SEMESTER VI - BIOCHEMISTRY

CARBOHYDRATES

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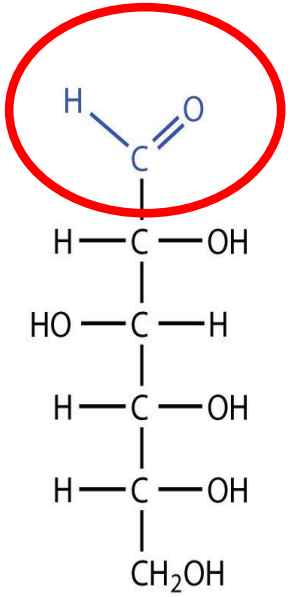
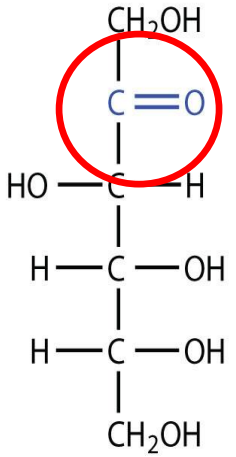
CARBOHYDRATES

- They are the most abundant organic molecules in nature and also referred to as “saccharides”.
- Most of them are sweet in taste are called as “sugars”.
- **They are polyhydroxy aldehyde or polyhydroxy ketones or substances which yield these compounds on hydrolysis**
- A carbohydrate molecule is essentially a chain of hydroxyl group with terminal aldehyde or ketone group.



Glucose
(an aldohexose)



Fructose
(a ketohexose)

CARBOHYDRATES

ALDOSES

- Contain aldehyde group
- Ultimate carbon is double bonded with O
- Ex.Glucose,Mannose,Arabinose etc

KETOSES

- Contain terminal keto group
- Penultimate carbonis double bonded with oxygen
- Ex.Fructose,erytrulose etc

- The general empirical structure for carbohydrates is $(CH_2O)_n$.

Ex. Ribose – $C_5H_{10}O_5$,

Glucose -$C_6H_{12}O_6$

There are some exceptions to the general formula

Ex, Deoxy Ribose – $C_5H_{10}O_4$

CLASSIFICATION OF CARBOHYDRATES

1.Based on Physico- Chemical properties :

1.Neutral sugars

- They only have hydroxyl and carboxyl groups
- Ex.glucose,fructose

2.Acidic sugars

- They have an additional carboxyl group
- Ex.Glucoronic acid

3.Basic sugars

- They have an additional amino group
- Also known as amino sugars or amino saccharides
- Ex. D- glucosamine

2.Based on molecular complexity

1.Monosaccharides

- Simplest sugars which cannot be hydrolysed into smaller units
- Ex. Glucose

2.Oligosaccharides

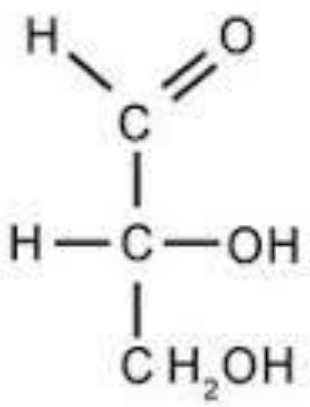
- These are compound sugars which yield 2-10 molecules of same monosaccharides on hydrolysis
- It include disaccharid,Trisaccharide ,tetrasaccharide etc.
- Ex.Sucrose,Lactose

3.Polysaccharides

- Compound sugars which yield more than 10 monosaccharide units on hydrolysis
- Two types – Homopolysaccharides and Heterosaccharides
- Ex. Starch,Glycogen

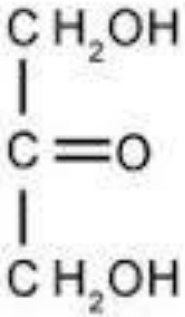
MONOSACCHARIDES

- Often called simple sugars
- They are compounds which possess a free aldehyde (-CHO) or ketone (=O) group and two or more Hydroxyl groups
- They can not be hydrolysed into smaller units
- General formula $(CH_2O)_n$.
- They simplest molecules of monosaccharides are Glyceraldehyde and dihydroxy acetone



D-Glyceraldehyde

Aldose Form



Dihydroxyacetone

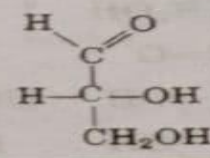
Ketose Form

- The backbone of monosaccharide is an unbranched single bonded Single bonded carbon chain .The carboxyl group is attached to the C1 in aldoses but with C2 in ketoses.
- Based on the number of carbon atoms ,Monosaccharide can be classified into trioses , tetroses, pentoses ,Hexoses etc.

Classification of monosaccharides		
Sugar groups	**Aldose forms**	**Ketose forms**
Dioses ($C_2H_4O_2$)	Glycolaldehyde	
Trioses ($C_3H_6O_3$)	Glyceraldehyde or glycerose	Dihydroxy acetone
Tetroses ($C_4H_8O_4$)	Erythrose Threose	Erythrulose
Pentoses ($C_5H_{10}O_5$)	Arabinose Xylose Lyxose Ribose Deoxyribose	Xylulose (xyloketose) Ribulose
Hexoses ($C_6H_{12}O_6$)	Glucose Mannose Galactose Gulose Iodose Talose Altrose Allose	Fructose Sorbose Tagatose
Heptoses ($C_7H_{14}O_7$)	Mannoheptose Glucoheptose Galactoheptose	Mannoketoheptose Glucoheptulose Galactoheptulose Altroheptulose (sedoheptose)
Octoses ($C_8H_{16}O_8$)	Gluco-octose Manno-octose Galacto-octose	
Nonoses ($C_9H_{18}O_9$)	Gluconononose Mannononose	
Decoses ($C_{10}H_{20}O_{10}$)	Glucodecose	

