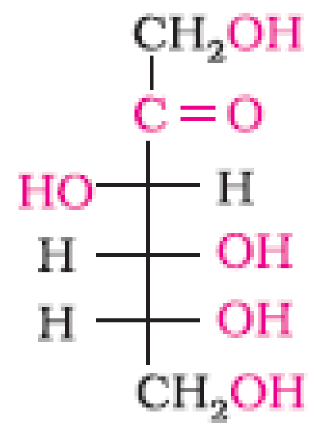
α – D – (+) – Glucopyranose



β – D – (+) – Glucopyranose

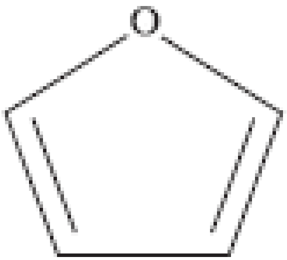
FRUCTOSE

- Fructose is an important ketohexose. It is obtained along with glucose by the hydrolysis of disaccharide, sucrose.
- Fructose also has the molecular formula $C_6H_{12}O_6$ and on the basis of its reactions it was found to contain a ketonic functional group at carbon number 2 and six carbons in straight chain as in the case of glucose.
- It belongs to D-series and is a laevorotatory compound.
- **It is appropriately written as**
- **D-(–)-fructose.**

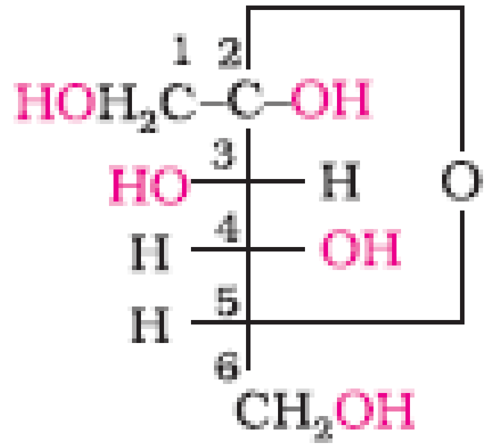


D – (–) – Fructose

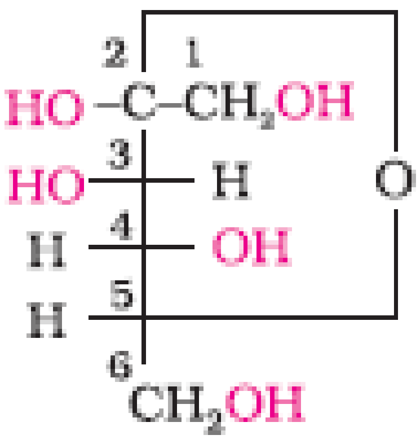
- It also exists in two cyclic forms which are obtained by the addition of —OH at C5 to the (>C=O) group.
- The ring, thus formed is a five membered ring and is named as furanose with analogy to the compound furan.
- Furan is a five membered cyclic compound with one oxygen and four carbon atoms.



