University of Al-Qadisiyah
College of Medicine

Medical Chemistry/ Part 1-Biochemistry

1st year / (2022-2023) / 1st Semester

L 3 – Monosaccharides, Di and Polysaccharides

((Structures, Reactions))

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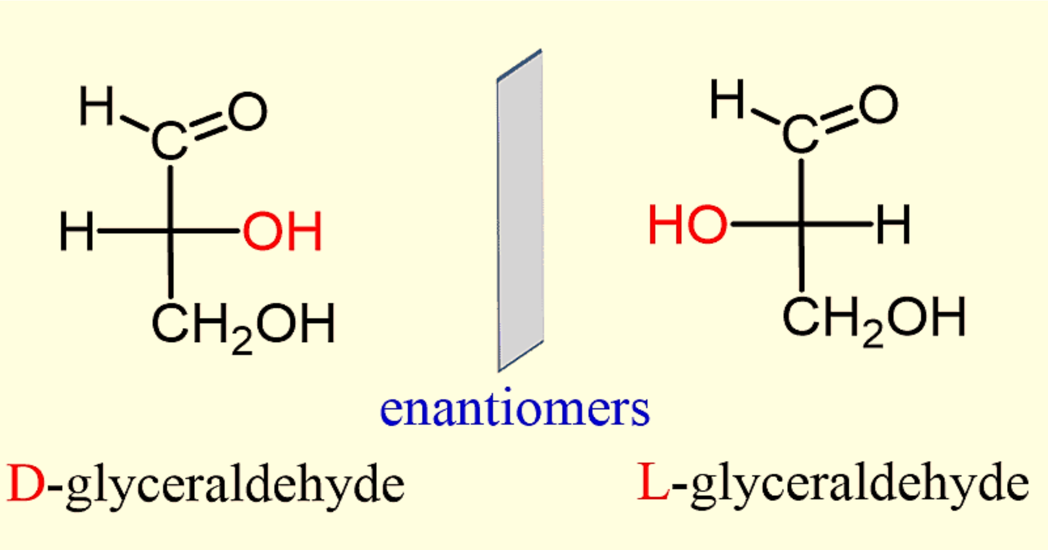
PhD. Medical Biochemistry

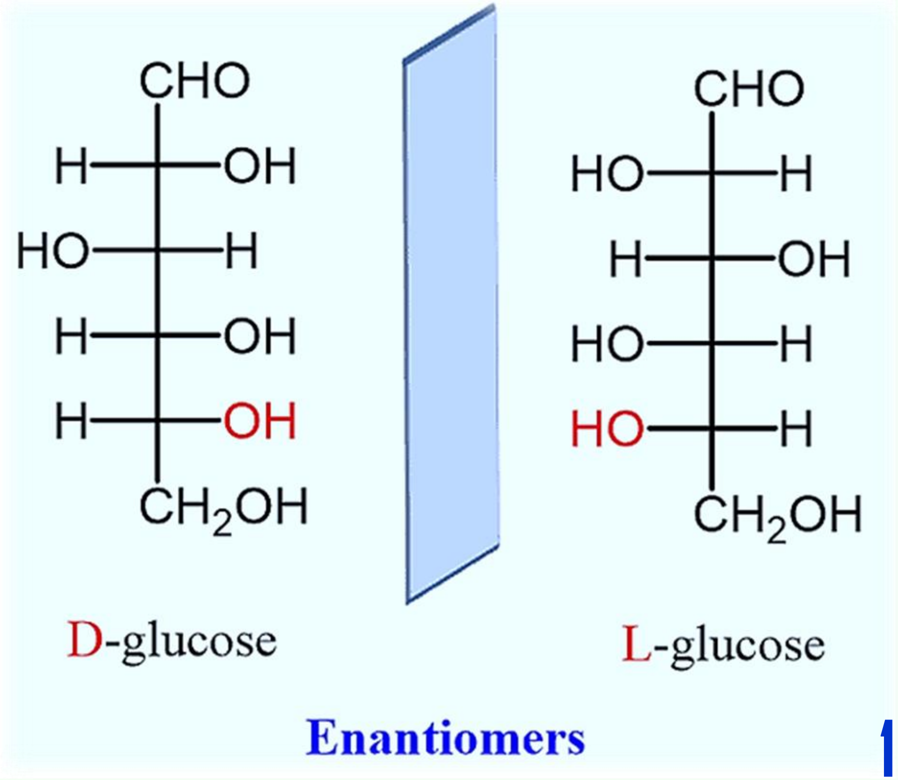
Monosaccharides

1- Structure of Glucose:

Optical activity of sugars: Optical activity is a characteristic feature of compounds with asymmetric carbon atom. The term dextrorotatory (d+) and levorotatory (l–) are used to compounds that respectively rotate the plane of polarized light to the right or to the left.

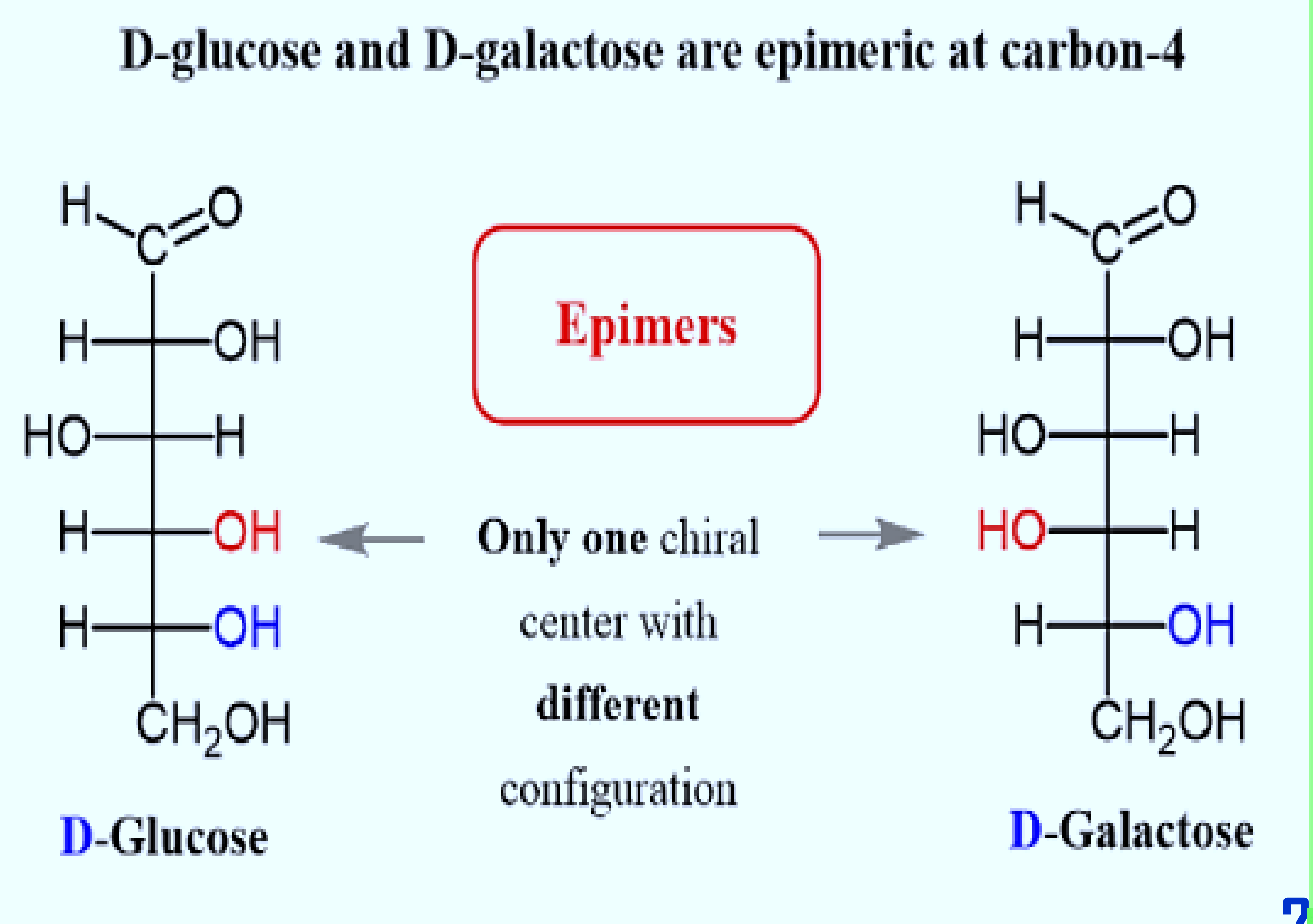
Enantiomers: are special types of stereoisomers that are mirror images of each other.





Epimers: If two monosaccharides differ from each other in their configuration around a single specific carbon atom, they are referred to as epimers to each other. E.g., glucose and galactose are epimers with regard to carbon 4 (C4-epimers).

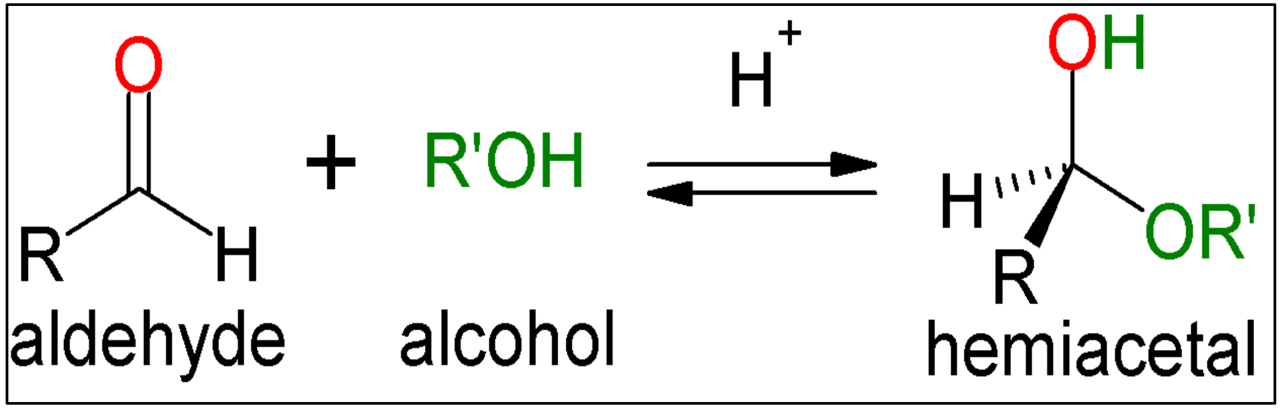
They differ in the arrangement of OH group at C4. The interconversion of epimers (e.g. glucose to galactose and vice versa) is known as epimerization, and enzymes namely epimerase catalyse this reaction.

