

Carbohydrates are hydrated carbon molecules with the general formula $C_nH_{2n}O_n$ or $(CH_2O)_n$ where n = number of carbon atoms.

Carbohydrates are defined as optically active polyhydroxy aldehydes or ketones or substance that yield one of these compounds on hydrolysis. They are also known as saccharides.

Structure of carbohydrates:

There are three types of structures that comprise carbohydrates:

① Open-chain form. ② Cyclic form ③ Ring form

① Open chain form:

The open chain form of carbohydrate discuss with the example of glucose. The open chain form sugar is linear with its functional group (aldehyde / ketone group) at one end and alcoholic group at the other end. In glucose, carbon atoms are linked one below the other in a linear fashion. The first carbon atom is linked to the aldehyde group ($-CHO$) and the sixth carbon is linked to the alcoholic group ($-CH_2OH$). Carbon 2 through 5 have H on one side and a hydroxy group on the other side. The 2, 4 and 5 carbon atoms have H on their left and OH on their right, whereas in the third carbon atoms, OH on the left and hydrogen is on the right.

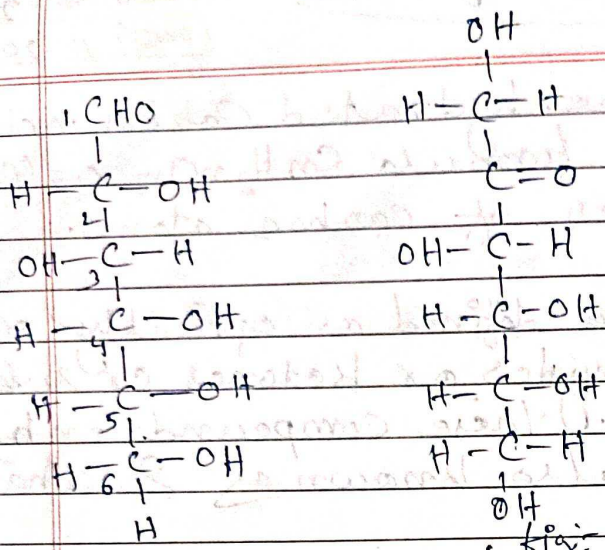


fig: Structure of open chain form of glucose.
 fig: Structure of open chain form of fructose.

② Cyclic form:

Cyclic form of sugar is formed due to cyclization and bond formation between different carbon atoms of that sugar residue. For example in glucose a bond is formed between the carbonyl group of the first carbon and hydroxyl group of the fifth carbon resulting in cyclization of the structure. The cyclic form is called hemiacetal form. If the -OH group of the first carbon of the hemiacetal is on the right side, the sugar is called α -form and if it is on the left side, the sugar is called β -form.

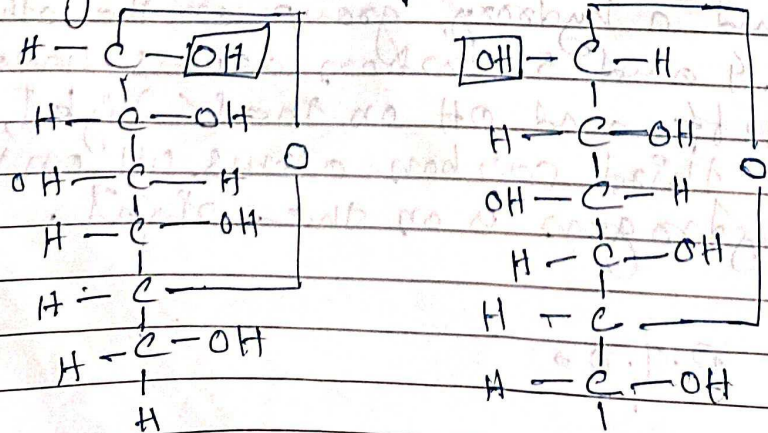


fig: Structure of α -form and β -form of glucose.

③ Ring form:

The ring form of aldoses resembles the structure of a pyran ring. Hence the ring form of aldoses is also known as the pyranose form. The ring form of ketoses resembles the structure of a furan ring. Hence, the ring form of ketoses is also known as the furanose form. If the -OH group of the first carbon of the ring is in the downward direction, that is, below the plane, the sugar is said to be an α -sugar, on the other hand if the -OH group is in the upward direction, that is above the plane, it is said to be an β -sugar.

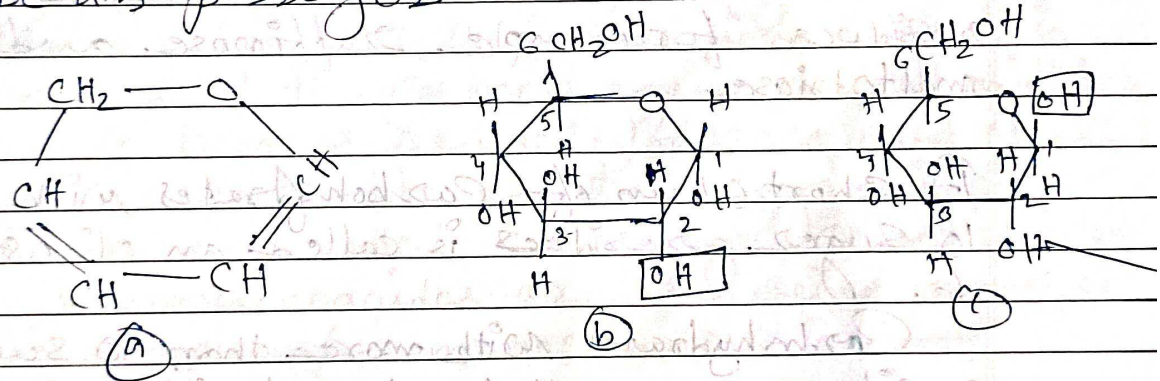


Fig: (a) pyran ring (b) α -D-glucose (c) β -D-glucose.

Classification of Carbohydrates:

Carbohydrates are optically active polyhydroxy aldehydes or ketoses.

Carbohydrates are classified into two groups namely, Sugars and non-sugars.

Classification of Carbohydrates on the basis of number of sugar residues:

Depending on the number of sugar residues carbohydrates can be classified into monosaccharides, disaccharides, trisaccharides and polysaccharides.

* Monosaccharides contain only one sugar residue, for example, glucose.

* Disaccharides contain two sugar residues, for example, maltose is made of two glucose residues, lactose of one glucose residue and one galactose residue, and sucrose of one glucose residue and one fructose residue.

* Trisaccharides have three sugar residues, for example, raffinose and maltotriose.

A short chain of carbohydrates with 4 to 10 sugar residues is called an oligosaccharide.

Carbohydrates with more than 10 sugar residues are called polysaccharides. Starch and cellulose are examples of polysaccharides.

