# UNIT-3 CARBOHYDRATES

## CARBOHYDRATES

Carbohydrates**,** together with lipids, proteins and nucleic acids, are one of the four major classes of biologically essential organic molecules found in all living organisms. Carbohydrates, all coming from the process of photosynthesis, represent the major part of organic substance on Earth, are the most abundant organic components in the major part of fruits, vegetables, legumes and cereal grains, carry out many functions in all living organisms and are the major energy source for humans.

They act as storehouses of chemical energy (glucose, starch, glycogen). Carbohydrates make up about three fourths of the dry weight of plants. Less than 1% of the body weight of animals is made up of carbohydrates. They are produced in photosynthesis by condensation of $CO_2$ and $H_2O$ in presence of light energy and the pigment chlorophyll.

$$nCO_2 + nH_2O + \text{energy} \xrightarrow[\text{chlorophyll}]{\text{sunlight}} C_nH_{2n}O_n + nO_2$$

The name carbohydrate means hydrate of carbon and derives from the formula $Cn(H_2O)n$. Not all carbohydrates, however, have this general formula. Some contain too few oxygen atoms to fit this formula, and some others contain too many oxygens.

The carbohydrates are a major source of metabolic energy, both for plants and for animals that depend on plants for food. Carbohydrates are called saccharides or if they are relatively small, sugars.

**Definition:** Carbohydrates are polyhydroxy aldehydes or ketones, or substances that yield such compounds on hydrolysis. Carbohydrates have the empirical formula $(CH_2O)$ n.

The term generated from carbonand hydrate; though some also contain nitrogen, phosphorus, or sulfur. Chemically, carbohydrates are molecules that are composed of carbon, along with hydrogen and oxygen- usually in the same ratio as that found in water ($H_2O$).

There are three major classes of carbohydrates:

1. **Monosaccharides**: Monosaccharides, or simple sugars, consist of a single polyhydroxy aldehyde or ketone unit. The most abundant monosaccharide in nature is the six-carbon sugar D-glucose, sometimes referred to as dextrose.

2. **Oligosaccharides:** Oligosaccharides consist of short chains of monosaccharide units, or residues, joined by characteristic linkages called glycosidic bonds. The most abundant are the disaccharides, with two monosaccharide units. Example: sucrose (cane sugar).

3. **Polysaccharides:** The polysaccharides are sugar polymers containing more than 20 or so monosaccharide units, and some have hundreds or thousands of units. Example: starch. Polysaccharides are of two types based on their function and composition. Based on function, polysaccharides are of two types, storage and structural.

A. Storage polysaccharide - starch.

B. Structural polysaccharide - cellulose.

**General properties of carbohydrates**

• Carbohydrates act as energy reserves, also stores fuels, and metabolic intermediates.

• Ribose and deoxyribose sugars forms the structural frame of the genetic material, RNA and DNA.

• Polysaccharides like cellulose are the structural elements in the cell walls of bacteria and plants.

• Carbohydrates are linked to proteins and lipids that play important roles in cell interactions.

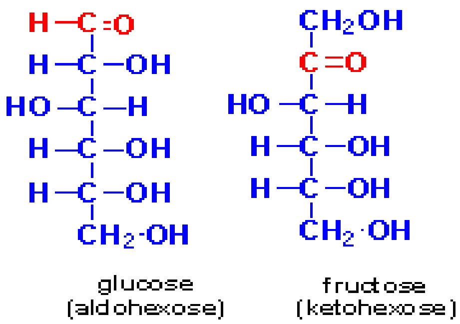
• Carbohydrates are organic compounds; they are aldehydes or ketones with many hydroxyl groups. Physical Properties of Carbohydrates

**Physical Properties of Carbohydrates**

**• Steroisomerism -** When the molecular formula is same in various substances, but the arrangement of same groups or atoms in space is different. This phenomenon is called stereo isomerism and these substances are called stereo isomers. Compounds that have the same structural formula but differ in spatial configuration are known as stereoisomers and the phenomenon is called sterioisomerism.

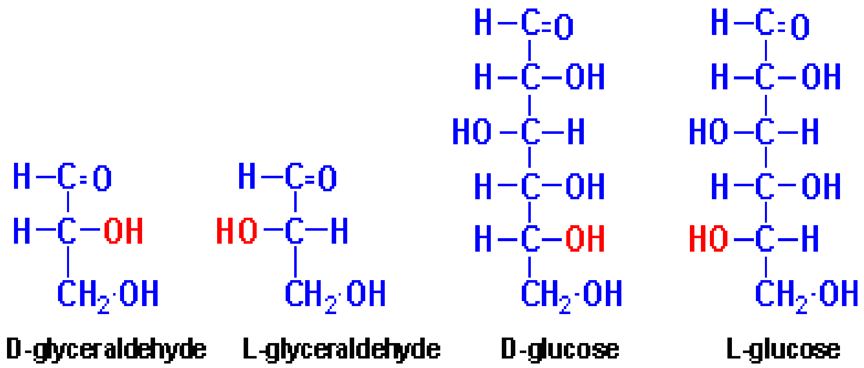
### 1. Aldose ketose isomers

In this type of isomerism the 2 isomers have same structural formula but differ in the carbonyl carbon; one contains aldehyde group and the other contains ketone group e.g. glucose and fructose each of them has the same structural formula C6(H2O)6 but glucose has aldehyde group and fructose has ketone group




### 2. D and L isomers

A monosaccharide can be found either in D form or L form; in D form the hydroxyl group at the penultimate carbon (the carbon before the last carbon) is on the right side while in L form the hydroxyl group at penultimate carbon is on the left side e.g. D-glyceraldehyde and L-glyceraldehyde, also D-glucose and L-glucose. D-sugars are the most abundant forms in humans

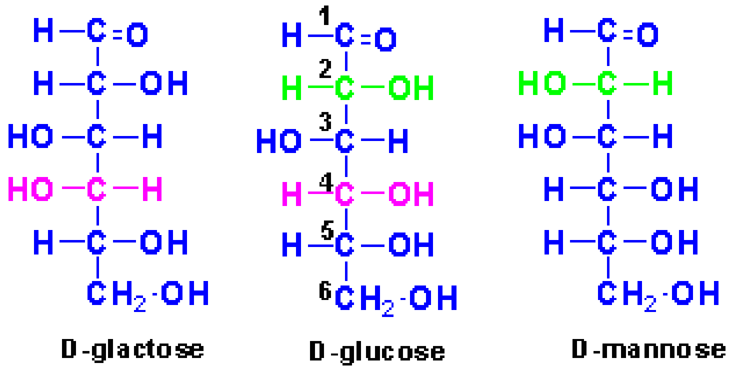



### 3. Epimers

Epimers differ in configuration around one carbon atom other than the carbonyl carbon and the penultimate carbon.