Furan

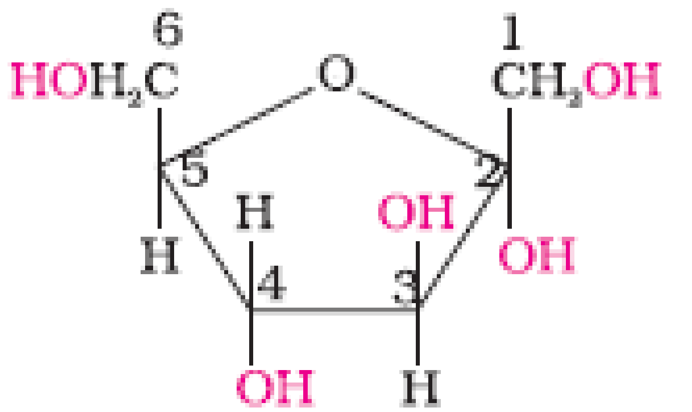


α – D – (–) – Fructofuranose

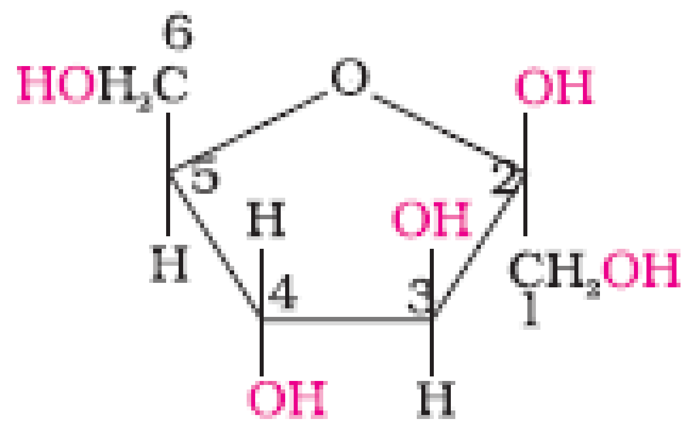


β – D – (–) – Fructofuranose

- The cyclic structures of two anomers of fructose are represented by Haworth structures as given.