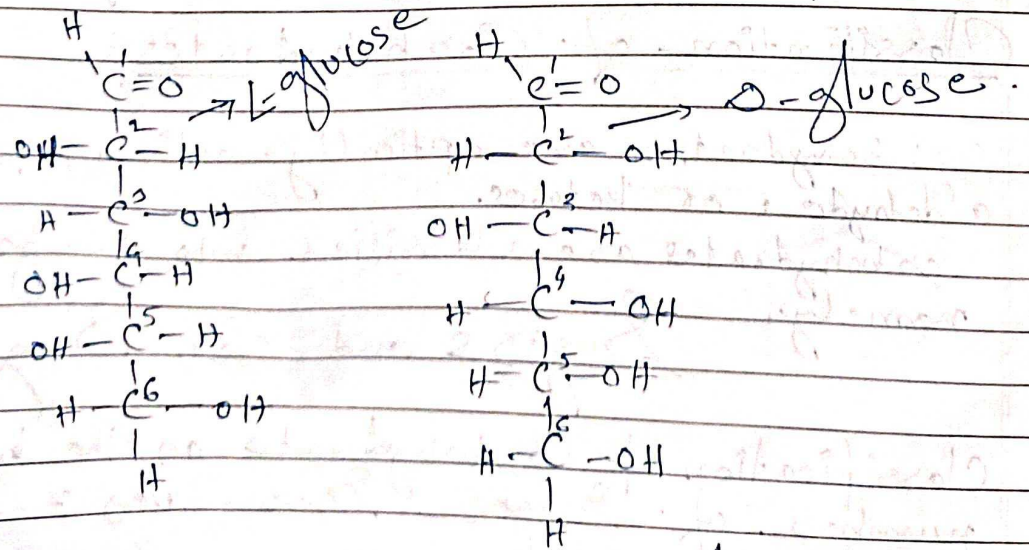


Fig: Structure of α and β glucose

Aldehyde (-CHO) Ketone (=CO)

Hydroxyl (-OH)

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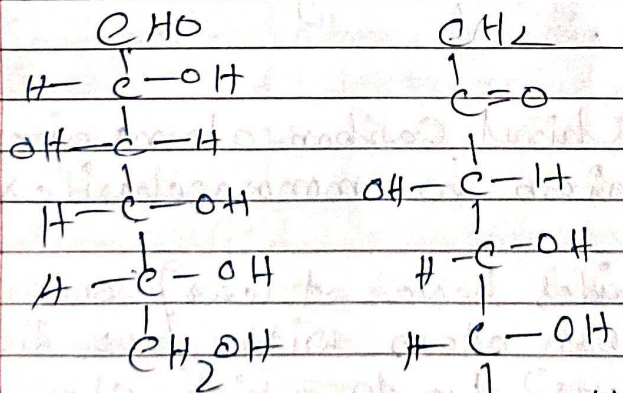
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Monosaccharides:

Monosaccharides are the simple sugars, which possess a free aldehyde (-CHO) or a ^{ketone} (=CO) group and 2 or more hydroxyl group (-OH). They contain 3 to 10 carbon atoms, 2 or more hydroxyl group and one aldehyde (-CHO) or one ketone (=CO) group.

They are represented by general formula $(C_6H_{12}O_6)_n$.

The important properties of monosaccharides is that they readily reduced oxidising agents such as ferricyanide, hydrogen peroxide or cupric ion. In such reactions sugar is oxidized at the carbonyl group and the oxidising agent becomes reduced. Glucose and other sugars capable of reducing oxidising agents are called reducing sugars. So monosaccharides are reducing agents. Example of monosaccharides is:



Glucose.

Fructose.

Based on the number of carbon atoms present, the monosaccharides are named as

Trioses, Tetroses, Pentoses, Hexoses etc.

Name	Formula	Aldose	Ketose
Triose	$C_3H_6O_3$	Glyceraldehyde	Dihydroxyacetone
Tetrose	$C_4H_8O_4$	Erythrose	Erythrulose
Pentose	$C_5H_{10}O_5$	Ribose	Ribulose
Hexose	$C_6H_{12}O_6$	Glucose	Fructose
Heptose	$C_7H_{14}O_7$	Glucoheptose	Sedoheptulose

Based on the type of carbonyl group present the monosaccharides are divided into two groups namely:

Aldoses

Ketoses

Functions of monosaccharides:

① Major source of energy.

Glucose supplies the immediate energy needed by the tissues.

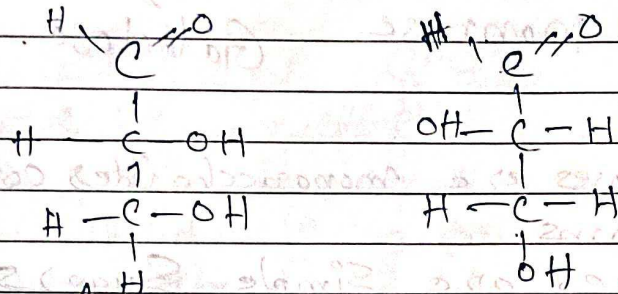
② Components of oligosaccharides and polysaccharides.

Monosaccharides are the structural and functional unit of oligosaccharides and polysaccharides.

Presence of a chiral carbon atom gives rise to stereoisomerism in monosaccharides.

All monosaccharides have at least one chiral atom (i.e. carbon atom with four different functional groups) due to which they exist as stereoisomers. Stereoisomers may be defined as different structural forms of same compound which differ in their spatial arrangement of groups. The possible number of stereoisomers for a monosaccharide depends on the number of chiral carbon atoms and is given by the formula 2^n .

where n = number of chiral atoms in the monosaccharide. For example glyceraldehyde has one chiral carbon atom and hence $2^n = 2^1 = 2$. This implies that there are two stereoisomers for glyceraldehyde. One is L-glyceraldehyde and other is D-glyceraldehyde.



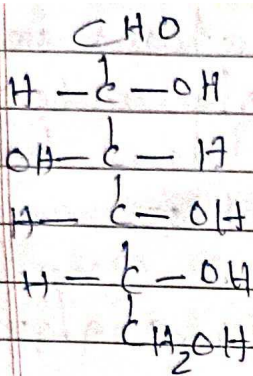
D-glyceraldehyde, L-glyceraldehyde.

Enantiomers:

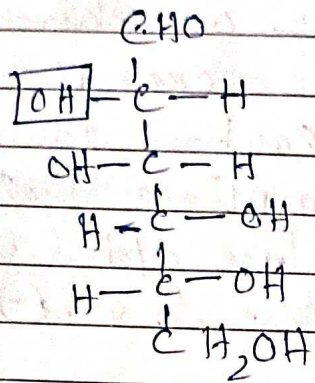
Compounds that deflect plane polarized light to either right or left direction are called enantiomers or optical isomers. Enantiomers are mirror image of each other. Monosaccharides are enantiomers. Monosaccharide that deflect plane polarized light to the right are called dextrorotatory sugars and are denoted as D(+). On the other hand sugars that deflect the light to the left are called levorotatory sugars and are denoted as L(-). Glucose is dextrorotatory sugar, while fructose is a levorotatory sugar.

Epimers:

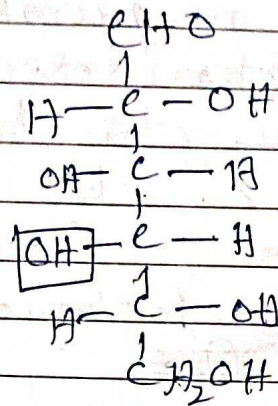
Monosaccharides which differ in the position of the -OH group around a single carbon are called epimers. For example, consider glucose, galactose and mannose. These sugars differ by one carbon which is highlighted in the fig.



Glucose



Mannose



Galactose

Trioses:

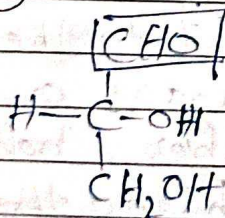
* Trioses are monosaccharides containing 3 carbon atoms.