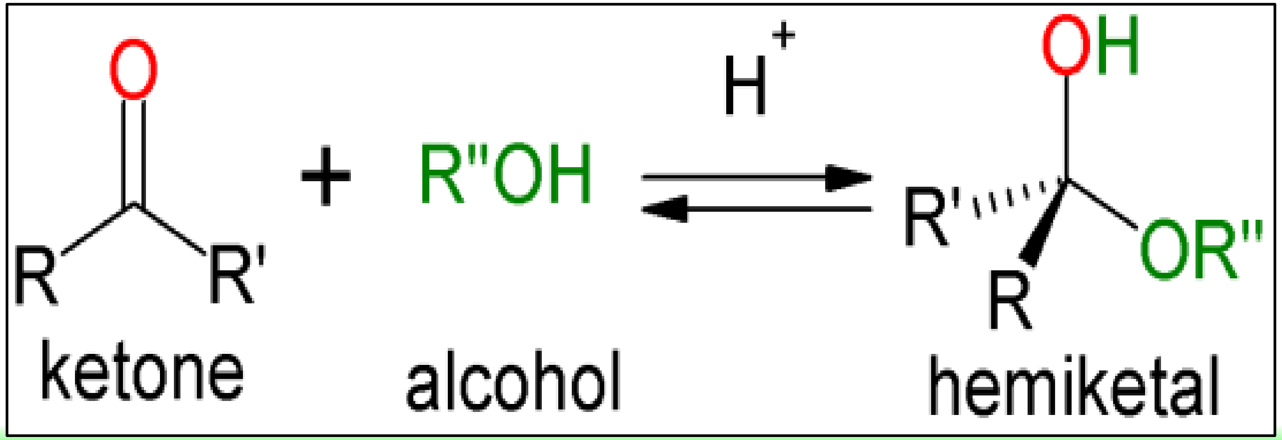


Hemiacetal and Hemiketal

For understanding of glucose structure, let us consider the formation of hemiacetals and hemiketals, respectively produced when an aldehyde or a ketone reacts with alcohol.

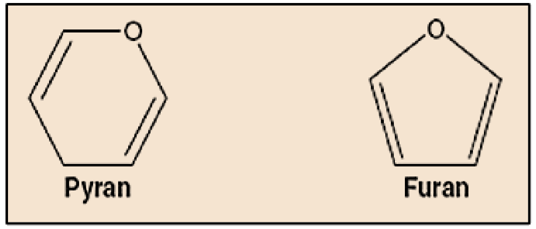
The hydroxyl group of monosaccharides can react with its own aldehyde or keto functional group to form hemiacetal and hemiketal. the aldehyde group of glucose at C1 reacts with alcohol group at C5 to form two types of cyclic hemiacetals namely α and β.

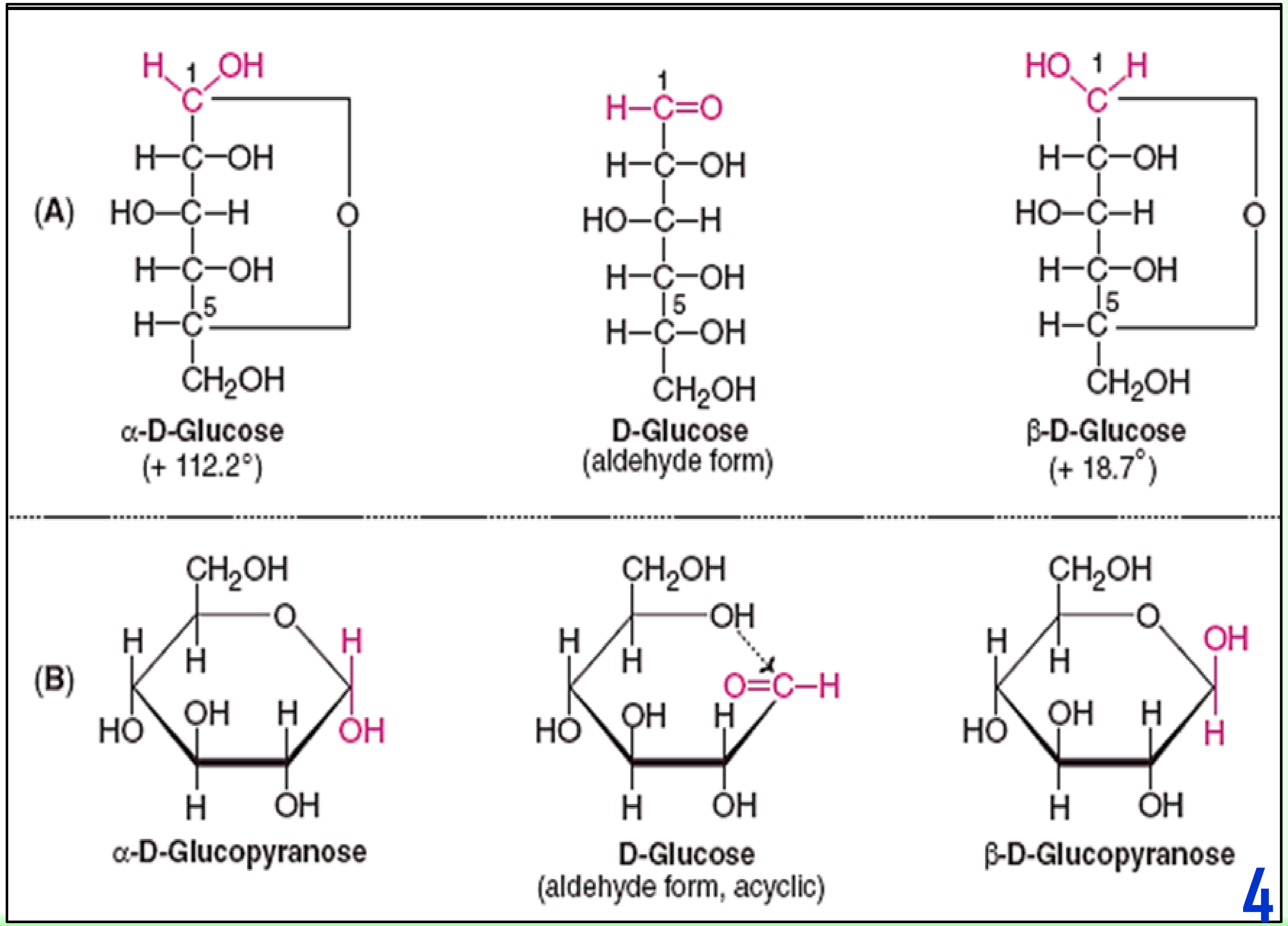




Pyranose and furanose structures: Haworth projection formulae are depicted by a six-membered ring pyranose (based on pyran) or a five-membered ring furanose (based on furan). The cyclic forms of glucose are known as α -D-glucopyranose and α -D-glucofuranose.

A- Fischer projection
B- Haworth projection





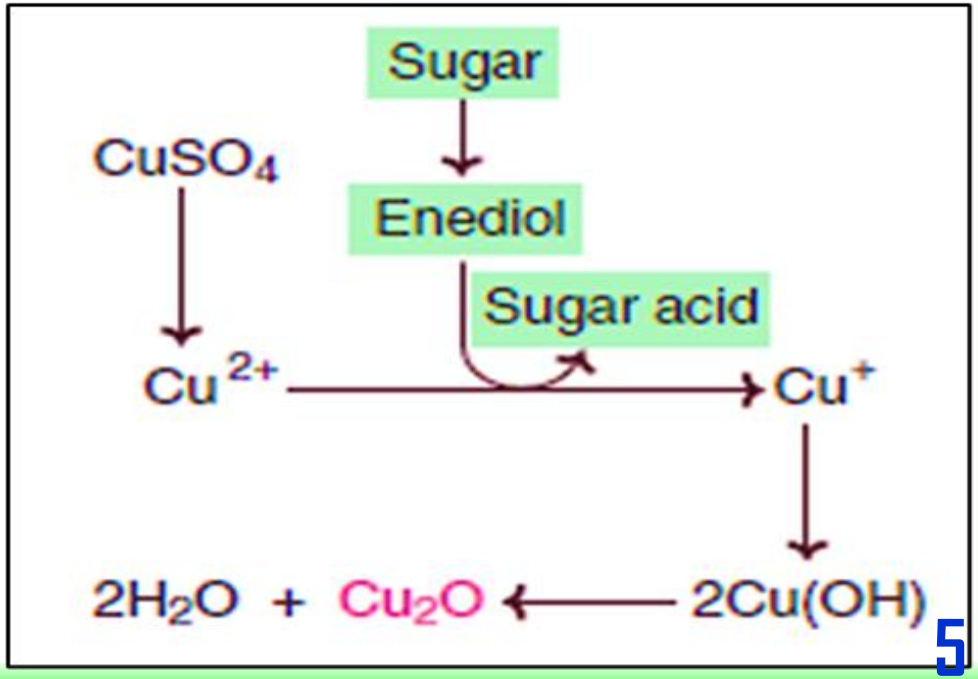
Mutarotation: The α and β anomers of glucose have different optical rotations. Mutarotation is defined as the change in the specific optical rotation representing the interconversion of α and β forms of D-glucose to an equilibrium mixture

Reactions of Monosaccharides

Reducing properties: The sugars are classified as reducing or nonreducing. The reducing property is attributed to the free aldehyde or keto group of anomeric carbon.

In the laboratory, many tests are employed to identify the reducing action of sugars. These include 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.

Sugars reduce cupric ions (Cu2+) of copper sulphate to cuprous ions (Cu+), which form a yellow precipitate of cuprous hydroxide or a red precipitate of cuprous oxide.



