

# MED-HUB

## BIOCHEMISTRY

### SUMMARY

### CARBS



**Carbohydrates:** are polyhydroxy aldehydes or ketones.

Functions of carbs:

1. major and first source of energy.
2. structure (like cellulose).
3. building blocks
4. cellular and immune recognition.

We have two classification systems:

**Classification I:** According to the number of sugars that constitute the molecule like:

1. monosaccharides = one sugar
2. disaccharides = two sugars
3. oligosaccharides = (3-10) sugars
4. polysaccharides = thousands or millions of sugars

**Classification II:** According to the number of carbon atoms they contain.  
Like: Triose, tetrose, pentose, hexose ...etc.

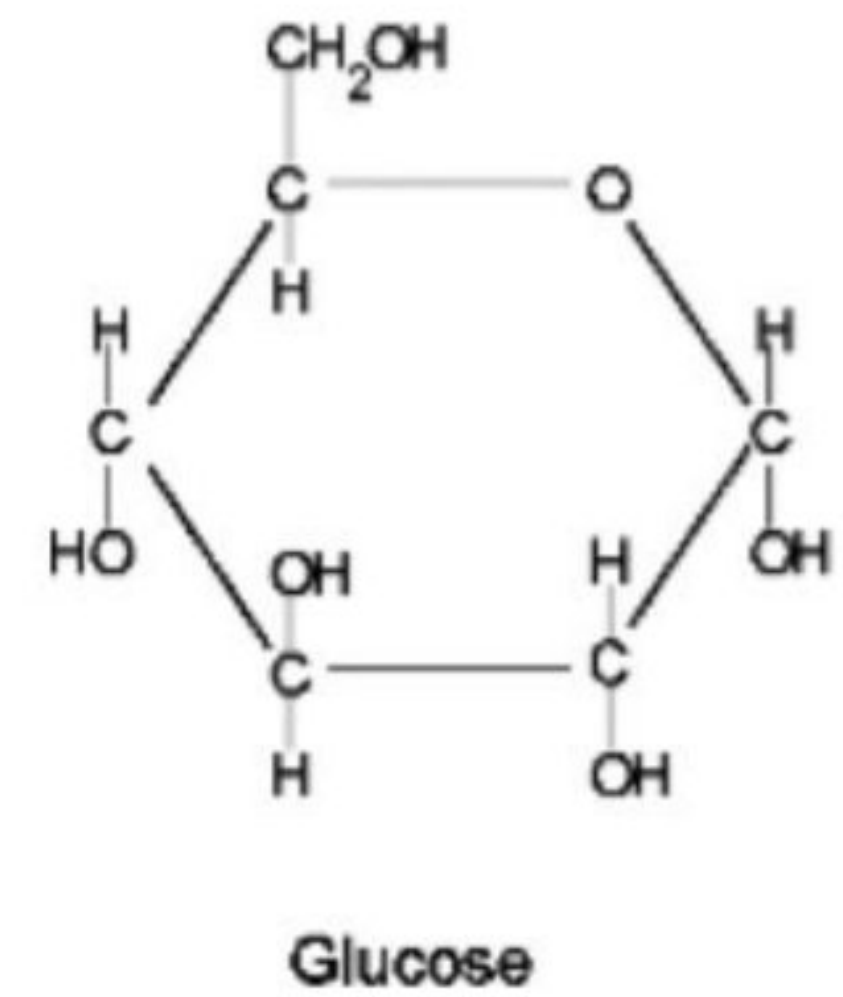
**Monosaccharides:**

- Basic chemical formula:  $C_n(H_2O)_n$ .
- The simplest aldose is Glyceraldehyde.
- The simplest ketose is Dihydroxyacetone.

Now we wanna talk about some common monosaccharides:

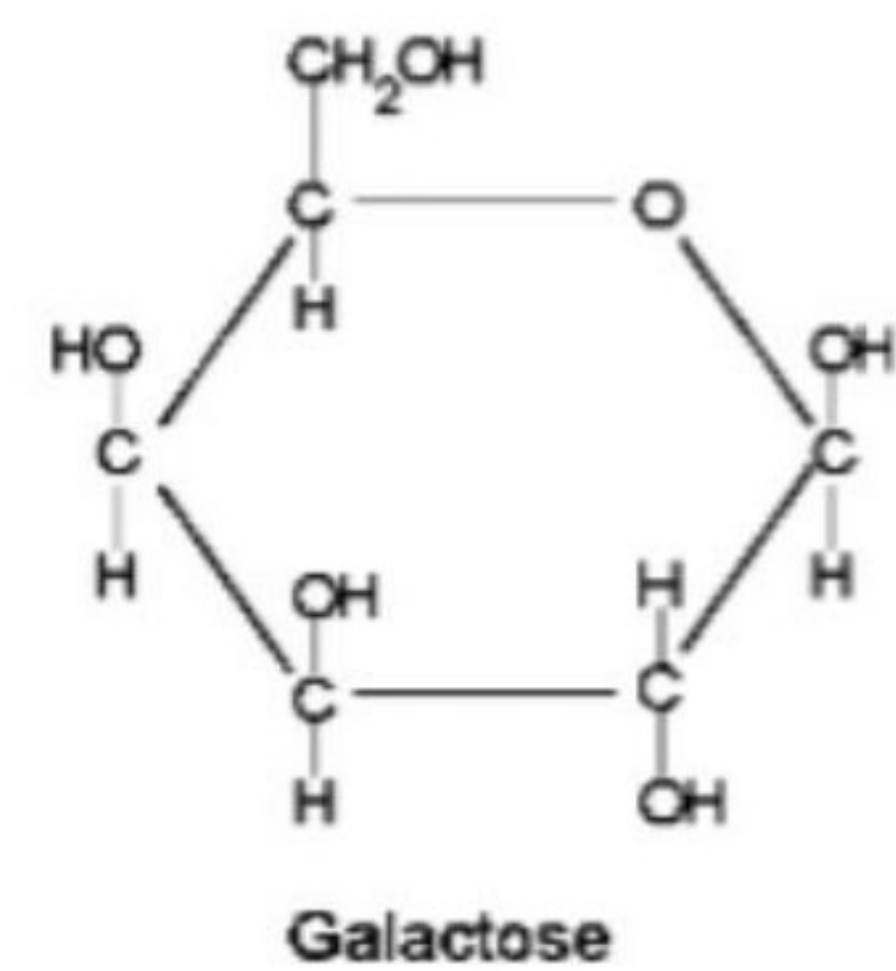
### 1. Glucose:

- Which is aldohexose.
- Known as blood sugar.
- Essential energy source.
- Found in every disaccharide and polysaccharide.