α – D – (–) – Fructofuranose



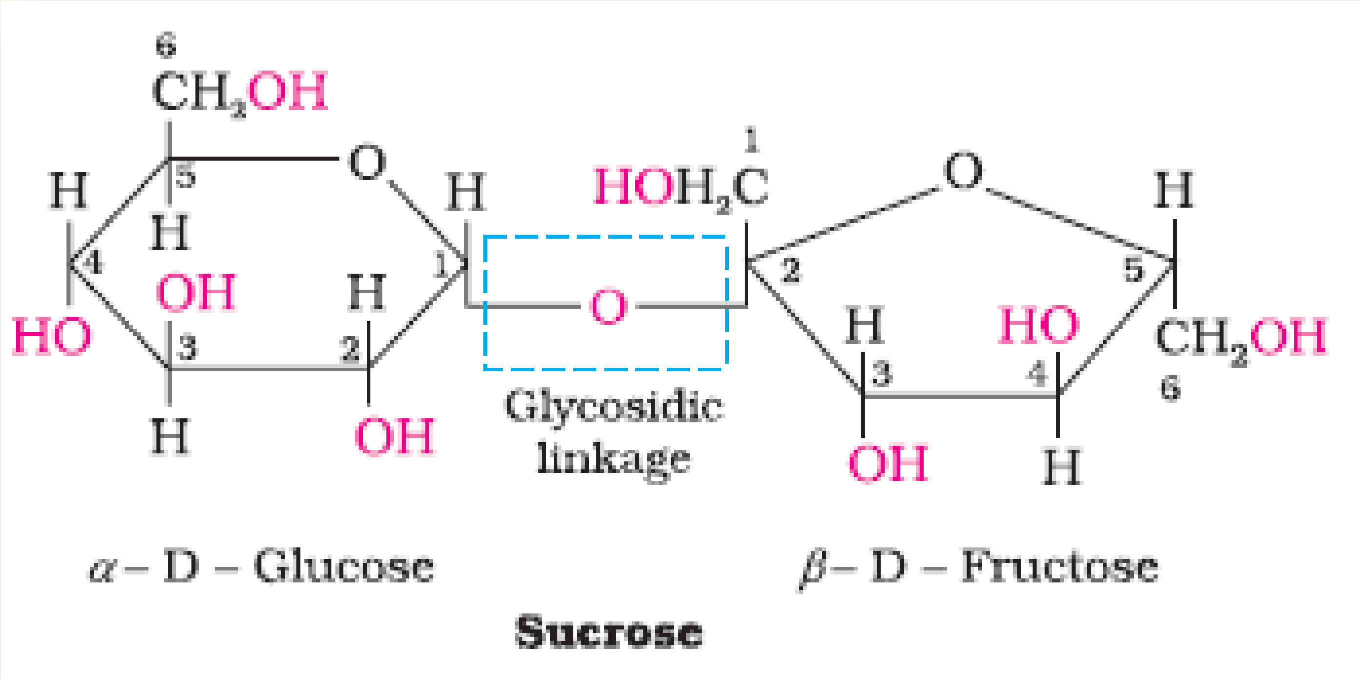
β – D – (–) – Fructofuranose

DISACCHARIDES

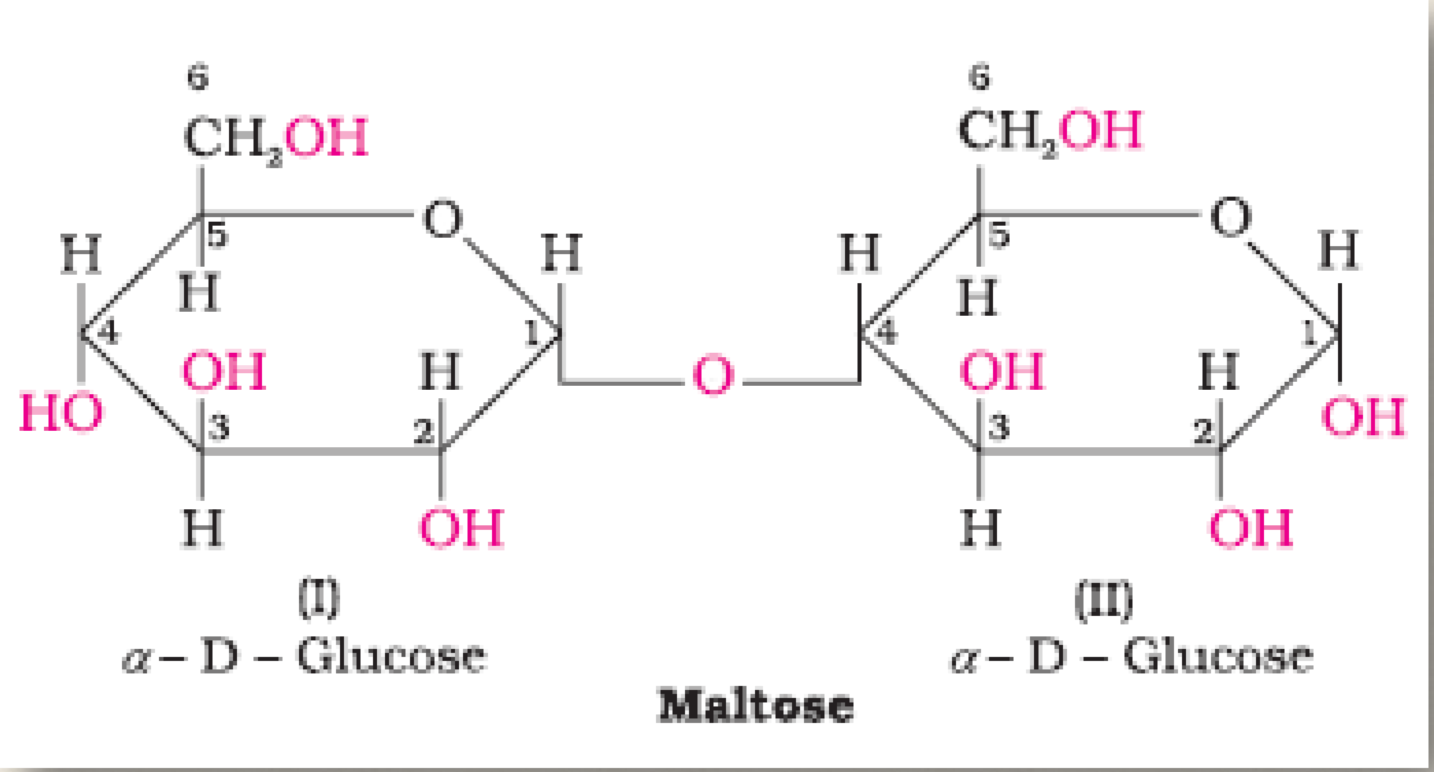
- disaccharides on hydrolysis with dilute acids or enzymes yield two molecules of either the same or different monosaccharides.
- The two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule.
- Such a linkage between two monosaccharide units through oxygen atom is called *glycosidic linkage*
- ***(i) Sucrose:*** *One of the common disaccharides is sucrose which on* hydrolysis gives equimolar mixture of D-(+)-glucose and D-(-)- fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{D-(+)-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(–)-Fructose}}{C_6H_{12}O_6}$$

- These two monosaccharides are held together by a glycosidic linkage between C1 of α-glucose and C2 of β-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non reducing sugar.



- Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory.
- Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as **invert sugar.**
- ***(ii) Maltose****: Another disaccharide, maltose is composed of two* α-D-glucose units in which C1 of one glucose (I) is linked to C4 of another glucose unit (II). The free aldehyde group can be produced at C1 of second glucose in solution and it shows reducing properties so it is a reducing sugar.