* Trioses are simple sugars.

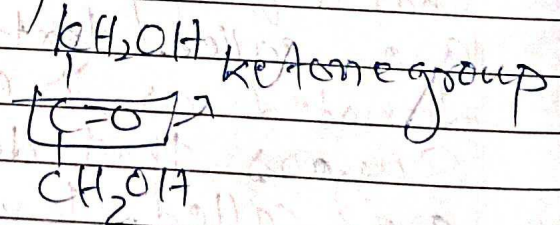
* Trioses are soluble in water.

* They are sweet in taste. They are crystalline forms.

* Trioses may contain an aldehyde (CHO) group or a ketone (CO) group. The trioses containing an aldehyde group is called aldotriose. The trioses containing a ketone group is called ketotrioses or triulose.



Glycerose



Dihydroxyacetone

Fig: Trioses.

Tetroses:

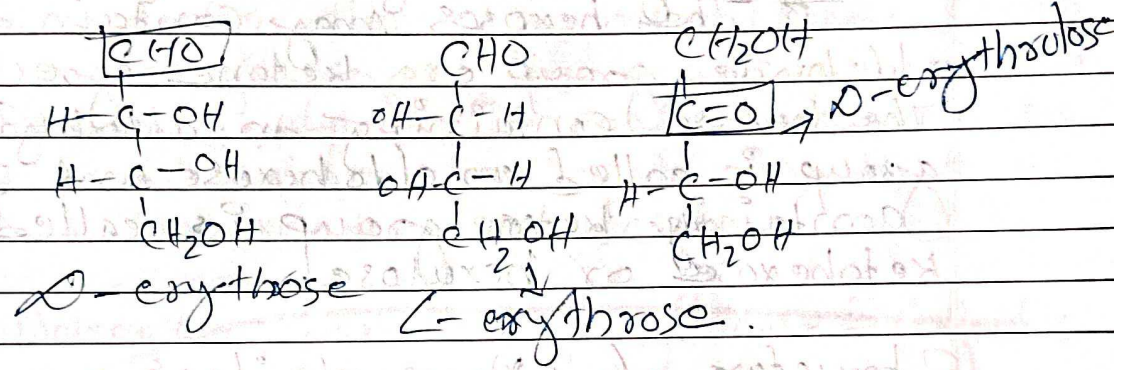
* Tetroses are monosaccharides containing 4 carbon atoms.

* Tetroses are simple sugars.

* Tetroses are soluble in water.

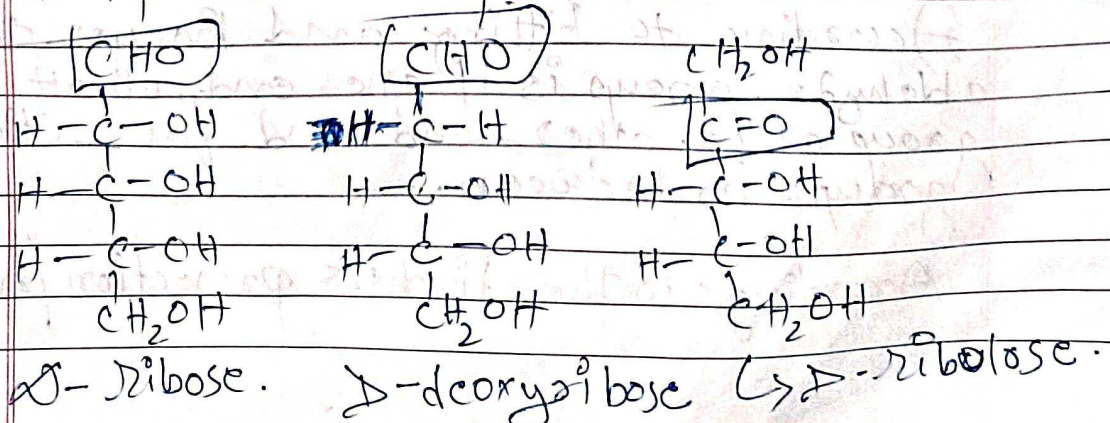
* They are sweet in taste.

- * They are crystalline forms.
- * The tetroses may contain an aldehyde or ketone group.
- * The tetroses containing aldehyde group is called an aldotetrose and the tetrose containing a ketone group is called a ketotetrose.



Pentoses :-

- * Pentoses are the monosaccharides containing 5 carbon atoms.
- * Pentoses are simple sugars.
- * They are soluble in water.
- * They are sweet in taste.
- * They are crystalline forms.
- * The pentose may contain an aldehyde group or a ketone group.
- * The pentose containing an aldehyde group is called an aldopentose and that containing a ketone group is called a ketopentose or pentulose.



Hexoses :-

* Hexoses are monosaccharides containing 6 carbon atoms.

* Hexoses are simple sugars.

* They are soluble in water.

* They are sweet in taste.

* They are crystalline form.

* The hexoses may contain an aldehyde group or a ketone group.

The hexose containing an aldehyde group is called an aldohexose and that containing ketone group is called ketohexose or hexulose.

Structure of a Monosaccharide :-

The monosaccharides may be represented by two structures. They are:

① Straight chain structure or open chain structure.

② Cyclic structure or ring structure.

① Straight chain structure :-

In straight chain structure the carbon atoms of glucose are arranged in a straight line. It is also called open chain structure because the two ends remain separate they are not linked.

According to Fittig and Baeyer, the aldehyde group is at one end, OH group at the other end and four OH groups in between.

According to the Fischer's projection formula

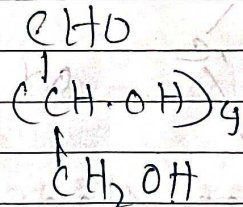
The aldehyde group is placed at one end and the remaining carbon atoms are arranged one behind the other.

The last carbon atom contains two hydrogen atoms and one -OH group (H_2OH). The remaining carbon atoms contain H atom on one side and OH group on the other side.

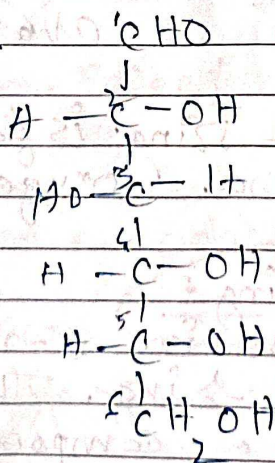
The carbon atoms are numbered from the aldehyde group. The carbon atom of the aldehyde group is the carbon atom number 1 and carbon atom containing H_2OH is the carbon atom number 6.

Molecular formula of glucose = $C_6H_{12}O_6$

According to the Fittling-Baeyer formula the glucose is



According to Fischer's projection formula the glucose is

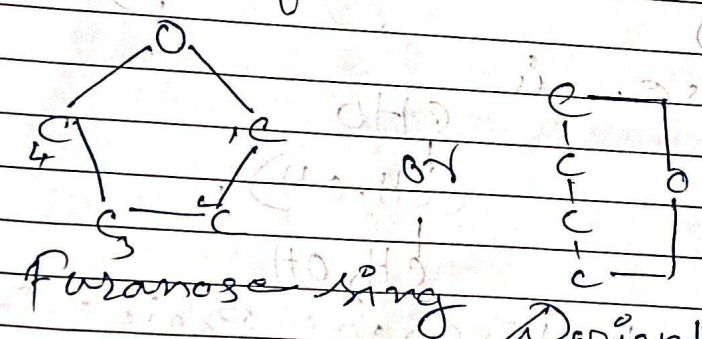


(2) Cyclic or Ring Structure :-

In cyclic structure, the atoms are arranged in the form of a ring. According to the Haworth's projection formula. The Sugar molecules exist in two types of rings. They are furanose ring and pyranose ring.