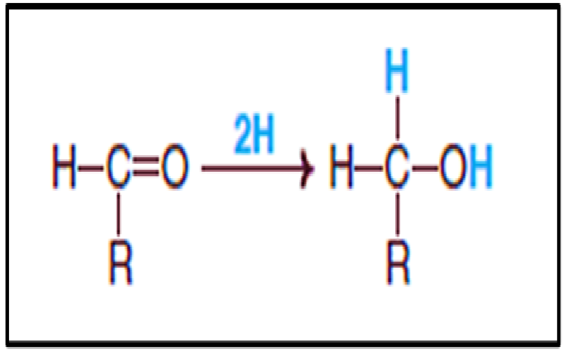
Oxidation: Depending on the oxidizing agent used, the terminal aldehyde (or keto) or the terminal alcohol or both the groups may be oxidized. For instance, Oxidation of glucose :

1. Oxidation of aldehyde group (CHO $\longrightarrow$ COOH) results in the formation of gluconic acid.

2. Oxidation of terminal alcohol group (CH_2OH $\longrightarrow$ COOH) leads to the production of glucuronic acid.

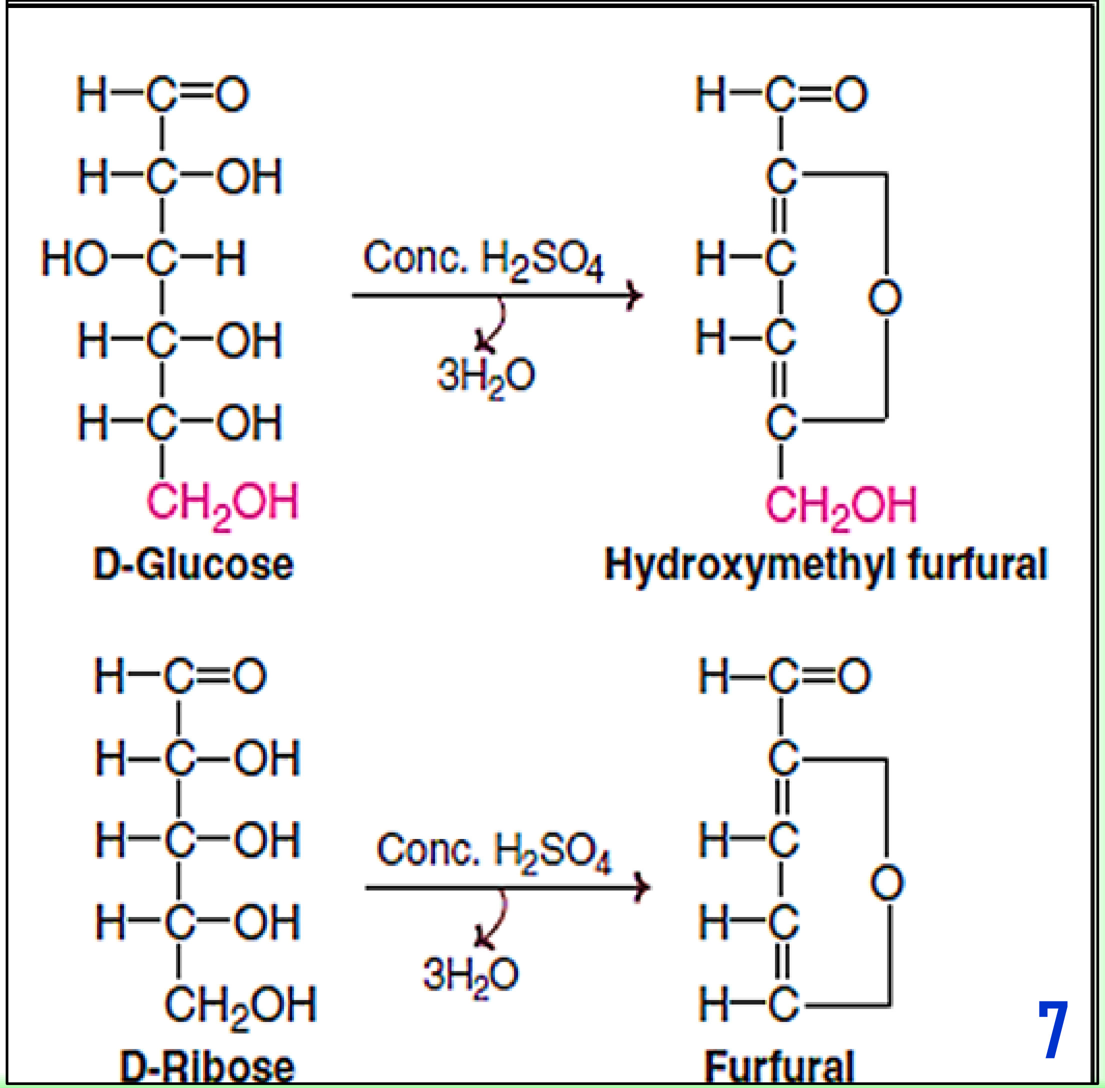
Reduction: When treated with reducing agents such as sodium amalgam, the aldehyde or keto group of monosaccharide is reduced to corresponding alcohol.

Sorbitol and dulcitol when accumulate in tissues in large amounts cause strong osmotic effects leading to swelling of cells, and certain pathological conditions



D-Glucose	$\longrightarrow$	D-Sorbitol
D-Galactose	$\longrightarrow$	D-Dulcitol
D-Mannose	$\longrightarrow$	D-Mannitol
D-Fructose	$\longrightarrow$	D-Mannitol + D-Sorbitol
D-Ribose	$\longrightarrow$	D-Ribitol

Dehydration: When treated with concentrated sulfuric acid, monosaccharides undergo dehydration with an elimination of 3 water molecules. Thus hexoses give hydroxymethyl furfural while pentoses give furfural on dehydration .



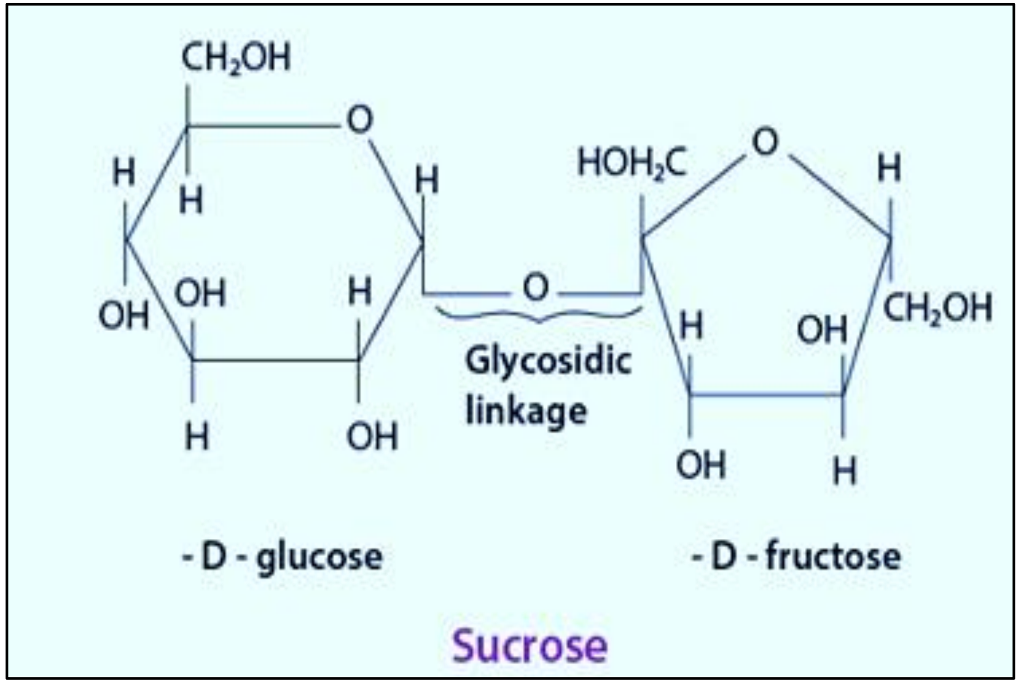
Formation of esters: The alcoholic groups of monosaccharides may be esterified by non-enzymatic or enzymatic reactions. Esterification of carbohydrate with phosphoric acid is a common reaction in metabolism.

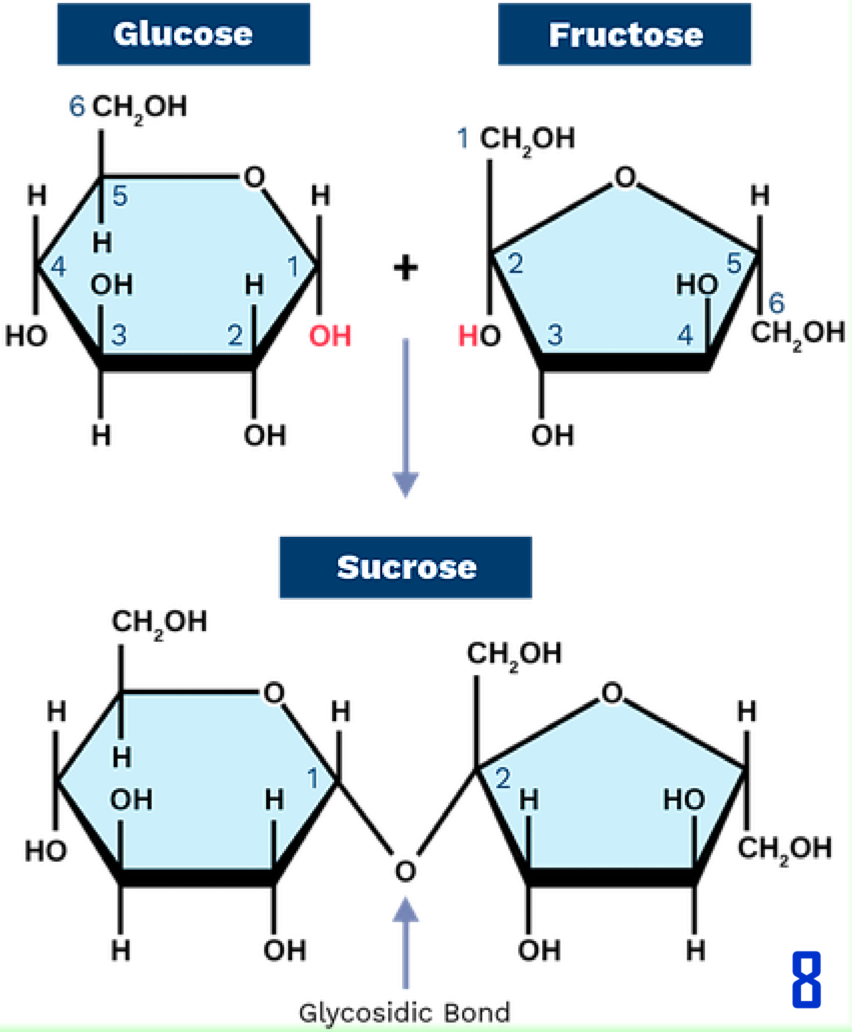
Glucose-6-phosphate and glucose-1-phosphate are good examples. ATP donates the phosphate moiety in ester formation.

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 noncarbohydrate (e.g. methyl alcohol, phenol, glycerol).

The bond formed is known as glycosidic bond and the non-carbohydrate moiety (when present) is referred to as aglycone

The monosaccharides are held together by glycosidic bonds to result in di-, oligo- or polysaccharide.