Glucose and galactose have the same structural formula $C_6 H_{12} O_6$ but differ only in the position of the hydroxyl group at C4; glucose has hydroxyl group at C4 on the right side while galactose has hydroxyl group at C4 on the left side. So glucose and galactose are C4 epimers.

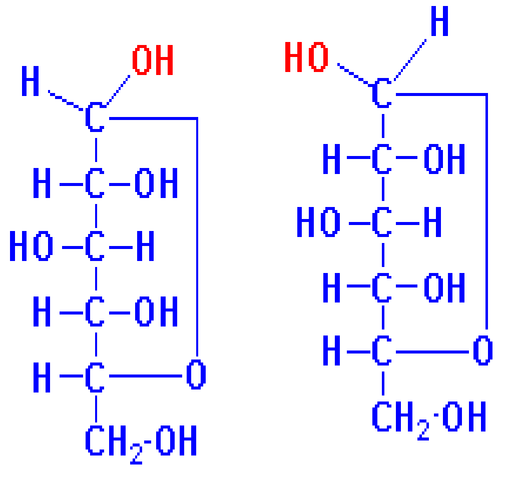
Also, glucose and mannose have the same structural formula $C_6 H_{12} O_6$ but differ only in the position of the hydroxyl group at C2; glucose has hydroxyl group at C2 on the right side while mannose has hydroxyl group at C2 on the left side. So glucose and mannose are C2 epimers.




**4. α and β isomers**

These are monosaccharides that differ in configuration only around the carbonyl carbon in cyclic structure. A monosaccharides in cyclic structure can exist either in α or β configuration.

- In α form the hydroxyl group attached to the carbonyl carbon is on the right side.
- In β form the hydroxyl group attached to the carbonyl carbon is on the left side.
- In monosaccharide solutions, in α or β forms are in equilibrium and can be readily converted to each other.



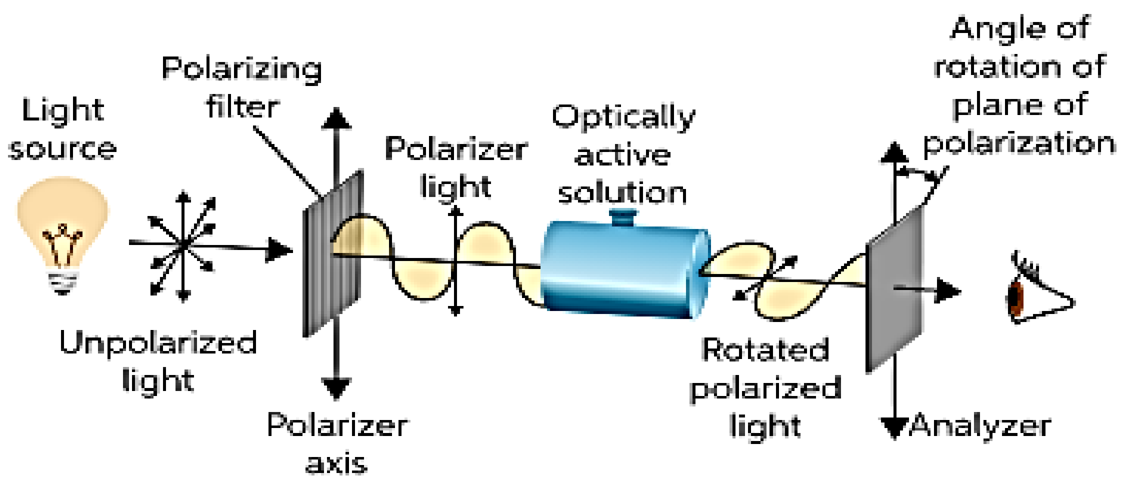
α D-glucose  β D-glucose

## III- Optical activity

It is the ability of the compound to rotate plane polarized light to the right or to the left. Plane polarized light is the light that its waves pass in the same plane by the action of special prisms.

- If the compound rotates plane polarized light to the right, it is dextrorotatory (d or +).
- If the compound rotates plane polarized light to the left, it is levorotatory (l or -).

The angle of rotation is measured by polarimeter and is affected by many factors such as the source of light, nature and concentration of substance and temperature.



Each optically active substance has a specific angle of rotation. For example, the specific rotation for glucose is +52.5 o and for fructose is -91 o.

**Biological Importance**

• Carbohydrates are chief energy source, in many animals; they are instant source of energy. Glucose is broken down by glycolysis/ kreb's cycle to yield ATP.

• Glucose is the source of storage of energy. It is stored as glycogen in animals and starch in plants.

• Stored carbohydrates act as energy source instead of proteins.

• Carbohydrates are intermediates in biosynthesis of fats and proteins.

• Carbohydrates aid in regulation of nerve tissue and are the energy source for brain.

• Carbohydrates get associated with lipids and proteins to form surface antigens, receptor molecules, vitamins and antibiotics.

• They form structural and protective components, like in cell wall of plants and microorganisms.

• In animals they are important constituent of connective tissues.

•They participate in biological transport, cell-cell communication and activation of growth factors.

• Carbohydrates those are rich in fibre content help to prevent constipation.

• Also they help in modulation of immune system.

**Monosaccharides**

• The word "Monosaccharides" derived from the Greek word "Mono" means Single and "saccharide" means sugar

• Monosaccharides are polyhydroxy aldehydes or ketones which cannot be further hydrolysed to simple sugar.

• Monosaccharides are simple sugars. They are sweet in taste. They are soluble in water. They are crystalline in nature.