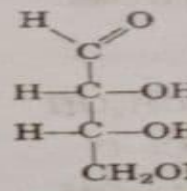
Aldose sugars

Trioses

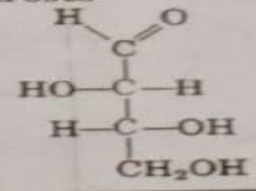


D-Glyceraldehyde

Tetroses

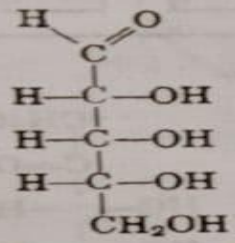


D-Erythrose

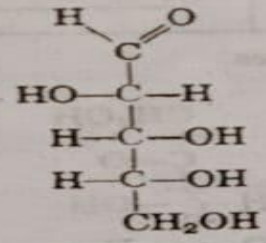


D-Threose

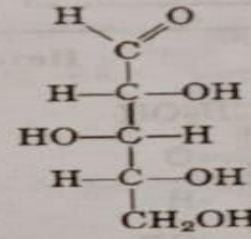
Pentoses



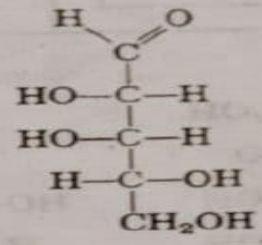
D-Ribose



D-Arabinose

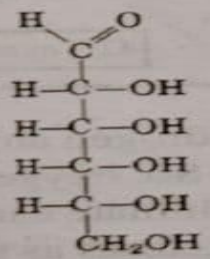


D-Xylose

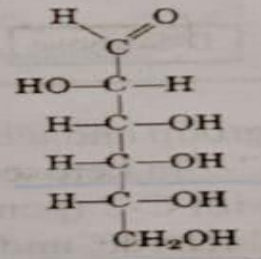


D-Lyxose

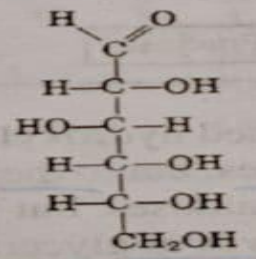
Hexoses



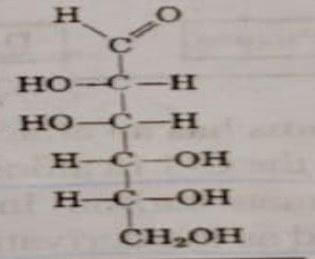
D-Allose



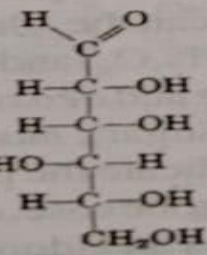
D-Altrose



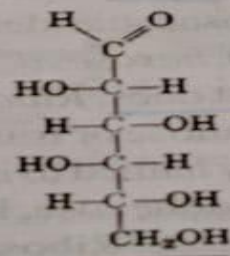
D-Glucose



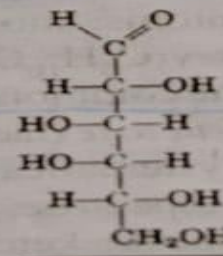
D-Mannose



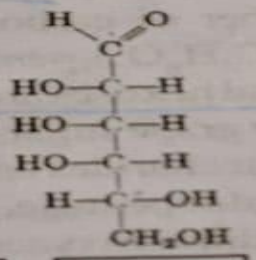
D-Gulose



D-Idose



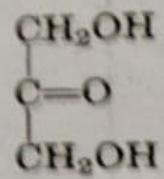
D-Galactose



D-Talose

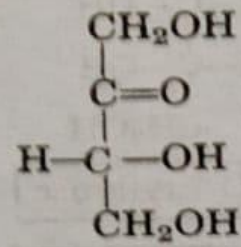
Ketose sugars

Trioses



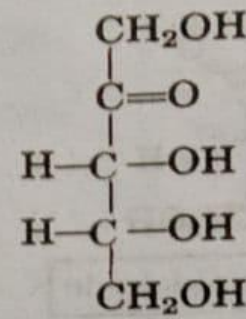
Dihydroxyacetone

Tetroses

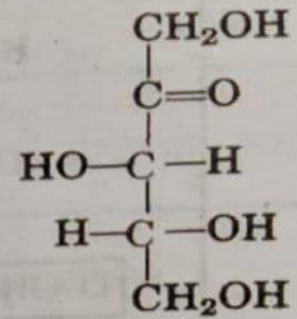


D-Erythrulose

Pentoses

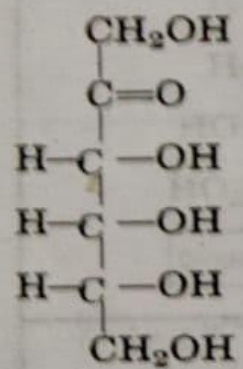


D-Ribulose

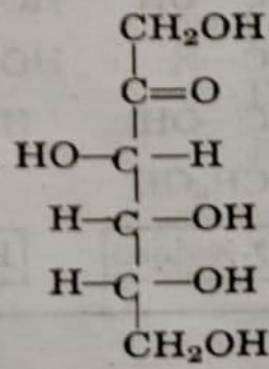


D-Xylulose

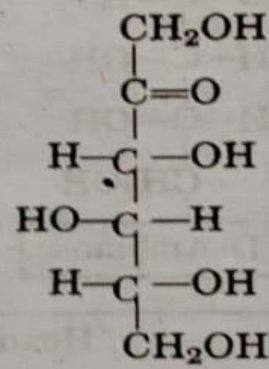
Hexoses



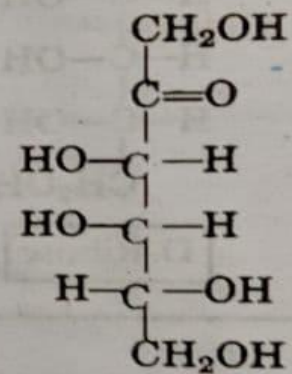
D-Psicose



D-Fructose



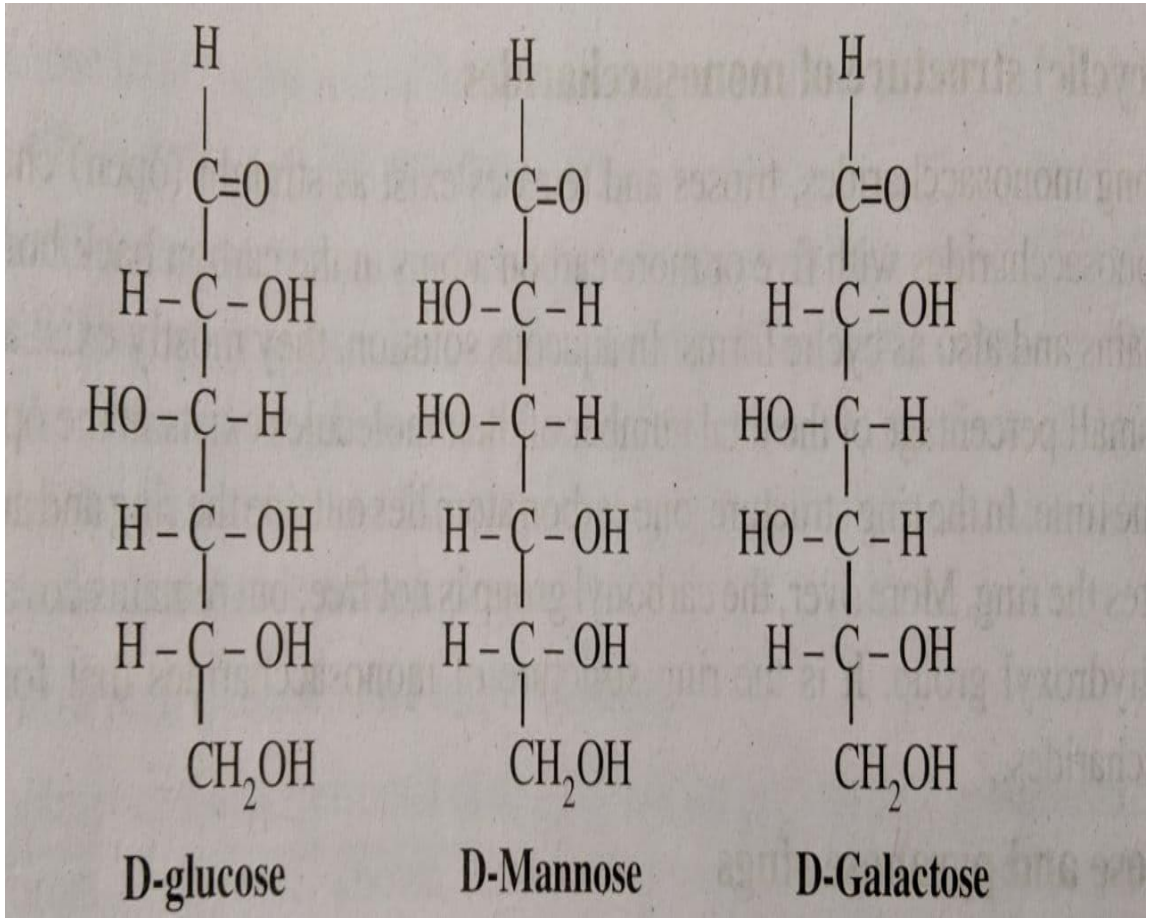
D-Sorbose



D-Tagatose

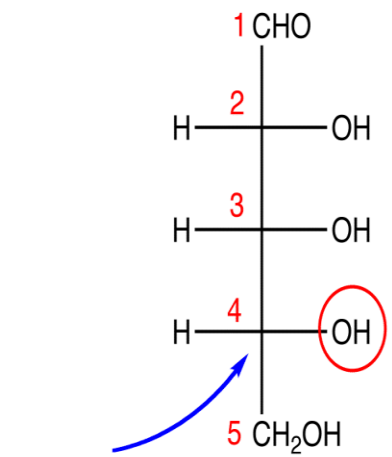
Stereoisomerism of carbohydrates

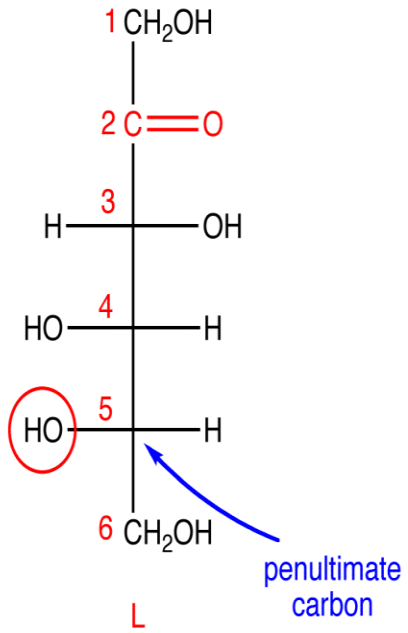
- Compounds having same structural formula but different arrangement in space is called as stereoisomers
- The number of stereoisomers depends upon the number of asymmetric carbon atoms by the formula 2^n ,Where n is the number of asymmetric carbon atoms



D and L isomerism of carbohydrates

- Left handed and right handed chiral forms of carbohydrates are indicated with reference to the penultimate carbon atom
- D sugars are naturally occurring sugars and body can only metabolize D sugars