(1) Furanose Ring :-

Furanose is a 5-membered ring. It is pentagonal ring. It resembles the ring of a compound called furan and hence it is called furanose ring. Sugar containing the furanose ring are called furanoses.



Derivation of furanose ring from straight chain structure.

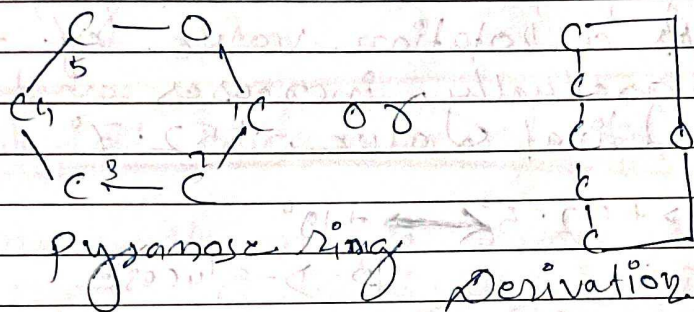
The furanose ring is formed of 4 carbon atoms and one oxygen atom.

(2) Pyranose Ring :-

Pyranose is a 6-membered ring. It is hexagonal ring. The ring resembles the ring of a compound called pyran and hence the ring is called pyranose ring. The sugars containing pyranose ring are called pyranose sugars.

The pyranose ring is more common among hexoses.

The pyranose ring is formed of 5 carbon atoms and one oxygen atom. The oxygen atom is called ring oxygen. The pyranose forms of the sugars are more stable than the furanose forms in solution.



Derivation of pyranose ring from straight chain structure

Properties of Monosaccharides

① Colour.

Monosaccharides are colourless.

② Shape.

They are crystalline compound.

③ Solubility.

They are readily soluble in water.

④ Taste.

They have sweet in taste.

⑤ Optical Activity.

They are optically active. They ^{can} rotate the plane polarized light.

⑥ Mutarotation.

Monosaccharides exhibit mutarotation. The change in specific rotation of an optically active compound is called mutarotation.

When a monosaccharide is dissolved in water, the optical rotatory power of the solution gradually changes until it

The value of mutarotation for α -D-glucose is $+52.5^\circ$. This is obtained by subtracting the final value from the original value. $[(+112.20) - (+52.7^\circ)]$

A freshly prepared solution of β -D-glucose has a rotation value of $+18.7^\circ$. It also gradually increases and reaches the same final value, $+52.7^\circ$

$+112^\circ \longrightarrow +52.5^\circ \longleftarrow +19^\circ$
 α -D-glucose β -D-glucose

fig: Mutarotation of α and β -glucose.

⑦ Glucoside formation:-

Glucose reacts with methyl alcohol in the presence of hydrogen chloride gas to give glucosides. Glucoside formation is due to the reaction of alcohol with the glucosidic OH of monosaccharides. In the same way, fructose, and forms fructosides.

Glucose + Methyl alcohol \rightarrow Methyl glucoside.

⑧ Esterification:-

Glucose reacts with 5 molecules of acetic anhydride to form esters

⑨ Reduction:-

Monosaccharides can be reduced by various reducing agents.

⑩ Reaction with concentrated HCl.

- ⑪ Reducing Agents.
- ⑫ Formation of Osazone.
- ⑬ Formation of Oximes.
- ⑭ Reaction with Hydrogen Cyanide.
- ⑮ Kilian's Synthesis.
- ⑯ Enolization.
- ⑰ Caramelization.
- ⑱ Phosphorylation of Hexoses.
- ⑲ Fermentation.

Biological Importance of Monosaccharides

Among the monosaccharides pentoses and hexoses are biologically important. Some biologically important monosaccharides are the following:

- ① D-glucose or Dextrose
- ② Ribose
- ③ Fructose
- ④ Galactose.
- ⑤ Mannose
- ⑥ Deoxyribose.

① D-Glucose or Dextrose.

* Glucose is simple sugar. It is a monosaccharide. It is also called ~~etc~~ dextrose.

* Glucose is colourless, crystalline solid highly soluble in water.

* Human blood contains 1mg per 100ml of blood.

* Glucose is an asymmetric or chiral compound because it contains asymmetric carbon atoms.

* Glucose is optically active and it is a dextro-rotatory compound and hence the name is D-glucose.

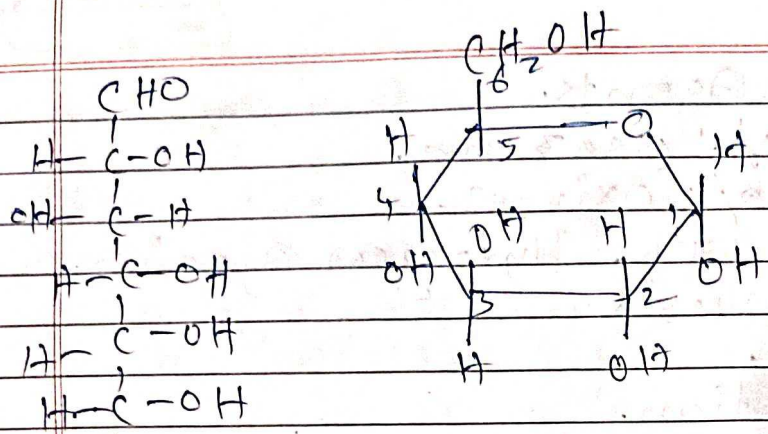
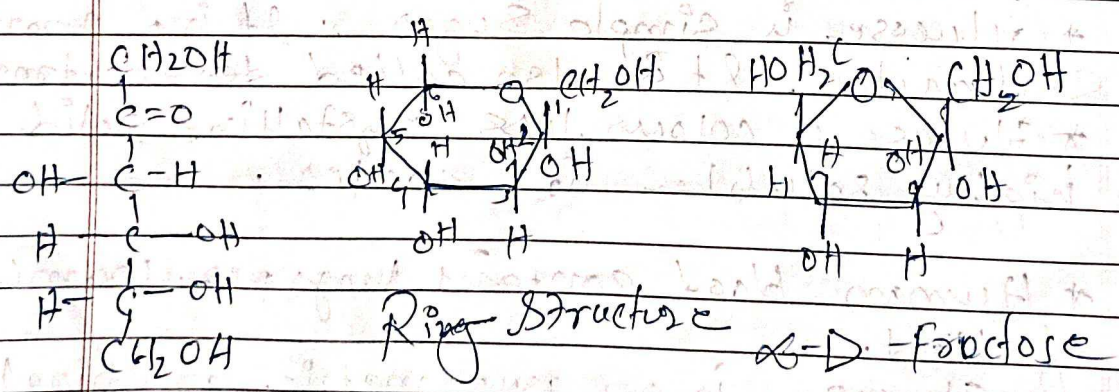


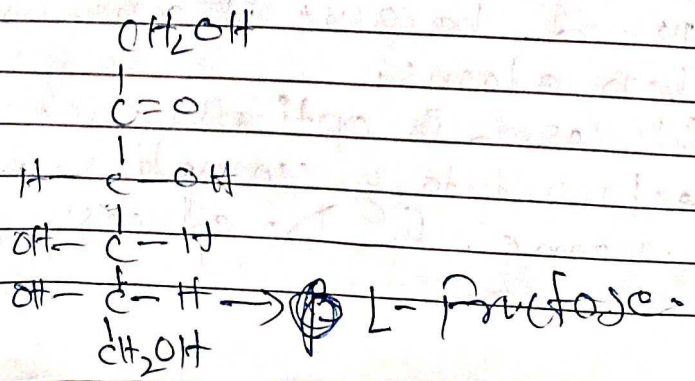
Fig: α -D-glucose.

