

# Biochemistry of Carbohydrates

# Introduction

- Carbohydrates may be defined as polyhydroxy aldehydes or ketones, or any substances that yield one of these compounds on hydrolysis.
- Carbohydrates are the most abundant biomolecules, distributed widely in plants and animals where, they perform structural and functional roles. They are hydrated carbon molecules. Generally the hydrogen and oxygen will be present in the proportion of 2:1.
- Many carbohydrates have the empirical formula  $(\text{CH}_2\text{O})_n$ , where  $n$  is 3 or larger.
- Some carbohydrates contain nitrogen, phosphorous or sulphur also.

# BIOLOGICAL IMPORTANCE

- Carbohydrates provide the majority of energy in most organisms. They are the most abundant dietary source of energy (4 Cal/g) for all organisms.
- Glucose is stored as **glycogen** in liver and muscle. Carbohydrates also serve as the storage form of energy (glycogen) to meet the immediate energy demands of the body.
- Carbohydrates (**e.g.** cellulose) give structure to cell walls (in plants) and cell membranes.
- Carbohydrates serve as metabolic intermediates (**e.g.** glucose 6-phosphate, fructose –1,6 biphosphate). The metabolic intermediates derived from glucose are used for the biosynthesis of amino acids, nucleic acid and nucleotides.
- Carbohydrates (**e.g.** ribose, deoxyribose) comprise large portions of the nucleotides that form DNA and RNA.
- Carbohydrates also play a role in lubrication, cellular intercommunication and immunity.
- It plays an important role in the metabolism of proteins and fatty acids.

# Classification

- Based on the sugar units they contain, carbohydrates are classified into four groups, as
  - Monosaccharides
  - Disaccharides,
  - Oligosaccharides (a small polymer of sugar)
  - Polysaccharides
- Monosaccharides are simple sugars, consisting of single polyhydroxy aldehyde or ketone unit. They cannot be hydrolyzed to yield simpler forms of sugar.
- They can be subdivided into trioses, tetroses, pentoses, hexoses, heptoses and octoses, depending upon the number of carbon atoms they possess.
- Carbohydrates with an aldehyde as their functional group are called as Aldoses. Those with keto as functional group are called as ketoses.

# Structures of Aldoses & Ketoses

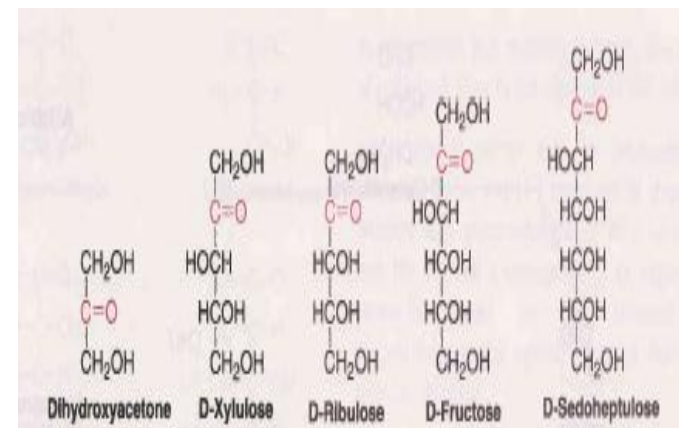
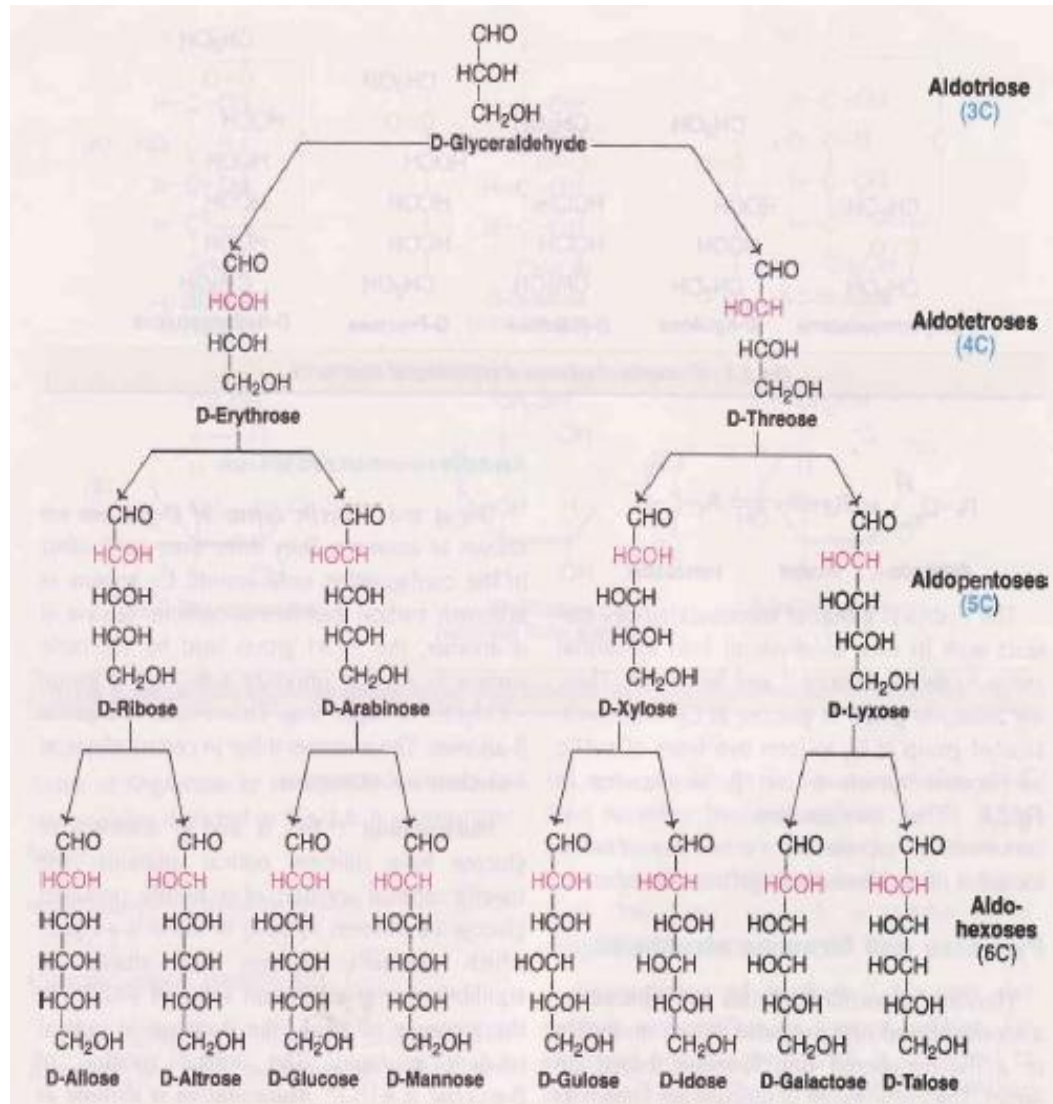


TABLE 2.1 Classification of monosaccharides with selected examples

<i>Monosaccharides (empirical formula)</i>	<i>Aldose</i>	<i>Ketose</i>
Trioses (C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> )	Glyceraldehyde	Dihydroxyacetone
Tetroses (C <sub>4</sub> H <sub>8</sub> O <sub>4</sub> )	Erythrose	Erythrulose
Pentoses (C <sub>5</sub> H <sub>10</sub> O <sub>5</sub> )	Ribose	Ribulose
Hexoses (C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> )	Glucose	Fructose
Heptoses (C <sub>7</sub> H <sub>14</sub> O <sub>7</sub> )	Glucoheptose	Sedoheptulose

- Disaccharides yield two molecules of the same or different monosaccharides when hydrolyzed. Examples are sucrose, lactose, and maltose.
- Oligosaccharides Yield 3–6 monosaccharide units on hydrolysis. Eg. maltotriose and raffinose
- Polysaccharides Yield more than 6 molecules of monosaccharide on hydrolysis. Examples of polysaccharides are starch, cellulose, glycogen and dextrans.
- The polysaccharides may be linear or branched eg. Cellulose is a **linear** polysaccharide and starch is a **branched** polysaccharide.
- Polysaccharides are sometimes called as hexosans or pentosans, depending upon the type of the monosaccharides they yield on hydrolysis eg., glycogen -hexosan.