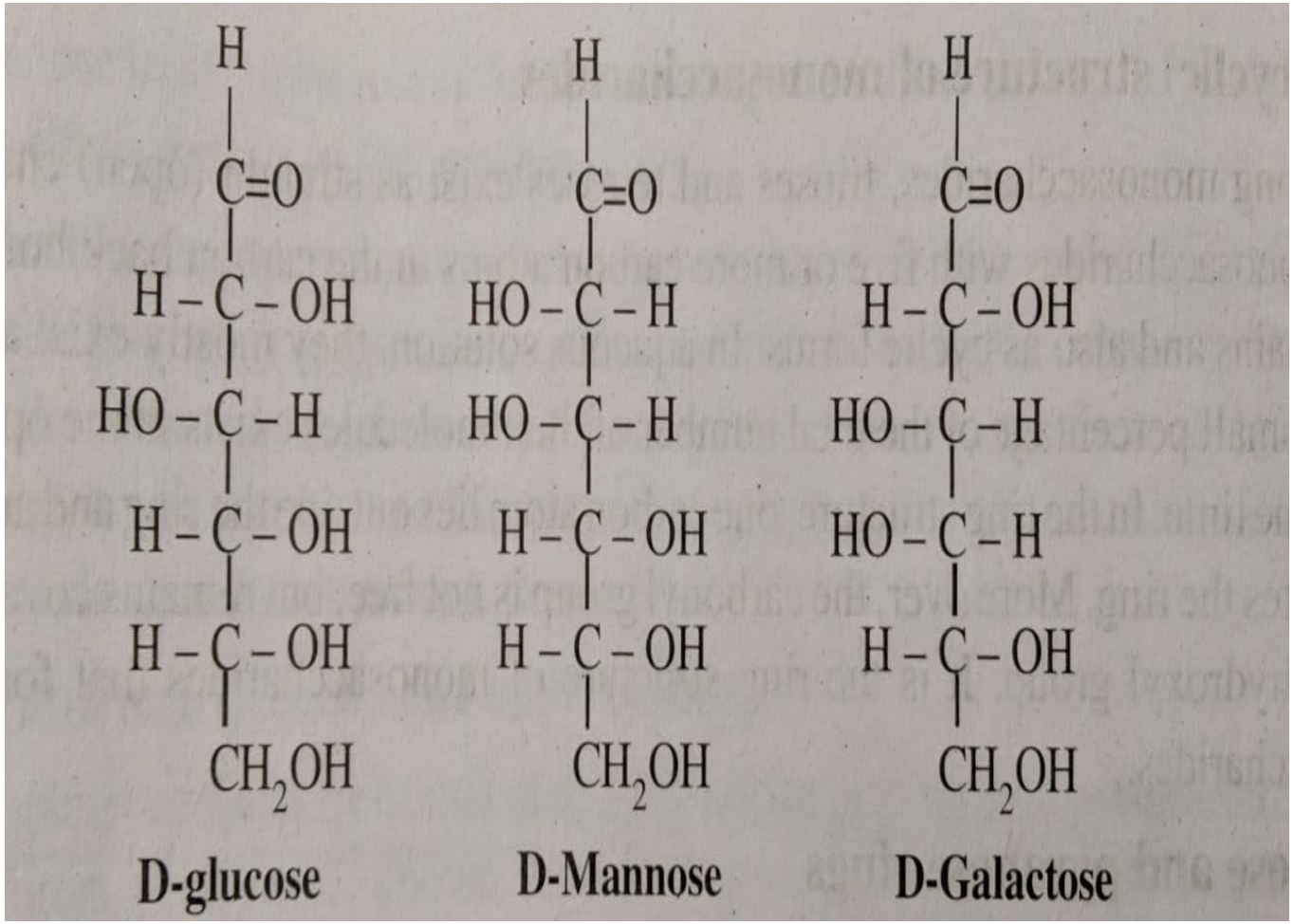


Optical isomerism of carbohydrates

- Optical activity is the ability to rotate plane polarised light either to left or right
- Depending on the rotation molecules are called dextro- rotatory (d or +) or laevorotatory (l or -)
- D Glucose is dextrorotatory but D Fructose is laevorotatory
- Equimolar mixture optical isomers has no net rotation (racemic mixture)

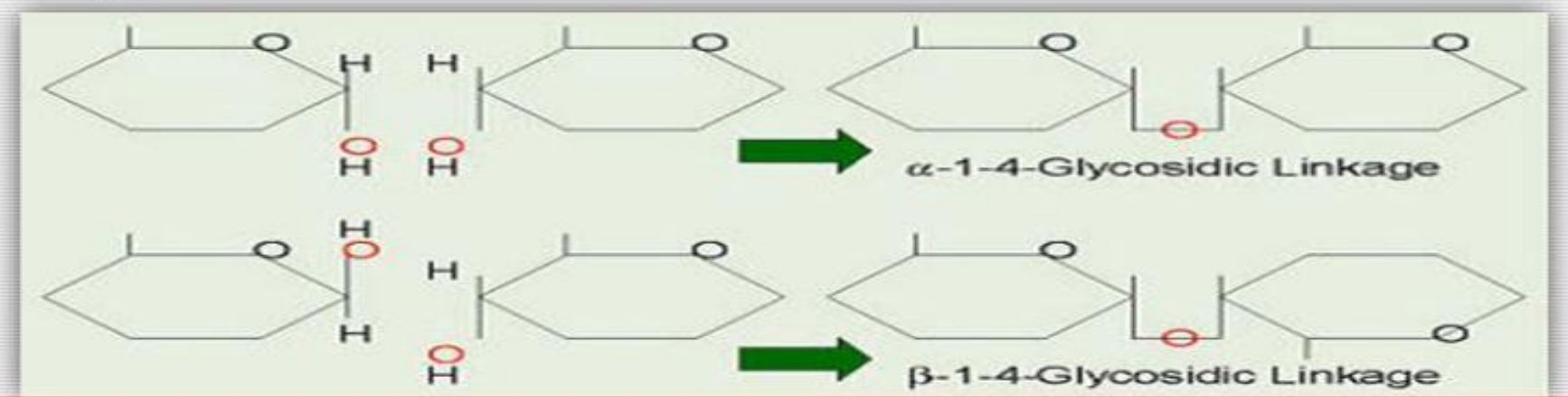
EPIMERISM

- Phenomenon in which diasteriomers of sugars differ from each other in their configuration with respect to only a single carbon atom other than the reference carbon atom.
- Glucose and mannose are epimeric pairs with respect to C2
- Glucose and Galactose are epimeric pairs with respect to C4
- Galactose and mannose are not epimers but diasteriomers.



Anomerism

- The predominant form of sugars like *glucose* & *fructose* in a solution cyclize into rings.
- During the conversion from straight-chain form to cyclic form, the C-1 of glucose becomes a chiral center which can form two possible configurations.
- These are *α* & *ß* .The C-1 carbon is called the anomeric *carbon* & so are *α* & *ß* forms are anomers.
- In the ***α* anomer**, the hydroxyl (-OH) group attached to C-1 is below the plane of the ring & in **ß anomer**, it is above the plane of the ring.

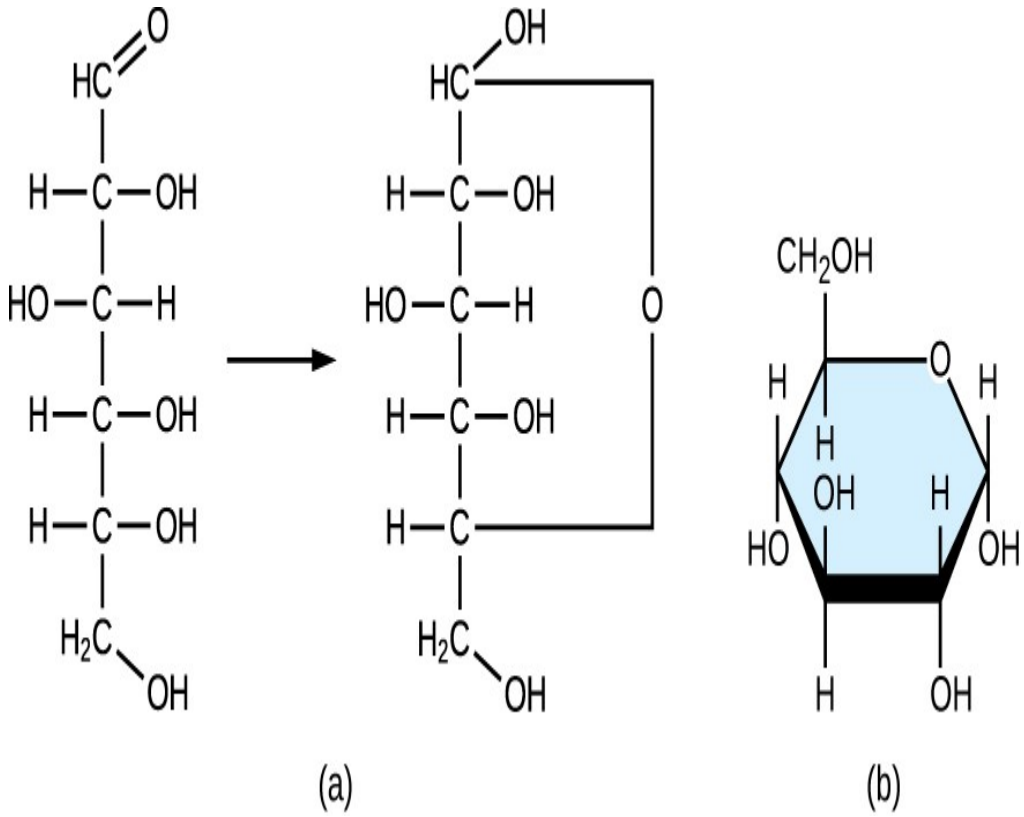


Mutarotation

- Mutarotation is the change in the specific optical rotation by the **interconversion** of α & ß forms to an *equilibrium* mixture.
- In water, α-D glucopyranose & ß-D glucopyranose interconvert through the open chain form of sugar. This interconversion was detected by optical rotation.
- The specific rotation $[\alpha]_D$ of the α & ß anomers of D-glucose are +112° & +18.7°. When crystalline sample of either anomers is dissolved in water, $[\alpha]_D$ changes with time until an equilibrium value of +52.7° is attained. This change called mutarotation.
- Enzymes called mutarotase catalyze the interconversion of anomeric sugars *in vivo*.
- Non-reducing sugar cannot show mutarotation due to the absence of the free anomeric OH group.