2) Fructose:

- * Fructose is commonly called fruit sugar.
- * It occurs in fruits.
- * It is monosaccharides and ketohexose.
- * It is a sugar with crystalline state and sweet in taste. It is highly soluble in water.
- * It is an isomer of glucose.
- * It is reducing sugar. It reduces Fehling's reagent and Fehling's solution.



D-Fructose.



③ Galactose:

- * It is a monosaccharides.
- * It is a simple sugar.
- * It is a component of a milk sugar.
- * In liver, galactose change into glucose.
- * It exhibits isomerism.
- * It is a reducing sugar.
- * It is crystalline form and sweet in taste.

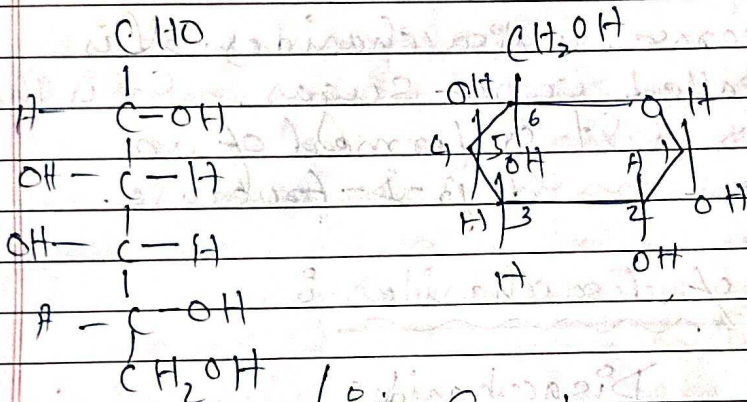


Fig: Galactose.

④ Ribose:

- * It is a pentose. It is a simple sugar.
- * It is sweet in taste. It is soluble in water.
- * It is a crystalline form.
- * It exhibits isomerism.

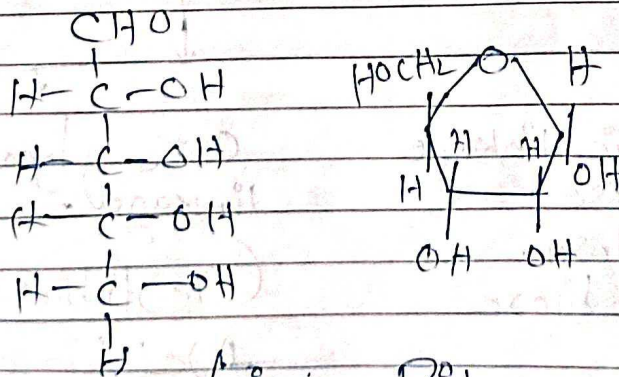


Fig: Ribose.

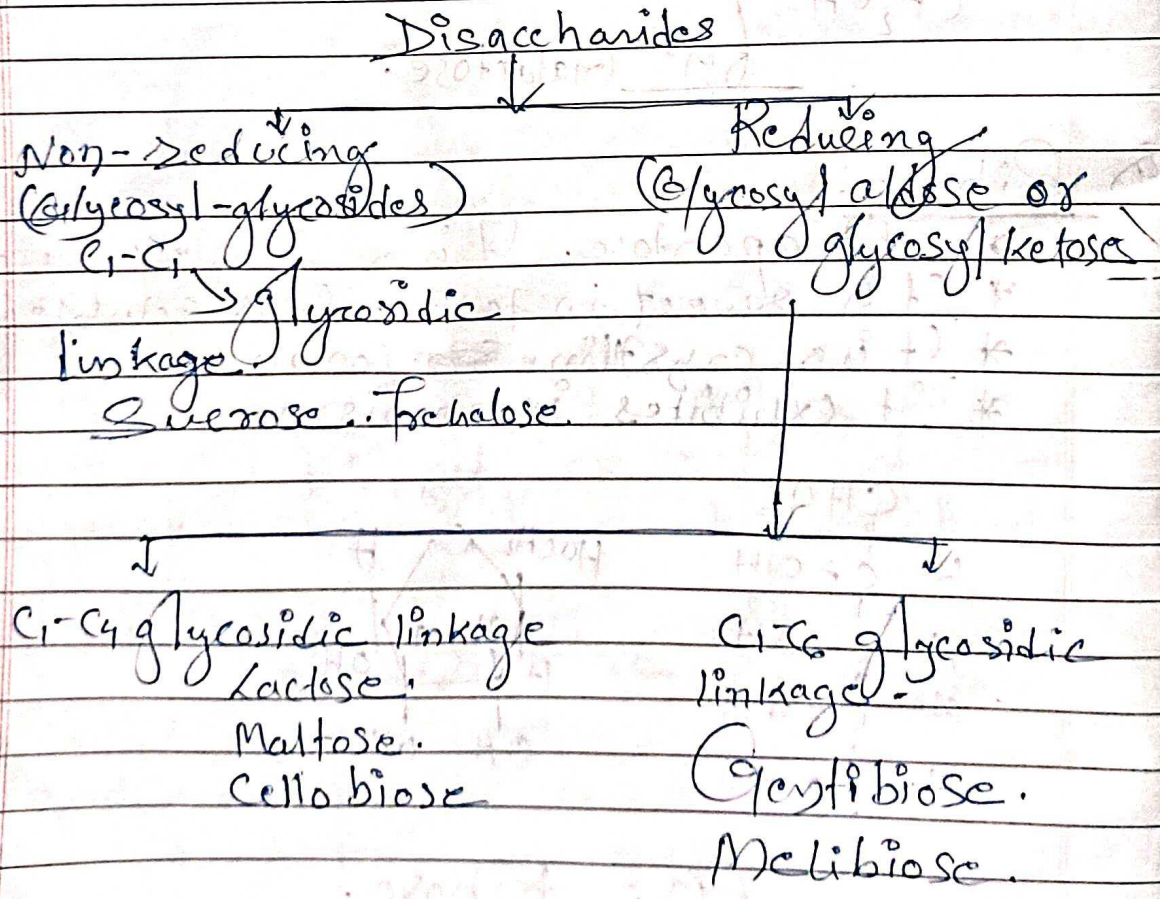
② Disaccharides:

Disaccharides are sugars which yield 2 molecules of monosaccharides on hydrolysis. They are sweet in taste and soluble in water. The important disaccharides are sucrose, lactose, maltose, cellobiose, trehalose, gentiobiose and melibiose.

① Sucrose:

Sucrose is disaccharides. It is commonly called cane-sugar. It is the table sugar. It is formed of an α -D-glucose and β -D-fructose.