# PHYSIOLOGICALLY IMPORTANT MONOSACCHARIDES

<i>Monosaccharides</i>	<i>Occurrence</i>	<i>Biochemical importance</i>
<b>Trioses</b>		
Glyceraldehyde	Found in cells as phosphate	Glyceraldehyde 3-phosphate is an intermediate in glycolysis
Dihydroxyacetone	Found in cells as phosphate	Its 1-phosphate is an intermediate in glycolysis
<b>Tetroses</b>		
D-Erythrose	Widespread	Its 4-phosphate is an intermediate in carbohydrate metabolism
<b>Pentoses</b>		
D-Ribose	Widespread as a constituent of RNA and nucleotides	For the structure of RNA and nucleotide coenzymes (ATP, NAD <sup>+</sup> , NADP <sup>+</sup> )
D-Deoxyribose	As a constituent of DNA	For the structure of DNA
D-Ribulose	Produced during metabolism	It is an important metabolite in hexose monophosphate shunt
D-Xylose	As a constituent of glycoproteins and gums	Involved in the function of glycoproteins
L-Xylulose	As an intermediate in uronic acid pathway	Excreted in urine in essential pentosuria
D-Lyxose	Heart muscle	As a constituent of lyxoflavin of heart muscle
<b>Hexoses</b>		
D-Glucose	As a constituent of polysaccharides (starch, glycogen, cellulose) and disaccharides (maltose, lactose, sucrose). Also found in fruits	The 'sugar fuel' of life; excreted in urine in diabetes. Structural unit of cellulose in plants
D-Galactose	As a constituent of lactose (milk sugar)	Converted to glucose, failure leads to galactosemia
D-Mannose	Found in plant polysaccharides and animal glycoproteins	For the structure of polysaccharides
D-Fructose	Fruits and honey, as a constituent of sucrose and inulin	Its phosphates are intermediates of glycolysis
<b>Heptoses</b>		
D-Sedoheptulose	Found in plants	Its 7-phosphate is an intermediate in hexose monophosphate shunt, and in photosynthesis

# Derivatives of the Monosaccharides

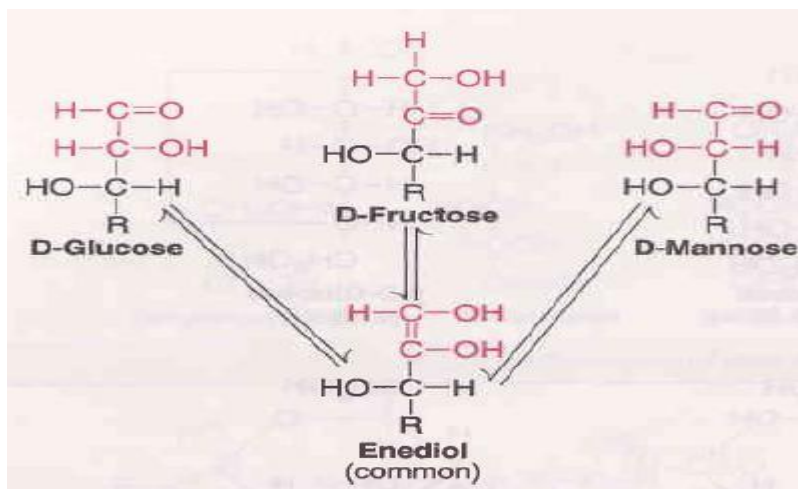
- Many derivatives of the monosaccharides are found in the systems, which include sugar phosphate, deoxy and amino sugars, sugar alcohol, and sugar phosphate, deoxy and amino sugar, sugar alcohols, and sugar acids.
- **Phosphate esters:** When monosaccharides are used as fuel they are metabolized as phosphate esters. For e.g., triose phosphate, ribose 5-phosphate and glucose 6-phosphate.
- **Deoxy sugars:** In these derivatives, a hydrogen atom replaces one of the hydroxyl groups in the parent monosaccharide. An example is deoxyribose occurring in nucleic acid DNA, L-Fucose (6-deoxy-L-galactose) is widely distributed in plants, animals and microorganisms. L-rhamnose (6-deoxy-L-mannose) is also found as components of cell wall.
- **Amino sugars:** In a number of sugars, an amino group replaces one of the hydroxyl groups in the parent monosaccharide. Some times the amino group is acetylated. Examples of amino sugars are D-glucosamine, D-galactosamine and D-mannosamine. They commonly occur in glycoconjugates. Several antibiotics contain amino sugars.
- **Sugar alcohols:** In sugar alcohols, the carbonyl oxygen of the parent monosaccharide has been reduced producing a polyhydroxy alcohol. For example glycerol and myo-inositol are the important components of lipids. Ribitol is a component of FMN and FAD.
- **Sugar acids:** Sugar acids are carboxylic acids derived from aldoses, either by the oxidation of C-1 (the aldehyde carbon or by the oxidation of carbon bearing the primary alcohol). Sugar acids are important components of many polysaccharides.
- **Ascorbic acid or Vitamin C:** It is derived from D-glucuronate . It is an essential cofactor for many hydroxylation processes.



# REACTIONS OF MONOSACCHARIDES

**Tautomerization or enolization:**-The process of shifting a hydrogen atom from one carbon atom to another to produce enediols is known as tautomerization. Sugars possessing anomeric carbon atom undergo tautomerization in alkaline solutions.

When glucose is kept in alkaline solution for several hours, it undergoes isomerization to form D-fructose and D-mannose. This reaction known as the **Lobry de Bruyn-von Ekenstein transformation**.



**Reducing properties:-** Benedict's test, Fehling's test, Barfoed's test etc. The reduction is much more efficient in the alkaline medium than in the acid medium.

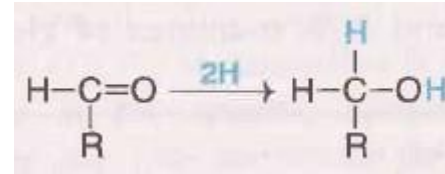
The enediol forms or sugars reduce cupric ions ( $\text{Cu}^{2+}$ ) of copper sulphate to cuprous ions ( $\text{Cu}^+$ ), which form a yellow precipitate of cuprous hydroxide or a red precipitate of cuprous oxide.

**Oxidation:-** Depending on the oxidizing agent used, the terminal aldehyde (or keto) or the terminal alcohol or both the groups may be oxidized.

1. Oxidation of aldehyde group ( $\text{CHO} \rightarrow \text{COOH}$ ) results in the formation of gluconic acid.

2. Oxidation of terminal alcohol group ( $\text{CH}_2\text{OH} \rightarrow \text{C OOH}$ ) leads to the production of glucuronic acid.

**Reduction:-** When treated with reducing agents such as sodium amalgam, the aldehyde or keto group of monosaccharide is reduced to corresponding alcohol.



The important monosaccharides and their corresponding alcohols are given below.