Ring structure of monosaccharides

- Monosaccharides with five or more carbon atoms in the carbon back bone can exist as open chains and also as cyclic forms
- In aqueous solution , they mostly exist as stable rings.
- In ring structure ,one carbon atom lies outside the ring and an oxygen atom completes the ring
- Carbonyl group is not free ,but remains covalently bonded with a hydroxyl group
- It is the ring structure of monosaccharides that forms oligo and poly saccharides



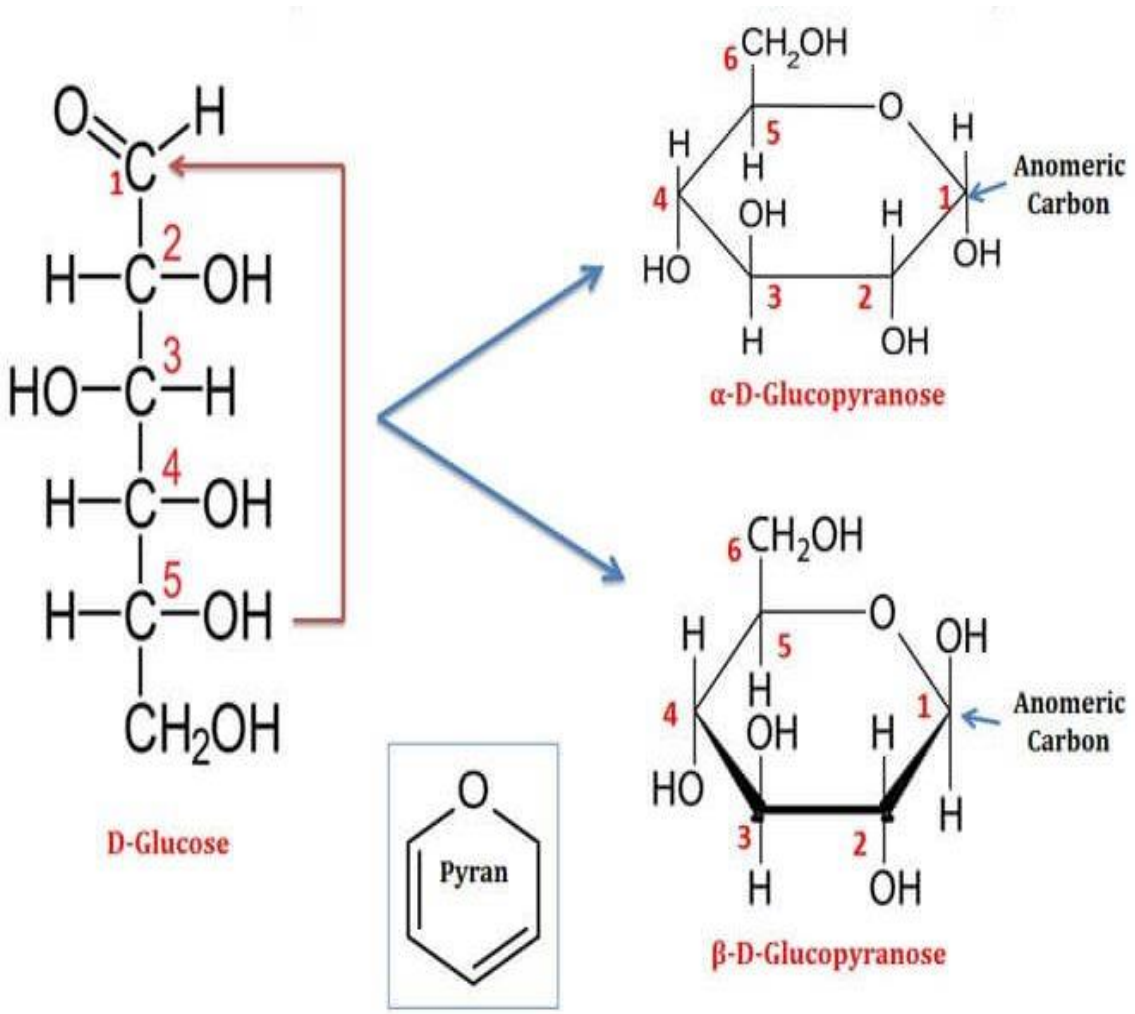
Furanose and Pyranose rings

- Cyclic sugars that contain a five membered ring are called "***furanoses***".
- The term is derived from the similarity with the aromatic compound furan and tetrahydrofuran.
- Both pentoses and hexoses can form this structure

- Cyclic sugars that contain a six membered ring are called "***pyranoses***"
- The term is derived from the similarity with the compound pyran and tetrahydropyran.
- Hexoses form this structure

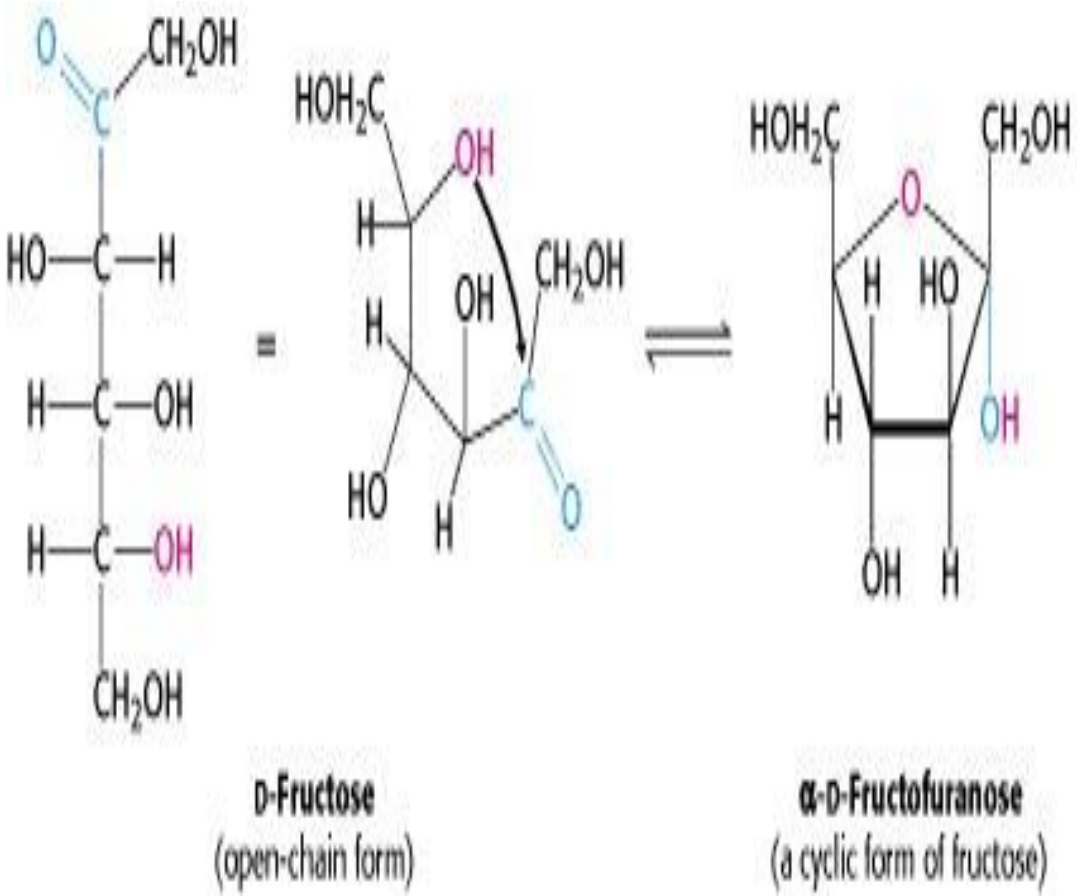
Pyranose ring

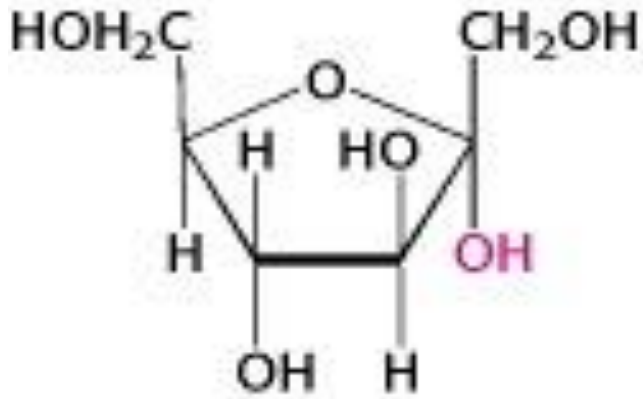
The ring in pyranose is formed due to the reaction of the hydroxyl group (OH) on the fifth carbon (C5) of the sugar with the aldehyde group at C1.



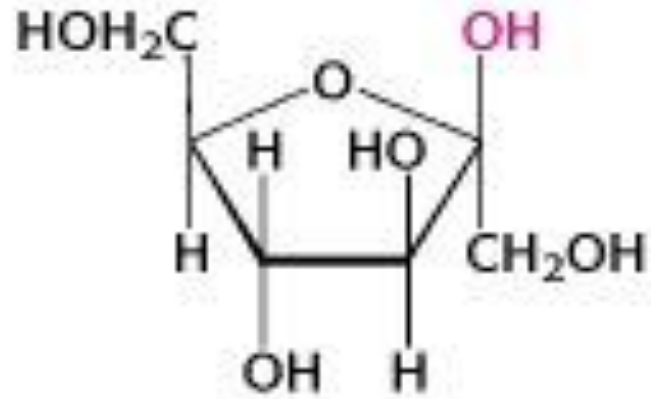
Furanose rings

- This molecule has a five-membered ring.
- It is formed due to the reaction between the hydroxyl group on C4 and the aldehyde.
- The furanose ring can have either alpha or beta configuration depending upon the direction of an anomeric hydroxyl group.
- In fructose the first carbon atom joins the oxygen on the fifth carbon and forms the furanose ring.