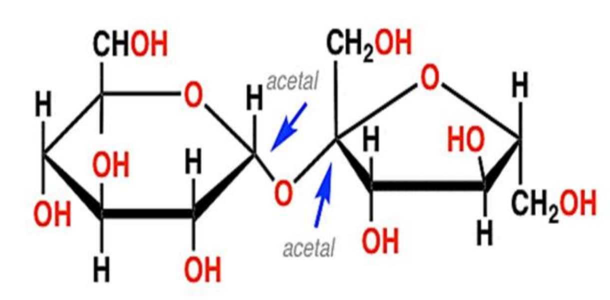


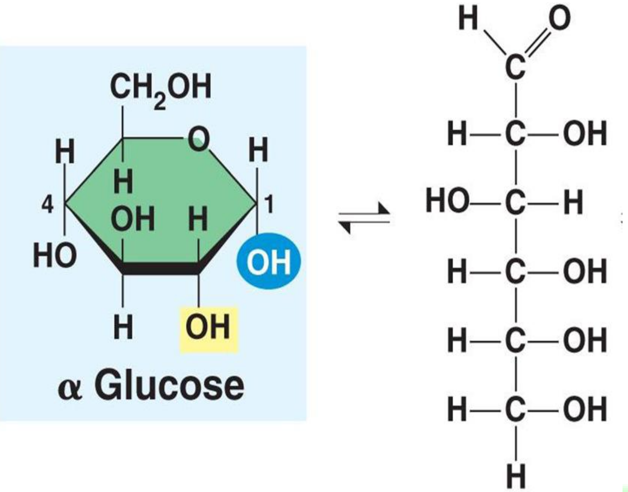
Disaccharides

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.

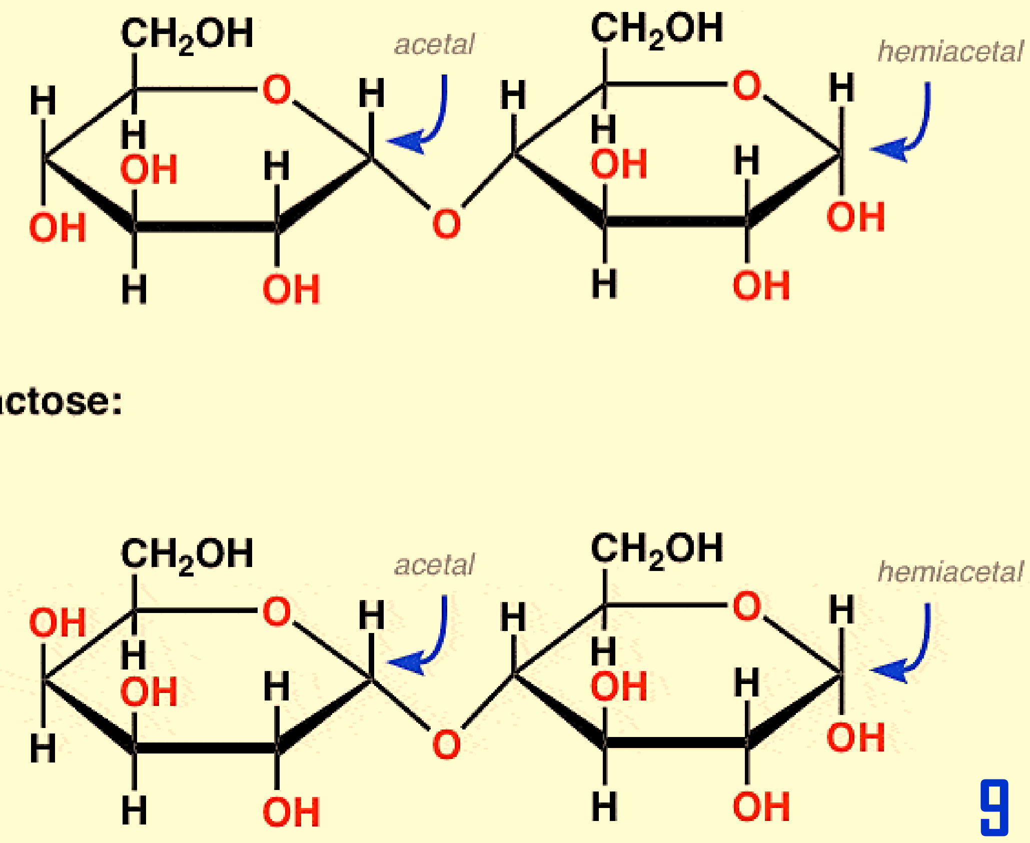
Sucrose is a non-reducing sugar



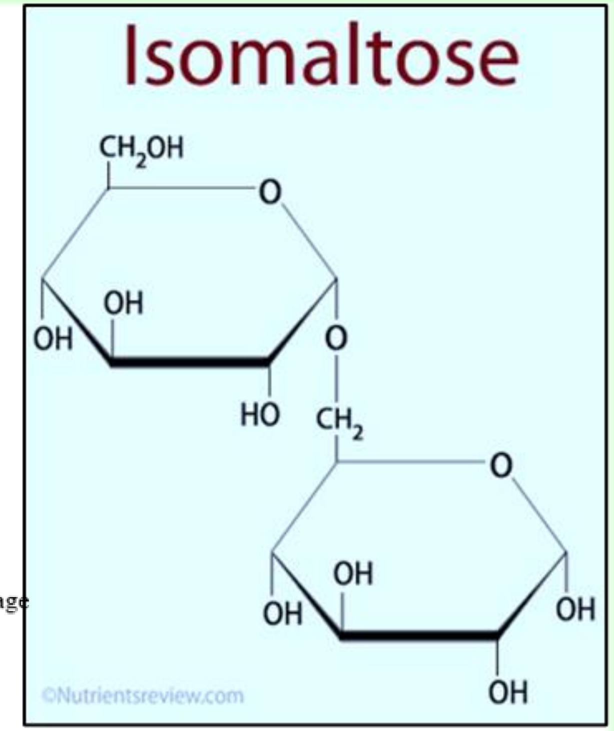


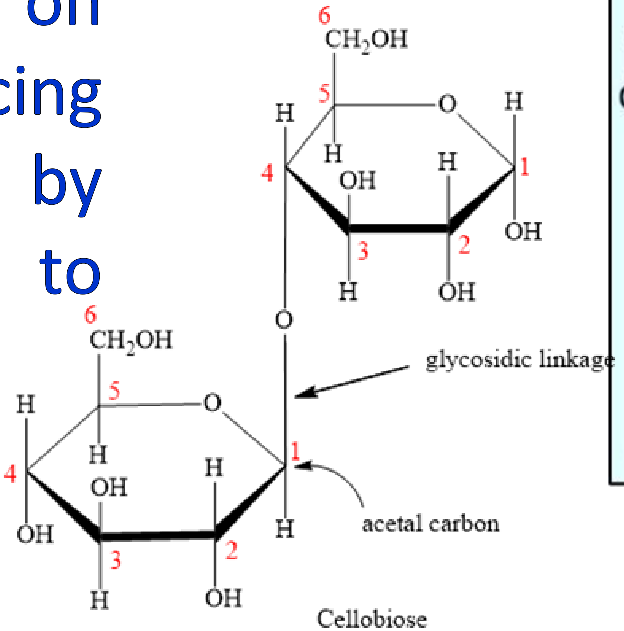
Maltose:

Lactose:



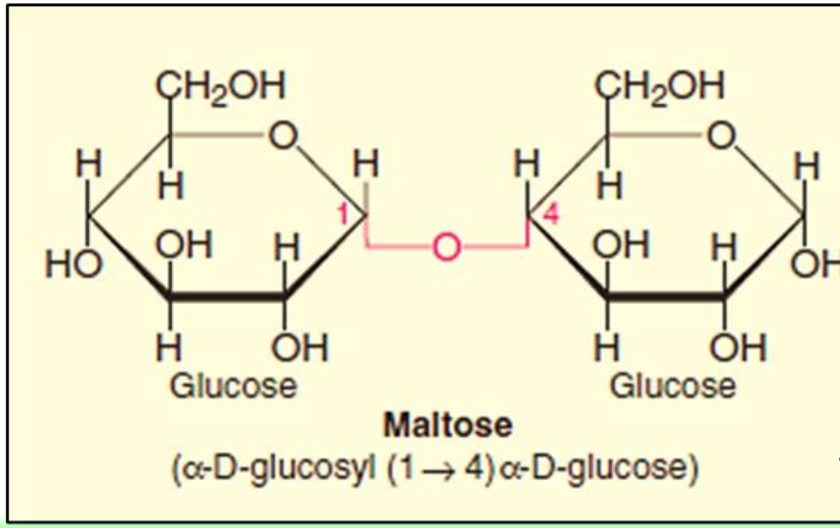
Maltose: is composed of two α-D-glucose units held together by α (1 ⟶ 4) glycosidic bond. The free aldehyde group present on C1 of second glucose answers the reducing reactions. Maltose can be hydrolysed by dilute acid or the enzyme maltase to liberate two molecules of α -D-glucose.





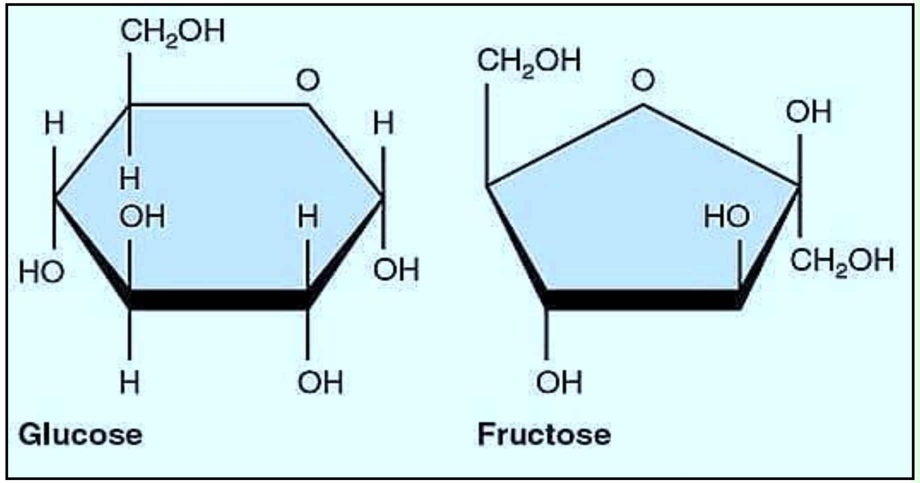
Cellobiose

Isomaltose, the glucose units are held together by α (1 ⟶ 6) glycosidic linkage. Cellobiose is another disaccharide, identical in structure with maltose, except that the former has β (1 ⟶ 4) glycosidic linkage. Cellobiose is formed during the hydrolysis of cellulose

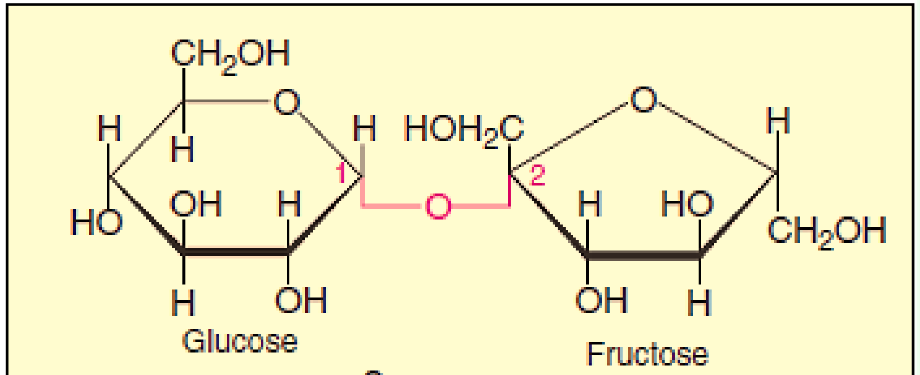


Sucrose: is made up of α -D-glucose and β - D-fructose. The two monosaccharides are held together by a glycosidic bond (α 1 ⟶ β2), between C1 of α -glucose and C2 of β -fructose.