D-Glucose-----> D-Sorbitol

D-Galactose -----> D-Dulcitol

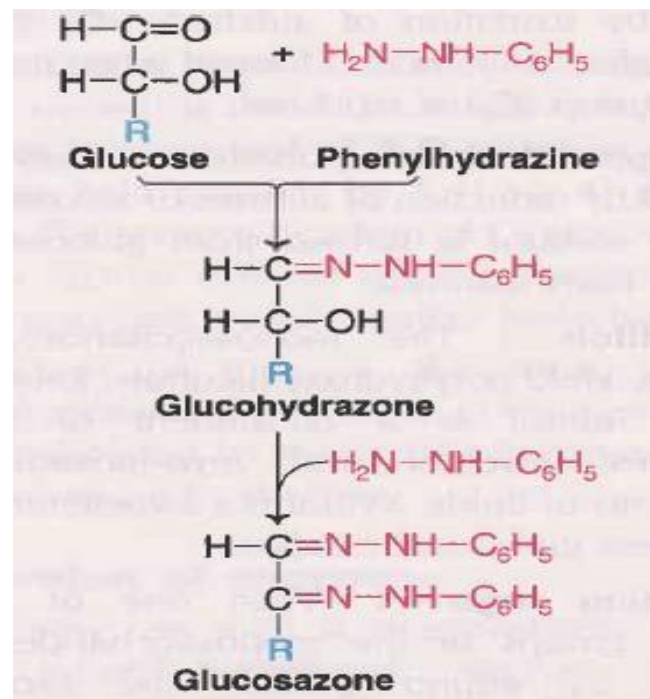
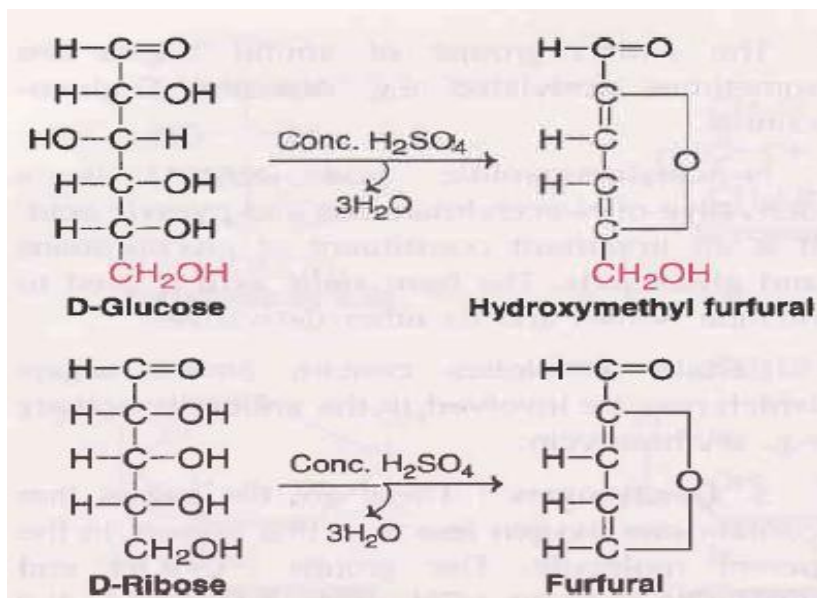
D-Mannose -----> D-Mannitol

D-Fructose ----> D-Mannitol + D-Sorbitol

D-Ribose -----> D-Ribitol

**Sorbitol and dulcitol** when accumulate in tissues in large amounts cause strong osmotic effects feading to swelling of cells, and certain pathological conditions. e.g. cataract, peripheral neuropathy, nephropathy. **Mannitol** is useful to reduce intracranial tension by forced diuresis.

# Dehydration:-



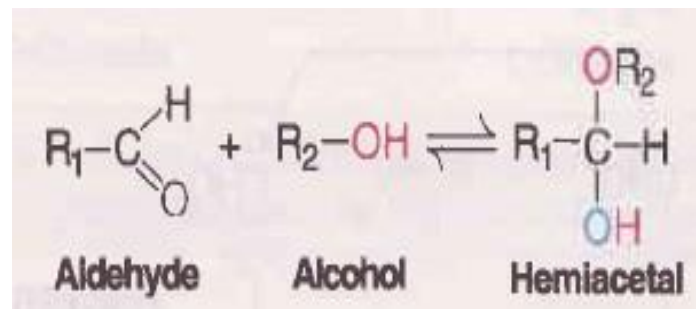
## Osazone formation:-

Phenylhydrazine in acetic acid, when boiled with reducing sugars, forms osazones. The first two carbons (**C1 and C2**) are involved in osazone formation.

Glucose, fructose and mannose give the same type (**needle-shaped**) osazones. Reducing disaccharides also give osazones **maltose sunflower-shaped**, and **lactose powderpuff shaped**.

**Formation of esters:-** The alcoholic groups of monosaccharides may be esterified by non-enzymatic or enzymatic reactions and formation of esters.

**GLYCOSIDES:-** Glycosides are formed when the hemiacetal or hemiketal hydroxyl group (of anomeric carbon) of a carbohydrate reacts with a hydroxyl group of another carbohydrate or a non carbohydrate (e.g. methyl alcohol, phenol, glycerol). The bond so formed is known as **glycosidic bond** and the non-carbohydrate moiety (when present) is referred to as aglycone.



# Physiologically important glycosides

1. **Glucovanillin** (Vanillin-D-glucosides) is a natural substance that imparts vanilla flavour.
2. **Cardiac glycosides** (steroidal glycosides):- **Digoxin** and **digitoxin** contain the aglycone steroid and they stimulate muscle contraction.
3. **Streptomycin**- An antibiotic used in the treatment of tuberculosis is a glycoside.
4. **Ouabain**- Inhibits  $\text{Na}^+ - \text{K}^+$  ATPase and blocks the active transport of  $\text{Na}^+$ .

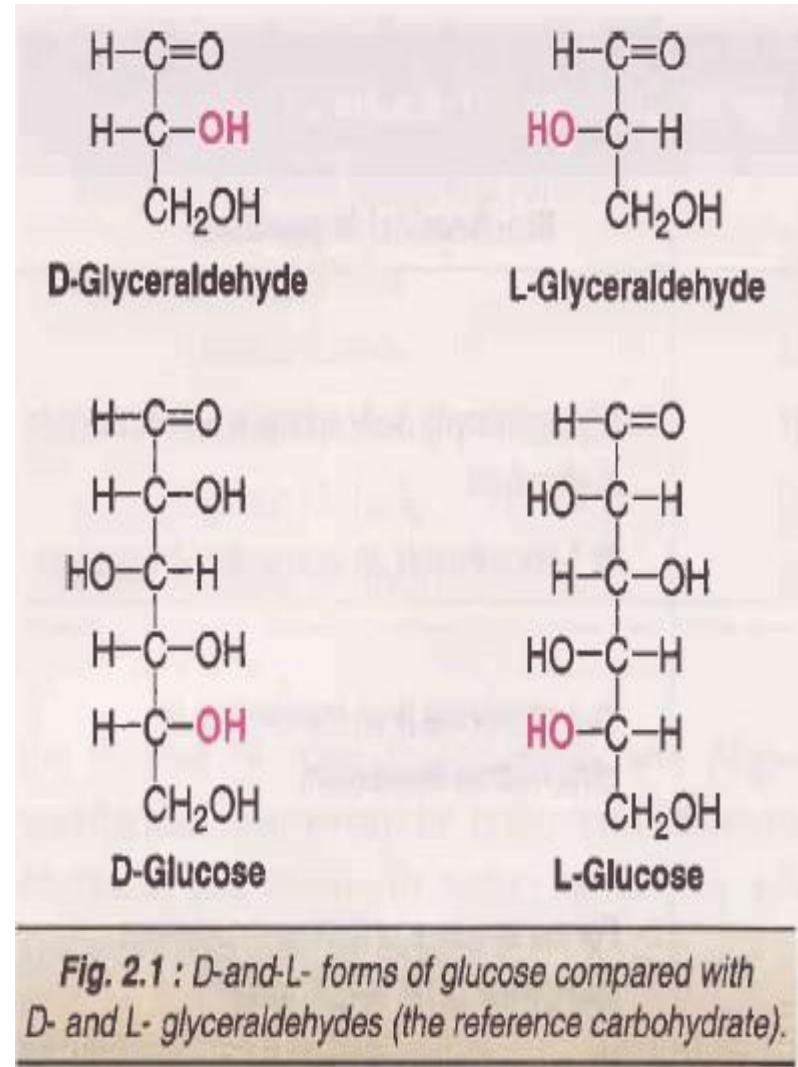


# Structures

**Racemic mixture** : If D- and L-isomers are present in equal concentration, it is known as racemic mixture or DL mixture. Racemic mixture does not exhibit any optical activity, since the dextro- and levorotatory activities cancel each other.