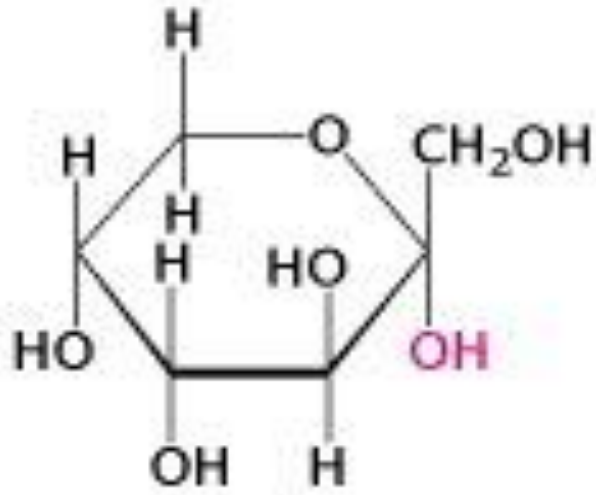




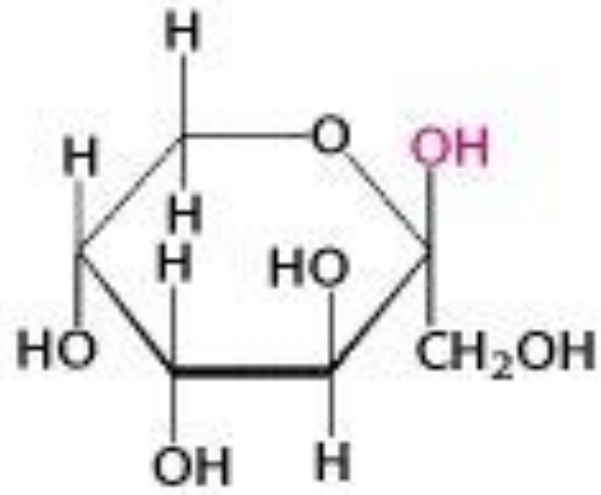
α-D-Fructofuranose



β-D-Fructofuranose



α-D-Fructopyranose

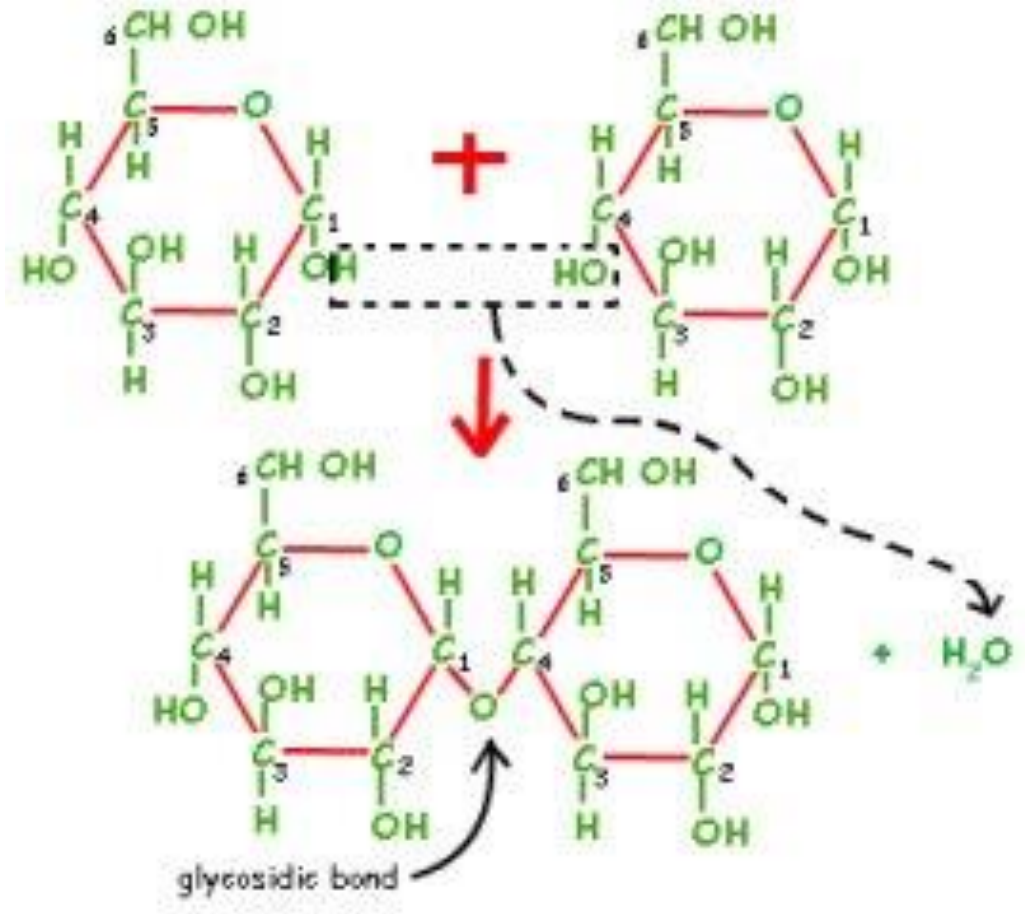


β-D-Fructopyranose

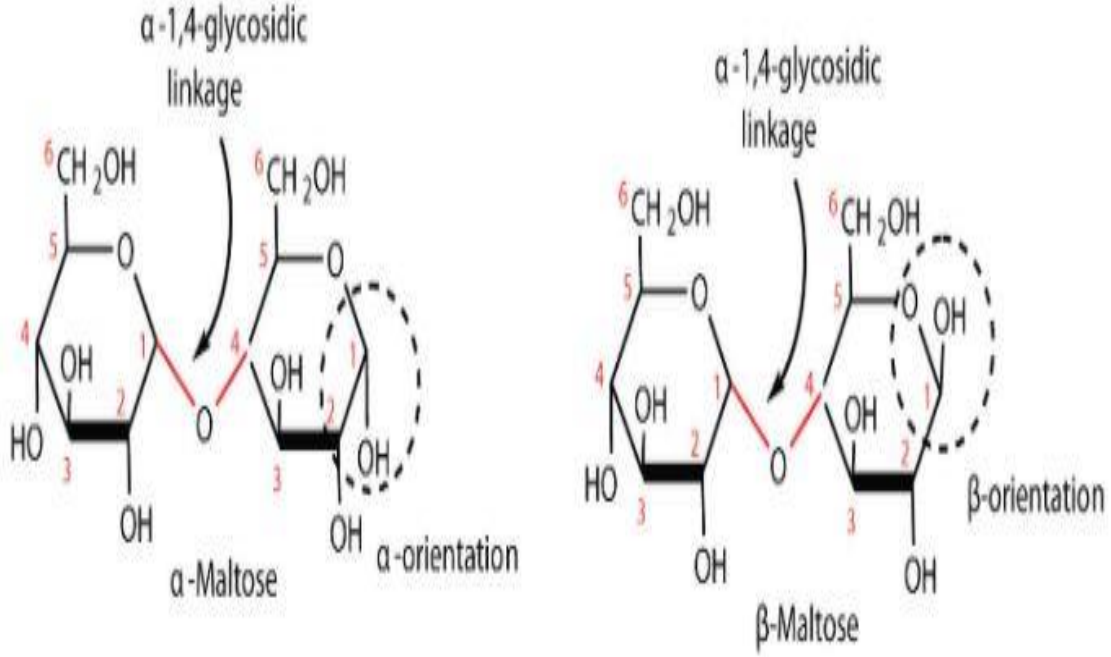
CHEMICAL PROPERTIES OF MONOSACCHARIDES

1.Formation of Glycosidic bond

- A **glycosidic bond** or **glycosidic linkage** is a type of covalent bond that joins a carbohydrate (sugar) molecule to another group, which may or may not be another carbohydrate.
- Glycosidic bond links monosaccharide with non –sugar substance to produce a glycoside. There the non- sugar moiety is called aglycone
- Glycosidic bond is formed by the dehydration condensation of anomeric carbon (C1) of one monosaccharide unit with the hydroxyl group of the C2,C4 OR C6 of another monosaccharide unit ,or with a non carbohydrate with the elimination of water
- The two monosaccharide units will be bonded by an oxygen



- Monosaccharide units getlinked by glycosidic linkage to form complex carbohydrates.
- Glycosidic bonds can be easily broken by acid hydrolysis
- Two kinds of glycosidic bonds can be recognised : alpha and beta glycosidic bonds .
- In alpha glycosidic bond, OH attached to C1 is below the plane of molecular ring
- In beta glycosidic bond, OH attached to C1 is above the plane of molecular ring



2.Reducing Power

- Is the ability of some sugars to readily reduce some oxidising agents ,such as hydrogen peroxide ,Ferric cyanide, Ferric ion ,Cupric ion etc. such sugars are known as reducing sugars.
- In these reactions sugar get oxidised at the carbonyl group, and the oxidising agent get reduced.
- The carbonyl carbon of the sugar is oxidised to carboxylic acid
- All monosaccharides and some disaccharides and trisaccharides are reducing sugars eg: maltose ,lactose etc.
- In disaccharides carbonyl carbon may be occupied by glycosidic bond . In such cases ,they can not act as reducing agents .They are known as non - reducing sugars Eg:Rffinose ,sucrose etc.