6
CH2OH
O
5
H
H
H
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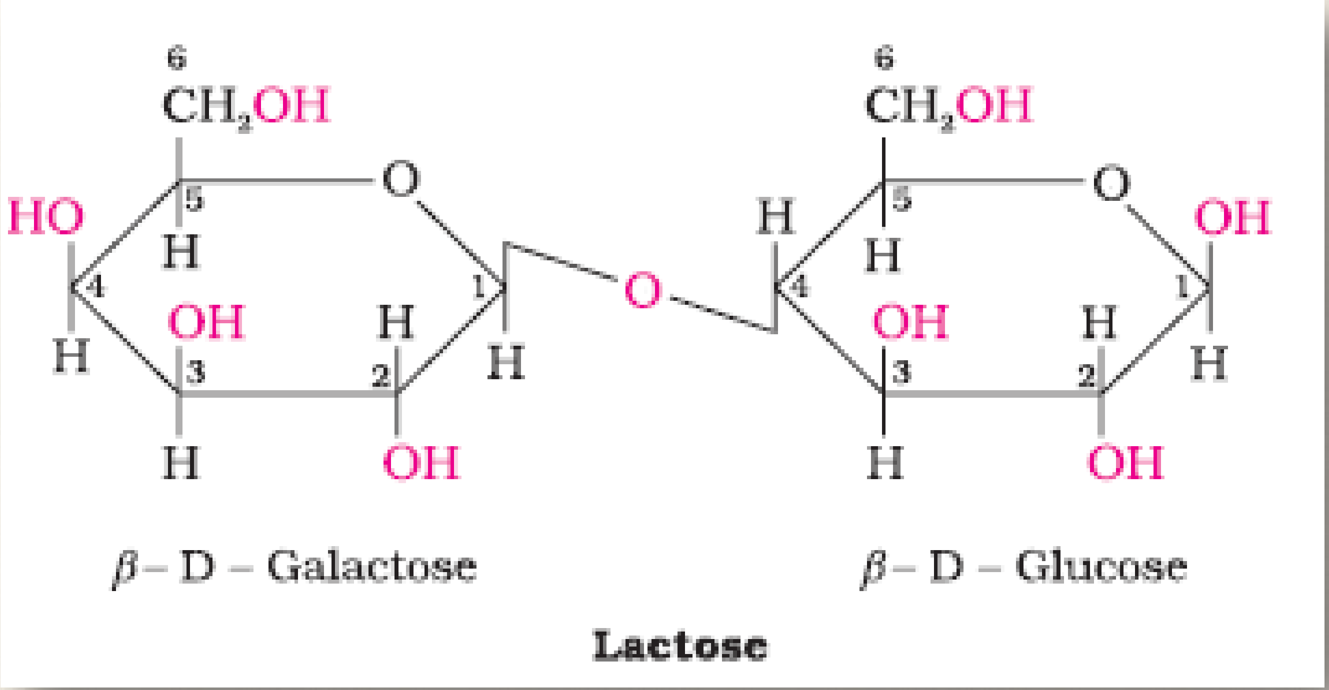
1
H
HO
OH
H
3
2
O
H
OH
6
CH2OH
O
5
H
H
H
4
1
OH
OH
H
3
2
H
OH
(I)
α – D – Glucose
(II)
α – D – Glucose
Maltose

- ***(iii) Lactose**: It is more commonly known as milk sugar since this* disaccharide is found in milk. It is composed of β-D-galactose and β-D-glucose.
- The linkage is between C1 of galactose and C4 of glucose. Hence it is also a reducing sugar.