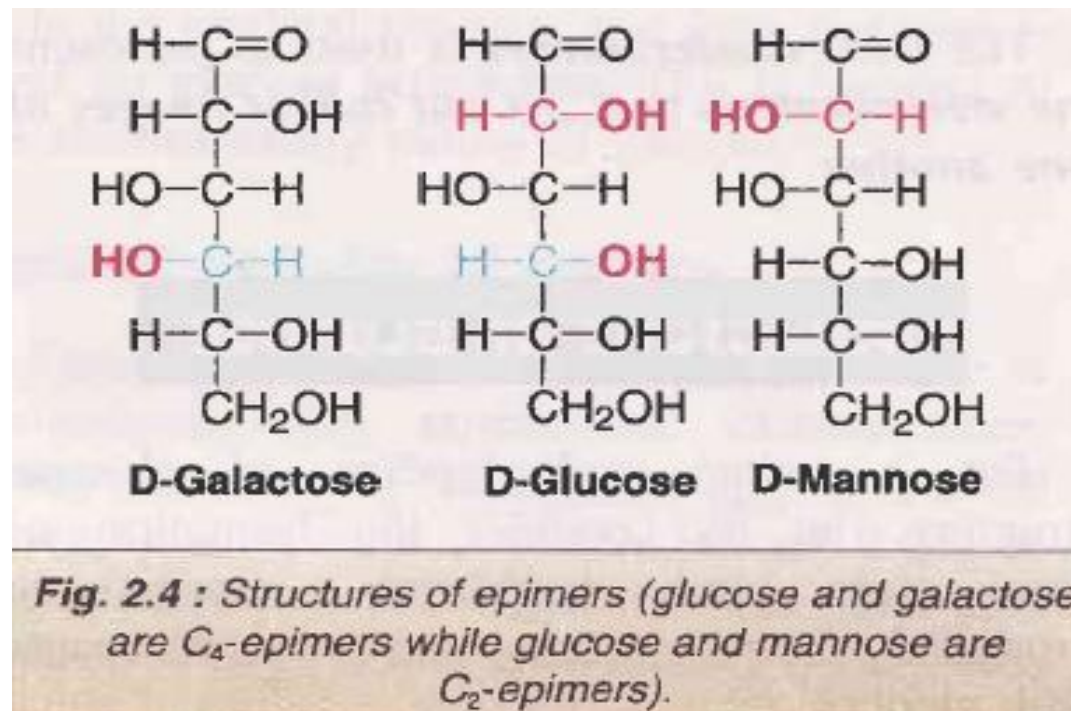
## D and L-isomers:-

The D and L isomers are mirror images of each other. The spatial orientation of -H and -OH groups on the carbon atom (C5 for glucose) that is adjacent to the terminal primary alcohol carbon determines whether the sugar is D- or L-isomer. If the -OH group is on the right side, the sugar is of D-series, and if on the left side, it belongs to L-series. The structures of D- and L-glucose based on the reference monosaccharide, D- and L-glyceraldehyde (glycerose) are denoted in Fig.2.1.



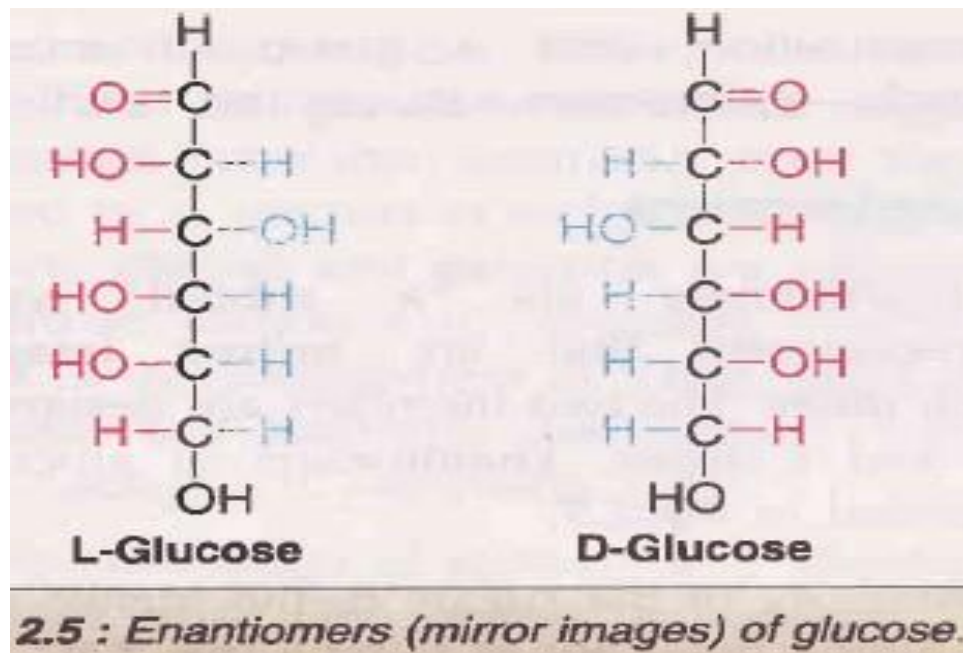
*Fig. 2.1 : D-and-L- forms of glucose compared with D- and L- glyceraldehydes (the reference carbohydrate).*

**Epimers:-** If two monosaccharides differ from each other in their configuration around a single specific carbon (other than anomeric) atom, they are referred to as epimers to each other. **Glucose and galactose** are epimers with regard to carbon 4 (**C<sub>4</sub>-epimers**). They differ in the arrangement of -OH group at C<sub>4</sub>. **Glucose and mannose** are epimers with regard to carbon 2 (**C<sub>2</sub>-epimers**).



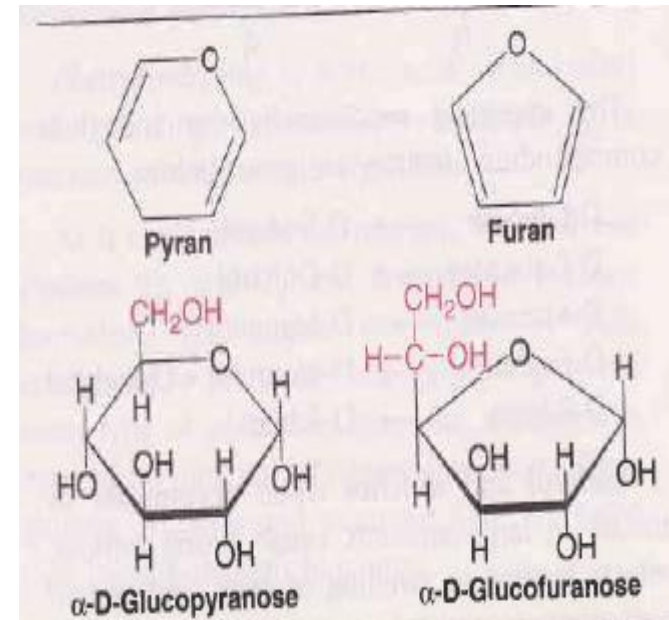
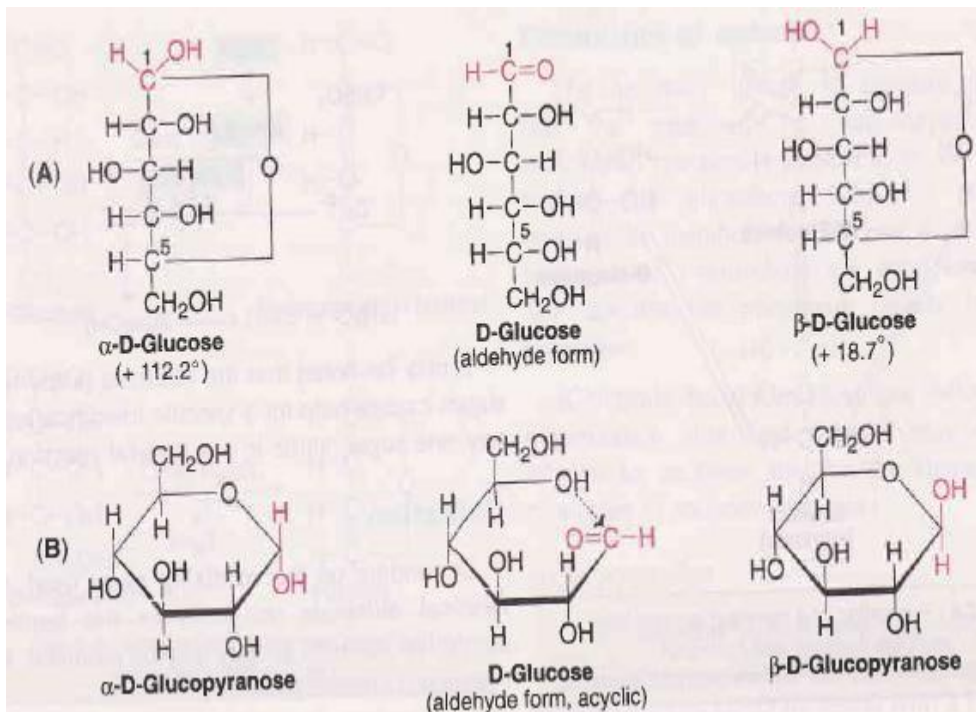
**Enantiomers:-** Enantiomers are a special type of stereoisomers that are mirror images of each other. The two members are designated as D- and L-sugars.