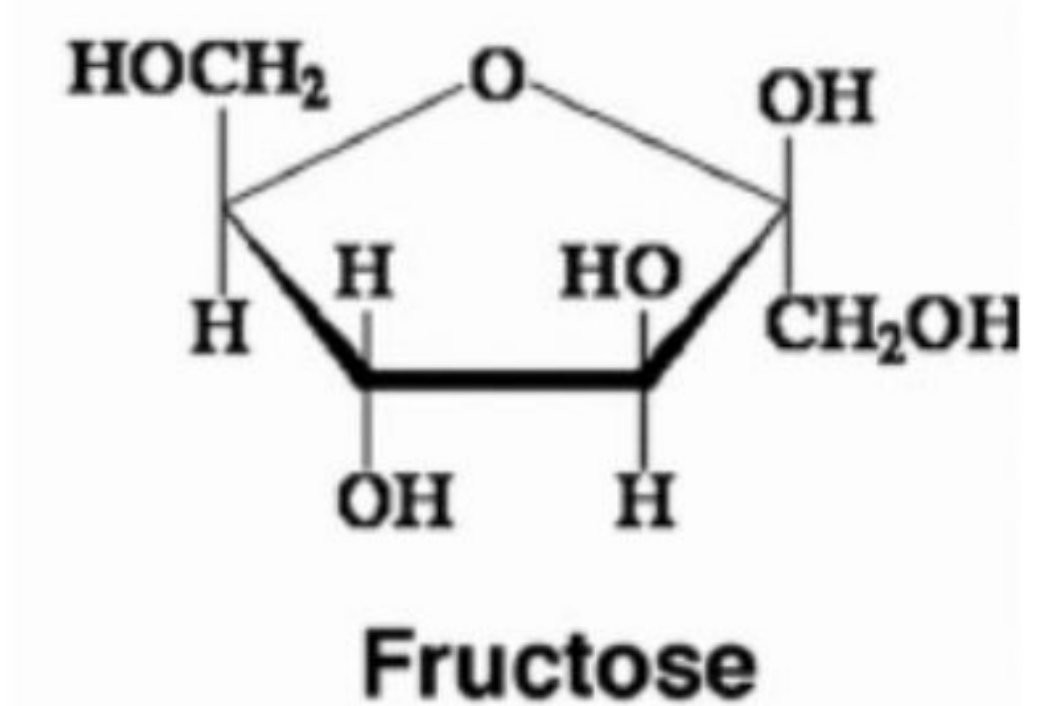
### 2. Galactose:

- Which is aldohexose.
- Hardly taste sweet.



### 3. Fructose:

- Ketohexose.
- Sweetest sugar.



How to calculate number of chiral centers:

1. In aldoses → Number of carbons – 2
2. In ketoses → Number of carbons – 3

### Isomerism:

Isomers: an isomer is a molecule with the same molecular formula as another molecule, but with different chemical structure.

We have two types of isomers:

1. Constitutional isomers: molecules with the same molecular formula, but have different bonding patterns and atomic organization.(like fructose and galactose)

Chiral center:

A carbon that is connected to four different groups not atoms

2. Stereoisomers: isomers that have the same molecular formula and sequence of bonded atoms, but differ in the three-dimensional orientations of their atoms in space. And we have two types of them:

A) Enantiomers (Complete mirror images) like D-isomer and L-isomer.

B) Diastereomers (Not complete mirror images) differ in one or more but if they only differ in the orientation of one chiral carbon we can call them Epimers.

**NOTE:** All epimers are diastereoisomers BUT not all diastereoisomers are epimers.

❖ How to calculate number of isomers?

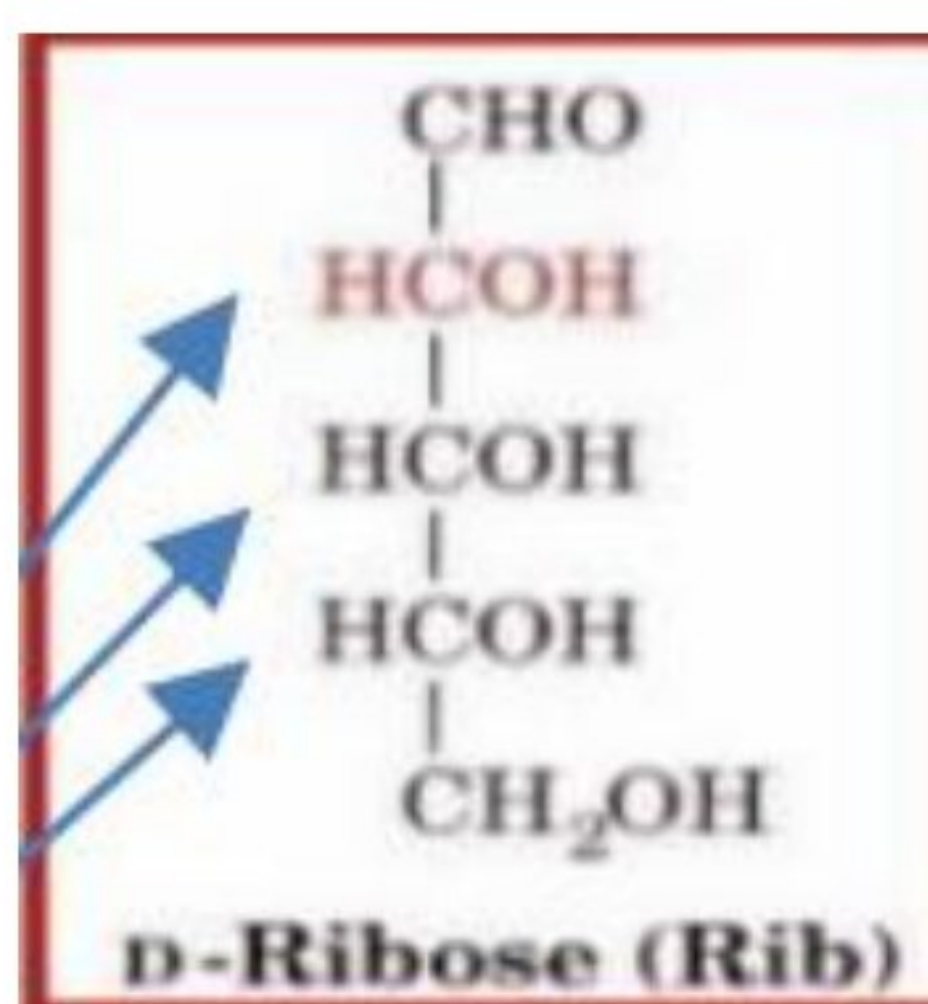
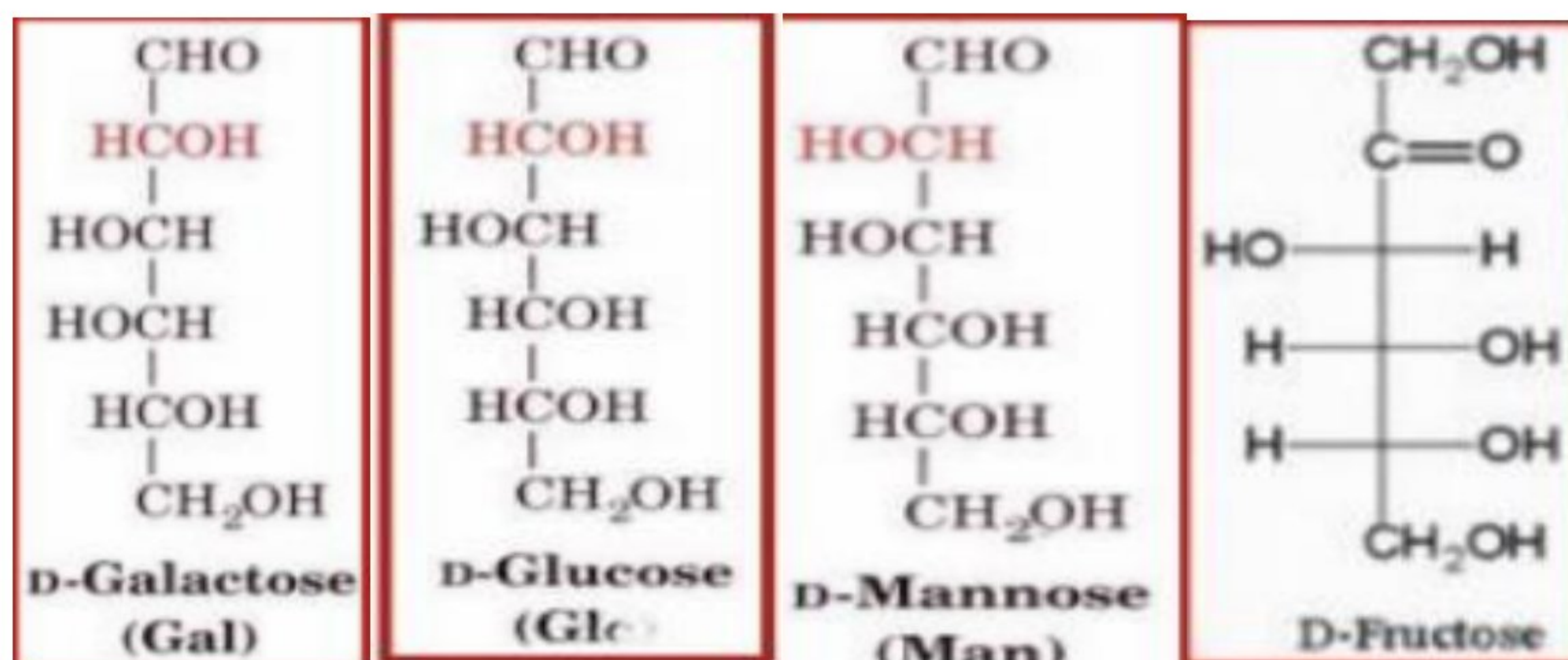
By  $2^n$