• They contain 3 to 10 carbon atoms, 2 or more hydroxyl (OH) groups and one aldehyde (CHO) or one ketone (CO) group.

**Classification of Monosaccharides**

Monosaccharides are classified in two ways.

a) First of all, based on the number of carbon atoms present in them and

b) Secondly based on the presence of carbonyl group.

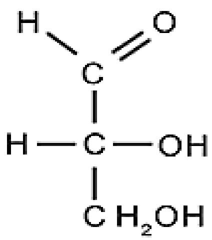
The naturally occurring monosaccharides contain three to seven carbon atoms per molecule. Monosaccharides of specific sizes may be indicated by names composed of a stem denoting the number of carbon atoms and the suffix -ose. For example, the terms triose, tetrose, pentose, and hexose signify monosaccharides with, respectively, three, four, five, and six carbon atoms. Monosaccharides are also classified as aldoses or ketoses. Those monosaccharides that contain an aldehyde functional group are called aldoses; those containing a ketone functional group on the second carbon atom are ketoses. Combining these classification systems gives general names that indicate both the type of carbonyl group and the number of carbon atoms in a molecule. Thus, monosaccharides are described as aldotetroses, aldopentoses, ketopentoses, ketoheptoses, and so forth. Glucose and fructose are specific examples of an aldohexose and a ketohexose, respectively.

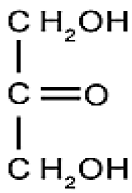
**Trioses**

Trioses are "Monosaccharides" containing 3 carbon atoms. The molecular formula of triose is $C_3H_6O_3$

**Characteristics**

- Trioses are simple sugars
- They are soluble in water
- They are sweet in taste.
- The triose may contain an aldehyde group (aldotriose) or a ketone group (ketotriose). Example Glycerose and Dehydroxyacetone





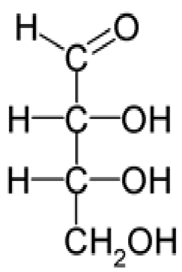
D-Glyceraldehyde Dihydroxyacetone

**Tetroses**

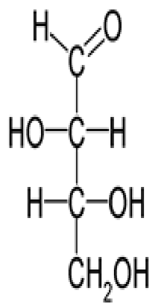
Tetroses are “Monosaccharides” containing 4 carbon atoms. The molecular formula of tetrose is $C_4H_8O_4$

**Characteristics**

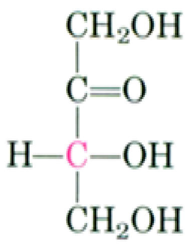
- Tetroses are simple sugars
- Tetroses are soluble in water
- They are sweet in taste.
- They are crystalline forms.
- The tetroses may contain an aldehyde group (aldotetrose) Erythrose forms. or a ketone group (ketotetrose) Erythrulose.



Erythrose



Treose



Erytrulose

**Pentoses**

Pentoses are “Monosaccharides” containing 5 carbon atoms. It is an important component of “nucleic acid”. The molecular formula of Pentose is $C_5H_{10}O_5$

**Characteristics**

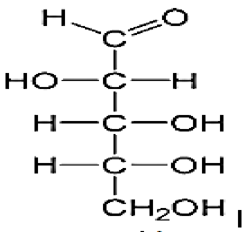
• Pentoses are simple sugars

• Pentoses are soluble in water

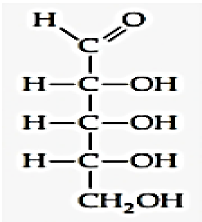
• They are sweet in taste.

• They are crystalline forms.

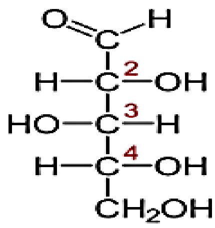
• The pentoses may contain an aldehyde group (aldopentose) or a ketone group (ketopentose).



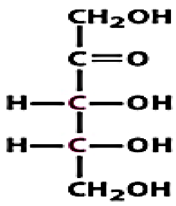
D- Arabinose



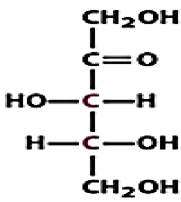
D – Ribose



D- Xylose



D-Ribulose



D-Xylulose

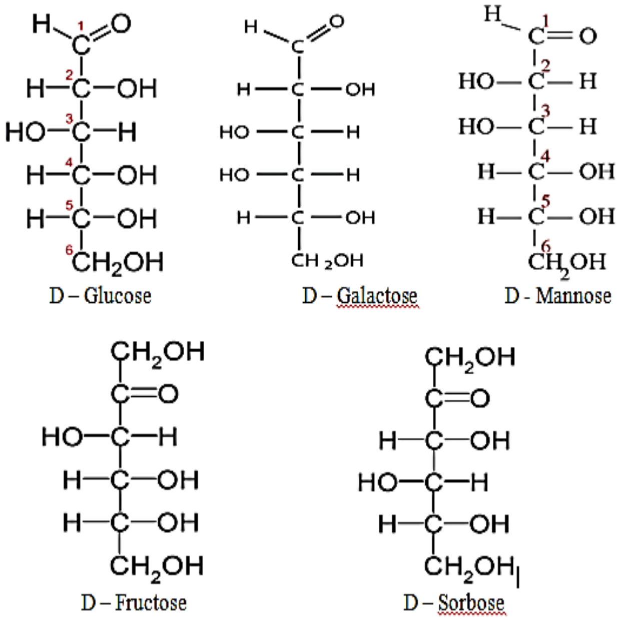
**Hexoses**

Hexoses are “Monosaccharides containing 6 carbon atoms. The molecular formula is of Hexose is $C_6H_{12}O_6$

**Characteristics**

• Hexoses are simple sugars
• Hexoses are soluble in water
• They are sweet in taste.
• They are crystalline forms.
• The Hexoses may contain an aldehyde group (aldohexose) or ketone group (ketohexose).