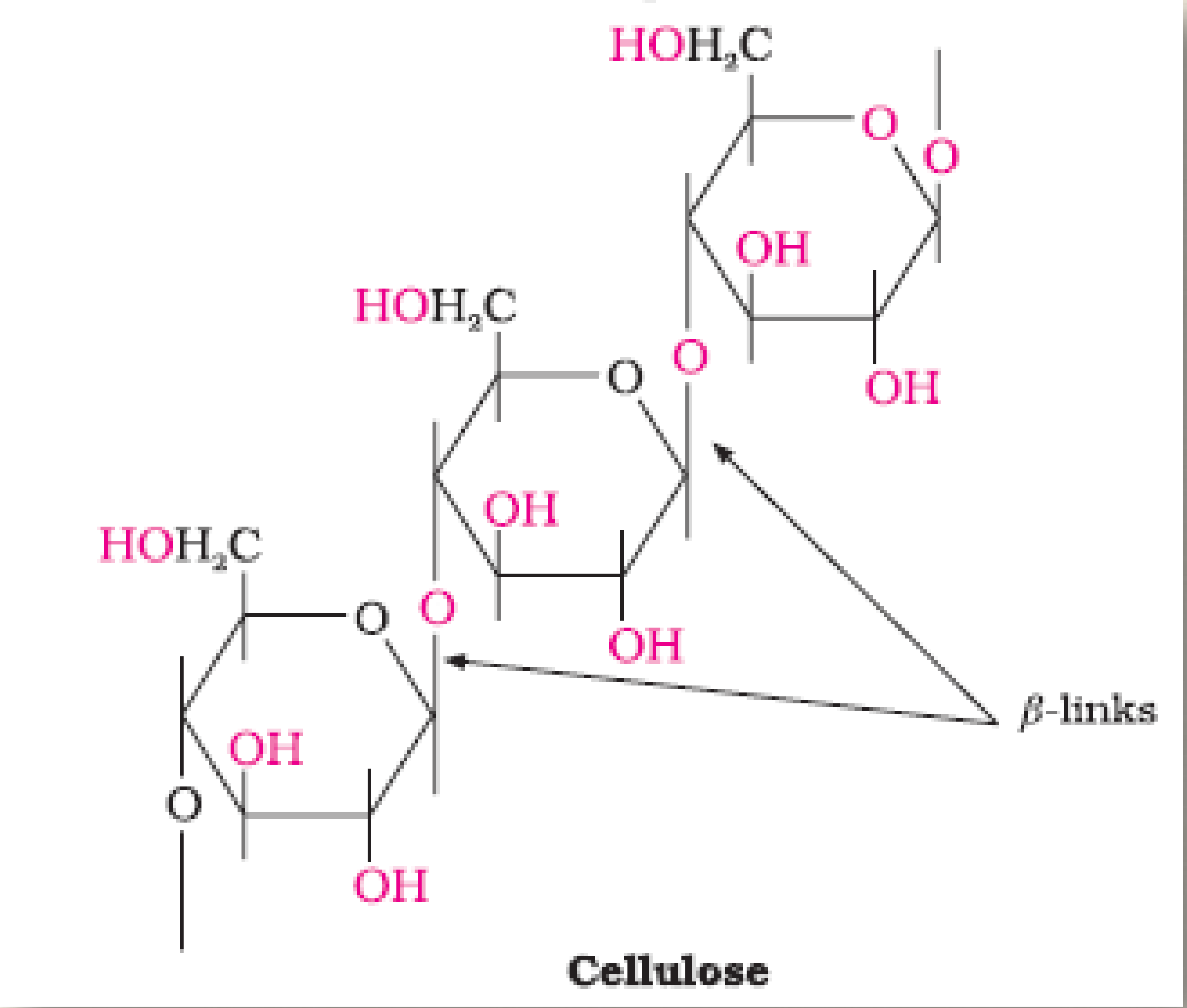
POLYSACCHARIDES

- Polysaccharides contain a large number of monosaccharide units joined together by glycosidic linkages.
- These are the most commonly encountered carbohydrates in nature. They mainly act as the food storage or structural materials
- ***(i) Starch***: *Starch is the main storage polysaccharide of plants. It is* the most important dietary source for human beings. High content of starch is found in cereals, roots, tubers and some vegetables. It is a polymer of α-glucose and consists of two components— **Amylose and Amylopectin.**
- ***Amylose is water soluble component*** which constitutes about 15-20% of starch.

- ***(ii) Cellulose**: Cellulose occurs exclusively in plants and it is the most* abundant organic substance in plant kingdom.

- It is a predominant constituent of cell wall of plant cells. Cellulose is a straight chain polysaccharide composed only of β-D-glucose units which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.