**Anomers:** are sugars that differ in the orientation of the OH group in the carbonyl carbon (carbon #1 for glucose, and carbon #2 in fructose).

- If the (OH) is facing upward → beta sugar
- If the (OH) is facing downward → alpha sugar

**NOTE:** Glucose spends more time in beta form than alpha and fructose spends more time as alpha.

**YOU SHOULD MEMORIZE THESE STRUCTERS:**



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## Modified Sugars:

**1. Sugar acids:** are products of sugar-oxidation reactions.

Ex: a glucose can be oxidized into carboxylic acid through the OH group at different sites on its' sugar structure.

Oxidation is done by oxidizing agents that can be:

1. Weak oxidizing agents.
2. Strong oxidizing agents like:  $\text{KMNO}_4$ ,  $\text{Cr}_2\text{O}_3$
3. Enzymes.

Sugar acid	Oxidation site	Oxidation agent	examples
-uronic acid	Carbon no.6	Enzymes	Glucuronic acid (glucuronate) Galacturonate
-aric acid	Carbon no.1 + no.6	Strong oxidizing agent	Galactaric acid
-onic acid	Carbon no.1	Weak oxidizing agent	Galactonic acid (Galactonate) Gluconic acid (gluconate)

❖ The difference between strong and weak oxidizing agents is:

The weak oxidizing agent can oxidize an aldehyde to carboxylic acid in one-step reaction, while strong oxidizing agent can oxidize a primary alcohol to a carboxylic acid which is two steps away.

**NOTE:** Ketoses can not be oxidized only by an indirect oxidation.

**indirect oxidation of ketoses:** ketoses can be oxidized when they isomerize to aldoses, in which they're converted into aldoses throughout bonds + electrons rearrangement causing the transfer of the carbonyl group from carbon.2 to carbon no.1.

We have two biochemical tests to distinguish between aldehydes and ketones:

### 1. Benedict's test:

a blue reagent that contains copper ion is going to be added to an aldehyde such as glucose, copper oxidizes it forming carboxylic acid and a brick red precipitate ( $\text{Cu}_2\text{O}$ ) that is used as an indication for aldehyde presence in solutions, if a ketone was added to the copper reagent no reaction would take place and the color would stay as it is rather than becoming brick red colored (No change).

### 2. Tollen's test :

Tollen's test reagent  $\text{Ag}(\text{NH}_3)_2^+$  contains silver (Ag), as it reacts with the ring structure of the aldose causing it to oxidize into **lactone**, leaving behind silver mirror.

(Ag precipitate), if a ketone was added to the  $\text{Ag}(\text{NH}_3)_2^+$  no reaction would take place.

**lactone:** is produced from aldose oxidation, a cyclic ester that has carboxyl and alcohol functional groups.

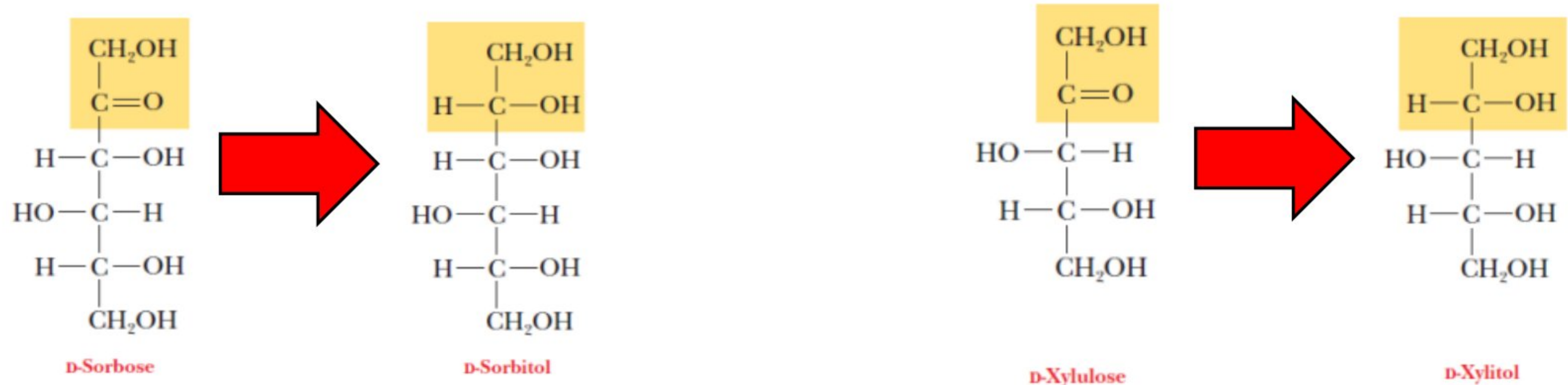
### Clinical Application on Tollen's Test:

- Vitamin C (ascorbic acid) is an unsaturated **lactone** that has an oxygen atom, a carbonyl group  $\text{C}=\text{O}$ , and a double bond in its ring structure.
- Vitamin C is important for uplifting and improving our immune system where it acts as antioxidant.
- Air oxidation of ascorbic acid, followed by hydrolysis of the ester bond, leads to loss of activity as a vitamin, so whenever ascorbic acid-containing food gets exposed to Air, the Vitamin C gets oxidized, causing it to deactivate because a new molecule is formed.
- A lack of fresh food can cause vitamin C deficiencies which leads to **scurvy**.

## 2.Sugar alcohol:

are products of ketose reduction, where the ketone group gets reduced back into a secondary alcohol.