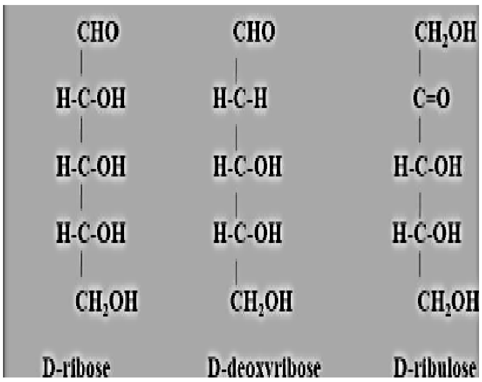
Hexoses- Consists of 6 carbons. Aldohexose D – Glucose, D-Galactose, D-Mannose and and Ketohexose D- Fructose, D- Sorbose.




## Structure of Monosaccharides

1. Straight or Open Chain Structure arranged in a straight line. It is also called open chain structure because the two ends remain separate and they are not linked. Open chain structures are of two types –

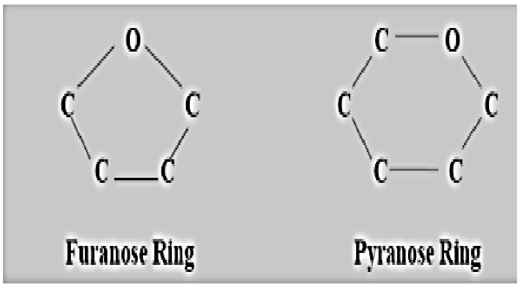
- a) Structure proposed by Fittig and Baeyer
- b) Structure proposed by Fischer known as Fischer's Projection Formula




2. Cyclic or Ring Structure: Haworth (1929) proposed this formula and hence the name Haworth's Projection Formula. The sugar molecules exist in two type of rings which are as follows

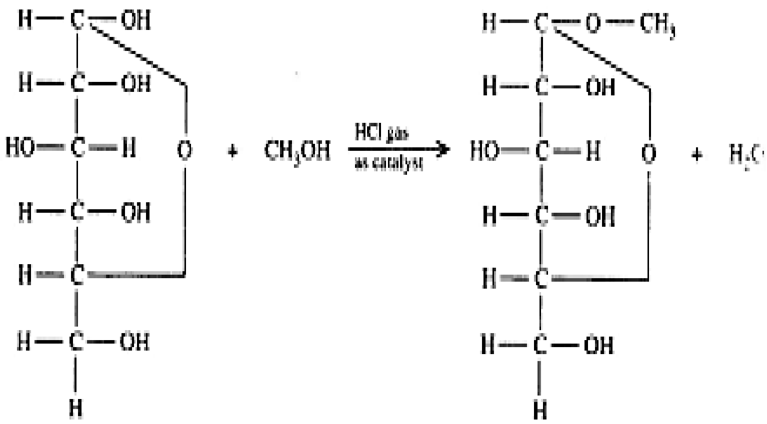
a) Furanose Ring – 5 membered rings

b) Pyranose Ring- 6 membered ring



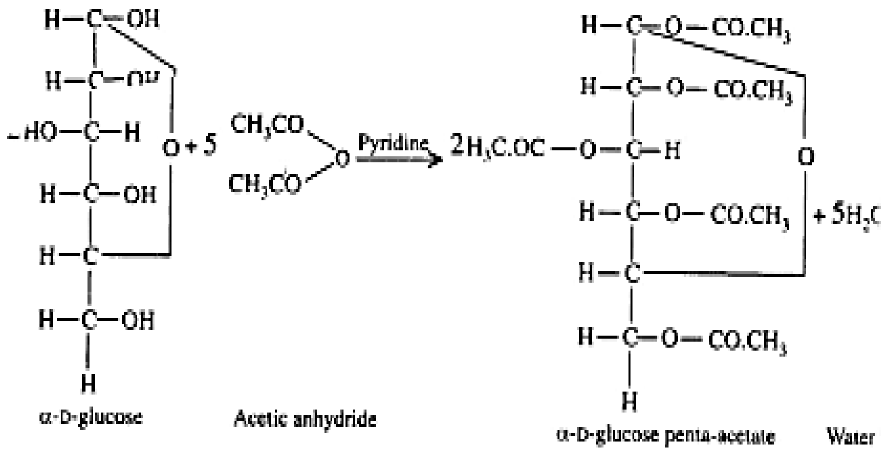

**Properties of Monosaccharides**

1. Colour – colourless
2. Shape - crystalline
3. Solubility – water soluble
4. Taste - sweet
5. Optical activity – Optically active. (a) Dextrorotatory ('d' form) and (b) Levorotatory ('l' form)
6. Mutarotation – The change in specific rotation of an optically active compound is called mutarotation. +1120 +52.50 +190 α-D-glucose β -D-glucose
7. Glucoside formation –