Majority of the sugars in the higher animals (including man) are of **D-type**.



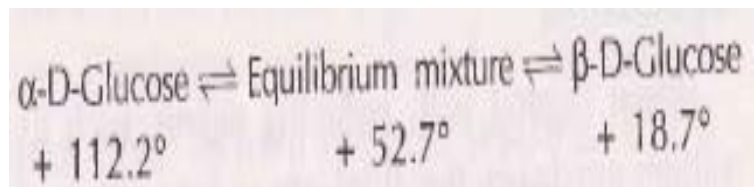
# Linear & Cyclic form

A six-membered ring pyranose (based on pyran) or a five-membered ring furanose (based on furan). The cyclic forms of glucose are known as  $\alpha$ -D-glucopyranose and  $\alpha$ -D-glucofuranos.



**Anomers-** The  $\alpha$  and  $\beta$  **cyclic forms** of D-glucose are known as anomers. They differ from each other in the configuration only around C1 known as anomeric carbon. In case of  $\alpha$  anomer, the -OH group held by anomeric carbon is on the opposite side of the group -CH<sub>2</sub>OH of sugar ring. The reverse is true for  $\beta$  -anomer. The anomers differ in certain physical and chemical properties.

**Mutarotation:-** The  $\alpha$  and  $\beta$  anomers of glucose have different optical rotations. The specific optical rotation of a freshly prepared glucose ( $\alpha$  anomer) solution in water is  $+112.2^\circ$  which gradually changes and attains an equilibrium with a constant value of  $+52.7^\circ$ . In the presence of alkali, the decrease in optical rotation is rapid. The optical rotation of  $\beta$ -glucose is  $+18.7^\circ$ . Mutarotation is defined as the change in the specific optical rotation representing the interconversion of  $\alpha$  and  $\beta$  forms of D-glucose to an equilibrium mixture.



# Disaccharides

A disaccharide consists of two monosaccharide units (similar or dissimilar) held together by a glycosidic bond. They are crystalline, water-soluble and sweet to taste.

The disaccharides are of two types:-

- 1.Reducing disaccharides with free aldehyde or keto group e.g. maltose, lactose.
- 2.Non-reducing disaccharides with no free aldehyde or keto group e.g. sucrose, trehalose.



**Maltose**- is composed of two  $\alpha$ -D-glucose units held together by  **$\alpha$  (1-4) glycosidic bond**. The free aldehyde group present on C1 of second glucose answers the reducing reactions besides the osazone formations (**sunflower-shaped**).

Maltose can be hydrolysed by dilute acid or the enzyme maltase to liberate two molecules of  **$\alpha$ -D-glucose**.

In **isomaltose**, the glucose units are held together by  **$\alpha$  (1-6) glycosidic linkage**.

**Cellobiose** is another disaccharide, identical in structure with maltose, except that the former has  **$\beta$  (1-4) glycosidic linkage**. Cellobiose is formed during the hydrolysis of cellulose.

**Sucrose** (cane sugar) is the sugar of commerce, mostly produced by sugar cane and sugar beets. Sucrose is made up of  $\alpha$ -D-glucose and  $\beta$ -D-fructose. The two monosaccharides are held together by a glycosidic bond ( $\alpha$ 1-  $\beta$ 2), between C1 of  $\alpha$  glucose and C2 of  $\beta$ -fructose. The reducing groups of glucose and fructose are involved in glycosidic bond, hence sucrose is a non-reducing sugar, and it cannot form osazones.

Sucrose is the major carbohydrate produced in photosynthesis. It is transported into the storage organs of plants (such as roots, tubers and seeds).

Sucrose is the most abundant among the naturally occurring sugars. It has distinct advantages over other sugars as a storage and transport form.

This is due to the fact that in sucrose, both the functional groups (aldehyde and keto) are held together and protected from oxidative attacks.

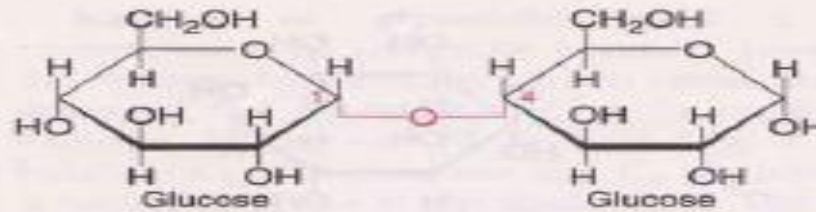
**Sucrose** is an important source of dietary carbohydrate. It is sweeter than most other common sugars (except fructose) namely glucose, lactose and maltose. Sucrose is employed as a sweetening agent in food industry. The intestinal enzyme-sucrase-hydrolyses sucrose to glucose and fructose which are absorbed.

**Lactose** is more commonly known as milk sugar since it is the disaccharide found in milk. Lactose is composed of  $\beta$ -D-galactose and  $\beta$ -D-glucose held together by  $\beta$  (1-4) glycosidic bond. The anomeric carbon of C1 glucose is free, hence lactose exhibits reducing properties and forms osazones (powder-puff or hedgehog shape). Lactose of milk is the most important carbohydrate in the nutrition of young mammals. It is hydrolysed by the intestinal enzyme lactase to glucose and galactose.

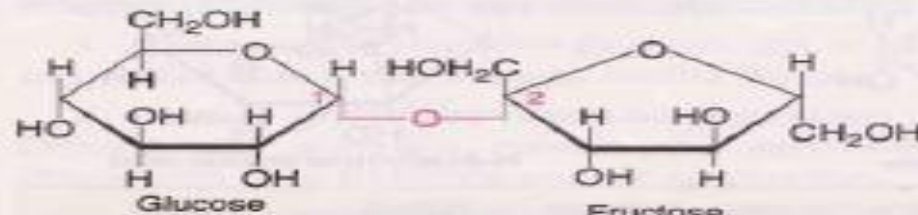
**Inversion of Sucrose:-** Sucrose, as such is dextrorotatory ( $+66.5^\circ$ ). But, when hydrolysed, sucrose becomes levorotatory ( $-28.2^\circ$ ). The process of change in optical rotation from dextrorotatory (+) to levorotatory (-) is referred to as inversion. The hydrolysed mixture of sucrose, containing glucose and fructose, is known as **invert sugar**.

Hydrolysis of sucrose by the enzyme sucrase (invertase) or dilute acid liberates one molecule each of glucose and fructose. It is postulated that sucrose (dextro) is first split into  $\alpha$ -D-glucopyranose ( $+52.5^\circ$ ) and  $\beta$ -D-fructofuranose, both being dextrorotatory.  $\beta$ -D-fructofuranose is less stable and immediately gets converted to  $\beta$ -D-fructopyranose which is strongly levorotatory ( $-92^\circ$ ). The overall effect is that dextro sucrose ( $+66.5^\circ$ ) on inversion is converted to levo form ( $-28.2^\circ$ ).

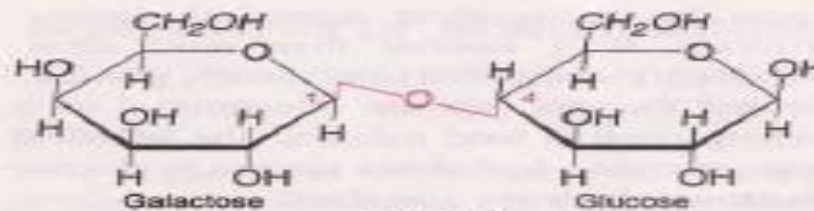
# Structures



**Maltose**  
( $\alpha$ -D-glucosyl (1  $\rightarrow$  4)  $\alpha$ -D-glucose)



**Sucrose**  
( $\alpha$ -D-glucosyl (1  $\rightarrow$  2)  $\beta$ -D-fructose)



**Lactose**  
( $\beta$ -D-galactosyl (1  $\rightarrow$  4)  $\beta$ -D-glucose)

# Polysaccharides

Polysaccharide (simply glycans) consist of repeat units of monosaccharides or their derivatives, held together by glycosidic bonds.