CELLULOSE



GLYCOGEN

- ***(iii) Glycogen**: The carbohydrates are stored in animal body as glycogen.*
- It is also known as *animal starch because its structure is similar* to amylopectin and is rather more highly branched.
- It is present in liver, muscles and brain. When the body needs glucose, enzymes break the glycogen down to glucose.
- Glycogen is also found in yeast and fungi.

IMPORTANCE OF CARBOHYDRATES

- Carbohydrates are essential for life in both plants and animals. They form a major portion of our food.
- Honey has been used for a long time as an instant source of energy by '**Vaids' in ayurvedic system of medicine.**
- Carbohydrates are used as storage molecules as starch in plants and glycogen in animals.
- Cell wall of bacteria and plants is made up of cellulose. We build furniture, etc. from cellulose in the form of wood and clothe ourselves with cellulose in the form of cotton fibre.

IMPORTANCE OF CARBOHYDRATES

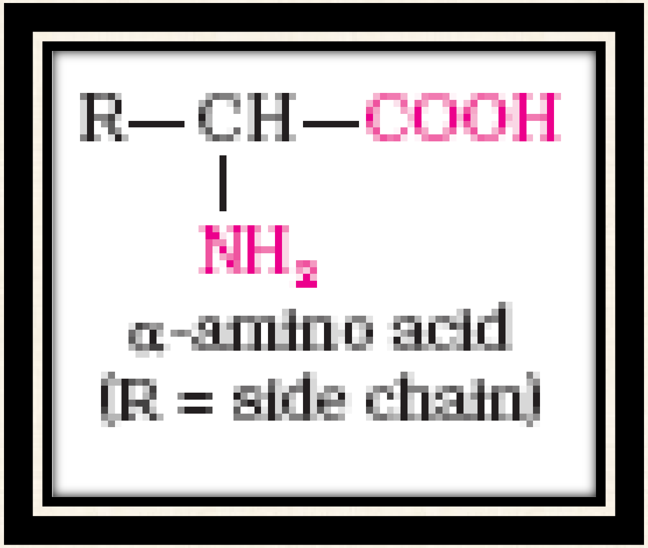
- They provide raw materials for many important industries like textiles, paper, lacquers and breweries.
- Two aldopentoses viz. D-ribose and 2-deoxy-D-ribose are present in nucleic acids.
- Carbohydrates are found in biosystem in combination with many proteins and lipids.

PROTEINS

- Proteins are the most abundant biomolecules of the living system.
- Chief sources of proteins are milk, cheese, pulses, peanuts, fish, meat, etc.
- They occur in every part of the body and form the fundamental basis of structure and functions of life.
- They are also required for growth and maintenance of body.
- The word protein is derived from Greek word, "**proteios" which means primary or of prime importance.**
- All proteins are polymers of α-amino acids.

AMINO ACIDS

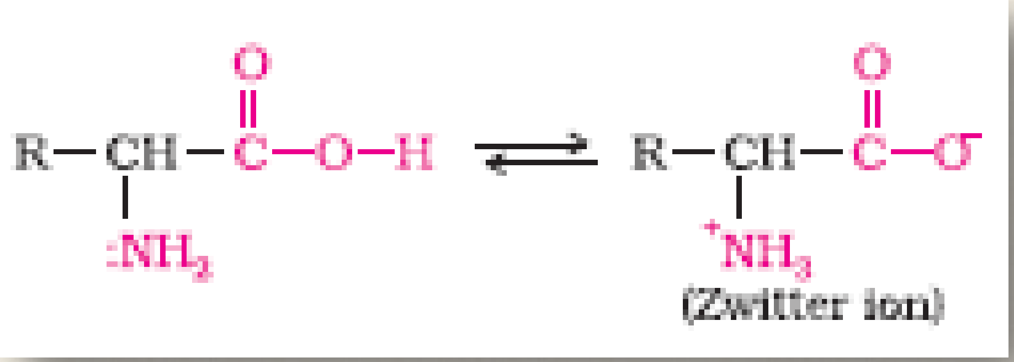
- Amino acids contain amino (–NH_2) and carboxyl (–COOH) functional groups.
- Depending upon the relative position of amino group with respect to carboxyl group, the amino acids can be classified as α, β, γ, δ and so on.
- Only α-amino acids are obtained on hydrolysis of proteins. They may contain other functional groups also.