Glucose + Methyl alcohol = Methyl glucoside + $H_2O$

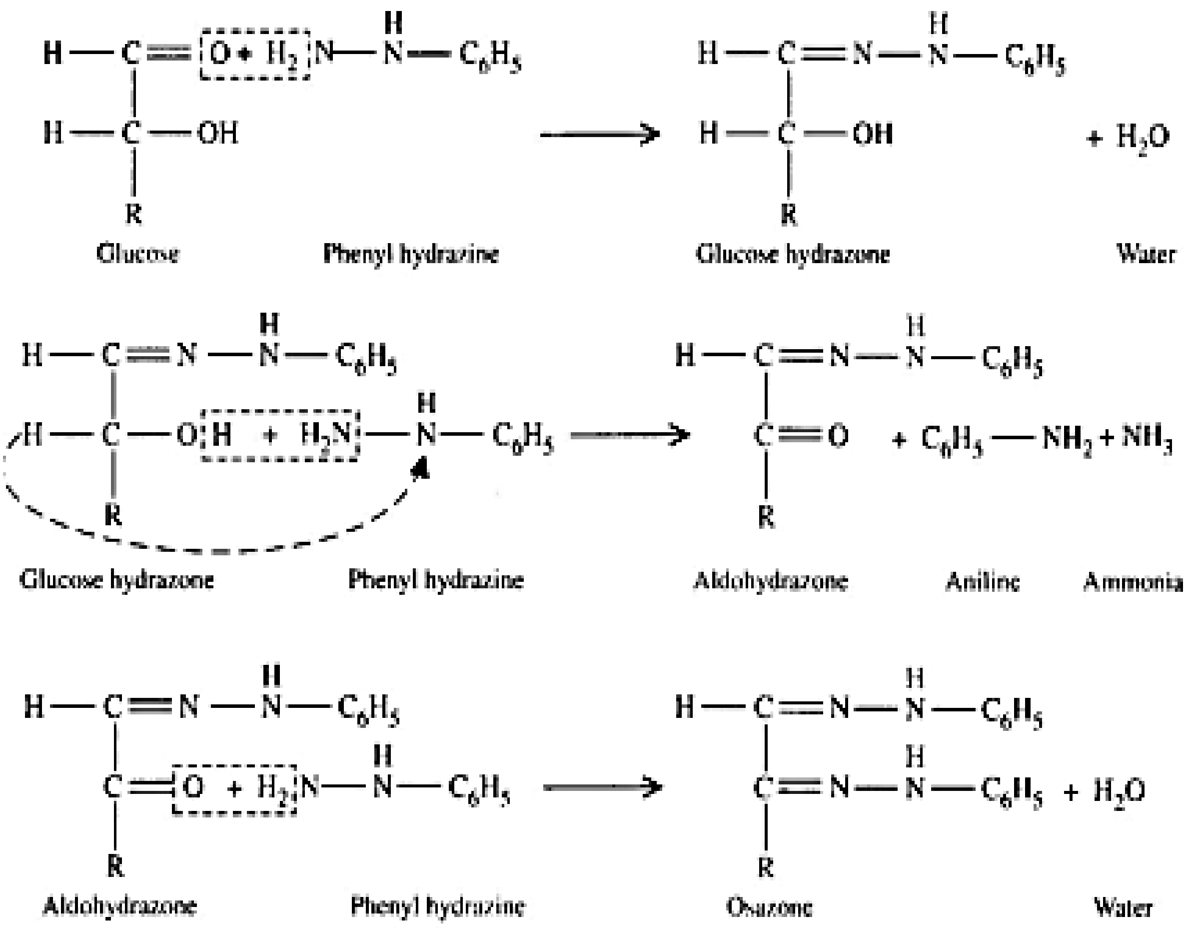
8. Esterification –




9. Reducing agents – Monosaccharides reduce oxidizing agent such as hydrogen peroxide. In such reaction, sugar is oxidized at the carbonyl group and oxidizing agent becomes reduced.

$C_6H_{12}O_6$ + 2 $Cu(OH)_2$→$C_6H_{12}O_7$ + $Cu_2O$ + $2H_2O$ Glucose Fehling's Gluconic Cuprous solution acid oxide

10. Formation of Osazone



**Disaccharides**

Disaccharides consist of two sugars joined by an O-glycosidic bond. The most abundant disaccharides are sucrose, lactose and maltose. Other disaccharides include isomaltose, cellobiose and trehalose.

The disaccharides can be classified into:
1. Homodisaccharides
2. Heterodisaccharides.

**Homodisaccharides** are formed of single monosaccharide units

| **Homodisaccharides** | **Maltose (malt sugar )** | **Isomaltose** | **Cellobiose** |
|---|---|---|---|
| **Structure** | 2α-glucose | 2 α-glucose | 2β-D-glucose |
| **Type of bond** | α-1-4 glucosidicbond | α1-6 glucosidicbond | β1-4 glucosidicbond. |
| **Anomeric Carbon** | Free | Free | Free |
| **Reducing Property** | Reducing | Reducing | Reducing |
| **Produced by** | It is produced from starch by the action of amylase | by the hydrolysis of some polysaccharides such as dextran | by the acid hydrolysis of cellulose |

**Heteropolysaccharides** are formed of two different monosaccharide units

| Heterodisaccharides | Sucrose | Lactose |
|---|---|---|
| Composition | α-D-glucose+ β–D-fructose | β-D-galactose and β-D-glucose |
| Type of bond | α-1-β-2 glucosidic bond OR β 2-α-1 fructosidic bond | a β (1 → 4) galactosidic bond |
| Anomeric C | no free aldehyde or ketone group | free |
| Reducing property | is not a reducing sugar | Reducing |
| Composition | α-D-glucose+β–D-fructose | β-D-galactose and β-D-glucose |
| Effect of hydrolysis | The hydrolysis of sucrose to glucose and fructose is catalysed by sucrase (also called invertase) | Hydrolysed by the intestinal lactase enzyme into galactose and glucose |
| Present in | Table sugar<br>Cane sugar,<br>beet sugar | Milk sugar<br>It may appear in urine in late pregnancy and |

## Polysaccharides

Polysaccharides contain hundreds or thousands of carbohydrate units

• Polysaccharides are not reducing sugars, since the anomeric carbons are connected through glycosidic linkages.

• Nomenclature: Homopolysaccharide- a polysaccharide is made up of one type of monosaccharide unit Heteropolysaccharide- a polysaccharide is made up of more than one type of monosaccharide unit

## Starch

• Starch is a polymer consisting of D-glucose units.

• Starches (and other glucose polymers) are usually insoluble in water because of the high molecular weight, but they can form thick colloidal suspensions with water.

• Starch is a storage compound in plants, and made of glucose units

• It is a homopolysaccharide made up of two components: amylose and amylopectin.

• Most starch is 10-30% amylose and 70-90% amylopectin.

• Amylose – a straight chain structure formed by 1,4 glycosidic bonds between α-D-glucose molecules. Structure of Amylose Fraction of Starch

• The amylose chain forms a helix.

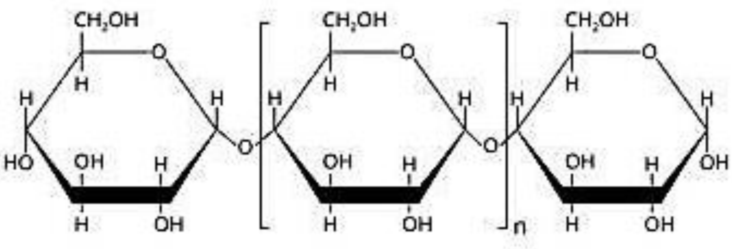
• This causes the blue colour change on reaction with iodine.