The reducing groups of glucose and fructose are involved in glycosidic bond, hence sucrose is a non-reducing sugar, and it cannot form osazones.

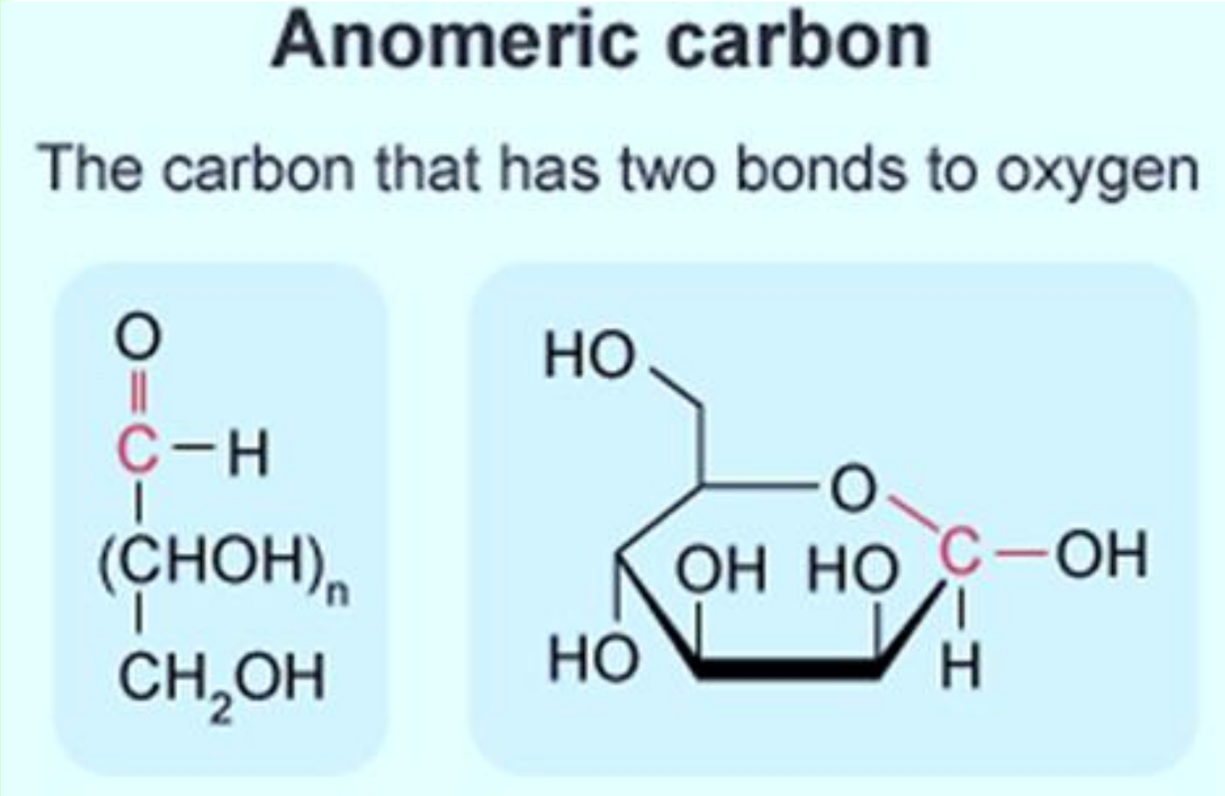


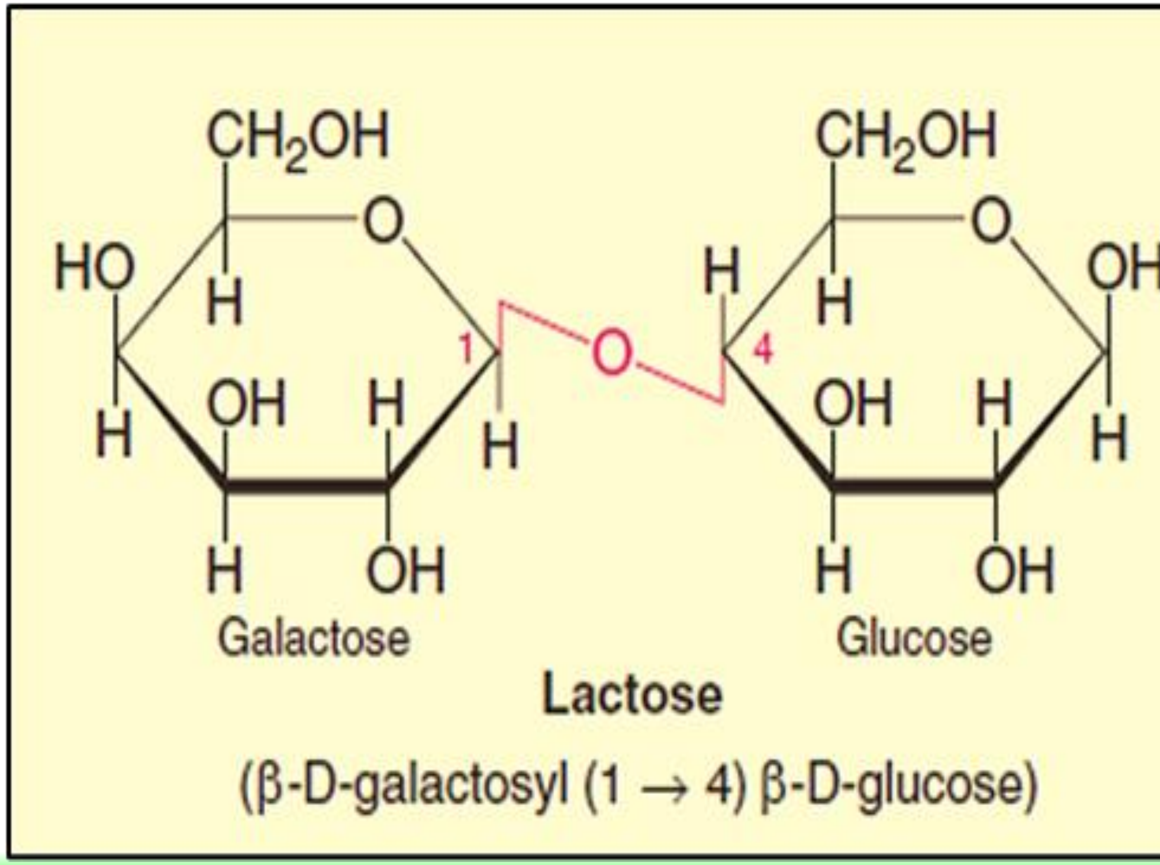
The intestinal enzyme sucrase hydrolyses sucrose to glucose and fructose which are absorbed



Sucrose
(α-D-glucosyl (1 → 2) β-D-fructose)

Lactose: (milk sugar) is the disaccharide found in milk. Lactose is composed of β -D-galactose and β -D-glucose held together by β (1 ⟶ 4) glycosidic bond. The anomeric carbon of C1 glucose is free, hence lactose exhibits reducing properties and forms osazones. 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.



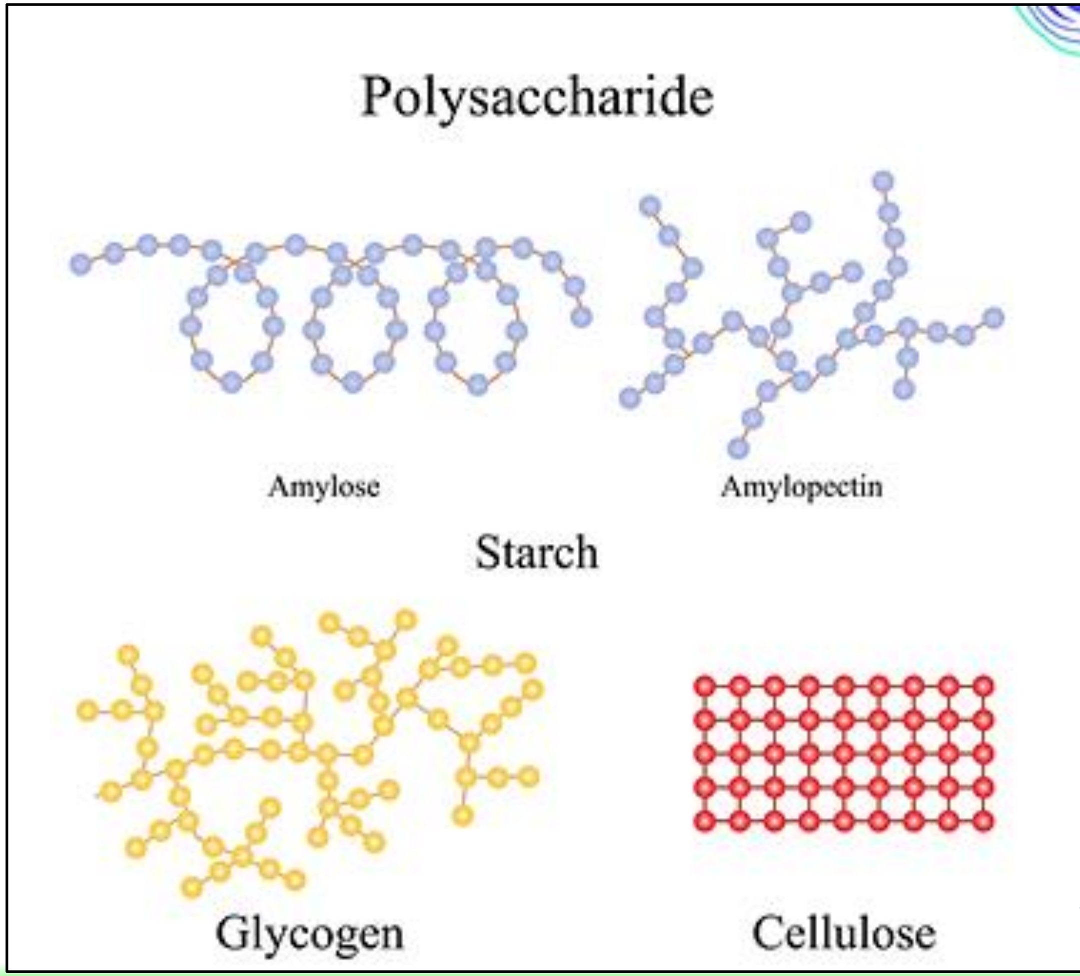


Polysaccharides

Polysaccharides: (or 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.