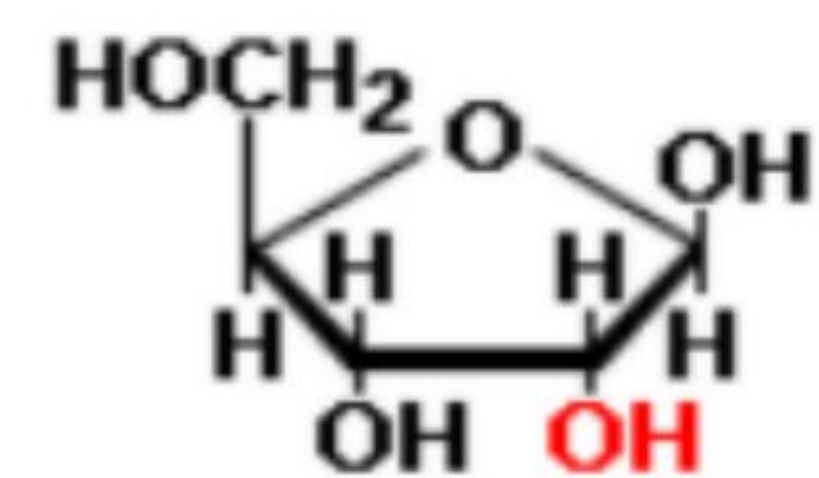
Ex.



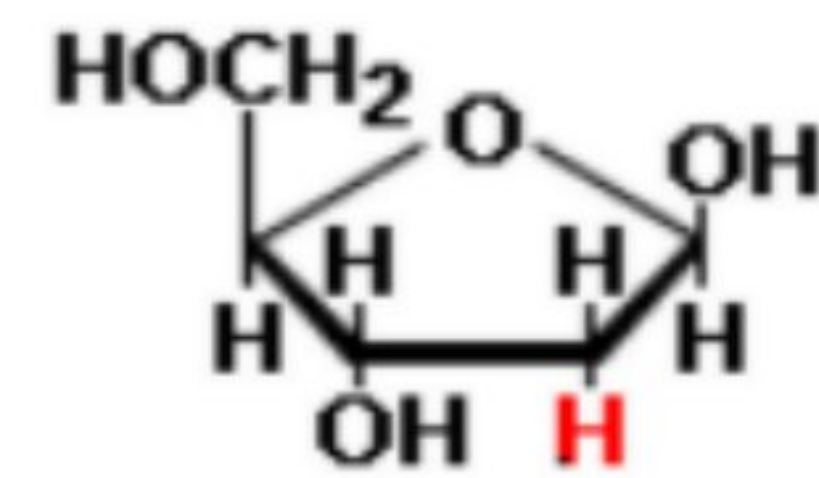
## 3.Deoxy-sugars:

an example on reduced sugars, have one or more hydroxyl groups that get replaced by hydrogens.

Ex.



Ribose



Deoxyribose

## 4.Sugar esters:

are products of sugar esterification; addition of phosphate groups to hydroxyl groups by phosphorylation. it's called esterification because the formula of the final product  $P=OOR$  is similar to esters' formula  $RC=OOR$ .

two different phosphorylation reactions can happen:

Reaction site	carbon no.6	carbon no.1
Sugar molecule	glucose-6-phosphate	glucose-1-phosphate
Type of linkage	Phosphate <b>ester</b> linkage	Phospho <b>acetal</b> linkage
Resulting molecule	Phosphate ester	phosphoacetal

when the reaction takes place at carbon no.6 in a glucose molecule, a phosphate ester is formed. however, adding the phosphate group to carbon no.1 would produce phosphoacetal which follows the formula of an acetal and has one O---P instead of O---R of a regular acetal.

❖ What is acetal?

Its a two ether groups at the same carbon (OR) + Hydrogen.



## 5.Glycosides:

We have two types of glycosides.

1. O-glycosides: result from an interaction between the anomeric carbon (carbon no.1) in a sugar molecule with an alcohol group (from another sugar or an alcohol molecule) via a glycosidic bond.

❖ Why we call it O-glycoside?

because the bonding occurred via oxygen atom the resulting molecule is called O-glycoside.

2. N-glycosides: are generated when a monosaccharide is attached to another sugar or a functional group through a nitrogen atom.

## 6.Amino sugars:

carbon of a sugar molecule gets modified by replacing the OH group by an amino group NH.

Another modification an amino sugar can form an amide bond with a acetyl group.

Ex. N-acetylneuraminate (sialic acid)

## Disaccharides:

Disaccharides are sugars that are made from two monosaccharides joined by glycosidic linkage, they could be made from the same type of monosaccharides, and called **homodisaccharides**, or they could be made from different types of monosaccharides, and called **hetero-disaccharides**.

- ❖ Disaccharides are synthesized by an enzyme called?  
Glycosyltransferase.

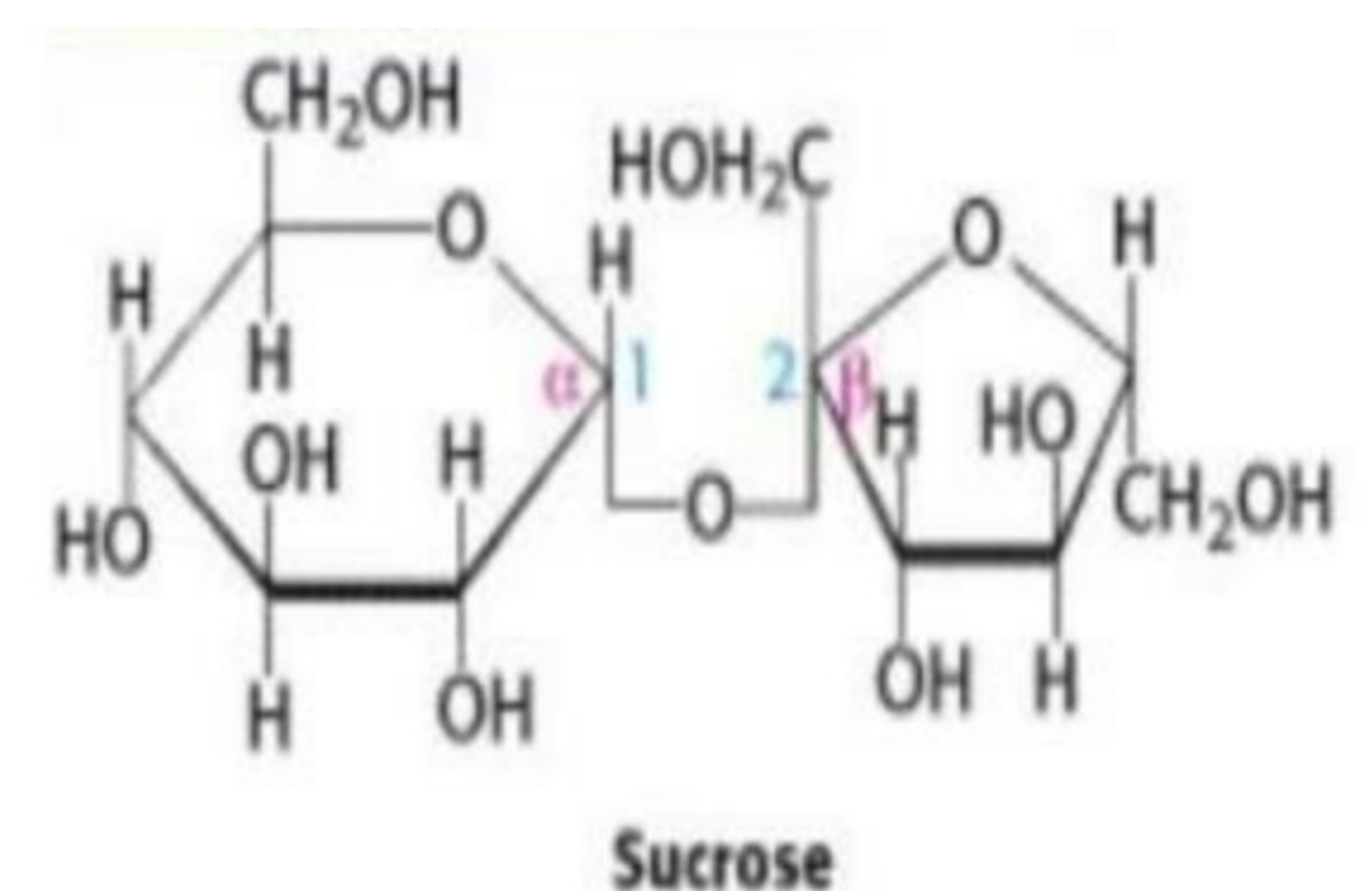
Distinctions of disaccharides:

1. The two specific sugar monomers involved and their stereo-configurations.
2. The carbons that make the linkage between disaccharides.
3. The order of the two monomer units.
4. The orientation of the OH group of the anomeric carbon whether it is upwards or downwards ( $\alpha$  or  $\beta$ ).

We have:

### 1. Sucrose (table sugar):

made from glucose (left) and fructose (right), the linkage is between the two anomeric carbons in each sugar (the carbon number 1 in glucose and carbon number 2 in fructose).  $\alpha$  (1—2) linkage.

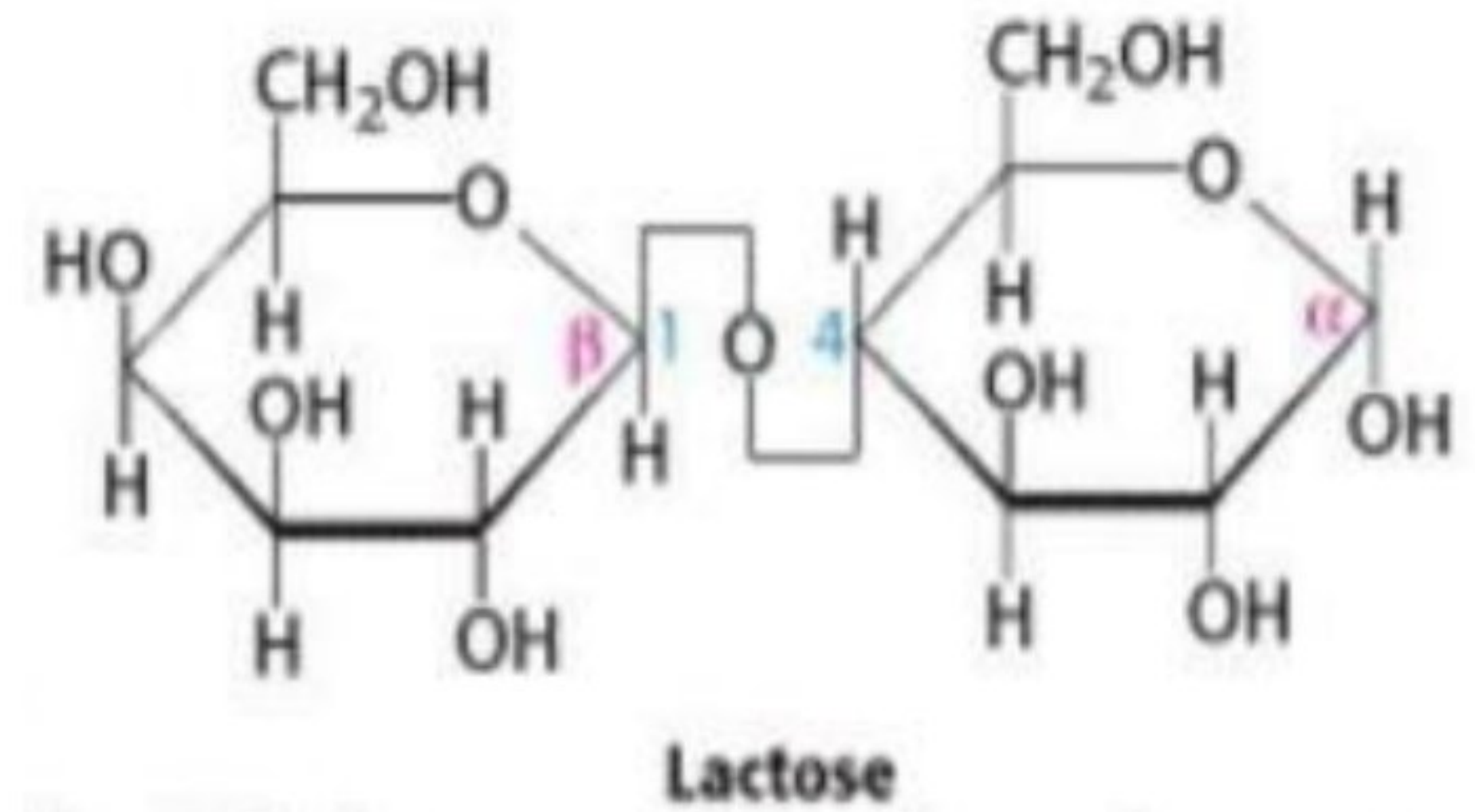


**Sucralose (artificial sweetener):** A molecule that is synthesized in terms of structure of sucrose, but in sucralose, some OH groups are replaced by CL.

## 2. Lactose (milk sugar):

It is made of galactose (left) and glucose (right), look at carbon number 1 in each sugar, The OH in galactose is upwards so  $\beta$ , and the OH in glucose is downwards so  $\alpha$ .

The linkage is between carbon number 1 in galactose and carbon number 4 in glucose, and remember that OH on C4 in glucose is directed downward, so the shape of the bond between them will be like the letter **N** in English. The bond is called  $\beta$  (1---4) linkage.