• Amylose is poorly soluble in water, but forms micellar suspensions

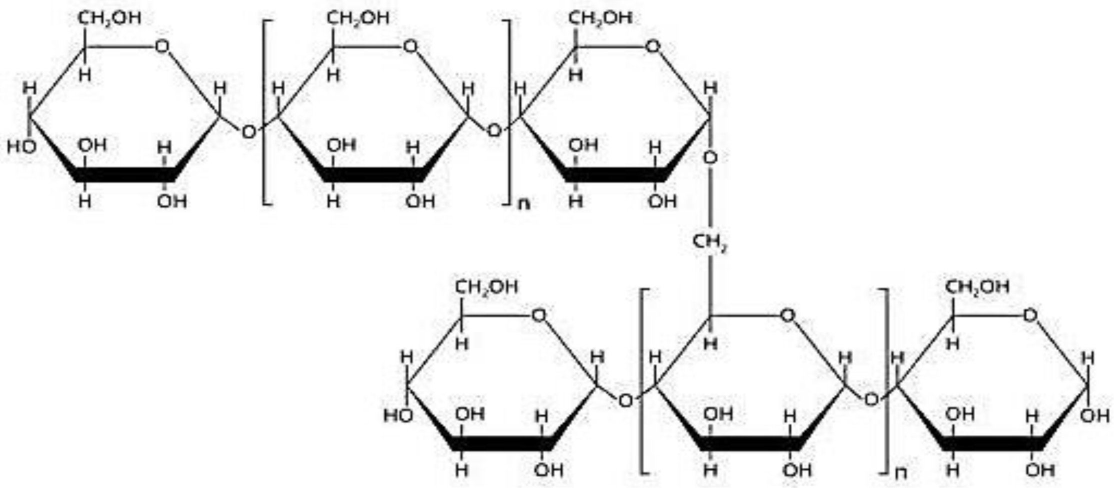
• Amylopectin-a glucose polymer with mainly α -(1→4) linkages, but it also has branches formed by α -(1→6) linkages. Branches are generally longer than shown above. Structure of Amylopectin Fraction of Starch

• Amylopectin causes a red-violet colour change on reaction with iodine.

• This change is usually masked by the much darker reaction of amylose to iodine.




Amylose




Amylopectin

**Glycogen**

• Storage polysaccharide in animals

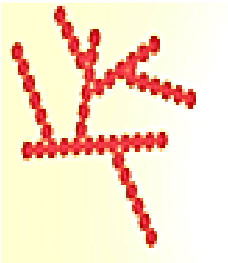
• Glycogen constitutes up to 10% of liver mass and 1-2% of muscle mass

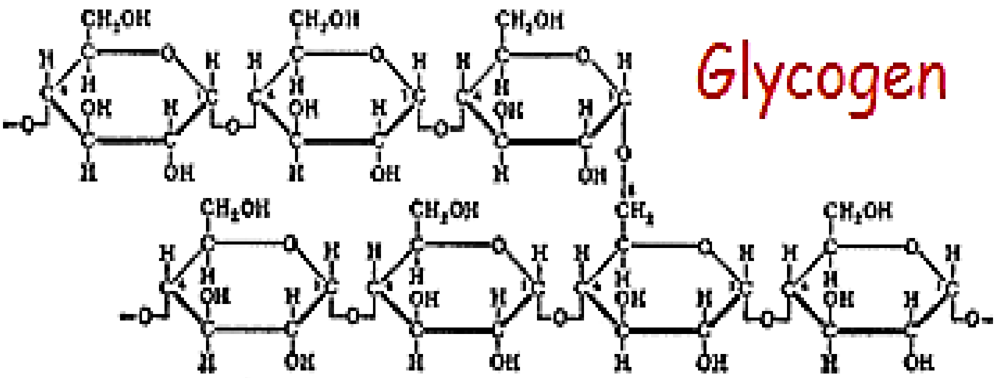
• Glycogen is stored energy for the organism

• Similar in structure to amylopectin, only difference from starch: number of branches

• Alpha (1,6) branches every 8-12 residues

• Like amylopectin, glycogen gives a red-violet color with iodine






**Cellulose**

• The β-glucose molecules are joined by condensation, i.e. the removal of water, forming β-(1, 4) glycosidic linkages.

•The glucose units are linked into straight chains each 100-1000 units long.

•Weak hydrogen bonds form between parallel chains binding them into cellulose microfibrils.

• Cellulose microfibrils arrange themselves into thicker bundles called microfibrils. (These are usually referred to as fibres.)

• The cellulose fibres are often “glued” together by other compounds such as hemicelluloses and calcium pectate to form complex structures such as plant cell walls.

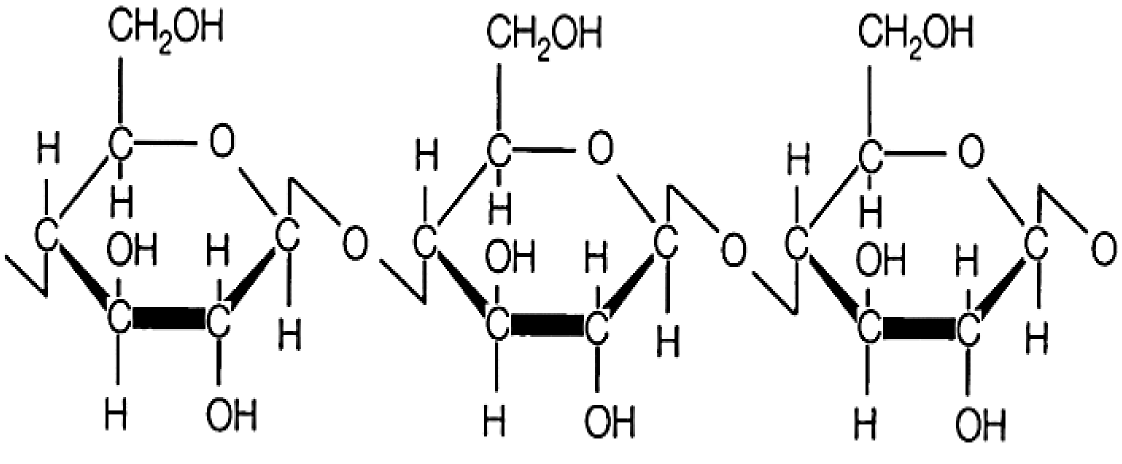
• Because of the β-linkages, cellulose has a different overall shape from amylose, forming extended straight chains which hydrogen bond to each other, resulting in a very rigid structure.