Reducing sugar

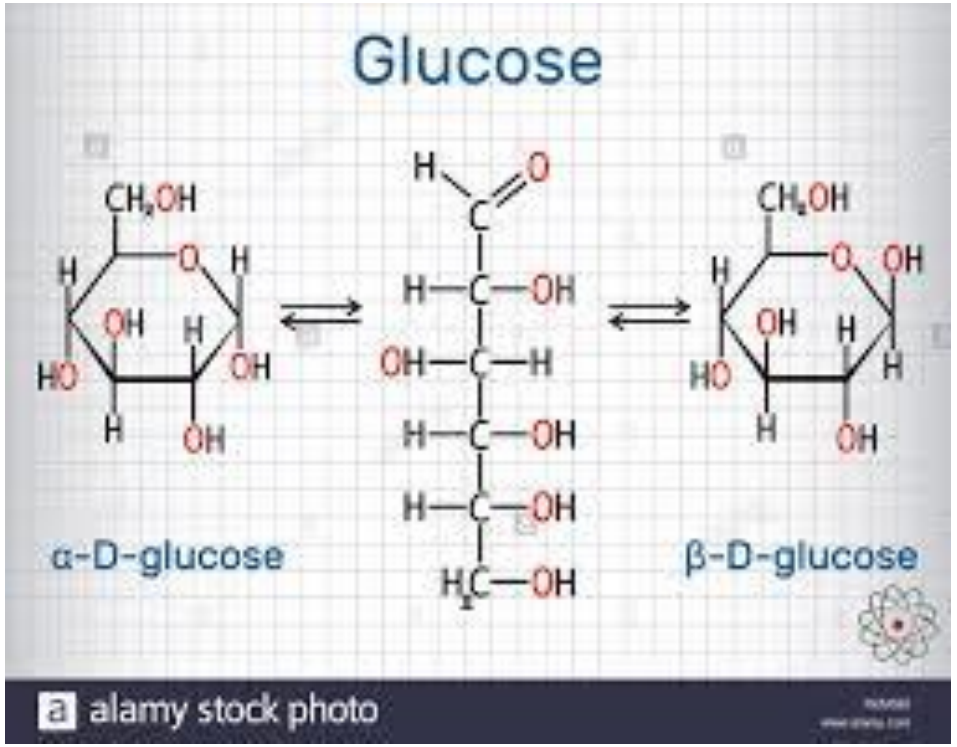
- Carbohydrate with free aldehyde or free ketone group
- They are in hemi acetal or hemi ketal form
- Do exhibit mutarotation
- Do form osazones with phenyl hydrazine
- Eg : Glucose,Fructose etc.

Non reducing sugar

- Aldehyde and ketone groups are not free but they are utilised in bonding
- They are in acetal or ketal form
- Do not exhibit mutarotation
- Do not form osazones
- Eg: Sucrose,Glycogen etc.

GLUCOSE $C_6H_{12}O_6$

- It is a polyhydoxy aldohexose
- With a free terminal aldehyde group ,hence it is a reducing sugar
- It is sweet in taste ,water soluble and crystalline monosaccharide
- Can exist in both chain form and ring form
- it is a chiral molecule with four asymmetric carbon atoms in positions 2,3,4 and 5
- As it has 4 asymmetric carbon atoms ,it can form 16 isomeric forms .
- Optical isomers of glucose can rotate plane polarised light to right hence they are called dextrorotatory.



Biological roles of glucose

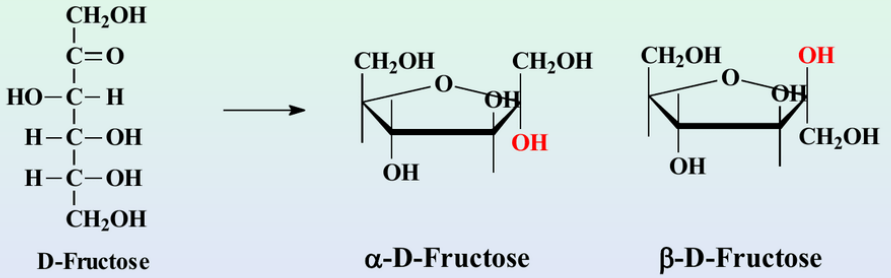
- Immediate source of energy for several metabolic functions
- In higher animals it is indispensable for the functioning of brain cells
- Glucose form storage products ,such as starch in plants and glycogen in animals which serve as rich source od reserve energy
- Cellulose ,the building block of plant cell wall is made up of glucose
- Proper concentration of blood glucose id=s necessary for the functioning of the body
- Glucose ,produced by photosynthesis is the primary source of energy for all the organisms

Fructose

- Fruit sugar
- Also known as *levulose* (as it is levorotatory)
- Poly hydroxy ketohexose
- Found abundantly in sweet fruits and in honey
- Sweetest of all natural common sugars
- Can be obtained from the hydrolysis of corn sugar and dahlia sugar and polysaccharide inulin
- It have the same empirical formula of glucose but it exist in keto form

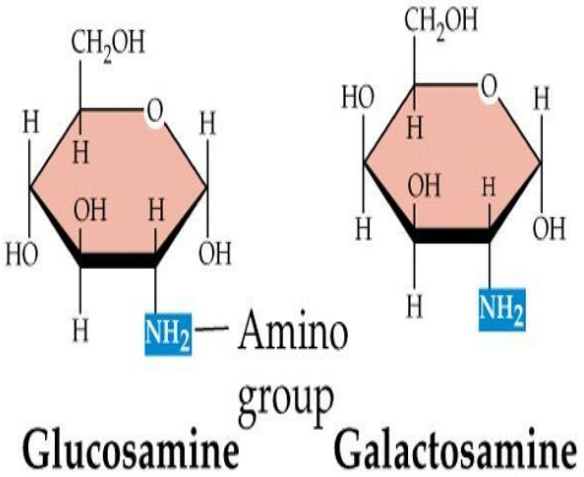
Cyclic Structure of Fructose

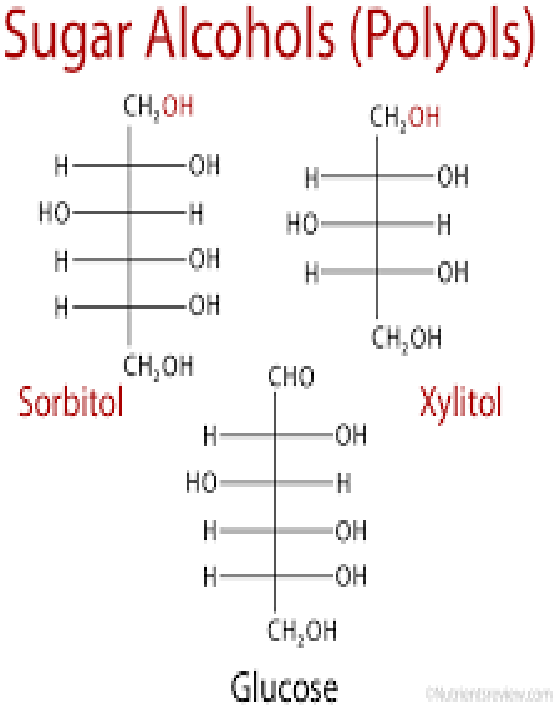
- As a ketohexose, fructose forms a 5-membered ring when the hydroxyl on C-5 reacts with the carbonly on C-2

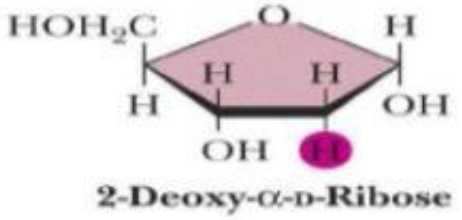


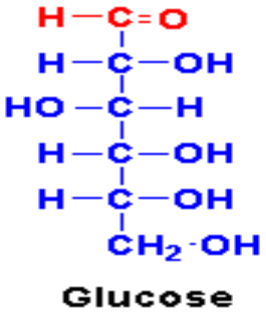
Derivatives of Monosaccharides

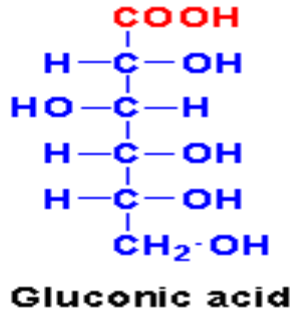
- Deoxy suagrs, amino sugars ,and sugar alcohols are some derivatives of monosaccharide
- Deoxy suagrs – formed by deoxygenation of –OH group eg . Deoxy ribose
- Amino sugars – Replacement of an –OH group by amino group eg: Glucosamine and galactosamine
- Sugar alcohols – Formed by the reduction of sugar eg: Mannitol ,sorbitol
- Sugar acid – Formed by the oxidation of sugar eg: Gluconic acid