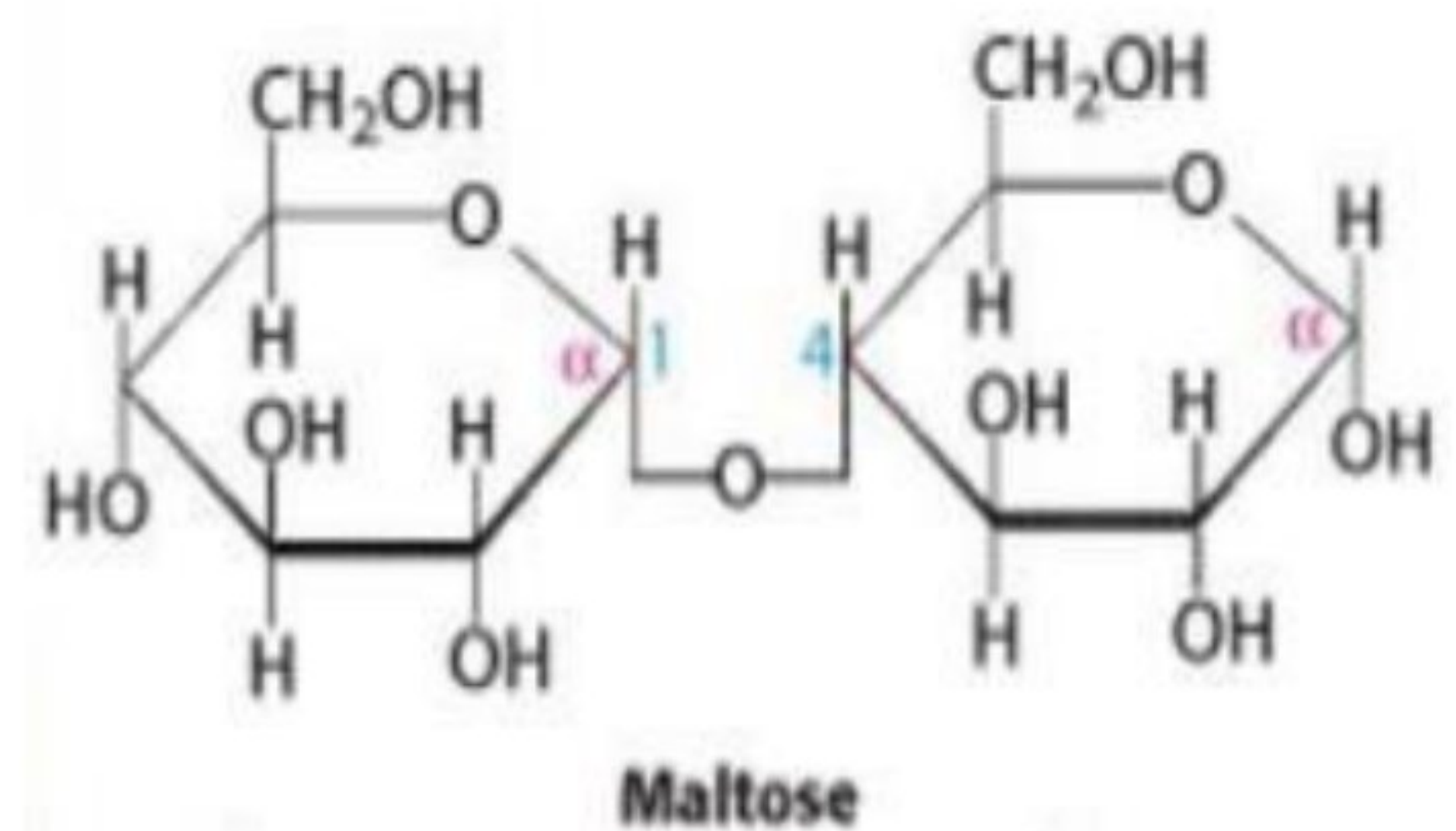


## 3. Maltose (malt sugar):

Maltose is a which is made of two glucose residues. The two residues are  $\alpha$  glucoses.

Recall that carbon number 1 in the first glucose has the  $\alpha$  configuration, so the OH is directed downwards. However, carbon number 4 in the other glucose is also

directed downwards, which makes the bond looks like the letter **V** in English. The bond is called  $\alpha$  (1---4) linkage.



## ❖ Milk problems:

### 1. Lactose intolerance:

the deficiency of an enzyme called “lactase (B-galactosidase)” which is protruded from the intestinal cells. This enzyme is responsible for breaking the  $\beta$  (1- -- 4) between the galactose and glucose in lactose, so the body can absorb them. So, whenever we have lactose accumulating in intestinal lumen, this is due to the deficiency in “lactase” enzyme.

The accumulating lactose will be used by the normal bacteria in metabolic reactions that produce side products, such as CO<sub>2</sub>, methane gas, etc. This will result in bloating.

What is the solution for this problem?

People drink milk to get their daily need of vitamin D, so you can get it by getting exposed to sun rather than obtaining it from milk.

Another solution is to drink milk that contain the enzyme “lactase”, or to drink a milk that is free from lactose.

**2. Galactosemia:** a genetic problem in which galactose-metabolizing enzyme is missing due to genetic mutation. This will result in accumulation of galactose, because it can't get metabolized, Accumulation of galactose will activate the transformation of galactose to an alcohol sugar called “galactitol”, this sugar can't exit the cell and will disturb the osmotic pressure inside the cell and attract water molecules towards the cell and damaging them at the end, resulting in severe retardation and cataract.

### **Oligosaccharides (3-10 sugar molecules):**

**Raffinose:** an oligosaccharide that is made of three sugars; galactose, glucose and fructose joined together by different bonds 1,6- and 1,2-. This oligosaccharide is present in beans and vegetables like cabbage, This sugar causes bloating, so why this happens?

That's because Humans lack the alpha -galactosidase enzyme that is needed to break down raffinose, but intestinal bacteria can ferment it into hydrogen, methane, and other gases

Also oligosaccharides can be synthesized and used as drugs.

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## Polysaccharides:

Polysaccharides are composed of a very large number of monosaccharides connected with each other.

Polysaccharides are two types depending on monomers that make up them:

- 1.Homopolysaccharides: Polysaccharides made up of the same monomer type.
- 2.Heteropolysaccharides: Polysaccharides made up of more than one type of monomers (different monosaccharides).

We have six polysaccharides:

### 1.Glycogen (Animal starch):

A highly branched storage polysaccharide, made of glucose units as monomers, synthesized by animal cells.

- Every 10 glucose residues, there is a branching point.
- It has so many layers of branching that it can reach 13 layers.
- it is the storage form of glucose.
- Glycogen is present in all cells, but the main store of glycogen is Liver and Muscles.
- The linkage between two monomers in glycogen is  $\alpha$  (1→4) glycosidic bond.
- The linkage on branching point is  $\alpha$  (1→6) glycosidic bond.
- Glycogen is a non-reducing sugar.

### 2.Starch:

A plant storage polysaccharide, that is made of glucose monomers.

- We can't synthesize starch in our cells, but we obtain it from diet.

➤ Starch is composed of two different forms of molecules:

**1. Amylopectin:** it makes (80-90) % of starch composition.

- It's the branched form of cellulose and it's made of long branched chains of glucose monomers.
- It has less branching layers.
- Every 25 glucose residues, there is a branching point.
- The linkage between two monomers in amylopectin is  $\alpha$  (1 $\rightarrow$ 4) glycosidic bond.
- The linkage on branching point is  $\alpha$  (1 $\rightarrow$ 6) glycosidic bond.
- Amylopectin is a non-reducing sugar.

### **GLYCOGEN VS AMYLOPECTIN**

➤ Both are made from the same monomer.

➤ Both are branched, but glycogen is more branched than amylopectin.

➤ Glycogen is synthesized by animals, whereas Amylopectin is synthesized by plants.

**2. Amylose:** it makes (10-20) % of starch composition.

- It's the unbranched form of cellulose and it's made of long chains of glucose monomers.
- Amylose chains form helices, similar in shape to  $\alpha$ -helix in protein structure.
- The linkage between glucose monomers is  $\alpha$ (1 $\rightarrow$ 4) glycosidic bond.

❖ What is the importance of branching?

1. Branching provides more free ends, so there will be more sites that enzymes can attack and break glycogen down, and this will increase the efficiency of breaking down this molecule.
2. Branching increases the solubility of molecules.

### 3.Dextran:

A storage polysaccharide, made of glucose residues, synthesized by bacteria and yeast.