• Cellulose is an important structural polysaccharide, and is the single most abundant organic compound on earth. It is the material in plant cell walls that provides strength and rigidity; wood is 50% cellulose.

• Most animals lack the enzymes needed to digest cellulose, although it does provide needed roughage (dietary fiber) to stimulate contraction of the intestines and thus help pass food along through the digestive system

• Some animals, such as cows, sheep, and horses, can process cellulose through the use of colonies of bacteria in the digestive system which are capable of breaking cellulose down to glucose; ruminants use a series of stomachs to allow cellulose a longer time to digest. Some other animals such as rabbits reprocess digested food to allow more time for the breakdown of cellulose to occur.

• Cellulose is also important industrially, from its presence in wood, paper, cotton, cellophane, rayon, linen, nitrocellulose (guncotton), photographic films (cellulose acetate), etc.



**CHITIN**

• Chitin is a polymer that can be found in anything from the shells of beetlesto webs of spiders. It is present all around us, in plant and animal creatures.

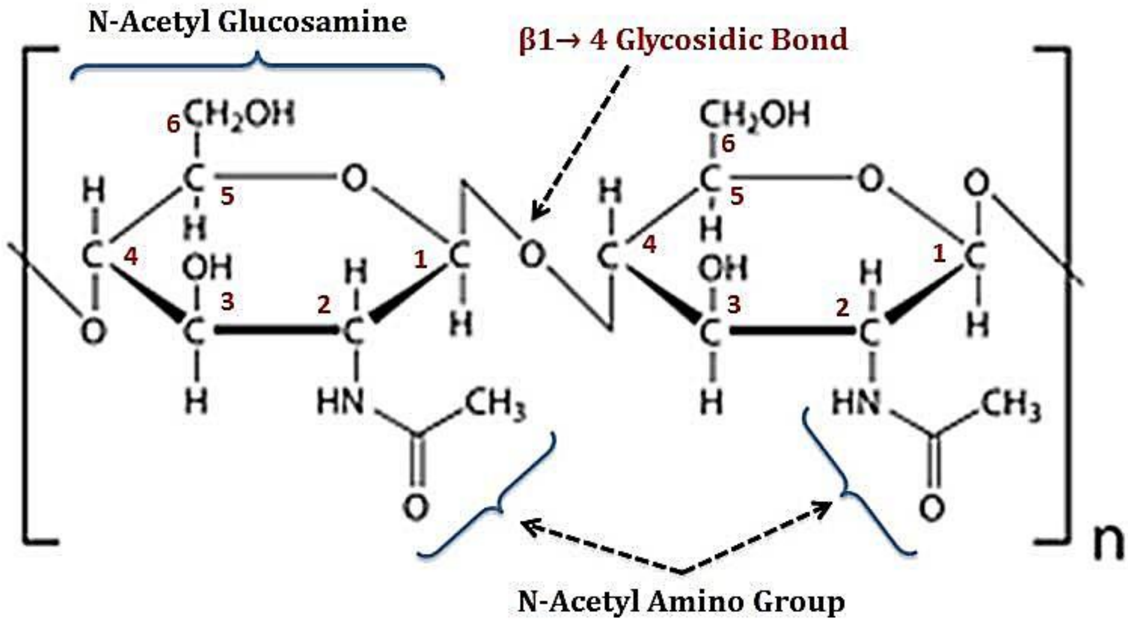
• It is sometimes considered to be a spinoff of cellulose, because the two are very molecularly similar.

• Cellulose contains a hydroxy group, and chitin contains acetamide.

• Chitin is unusual because it is a "natural polymer," or a combination of elements that exists naturally on earth.

• Usually, polymers are man-made. Crabs, beetles, worms and mushrooms contain large amount of chitin.

• Chitin is a very firm material, and it help protect an insect against harm and pressure



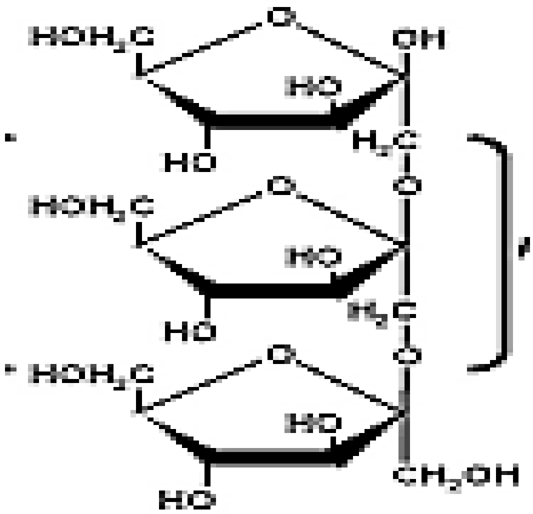

**Chitin**

**Inulin**

• Inulin is stored in the tubers of the dahlia and artichoke and in the roots of dandelion. It is also found in onion and garlic.

• Inulin has a molecular weight of about 5,000 and consists of about 30–35 fructose units per molecule.

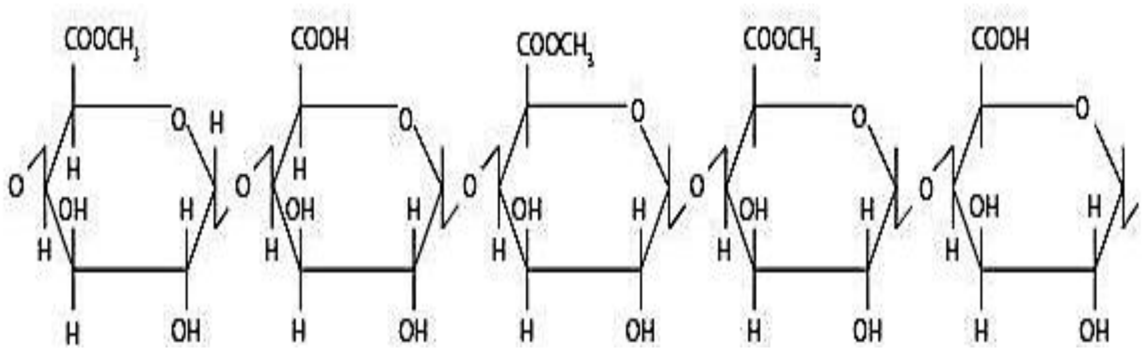
• It is formed in the plants by eliminating a molecule of water from the glycosidic OH group on carbon atom 2 of one group on carbon atom 1 of the adjacent




**Pectin**

• Pectins are found as intercellular substances in the tissues of young plants and are especially abundant in ripe fruits such as guava, apples and pears.