Classification of disaccharides:



- (2) It is the common sugar and widely distributed in all photosynthetic plants.
- (3) It is found in sugarcane, beet root, apple, pineapple, carrot and ripe fruits.
- (4) It is the only food stuff used in crystalline form.
- (5) It is the pre-dominant form in which sugar is transported from leaves to the other organs of the plant through their vascular system.
- (6) Sucrose on hydrolysis by dilute acids or the enzyme invertase gives invert sugar. It is a ~~mixed~~ mixture of glucose and fructose. Glucose is dextrorotatory. Fructose is levorotatory. There is inversion of the sign of rotation. This process is called inversion and mixture is called invert sugar.
- (7) Sucrose is formed by the combination of α -D-glucose and β -D-fructose with the elimination of a molecule of a water.
- (8) It is sweeter than lactose, maltose and glucose.
- (9) Sucrose doesn't possess mutarotation and it is not a reducing sugar. It is not reactive.

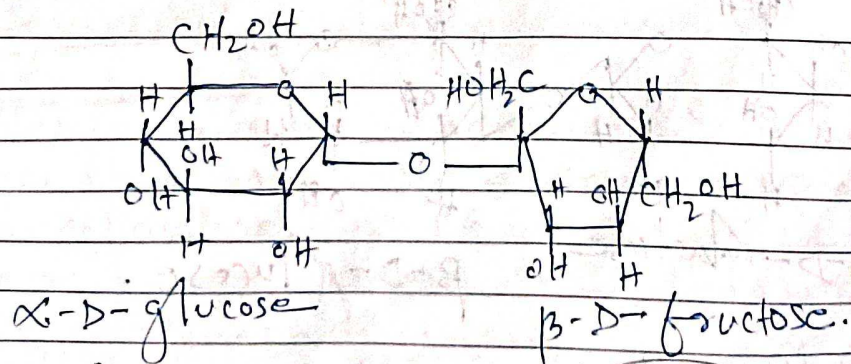


fig: formation of Sucrose

Lactose:

* It is disaccharides purely of animal origin.

* It is commonly called milk sugar. It is present in milk of mammals.

* It is present in mammary gland. However, it is also found in urine during pregnancy.

* It is formed by combination of galactose and glucose. The two sugars are linked by a glycosidic bond.

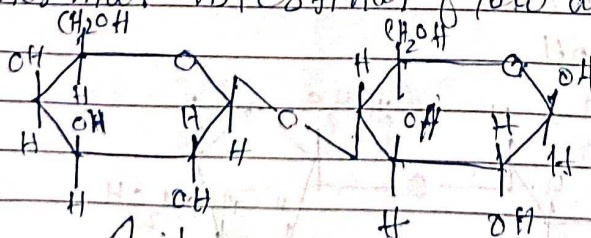
* It is less soluble in water and less sweeter than sucrose.

* It exhibits mutarotation due to the presence of a carbonyl group on the carbon atoms of glucose unit.

* The enzyme lactase hydrolyses lactose to glucose and galactose.

* The intestine of milk sucking infant has the enzyme lactase. This converts lactose to glucose and galactose. Then only, it is absorbed in the body.

Excess of lactose in the milk ingested into the body causes watery diarrhoea, abnormal intestinal flow and colic pain.



β -D-galactose

β -D-glucose.

Fig: Lactose.

③ Maltose

① It is a disaccharides. It is commonly called malt sugar. Malt from sprouting barley is the major source of maltose.

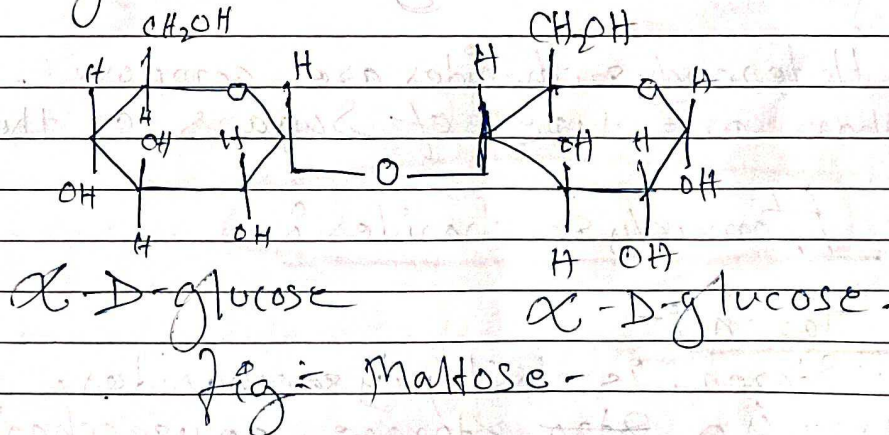
② It is produced during the digestion of starch by the enzyme α -amylase.

③ Maltose is formed by the removal of a molecule of water from the glycosidic OH group of α -D-glucose and the alcoholic OH group on the carbon atom 4 of another D-glucose.

④ Maltose is formed of two molecules of D-glucose.

⑤ The linkage in maltose is found to be an α -1,4-glycosidic.

⑥ It is a reducing sugar. It reduces Fehling's solution and Tollen's reagent.



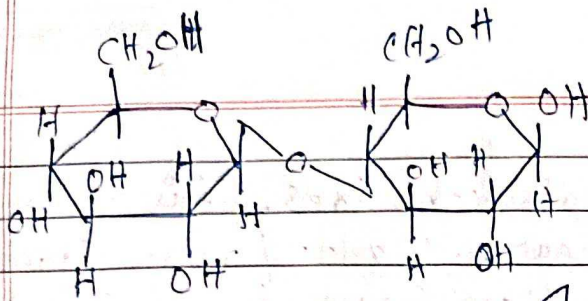
④ Cellobiose

① It is a disaccharides, It is identical with maltose. It is made up of β -D-glucose. In cellobiose β -1,4-glycosidic linkage is present. In maltose the linkage is α -1,4-glycosidic.

② It is present in traces amount.

③ It is released during the digestion of the polysaccharides cellulose by cellulases.

④ on hydrolysis it gives glucose unit only.



β -D-glucose β -D-glucose

Fig: Cellobiose.

③ Polysaccharides :-

Polysaccharides are polymers of several sugar residues, usually more than ten.

There are two types of polysaccharides: Homopolysaccharides and Heteropolysaccharides.

Homopolysaccharides are composed of the same type of sugars, for example, starch, glycogen, and cellulose, which are made of glucose units only.

Heteropolysaccharides are composed of more than one type of sugars or their derivatives.

Homopolysaccharides :-

① Starch :-

① Starch is plant polysaccharides.

② It is a storage polysaccharide which occurs in the form of granules.

③ It is structurally made of two compounds - amylose and amylopectin.

④ Amylose is made of a linear chain of α -D-glucose units linked by $\alpha(1 \rightarrow 4)$ glycosidic linkage.

⑤ Amylopectin is made of a branched chain of α -D-glucose units, similar

to amylose, linked by α (1 \rightarrow 6) glycosidic linkage at the branching points. Branching occurs at every 25 to 30 residues. All sugars present in starch are oriented in the same direction.