They are primarily concerned with two important functions-structural, and storage of energy. Polysaccharides are linear as well as branched polymers. This is in contrast to structure of proteins and nucleic acids which are only linear polymers. The occurrence of branches in polysaccharides is due to the fact that glycosidic linkages can be formed at any one of the hydroxyl groups of a monosaccharide.

Polysaccharides are of two types-

**1.Homopolysaccharides:** Which on hydrolysis yield only a **single type** of monosaccharide. They are named based on the nature of the monosaccharide unit. Thus, glucans are polymers of glucose whereas fructosans are polymers of fructose.

**2.Heteropolysaccharides:** Which on hydrolysis yield a mixture of a few monosaccharides or their derivatives.



# Homopolysaccharides

## Starch-

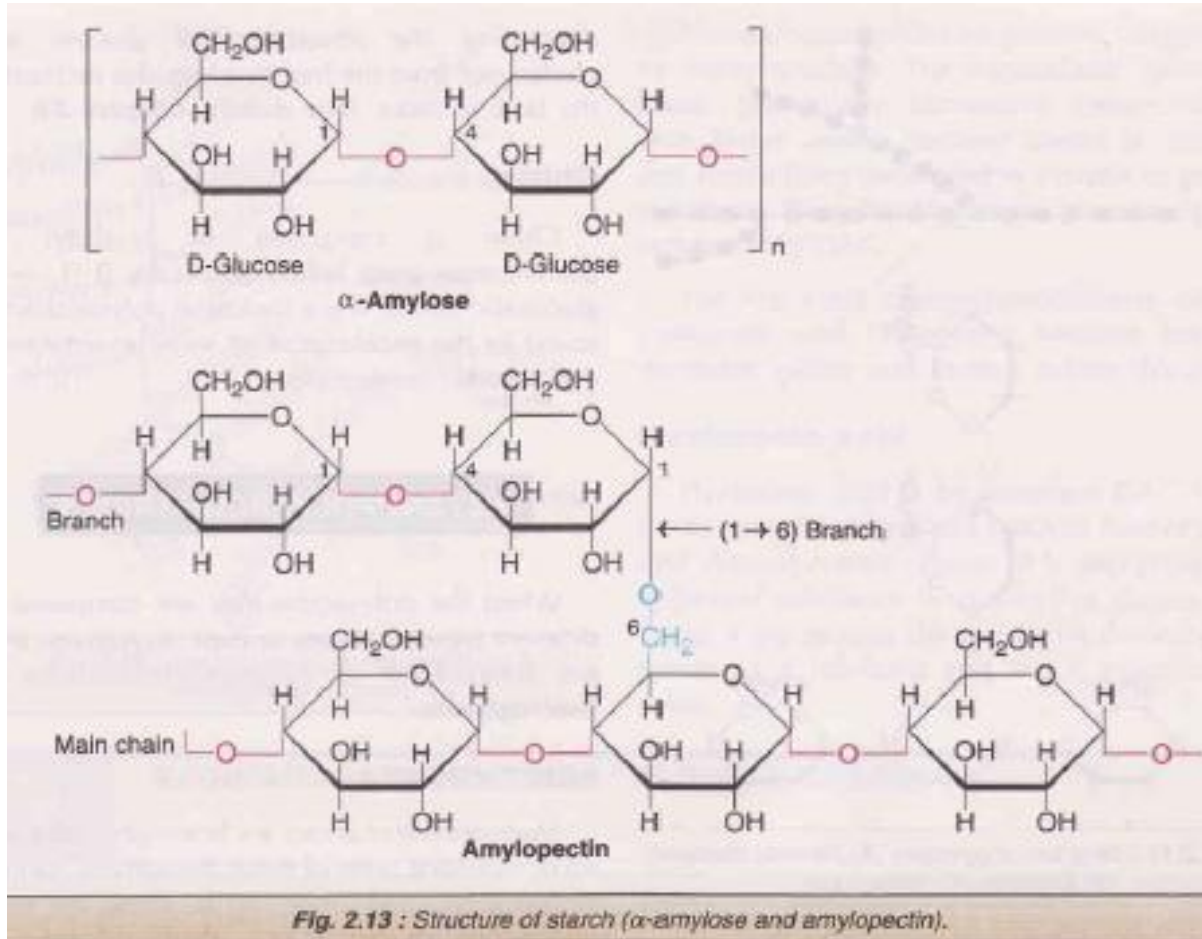
Starch is the carbohydrate reserve of plants which is the most important dietary source for higher animals, including man. High content of starch is found in cereals, roots, tubers, vegetables etc. Starch is a homopolymer composed of D-glucose units held by  $\alpha$ -glycosidic bonds. It is known as glucosan or glucan.

Starch consists of two polysaccharide components-water soluble amylose (15-20 %) and a water insoluble amylopectin (80-85 %). Chemically, amylose is a long unbranched chain with 200-1,000 D-glucose units held by  $\alpha$  (1--->4) glycosidic linkages.

**Amylopectin** is a branched chain with  $\alpha$  (1---->6) glycosidic bonds at the branching points and  $\alpha$  (1--->4) linkages. Amylopectin molecule containing a few thousand glucose units looks like a branched tree (20-30) glucose units per branch).

Starches are hydrolysed by amylase (pancreatic or salivary) to liberate dextrans, and finally maltose and glucose units. Amylase acts specifically on  $\alpha$  (1--->4) glycosidic bonds.

# Structures



## Dextrins-

Dextrins are the breakdown products of starch by the enzyme amylase or dilute acids. Starch is sequentially hydrolysed through different dextrins and, finally, to maltose and glucose.

The various intermediates (identified by iodine colouration) are soluble starch (blue), amyloextrin (violet), erythroextrin (red) and achroextrin (no colour).