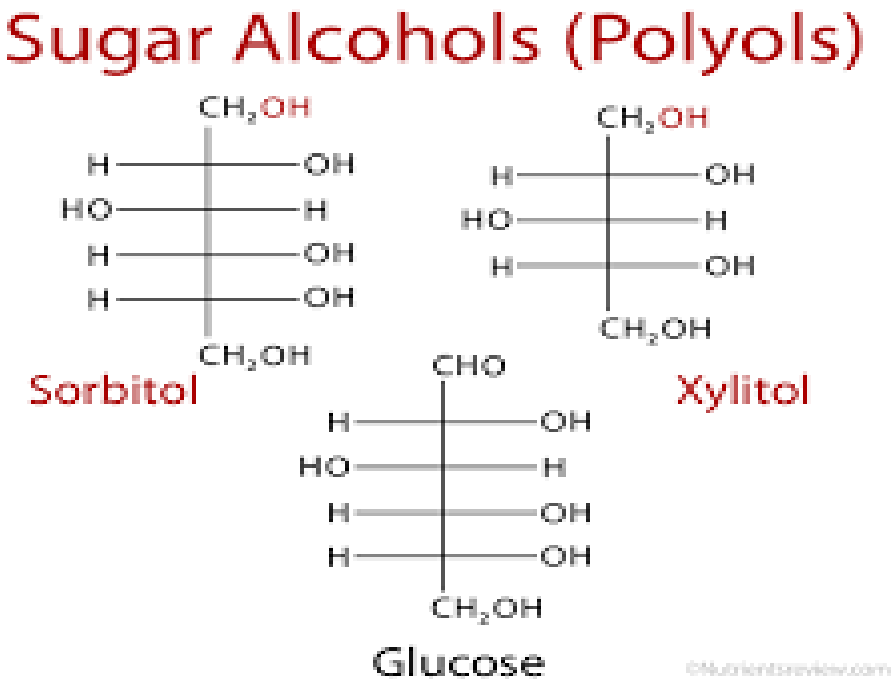






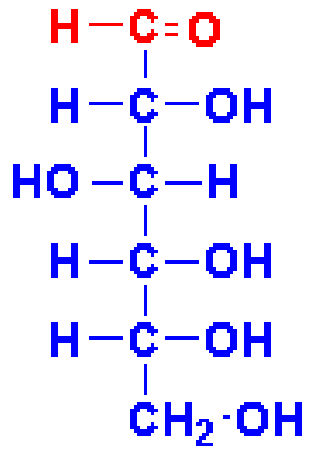
Reduction of monosaccharides

- Reduction of aldehyde or ketone functional group of monosaccharides convert them to polyhydric alcohols

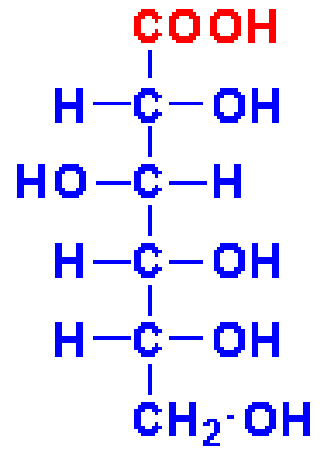


Oxidation of monosaccharides

- In this reaction the aldehyde group or primary alcohol get converted to an acid group



Glucose



Gluconic acid

OLIGOSACCHARIDES

- Oligosaccharides are a type of carbohydrate formed when three to 10 simple sugars are linked together by glycosidic bonds
- The common oligosaccharides are disaccharides ,tri saccharides and tetra saccharides
- Most oligosaccharides ,having three or more units are seen complexed with non- sugar molecules forming glycolipids and glycoproteins

Some oligoaccharides

		Constituent monomers
I. Disaccharide ($C_{12}H_{22}O_{11}$)		
A. Reducing forms		
1. Maltose	..	Glucose – glucose
2. Cellobiose	..	Glucose – glucose
3. Lactose	..	Glucose – galactose
4. Meliobiose	..	Glucose – galactose
5. Gentiobiose	..	Glucose – glucose
6. Turanose	..	Glucose – fructose
B. Non-reducing forms		
1. Sucrose	..	Glucose – fructose
2. Trehalose	..	Glucose – glucose.
II. Trisaccharides		
A. Reducing forms		
1. Mannotriose	..	Galactose - galactose - glucose
2. Robinose	..	Galactose - rhamose - rhamnose
3. Rhamninose	..	Galactose - rhamnose - rhamnose
B. Non-reducing forms		
1. Raffinose	..	Fructose - glucose - glucose
2. Gentianose	..	Fructose - glucose - glucose
3. Melezitose	..	Glucose - fructose - glucose

III. Tetrasaccharides

Only two are known, stachyose and scorodose

IV. Pentasaccharides

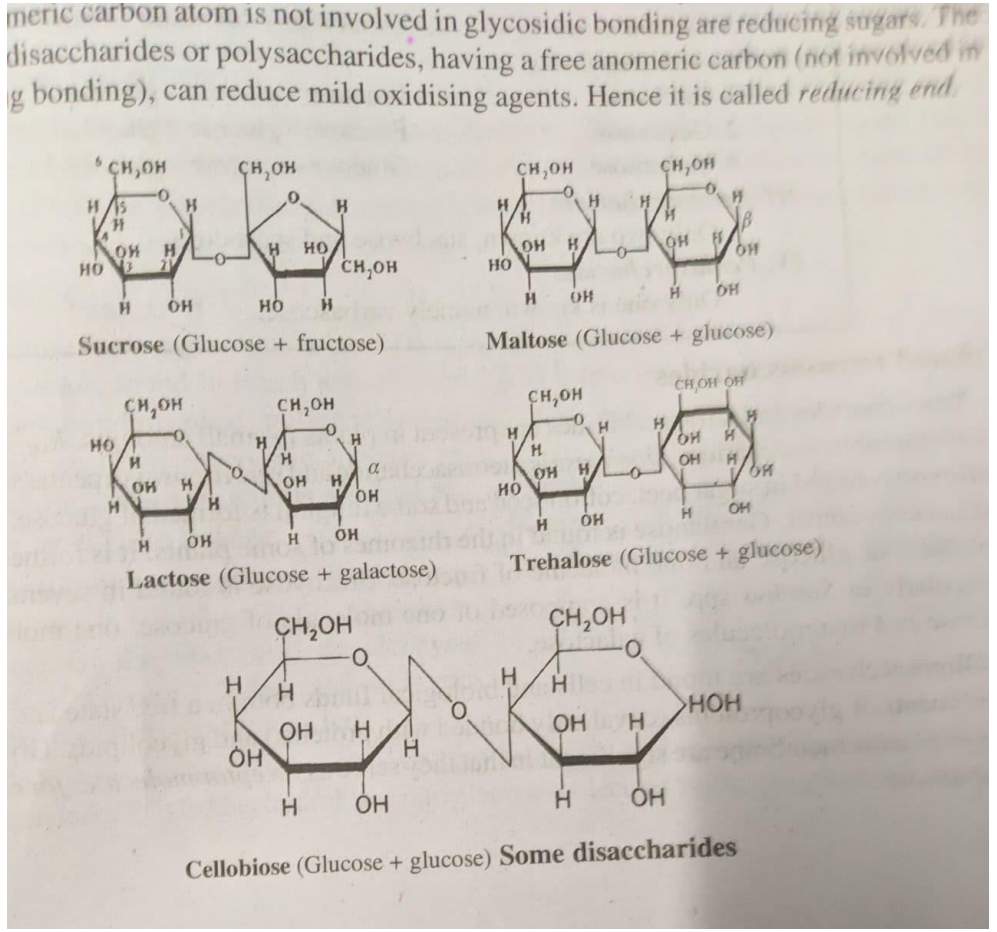
Only one is known, namely verbascose.

Disaccharides

- When two monosaccharides are combined together with glycosidic linkage a disaccharide is formed
- General formula $C_{11}H_{22}O_{11}$
- Eg: Maltose (malt sugar)