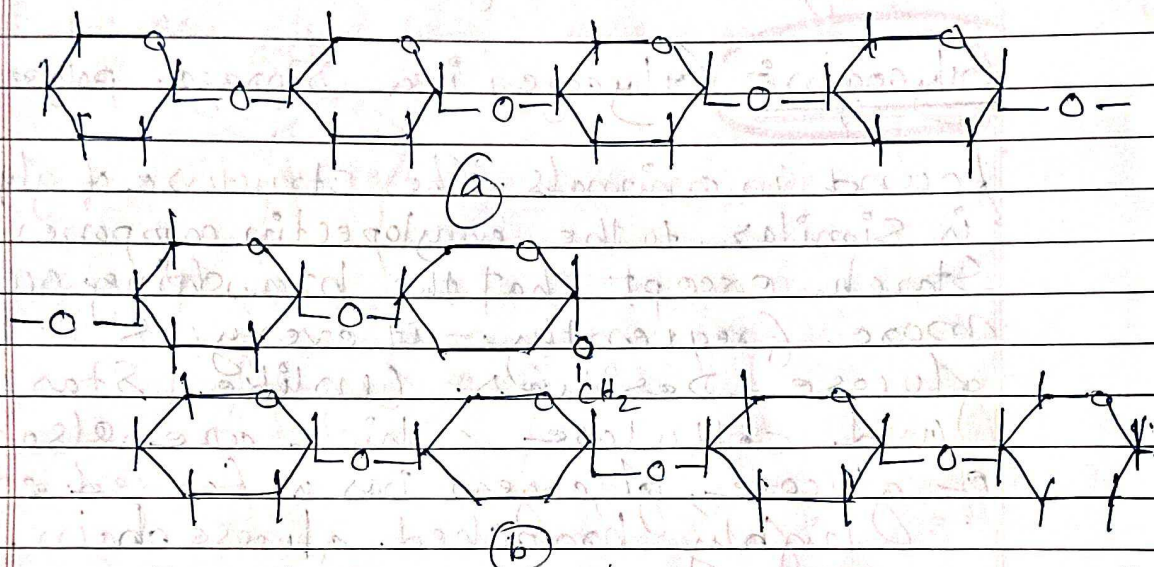


Fig: Structure of starch (a) Amylose (b) Amylopectin

② Cellulose:

(a) Cellulose is a structural polysaccharides found in wood, paper and cotton.

(b) It is formed by polymerization of β -D-glucose unit via β (1 \rightarrow 4) glycosidic linkage.

(c) The orientation of every alternative glucose ring in the cellulose is upside down.

(d) Cellulose is not digested by human beings because of the lack of the enzyme cellulase.

(e) In animals, cellulose can be digested due to the presence of cellulase.

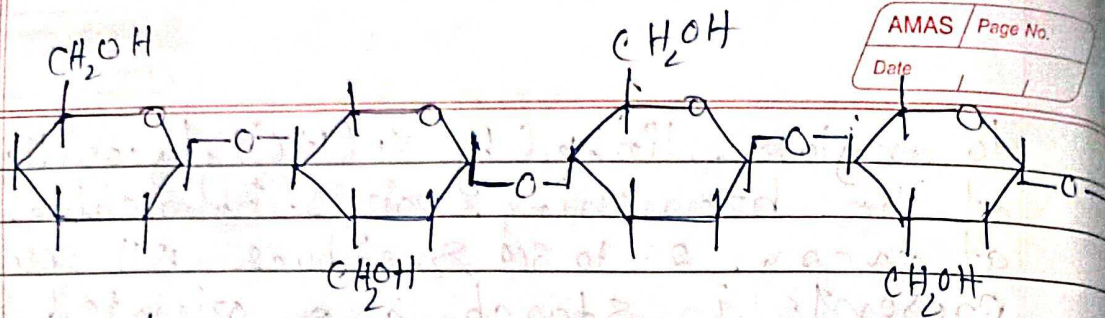


fig: Structure of cellulose.

Glycogen:

Glycogen is a storage polysaccharide found in animals. The structure of glycogen is similar to the amylopectin component of starch except that the branching occurs more frequently - at every 8 to 12 glucose residues. Unlike starch and cellulose, which are also made of glucose, glycogen has a forked or highly branched glucose chain.

Chitin:

(a) Chitin is a homopolysaccharide made up of N-acetylglucosamine units linked by $\beta(1 \rightarrow 4)$ glycosidic linkage.

(b) It is hard and tough and found in exoskeleton.

(c) It plays a structural role due to its high matrix strength and rigidity.

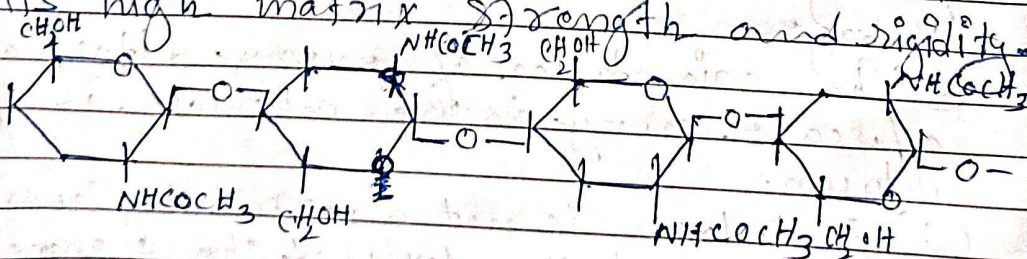


fig: Structure of chitin.

Inulin :-

Inulin is a polymer of fructose units and is also called polyfructosan. It is found in plants, typically in roots and rhizomes. It serves as a stored energy source.

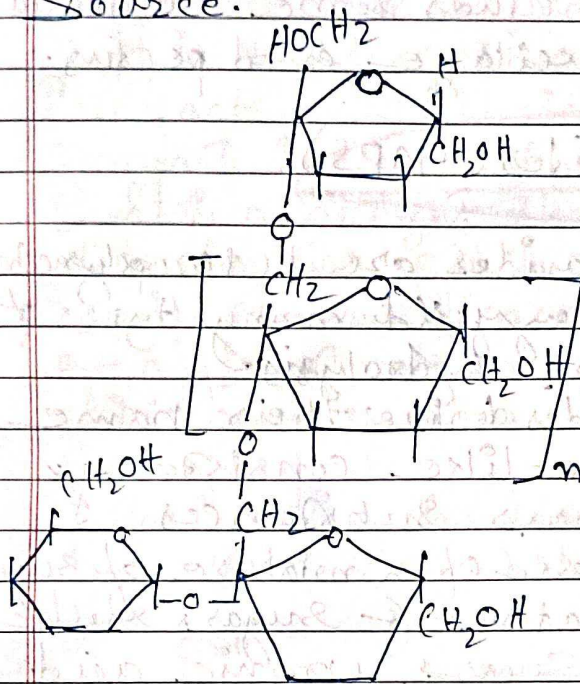


Fig. 2.0 Structure of Inulin.

Heteropolysaccharides :-

Heteropolysaccharides are composed of a mixture of monosaccharides. On hydrolysis they yield a mixed mixture of monosaccharides.

Example: Neutral sugars such as hemicellulose, gums etc. Mucopolysaccharides such as hyaluronic acid, chondroitin, chondroitin sulfate A, B and C, keratosulfate, heparin etc.

Heteropolysaccharides are further classified into two types, namely neutral sugars and mucopolysaccharides.

① Neutral Sugars:

Neutral Sugars give more than one type of sugar units on hydrolysis and sometimes non-sugar components also.