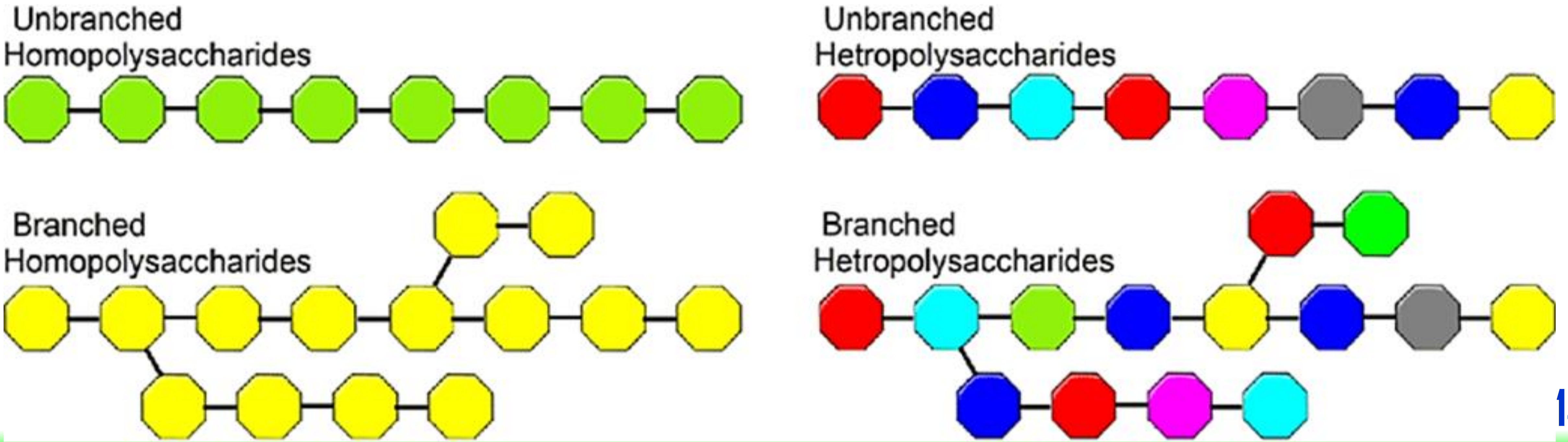
The occurrence of branches in polysaccharides is due to the fact that glycosidic linkages can be formed at any one of the hydroxyl groups of a monosaccharide.



Polysaccharides are of two types:

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

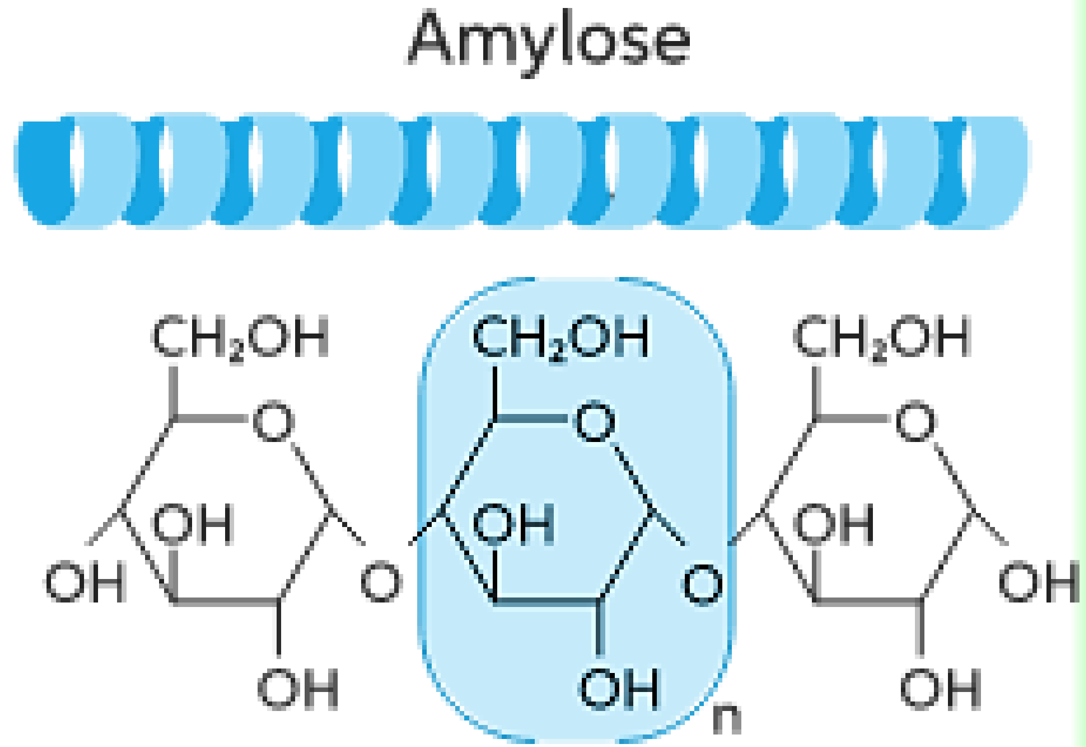
2. Heteropolysaccharides on hydrolysis yield a mixture of a few monosaccharides or their derivatives.



Starch (Homopolysaccharides): 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 α -glycosidic bonds. It is known as glucosan or glucan.

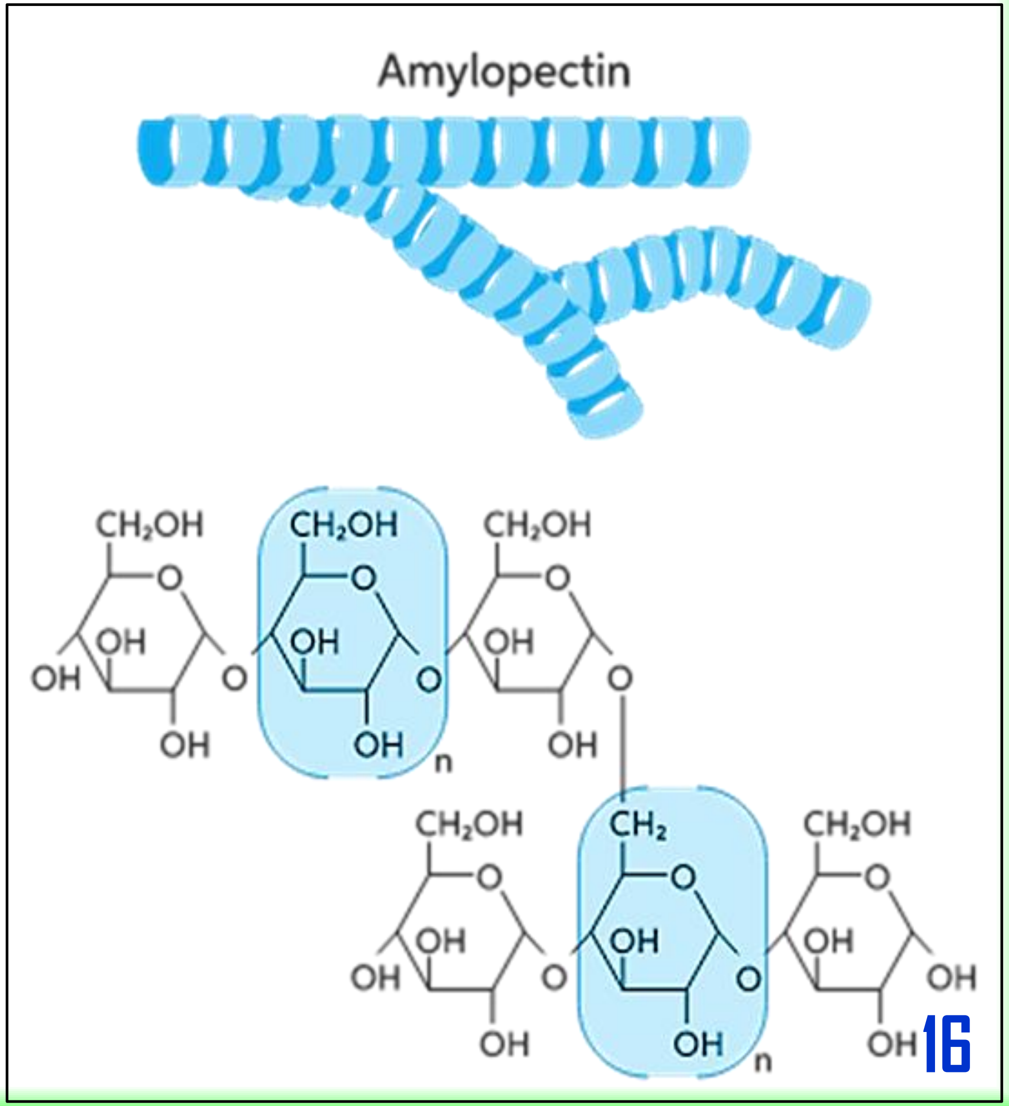
Starch consists of two polysaccharide components water soluble amylose (15-20%) and a water insoluble amylopectin (80-85%).

Chemically, amylose is a long unbranched chain with 200–1,000 D-glucose units held by α (1 ⟶ 4) glycosidic linkages.

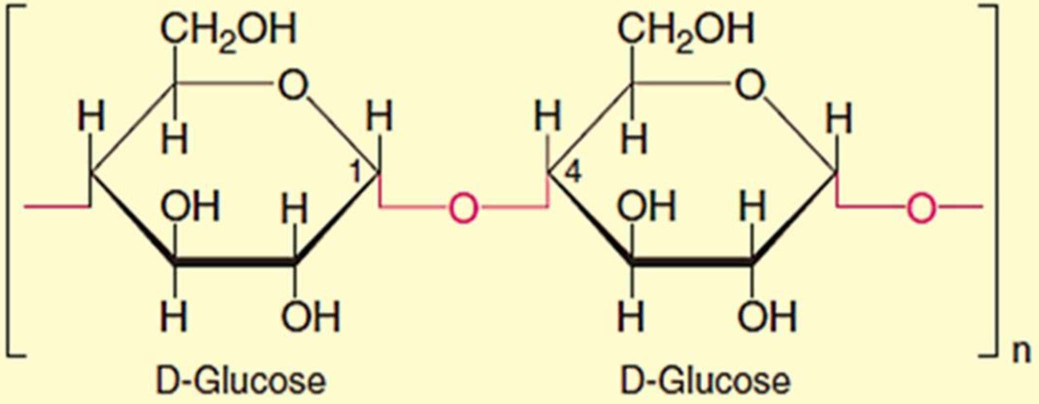


Amylopectin is a branched chain with α (1 ⟶ 6) glycosidic bonds at the branching points and α (1 ⟶ 4) linkages everywhere else.