• Pectin is a polysaccharide of carboxyl groups are, either partly or completely, esterified with methyl alcohol and others are combined with calcium or magnesium ions. Chemically, they are called polygalacturonides.

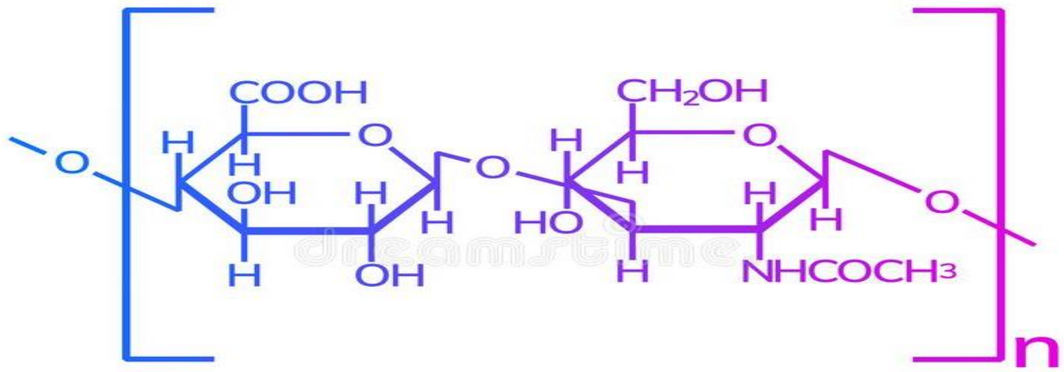



**Mucopolysaccharides**

that are composed not only of a mixture of simple sugars but also of derivatives of sugars such as amino sugars and uronic sugars are called mucopolysaccharides.

**Hyaluronic acid**

It is the most abundant member of mucopolysaccharides and is found in higher animals as a component of various tissues such as the vitreous body of the eye, the umbilical cord and the synovial fluid of joints.It is a straight-chain polymer of D-glucuronic acid and N-acetyl- Dglucosamine (NAG) alternating in the chain. Its molecular weight approaches approximately, 5,000,000. linkages invloved, β-1 → 3 and β-1 → 4



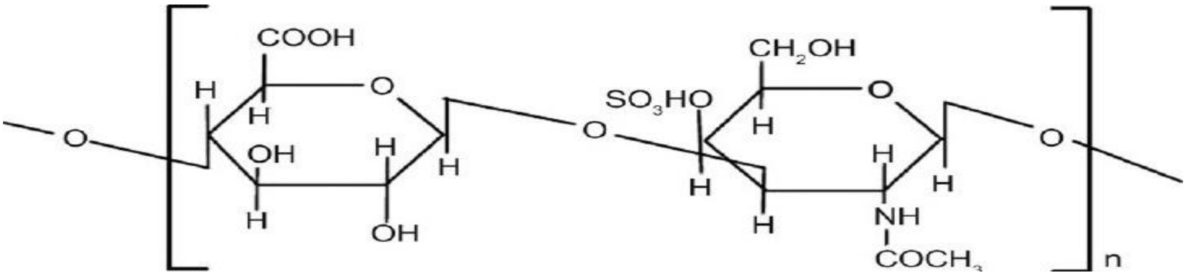

**Chondroitin**

• Chondroitin is of limited distributioin. It is found in cartilage and is also a component of cell coats. It is a parent substance for two more widely distributed mucopolysaccharides, chondroitin sulfate A and chondroitin sulphate B.

• Chondroitin is similar in structure to hyaluronic acid except that it contains galactosamine rather than glucosamine. It is, thus, a polymer of βDglucuronido-1, 3-N-acetyl-D-galactosamine joined by β- 1 → 4 linkages.

• The two chondroitin sulfate A and C are widely distributed and form major structural components of cartilage, tendons and bones.

• Chondroitin sulfates may be regarded as derivatives of chondroitin where, in thegalactosamine moiety, a sulfate group is esterified either at carbon 4 as in chondroitin sulfate A or at carbon 6 as in chondroitin sulfate C • The two linkages involved in both types of chondroitin sulfate would, obviously, be the same. These are β-1 → 3 and β-1 → 4




**Dermatan Sulfate**

Dermatan sulfate is a mucopolysaccharide structurally similar to chondroitinsulfate A except that the D-glucuronic acid is replaced by L-iduronic acid. The two linkages involved are α-1 → 3 and β-1 → 4. Dermatan sulfate is also known byits conventional name, chondroitin sulfate B.

**Keratosulfate**

Keratosulfate differs from other mucopolysaccharides in that the uronic acid component is replaced by D-galactose. Here, the second acetylated amino sugar component (which is N-acetyl-D-glucosamine in this case) is esterified by a sulfate group at carbon 6. Although, the two alternating linkages involved are β-1 → 4 and β-1 → 3, in this case the linkage between the repeating disaccharide units is β-1 →3 rather than β-1 → 4.

**Heparin**

Heparin is composed of D-glucuronic acid units, most of which (about 7 out of every 8) are esterified at $C_2$ and D-glucosamine-N-sulfate units with an additional O-sulfate group at C6. Both the linkages of the polymer are alternating α-1 → 4. Thus, the sulfate content is very high and corresponds to about 5–6 molecules per tetra-saccharide repeating unit.

Heparin acts as an anticoagulant. It prevents coagulation of blood by inhibiting the prothrombin thrombin conversion. This eliminates the effect of thrombin on fibrinogen.