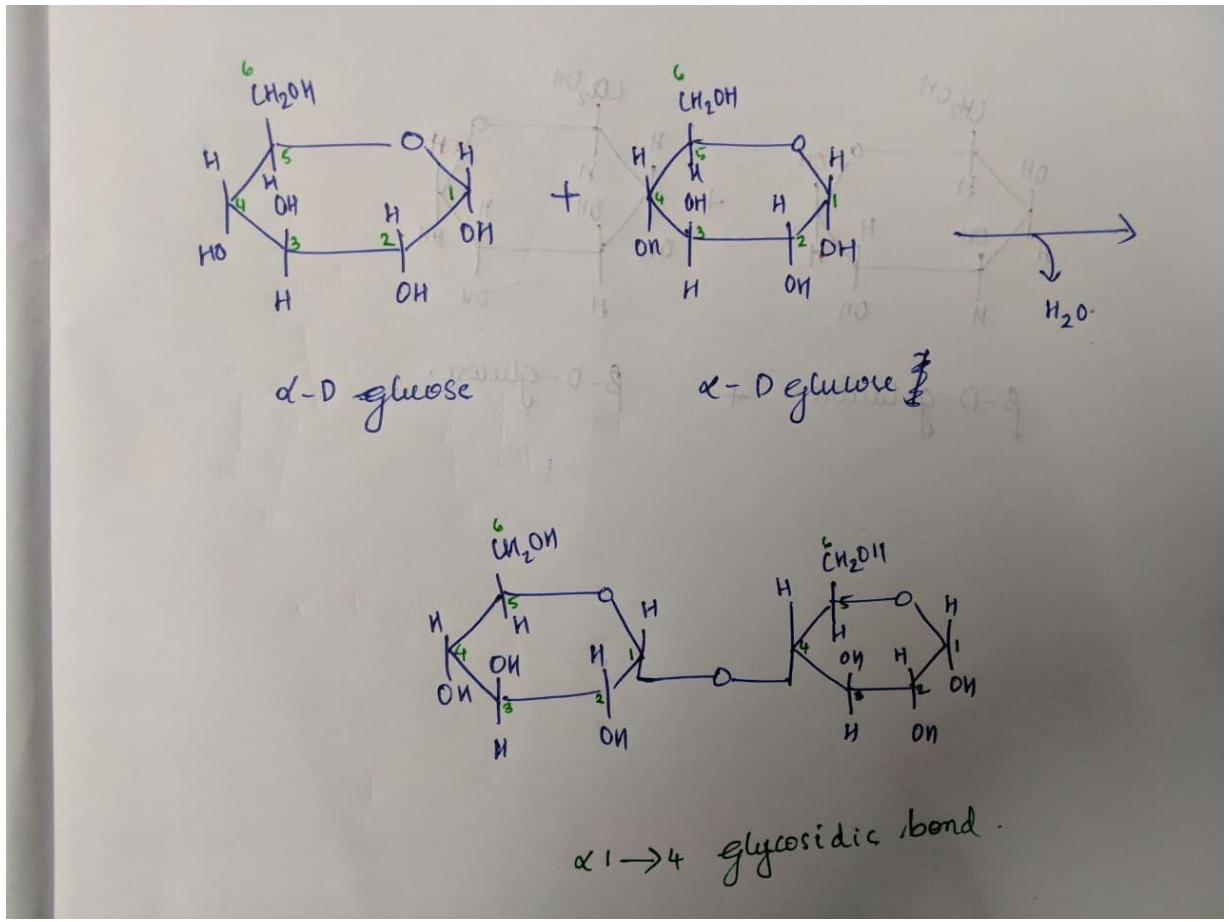
Lactose (Milk sugar)

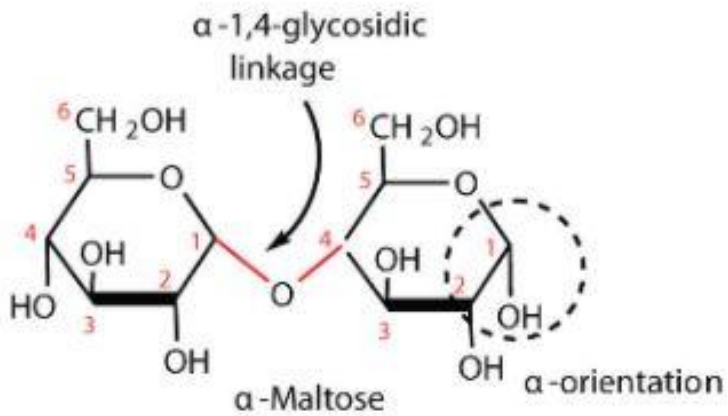
Sucrose (cane sugar or beet sugar)

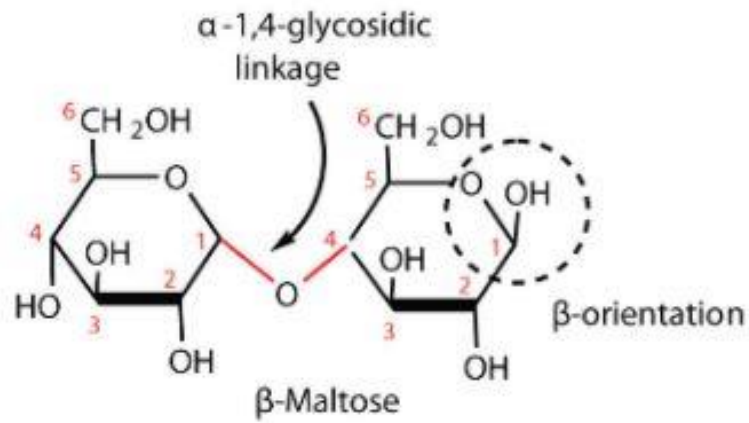


Maltose

- Disaccharide formed by the glycosidic linkage between two glucose residues (α 1→4)
- It is a reducing disaccharide
- In isomaltose two glucose units are linked together by (α 1→6)glycosidic linkage
- In higher animals ,maltose is the end product of oral and intestinal digestion of starch by amylases .

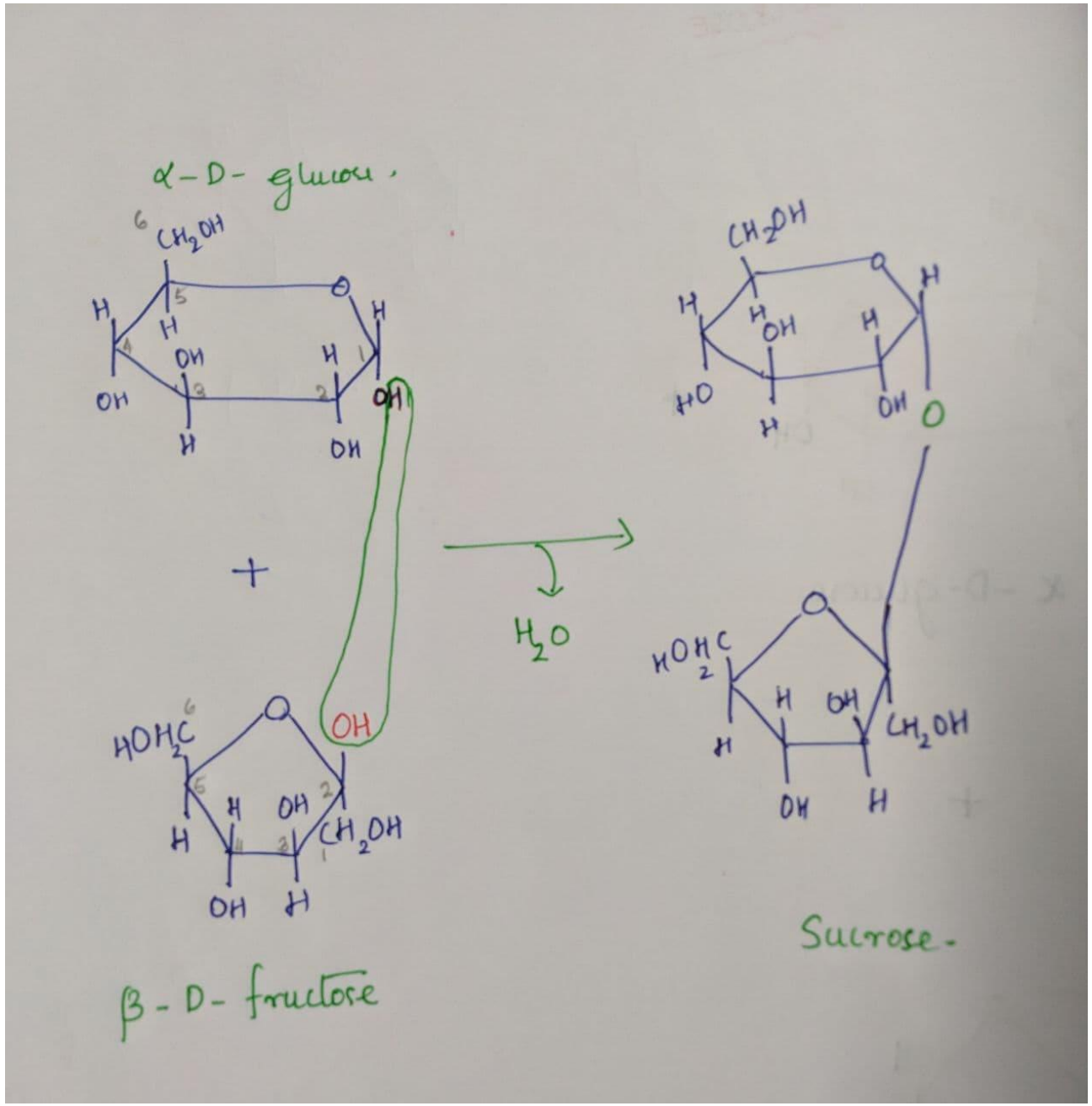

α-D glucose
α-D glucose
H_2O
α 1 → 4 glycosidic bond.


α -1,4-glycosidic
linkage
α -Maltose
α -orientation


α -1,4-glycosidic
linkage
β-Maltose
β-orientation

Sucrose

- It is the sweetening agent known as cane sugar
- Present in sugar cane and various fruits
- It is formed by the glycosidic linkage between α D Glucose and βD Fructose (α1→ β2)
- Sucrose is not a reducing sugar because the linkage involves first carbon of glucose and second carbon of fructose and no free groups are available
- When sucrose is hydrolysed the resulting solution will have the reducing action
- Sucrose is dextrorotatory but after hydrolysis the product formed ,fructose is laevorotatory thus sucrose is also called as invert sugar
- The enzyme producing hydrolysis of sucrose is called sucrase or invertase


α-D- glucose.
β-D- fructose
H_2O
Sucrose.

Polysaccharides