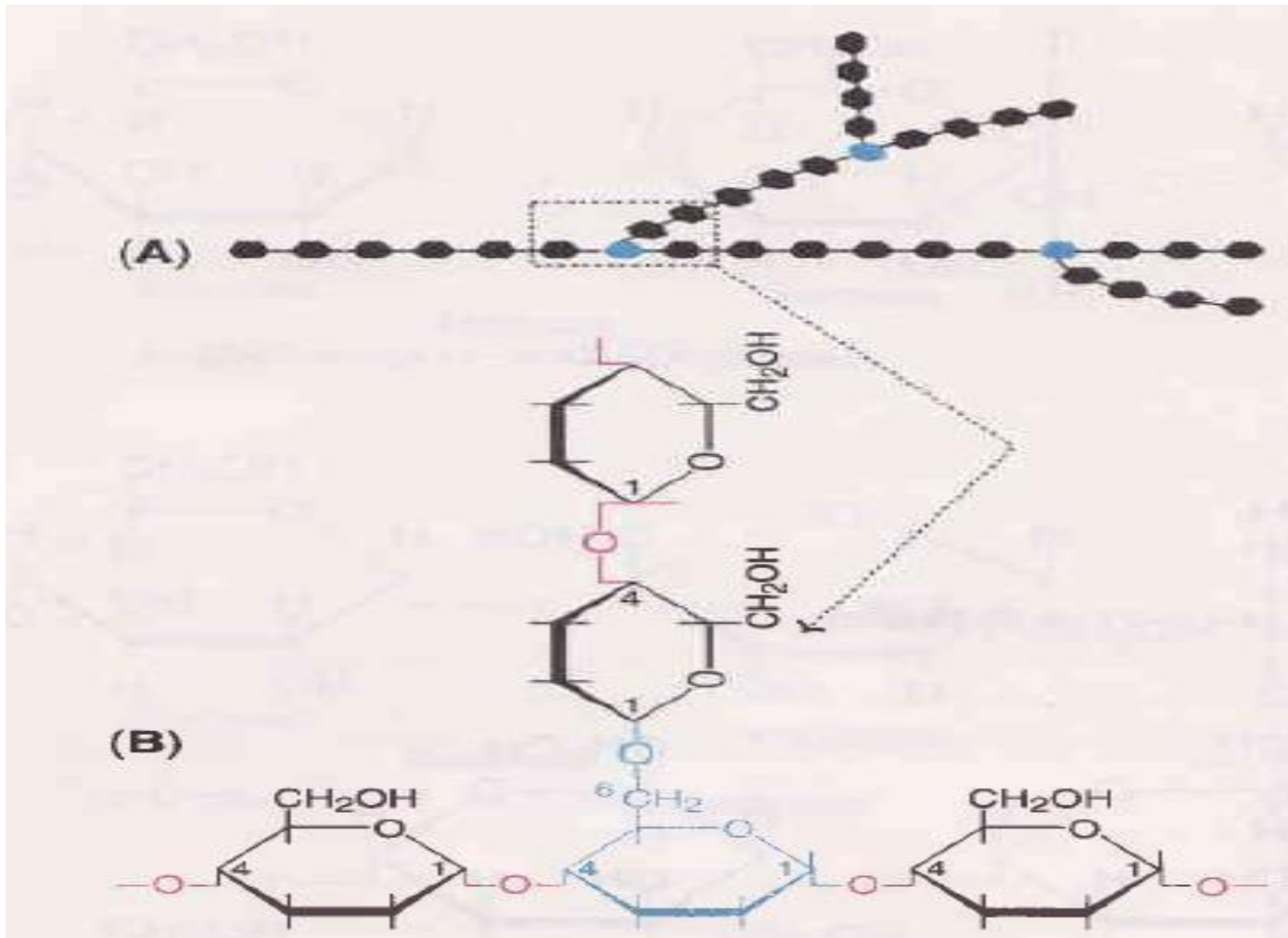
## Inulin-

Inulin is a polymer of fructose i.e., fructosan. It occurs in dahlia bulbs, garlic, onion etc. It is a low molecular weight (around 5,000) polysaccharide easily soluble in water. Inulin is not utilized by the body. It is used for assessing kidney function through measurement of **glomerular filtration rate (GFR)**.

# Glycogen-

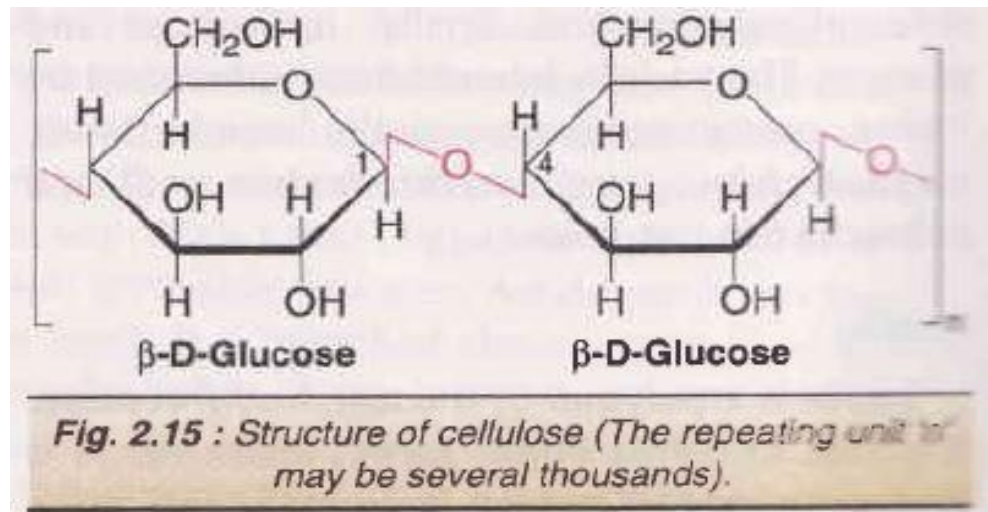
Glycogen is the carbohydrate reserve in animals, often referred to as **animal starch**. It is present in high concentration in liver, followed by muscle, brain etc. Glycogen is also found in plants that do not possess chlorophyll (e.g. yeast, fungi).

The structure of glycogen is similar to that of amylopectin with more number of branches. Glucose is the repeating unit in glycogen joined together by  $\alpha$  (1 $\rightarrow$ 4) glycosidic bonds, and  $\alpha$  (1 $\rightarrow$ 6) glycosidic bonds at branching points. The molecular weight (up to  $10^8$ ) and the number of glucose units (up to 25,000) vary in glycogen depending on the source from which glycogen is obtained.



Structure of glycogen

# Cellulose-



Cellulose occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. It is a predominant constituent of plant cell wall. Cellulose is totally absent in animal body.

Cellulose is composed of  $\beta$ -D-glucose units linked by  $\beta$  (1 $\rightarrow$ 4) glycosidic bonds.

Cellulose cannot be digested by mammals including man-due to lack of the enzyme that cleaves  $\beta$ -glycosidic bonds (a amylase breaks bonds only).

Ruminants and herbivorous animals contain microorganisms in the gut which produce enzymes that can cleave  $\beta$ -glycosidic bonds. Hydrolysis of cellulose yields a disaccharide cellobiose, followed by  $\beta$ -D-glucose.

Cellulose, though not digested, has great importance in human nutrition. It is a major constituent of fiber, the non-digestible carbohydrate. The functions of dietary fiber include decreasing the absorption of glucose and cholesterol from the intestine, besides increasing the bulk of faeces.

## **Chitin:-**

Chitin is composed of N-acetyl D glucosamine units held together by  $\beta$  (1 $\rightarrow$ 4) glycosidic bonds. It is a structural polysaccharide found in the exoskeleton of some invertebrates e.g. insects, crustaceans.



# Heteropolysaccharides

When the polysaccharides are composed of different types of sugars or their derivatives, they are referred to as heteropolysaccharides or heteroglycans.

## MUCOPOLYSACCHARIDES-

Mucopolysaccharides are heteroglycans made up of repeating units of sugar derivatives, namely amino sugars and uronic acids. These are more commonly known as **glycosaminoglycans (GAG)**. Acetylated amino groups, besides sulfate and carboxyl groups are generally present in GAG structure. The presence of sulfate and carboxyl groups contributes to acidity of the molecules, making them acid mucopolysaccharides.

Some of the mucopolysaccharides are found in combination with proteins to form mucoproteins or mucoids or proteoglycans.

**Mucoproteins** may contain up to **95 % carbohydrate** and **5 % protein**.

Mucopolysaccharides are essential components of tissue structure. The extracellular spaces of tissue (particularly connective tissue-cartilage, skin, blood vessels, tendons) consist of collagen and elastin fibers embedded in a matrix or ground substance. The ground substance is predominantly composed of GAG.

The important mucopolysaccharides include hyaluronic acid, chondroitin 4- sulfate, heparin, dermatan sulfate and keratan sulfate.

### **Hyaluronic acid:-**

Hyaluronic acid is an important GAG found in the ground substance of synovial fluid of joints and vitreous humor of eyes. It is also present as a ground substance in connective tissues, and forms a gel around the ovum. Hyaluronic acid serves as a lubricant and shock absorbant in joints.

Hyaluronic acid is composed of alternate units of D-glucuronic acid and N-acetyl D-glucosamine. These two molecules form disaccharides units held together by  **$\beta$  (1--->3) glycosidic bond**. Hyaluronic acid contains about 250-25,000 disaccharides unit (held by  $\beta$  1--->4 bonds) with a molecular weight up to 4 million.

## **Hyaluronidase:-**

It is an enzyme that breaks ( $\beta$  1--->4 linkages) hyaluronic acid and other GAG. This enzyme is present in **high concentration in testes, seminal fluid, and in certain snake and insect venoms.** Hyaluronidase of semen is assigned an important role in fertilization as this enzyme clears the gel (hyaluronic acid) around the ovum allowing a better penetration of sperm into the ovum. Hyaluronidase of bacteria helps their invasion into the animal tissues.