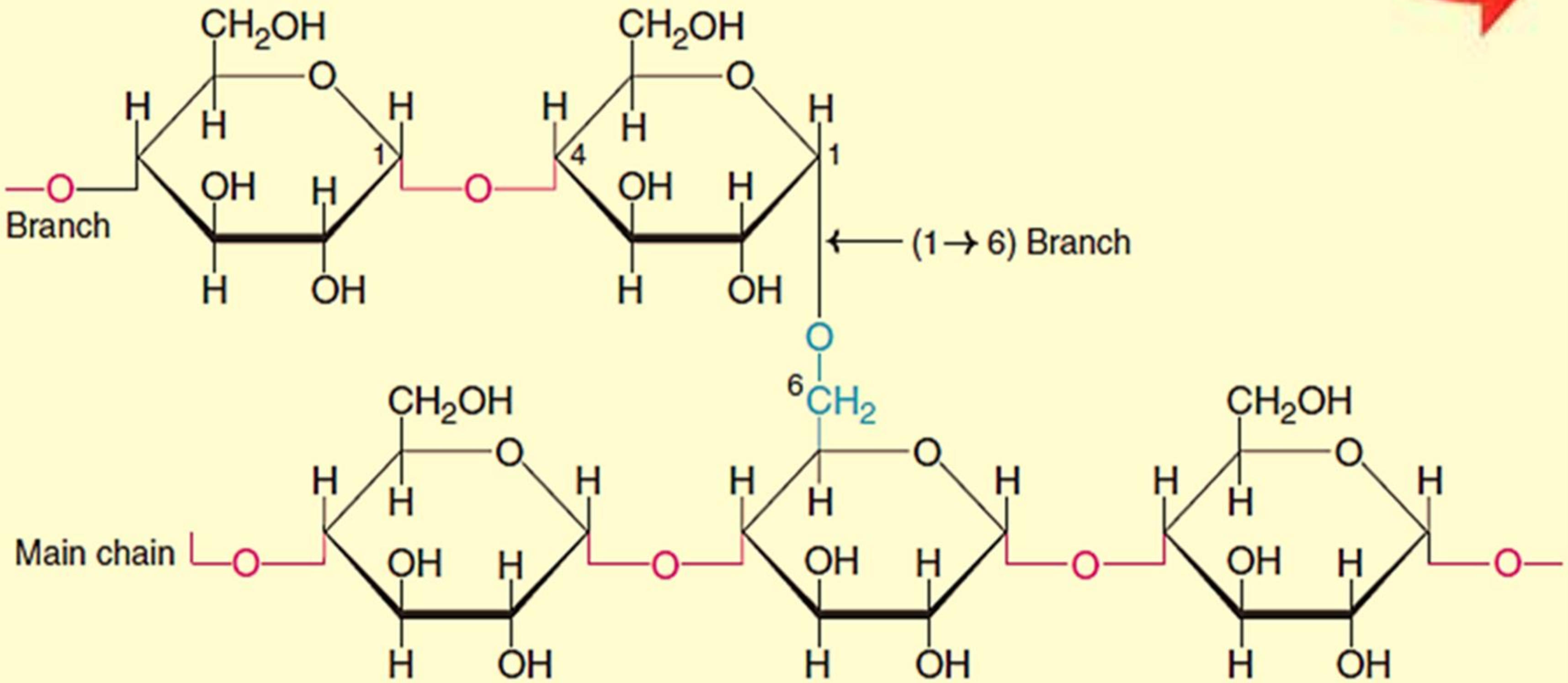
Amylopectin molecule containing a few thousand glucose units looks like a branched tree (20–30 glucose units per branch).



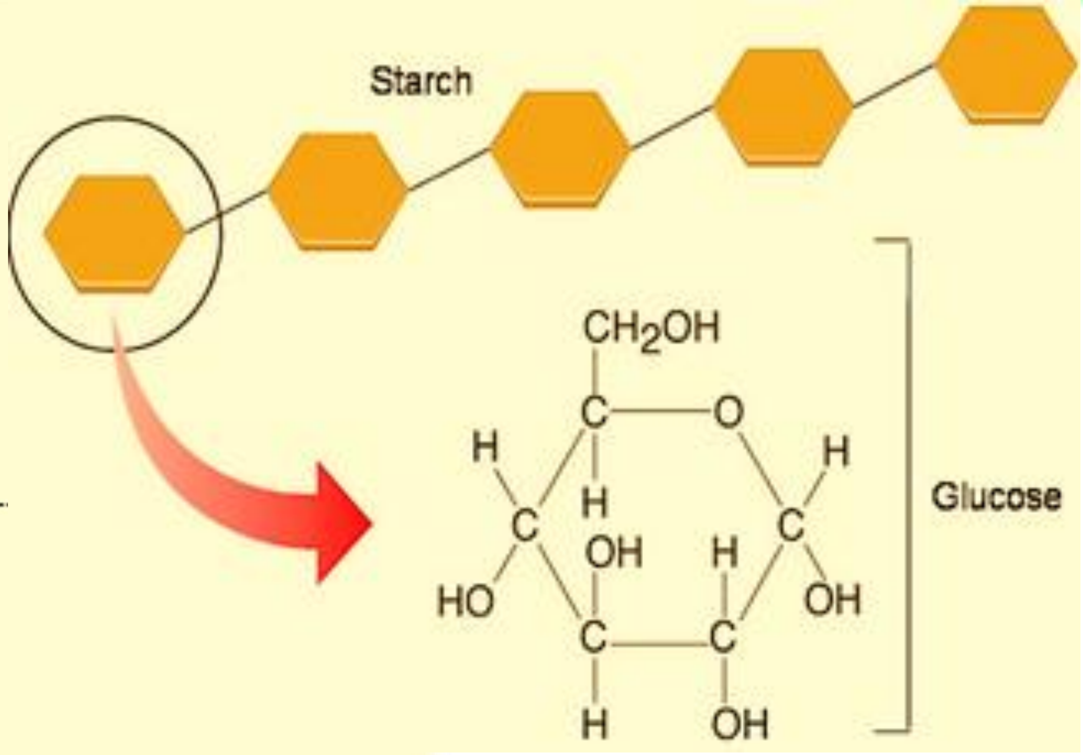
Starches are hydrolysed by amylase (pancreatic or salivary) to liberate dextrins, and finally maltose and glucose units. Amylase acts specifically on α (1 ⟶ 4) glycosidic bonds.

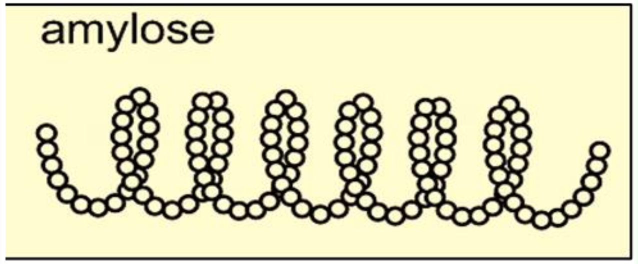


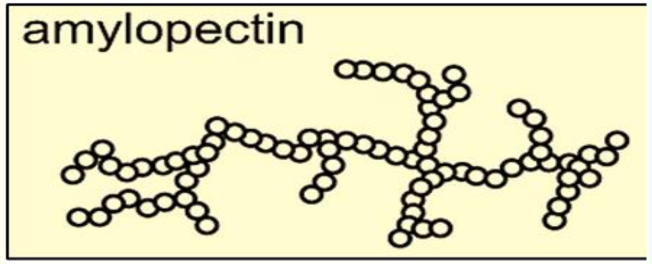
α-Amylose



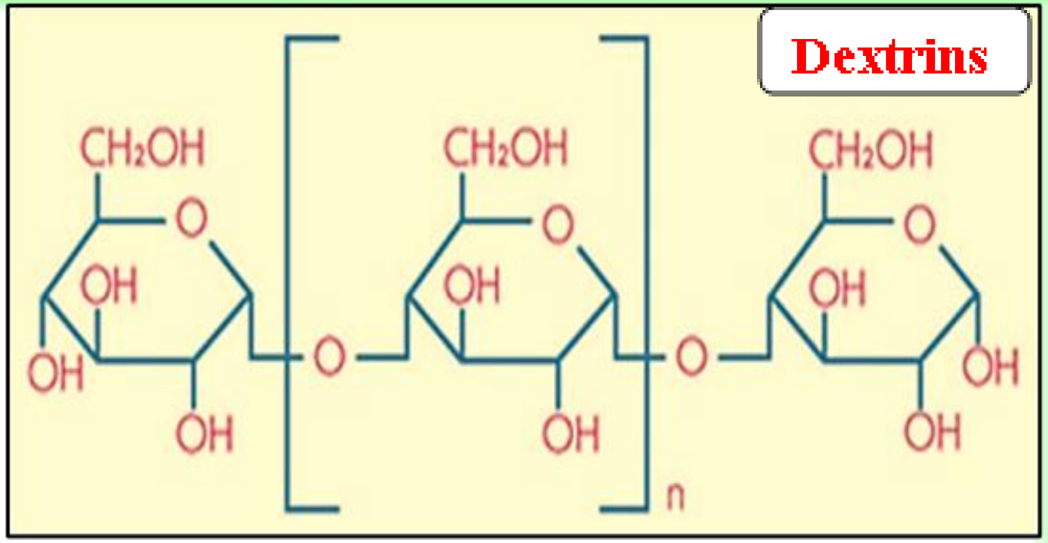
Amylopectin



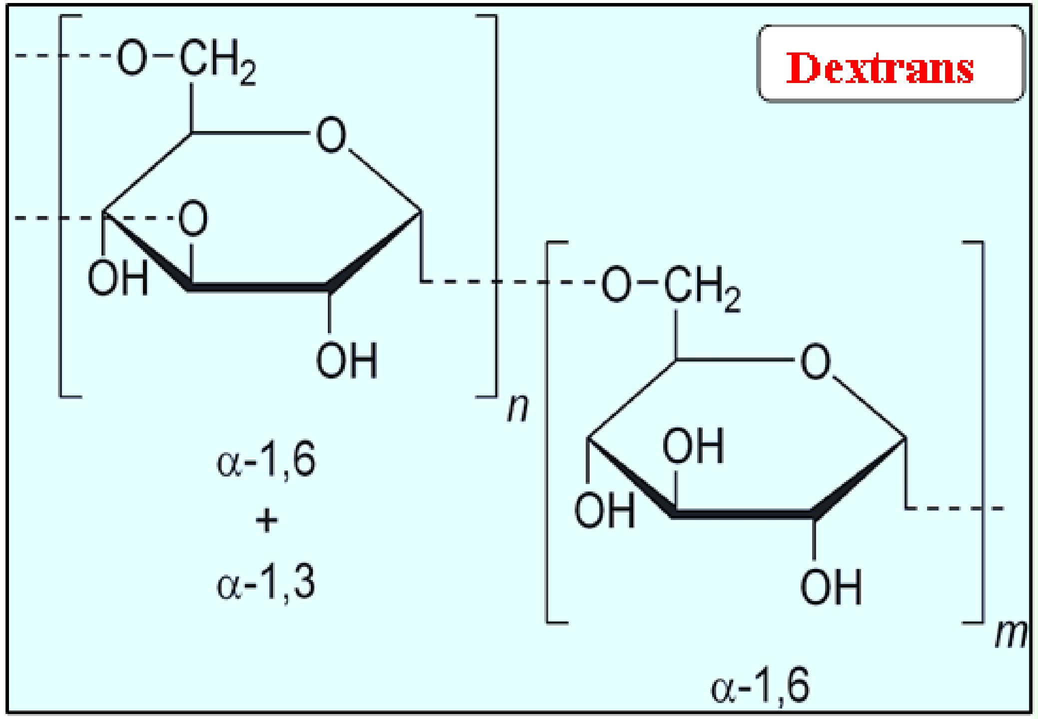




Dextrins: Dextrins are the breakdown products of starch by the enzyme amylase or dilute acids.