CLASSIFICATION OF AMINO ACIDS

- Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule.
- Equal number of amino and carboxyl groups makes it neutral; more number of amino than carboxyl groups makes it basic and more carboxyl groups as compared to amino groups makes it acidic.
- The amino acids, which can be synthesised in the body, are known as **nonessential amino acids.**
- **On the other hand, those which cannot be** synthesised in the body and must be obtained through diet, are known as **essential amino acids**

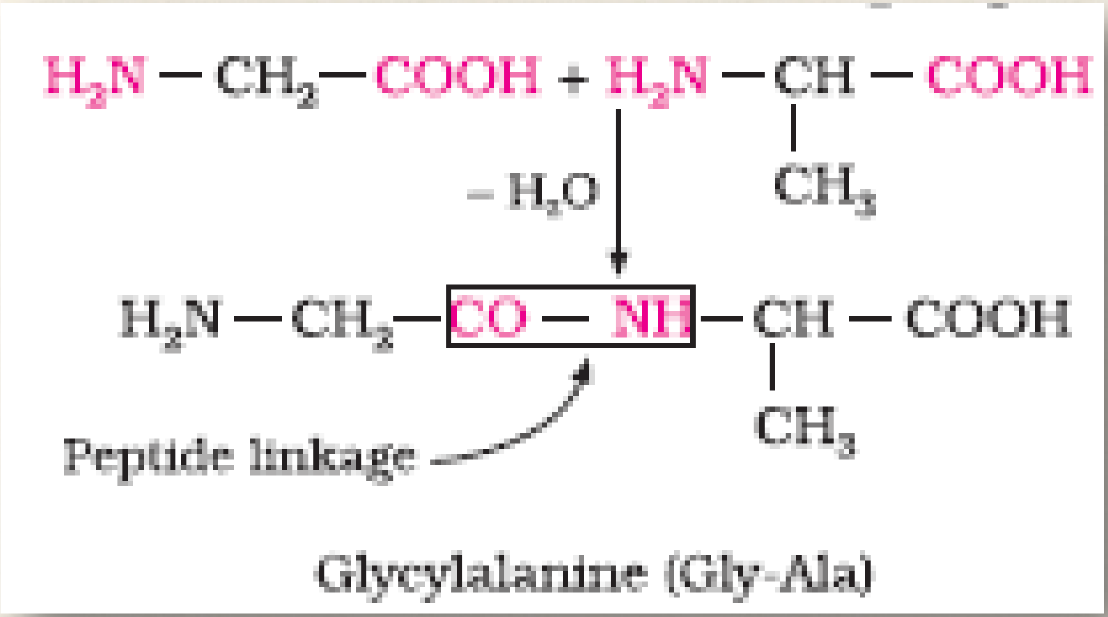
- Amino acids are usually colourless, crystalline solids.
- These are water-soluble, high melting solids and behave like salts rather than simple amines or carboxylic acids.
- This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule.
- In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as ***zwitter ion***.
- *This is* neutral but contains both positive and negative charges.



- In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.
- Except glycine, all other naturally occurring α-amino acids are optically active, since the α-carbon atom is asymmetric.
- These exist both in 'D' and 'L' forms. Most naturally occurring amino acids have L-configuration.
- L-Aminoacids are represented by writing the $-NH_2$ group on left hand side.

STRUCTURE OF PROTEINS

- Proteins are the polymers of α-amino acids and they are connected to each other by **peptide bond or peptide linkage.**
- **Chemically, peptide linkage is an amide formed between** –COOH group and $–NH_2$ group.



Classification of Proteins

- **Proteins can be classified into two types on the basis of their** molecular shape.

(a) Fibrous proteins

- When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre– like structure is formed.
- Such proteins are generally insoluble in water. Some common examples are keratin (present in hair, wool, silk) and myosin (present in muscles), etc.

(b) Globular proteins

- This structure results when the chains of polypeptides coil around to give a spherical shape.
- These are usually soluble in water.
- Insulin and albumins are the common examples of globular proteins.

ENZYMES

- 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.
- They are generally named after the compound or class of compounds upon which they work.
- For example, the enzyme that catalyses hydrolysis of maltose into glucose is named as *maltase*.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2\,C_6H_{12}O_6}$$

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.
- 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.
- **(i) *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.
- **(ii) *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.

NUCLEIC ACIDS

- 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.

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.

Thank you