- The linkage between its glucose monomers is  $\alpha$  (1 $\rightarrow$ 6) glycosidic linkage.
- Branches can be (1-2), (1-3) or (1-4).
- Can be found in mouth.

### 4.Cellulose:

An unbranched plant structural polysaccharide, made of  $\beta$ -glucose monomers.

- The linkage between cellulose monomers is  $\beta$  (1 $\rightarrow$ 4) glycosidic linkage. And this bond can be broken down by an enzyme known as cellulase, which human doesn't have it.
  - ❖ So why do we eat it?
    1. When we ingest cellulose fibers, like in fruits, they're going to stay as they are, not digested, in the intestinal tract, then they attract water molecules toward intestines to maintain osmotic pressure, thus facilitating getting rid of waste products (feces).

2. Cellulose attracts water molecules, interacting with them through hydrogen bonds. This will enlarge the structure, filling up the intestines, what gives you a feeling of satiety. (for people who want to lose weight)

3. Cellulose acts like a network that can fish cholesterol molecules, toxins, etc. so they are not absorbed by the intestine, rather we get rid of them into feces.

➤ Cellulose chains → Microfibrils → Macrofibrils → Cellulose fibers

This organization makes cellulose structure stronger and better in terms of mechanical properties, thus cellulose function as a structural polysaccharide is related to its structure.

## 5. Chitin:

A structural polysaccharide presents in the exoskeleton of different animals.

- Made of repeated units of N-Acetyl- $\beta$ -D-glucosamine.
- connected with each other via  $\beta(1 \rightarrow 4)$  linkage.

## 6. Pectin:

A structural polysaccharide, composed of two types of modified galactose residues, produced by plant cells and bacterial cells.

- Pectin is heteropolysaccharide, since it has two different types of monosaccharides.
- The linkage between its monomers is  $\beta(1 \rightarrow 4)$  glycosidic linkage.
- Pectin is used as gelling agent in plant-based jello.

**NOTE:** Polysaccharides are non-reducing → They will test negative in oxidation tests.

### 7. Glycosaminoglycans (GAGs):

are Polysaccharides with disaccharide repeating units these disaccharides are made of monomers and these monomers are modified sugars either with carboxyl group sulfate group in addition to the amino group.

- They are heteropolysaccharides.
- Has a negatively charged carboxylate.
- Found in ECM.

GAG	Localization	Comments
Hyaluronate	synovial fluid, <b>vitreous humor</b> , <b>ECM of loose connective tissue</b>	<b>the lubricant fluid , shock absorbing</b> As many as 25,000 disaccharide units
Chondroitin sulfate	<b>cartilage</b> , bone, heart valves	<b>most abundant GAG</b>
Heparan sulfate	basement membranes, components of cell surfaces	contains higher acetylated glucosamine than heparin
Heparin	component of intracellular granules of mast cells lining the arteries of the lungs, liver and skin	<b>A natural anticoagulant</b>
Dermatan sulfate	skin, blood vessels, heart valves	
Keratan sulfate	cornea, bone, cartilage aggregated with chondroitin sulfates	Only one not having uronic acid

**YOU SHOULD MEMORIZE IT**

➤ Proteoglycans:

- Made of GAGs associated with small protein part.
- The major component is the sugar, and the minor component is the core protein.
- Their main function is to lubricate through their GAG component.
- Essential for adhesion and Interaction between cells.

➤ Peptidoglycans:

- They contain peptides not long proteins so they are not proteoglycans.
- It is composed of muramic acid extending from it 4 amino acids (alanine, glutamine, lysine, alanine)
- Attached to number 3 (lysine) five glycine residues.
- The last glycine interacts with the last amino acid (alanine) in the adjacent chain which is connected to another muramic acid.
- This complicated structure makes the bacterial cell wall highly rigid.

**Glycoproteins:**

They are molecules that contain sugar components but they are not polysaccharides, actually they are oligosaccharides connected to a protein component.

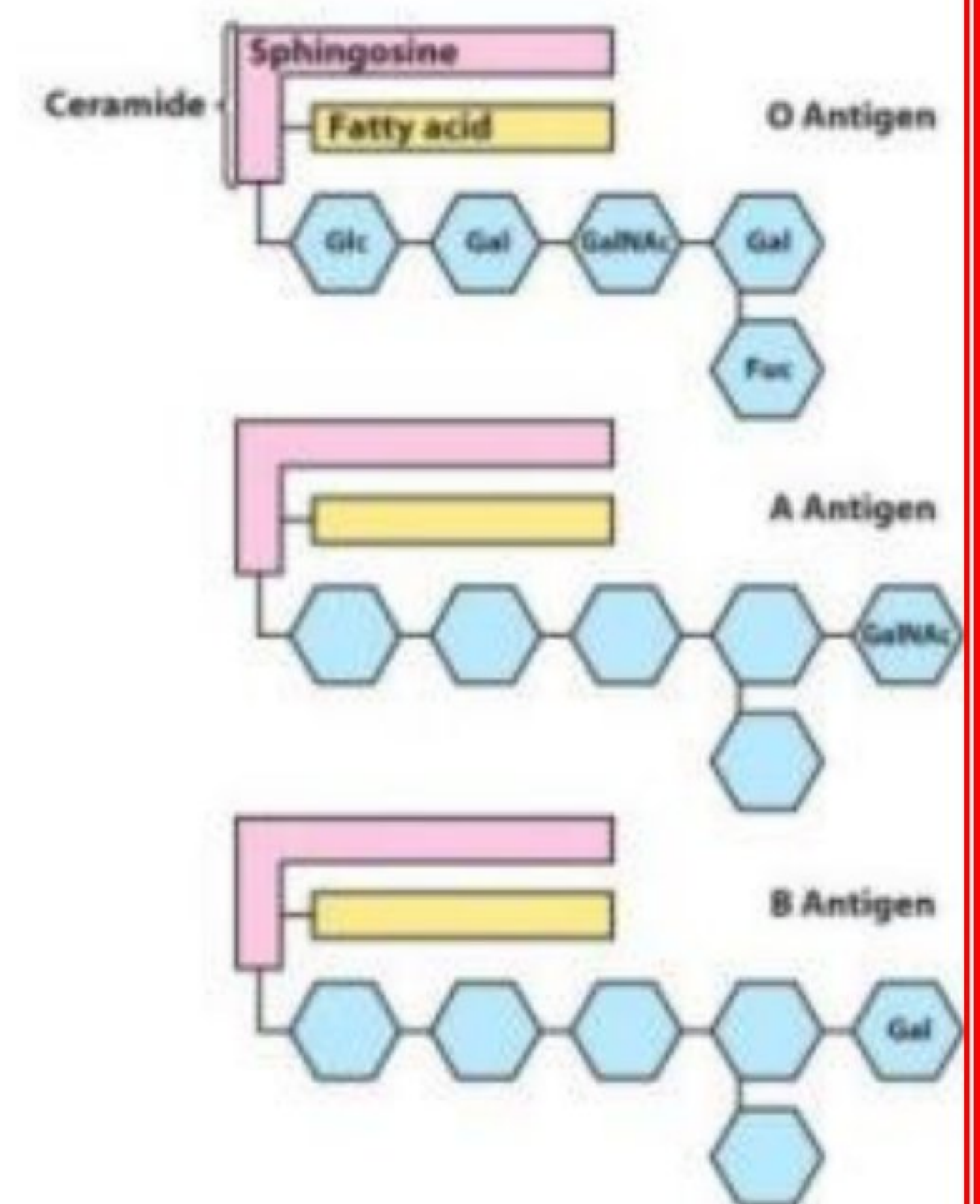
- The major component is protein while the minor one is sugar.