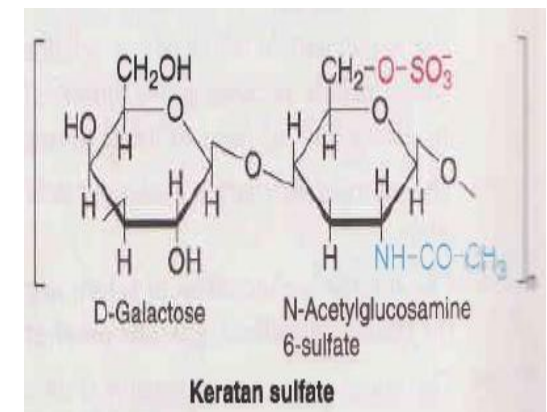
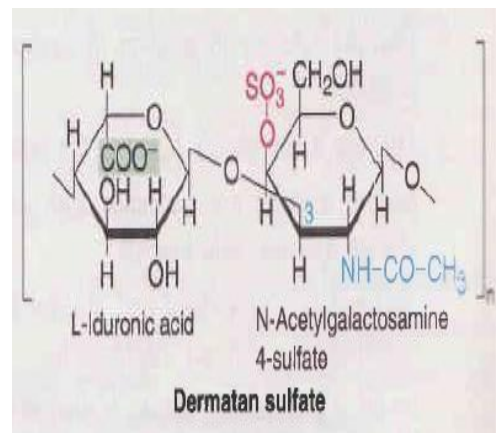
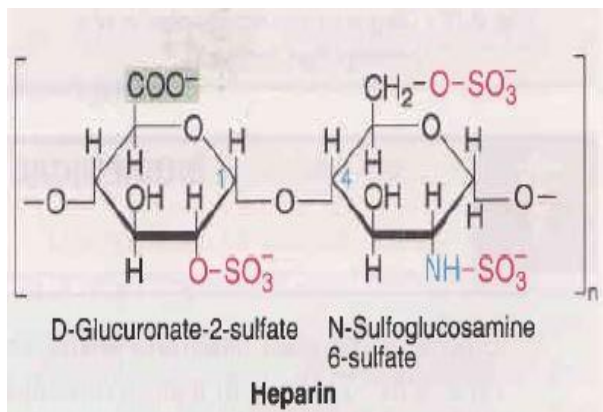
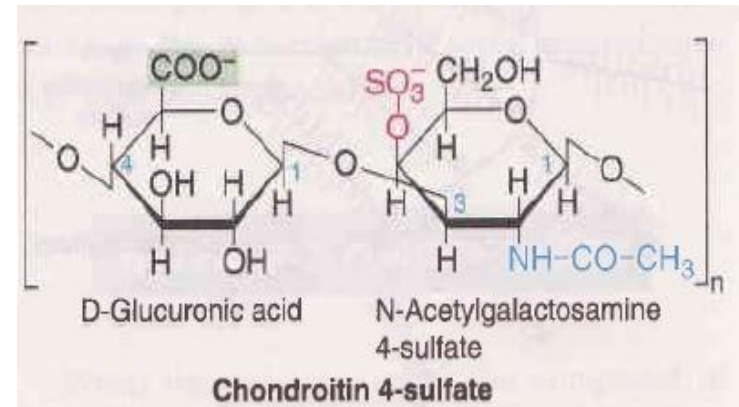
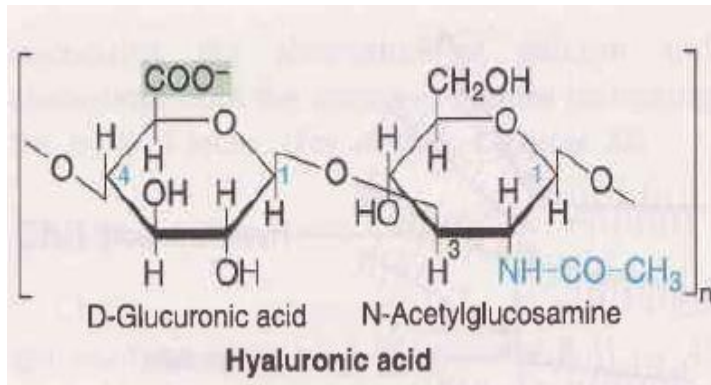
## **Chondroitin sulfates:-**

**Chondroitin 4-sulfate** (Greek: Chondroscartilage) is a major constituent of various mammalian tissues (bone, cartilage, tendons, heart, valves, skin, cornea etc.).

Structurally, it is comparable with hyaluronic acid. Chondroitin 4-sulfate consists of repeating disaccharide units composed of D-glucuronic acid and N-acetyl D-galactosamine 4-sulfate.

**Chondroitin 6-sulfate** is also present in many tissues. As evident from the name, the sulfate group is found on C6 instead of C4.

# Structures of common glycosaminoglycans



## **Heparin:-**

Heparin is an anticoagulant( prevents blood clotting) that occurs in blood, lung, liver, kidney, spleen etc. Heparin helps in the release of the enzyme lipoprotein lipase which helps in clearing the turbidity of lipemic plasma.

Heparin is composed of alternating units of N-sulfo D-glucosamine 6-sulfate and glucuronate 2-sulfate.

## **Dermatan sulfate:-**

The name dermatan sulfate is derived from the fact that this compound mostly occurs in the skin. It is structurally related to chondroitin 4-sulfate. The only difference is that there is an inversion in the configuration around C5 of D-glucuronic acid to form L-iduronic acid.

# Keratan sulfate:-

It is a heterogeneous GAG with a variable sulfate content, besides small amounts of mannose, fructose, sialic acid etc. Keratan sulfate essentially consists of alternating units of D-galactosamine and N-acetylglucosamine 6-sulfate.

TABLE 2.3 A summary of glycosaminoglycans – composition, distribution and functions

<i>Glycosaminoglycan</i>	<i>Composition</i>	<i>Tissue distribution</i>	<i>Function(s)</i>
Hyaluronic acid	D-Glucuronic acid, N-acetylglucosamine	Connective tissue, synovial fluid, vitreous humor	Serves as a lubricant, and shock absorber. Promotes wound healing
Chondroitin sulfate	D-Glucuronic acid, N-acetylgalactosamine 4-sulfate	Cartilage, bone, skin, blood vessel walls	Helps to maintain the structure and shapes of tissues
Heparin	D-Glucuronate 2-sulfate, N-sulfoglucosamine 6-sulfate	Blood, lung, liver, kidney, spleen	Acts as an anticoagulant
Dermatan sulfate	L-Iduronic acid, N-acetyl-galactosamine 4-sulfate	Blood vessel valves, heart valves, skin	Maintains the shapes of tissues
Keratan sulfate	D-Galactose, N-acetyl-glucosamine 6-sulfate	Cartilage, cornea, connective tissues	Keeps cornea transparent

# BACTERIAL CELL WALL POLYSACCHARIDE

The cell walls of many bacteria are made of peptidoglycans, which are heteroglycan chains linked to peptides (murein is another name for peptidoglycan).

The heteroglycan component is composed of alternating residues of N-acetylglucosamine and N-acetylmuramic acid joined by  $\beta(1\rightarrow4)$  linkage. N-acetylmuramic acid consists of N-acetylglucosamine in an ether link with D-lactic acid.

Many such linear polymers lie side by side in the cell wall, cross-linked by short peptides.

The antibacterial action of lysozyme (present in tears) is due to its ability to catalyze the hydrolysis of polysaccharide chain of peptidoglycan.



# Glycoproteins

Proteins are covalently bound to carbohydrates which are referred to as glycoproteins.

The carbohydrate content of glycoprotein varies from 1 % to 90 % by weight.

The term mucoprotein is used for glycoprotein with carbohydrate concentration more than 4 %. Glycoproteins are very widely distributed in the cells and perform variety of functions. These include their role as enzymes, hormones, transport proteins, structural proteins and receptors.

The carbohydrates found in glycoproteins include mannose, galactose, N-acetylglucosamine, N-acetylgalactosamine, xylose, L-fucose and **N-acetylneuraminic acid (NANA)**.

NANA is an important **sialic acid**.

# Functions of Glycoproteins

**Antifreeze glycoproteins** :-The Antarctic fish live below  $-2^{\circ}\text{C}$ , a temperature at which the blood would freeze. It is now known that these fish contain antifreeze glycoprotein which lower the freezing point of water and interfere with the crystal formation of ice. Antifreeze glycoproteins consist of 50 repeating units of the tripeptide, alanine-alanine-threonine.

**Blood group substances**:- The blood group antigens (of erythrocyte membrane) contain carbohydrates as glycoproteins or glycolipids. N-Acetylgalactosamine, galactose, fucose, sialic acid etc. are found in the blood group substances. The carbohydrate content also plays a determinant role in blood grouping.

<i>Glycoprotein(s)</i>	<i>Major function(s)</i>
Collagen	Structure
Hydrolases, proteases, glycosidases	Enzymes
Ceruloplasmin	Transport
Immunoglobulins	Defense against infection
Synovial glycoproteins	Lubrication
Thyrotropin, erythropoietin	Hormones
Blood group substances	Antigens
Fibronectin, laminin	Cell-cell recognition and adhesion
Intrinsic factor	Absorption of vitamin B <sub>12</sub>
Fibrinogen	Blood clotting

**THANKS**