This group includes some hemicellulose, some gums, mucilage and pectin.

② Mucopolysaccharides: (MPS)

① Mucopolysaccharides are heteropolysaccharides because, they yield many types of monosaccharides on hydrolysis.

② Mucopolysaccharides derive their name from their slime-like consistency.

They are gelatinous substances.

③ They are composed of a mixture of sugars as well as derivatives of sugars, such as amino acid sugars, uronic acid.

④ Mucopolysaccharides are highly molecular weight up to 5 million.

⑤ They are found in the extracellular materials.

⑥ They serve as lubricants and biological cements. They cement the adjacent cells.

⑦ Mucopolysaccharides are acidic in nature as they contain uronic acid and sulfuric acid. Hence, they are also called - acidic heteropolysaccharides.

⑧ The common examples of mucopolysaccharides are -

(i) Hyaluronic acid (ii) Heparin.

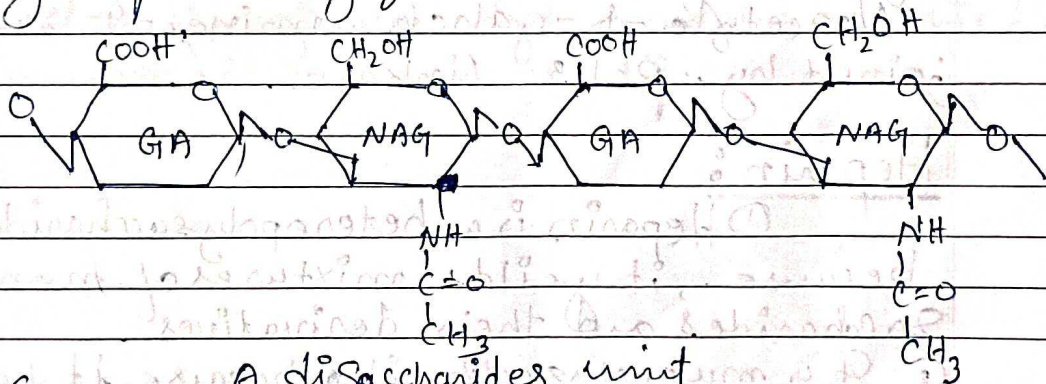
(iii) Chondroitin (iv) Blood group substances (v) Chondroitin sulfate

(vi) Bacterial polysaccharides (vii) Dermatan sulfate (viii) Vegetable gums (ix) Agar

Agar.

Hyaluronic Acid

- ① It is heteropolysaccharides.
- ② It is found in the skin, vitreous body of the eye, the umbilical cord, a coating around ovum, synovial fluid of joints and in some bacteria.
- ③ It is highly viscous substance.
- ④ It acts as a lubricant and as a biological cement in connective tissues.
- ⑤ It is a straight chain polymer of disaccharides which form the repeating unit. Each disaccharides unit is formed of a β -glucuronic acid and N -acetyl β -glucosamine linked by β -1,3, α -linkage.
- ⑥ Each disaccharides is linked to the next by a β -1,4-glycosidic bond.



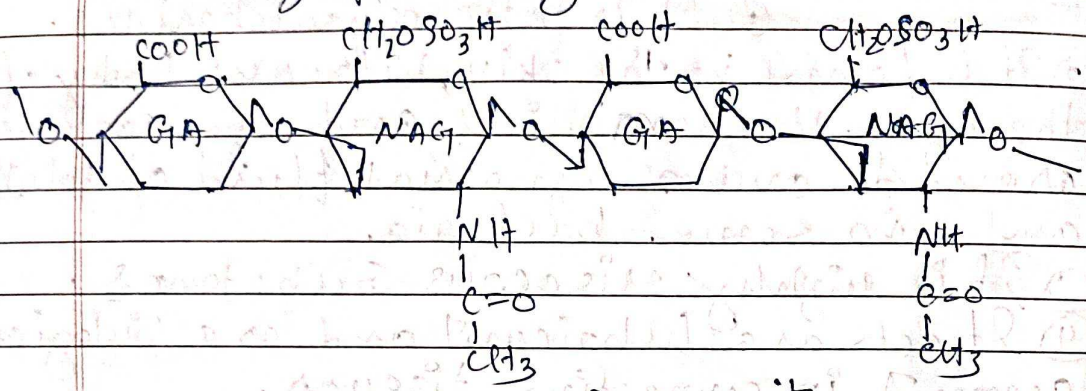
A disaccharides unit

fig: Hyaluronic acid.

Chondroitin

- ① It is a mucopolysaccharides
- ② It is found in cartilages and is also a component of cell coats.
- ③ It is parent substance for Chondroitin Sulfate A, B and C.
- ④ It is a straight chain of polymer of disaccharides which is form the repeating units. Each disaccharides is linked to the

next by β -1:4-glycosidic bond.



A disaccharides unit

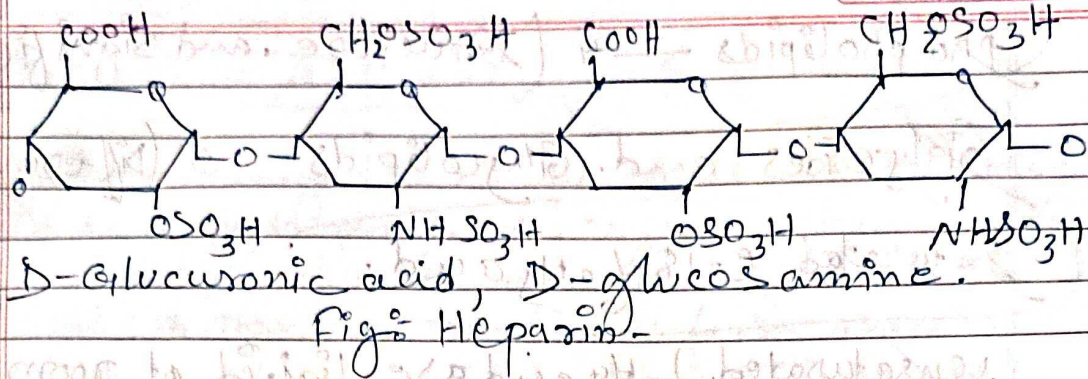
where GA = glucuronic acid
NAG = N-acetyl D-galactosamine-4-Sulphate

Fig: Chondroitin sulfate.

Each disaccharides unit is formed of a D-glucuronic acid and N-acetyl-D-galactosamine-4-sulphate joined by β -1:3 linkage.

Heparin:

- ① Heparin is a heteropolysaccharide because it yields mixtures of mono-saccharides and their derivatives.
- ② It is mucopolysaccharides because it has gel-like consistency.
- ③ It contains uronic acid and sulfuric acid and is acidic in nature. Hence it is also called acidic heteropolysaccharides.
- ④ It is present in liver, lungs, arterial walls, spleen, kidney and intestinal mucosa. They are secreted by the mast cells of connective tissue.



- (5) It functions as an anticoagulant because it prevents coagulation of blood. It prevents the conversion of prothrombin into thrombin and thus eliminates the effect of thrombin on fibrinogen.
- (6) It is a straight chain polymer composed of D-glucuronic acid and D-glucosamine N-sulphate.
- (7) The two molecules are linked by 1-4 linkage only, and 1-3 linkage absent.
- (8) The D-glucuronic acid is esterified at carbon atom number 2.