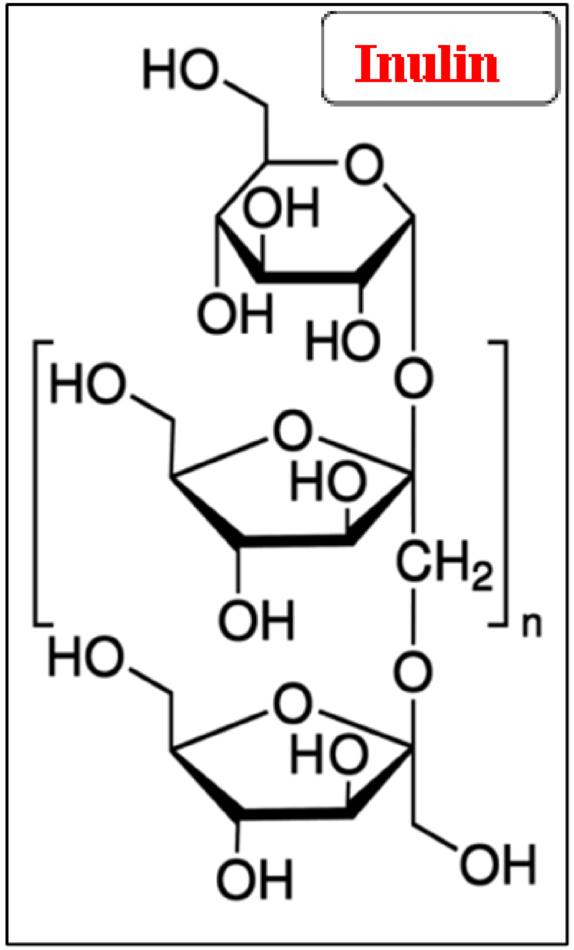


Starch is sequentially hydrolysed through different dextrins and, finally, to maltose and glucose.



Dextrans: are polymers of glucose, produced by microorganisms. They are used as plasma volume expanders in transfusion, and chromatography (e.g. gel filtration).

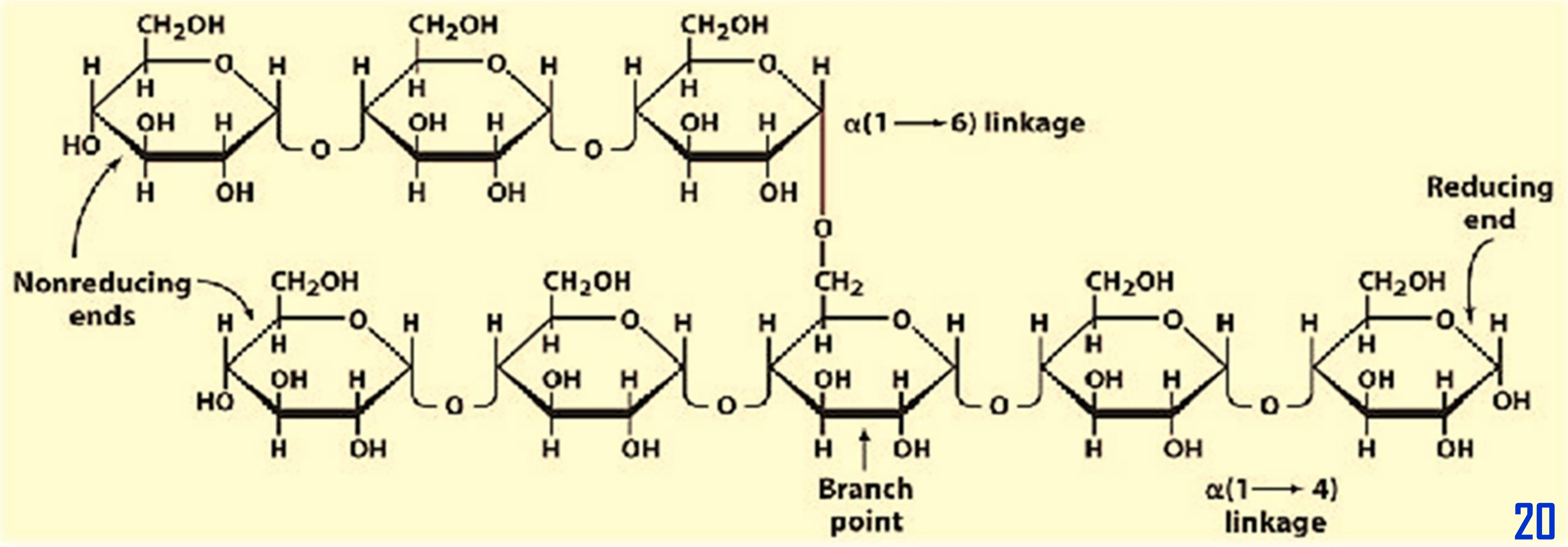
Inulin: is a polymer of fructose i.e., fructosan. It occurs in garlic, onion etc. It is a low molecular weight (around 5,000) polysaccharide easily soluble in water. Inulin is not utilized by the body. It is used for assessing kidney function through measurement of glomerular filtration rate (GFR).



Glycogen: is the carbohydrate reserve in animals, 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).

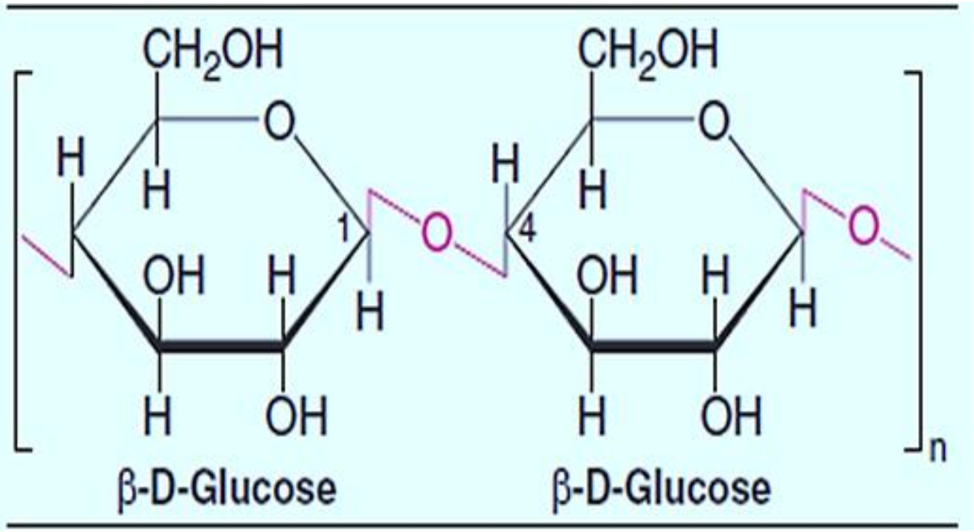
The structure of glycogen is similar to that of amylopectin with more number of branches.

Glucose is the repeating unit in glycogen joined together by α (1 → 4) glycosidic bonds, and α (1 → 6) glycosidic bonds at branching points. The molecular weight (up to 1 × 108) and the number of glucose units (up to 25,000) vary in glycogen depending on the source from which glycogen is obtained.

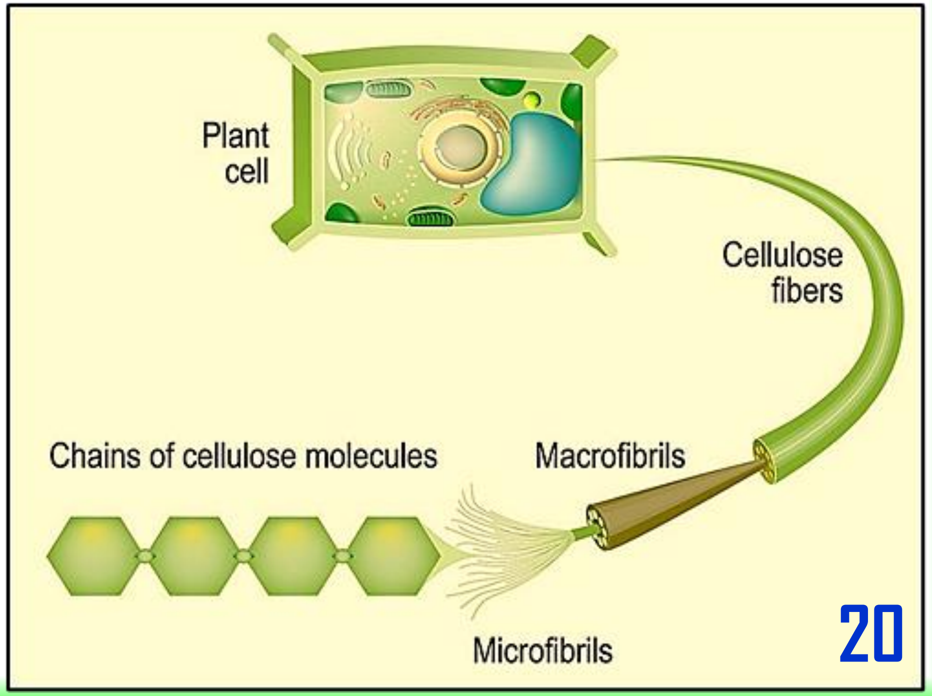


Cellulose: occurs exclusively in plants. It is a predominant constituent of plant cell wall. Cellulose is totally absent in animal body. Cellulose is composed of β -D-glucose units linked by β (1 → 4) glycosidic bonds.

Cellulose cannot be digested by mammals including man due to lack of the enzyme that cleaves β -glycosidic bonds (α amylase breaks α bonds only). Hydrolysis of cellulose yields a disaccharide cellobiose, followed by β -D-glucose



Cellulose



For your listening..

Dr. Ahmed Ghdhban Al-Ziaydi

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