➤ Significance of glycoproteins:

1. They are important for protein folding, the presence of the sugar component may guide or facilitate the folding and formation of the final 3D shape of a protein.
2. Protein targeting
3. Prolonging protein half-life and functionality.
4. For cell-cell communication and cell signaling.

## BLOOD TYPING:

- It's an application on the importance of sugars, specifically glycoproteins and glycolipids.
- In the cell membrane of RBCs, we have glycoproteins and glycolipids which contain a sugar component, specifically an oligosaccharide. This oligosaccharide is variable among individuals, and actually it's what determines the blood group. As in the picture:



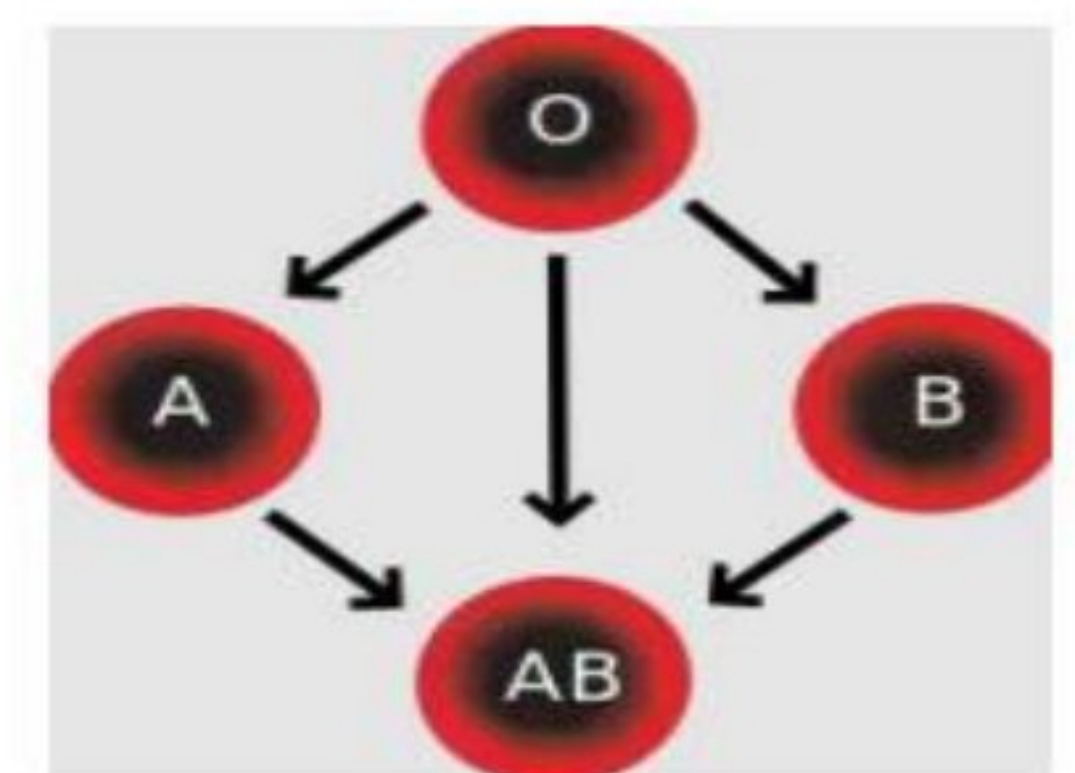
Glc - Gal - GalNAc - Gal - Fuc is found in all blood types, but the difference is:

- O blood type → No extra monosaccharides.
- A blood type → Extra GalNAc.
- B blood type → Extra Gal.
- AB blood type → Extra GalNAc and Gal.

Glc = Glucose  
Gal = Galactose  
GalNAc = Galactosamine  
Fuc = Fucose (Reduced galactose)

This picture summarizes blood transfusion: ➡

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# MED-HUB

## BIOCHEMISTRY

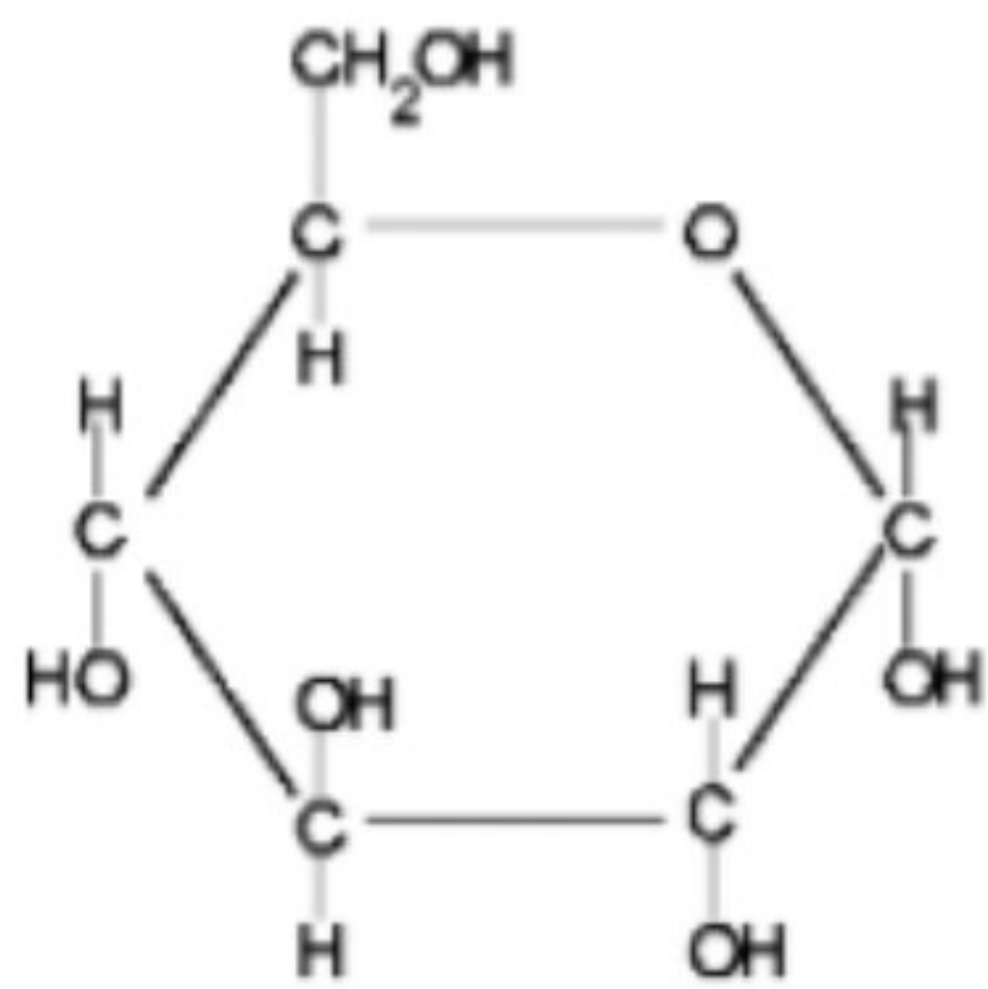
### SUMMARY

### CARBS



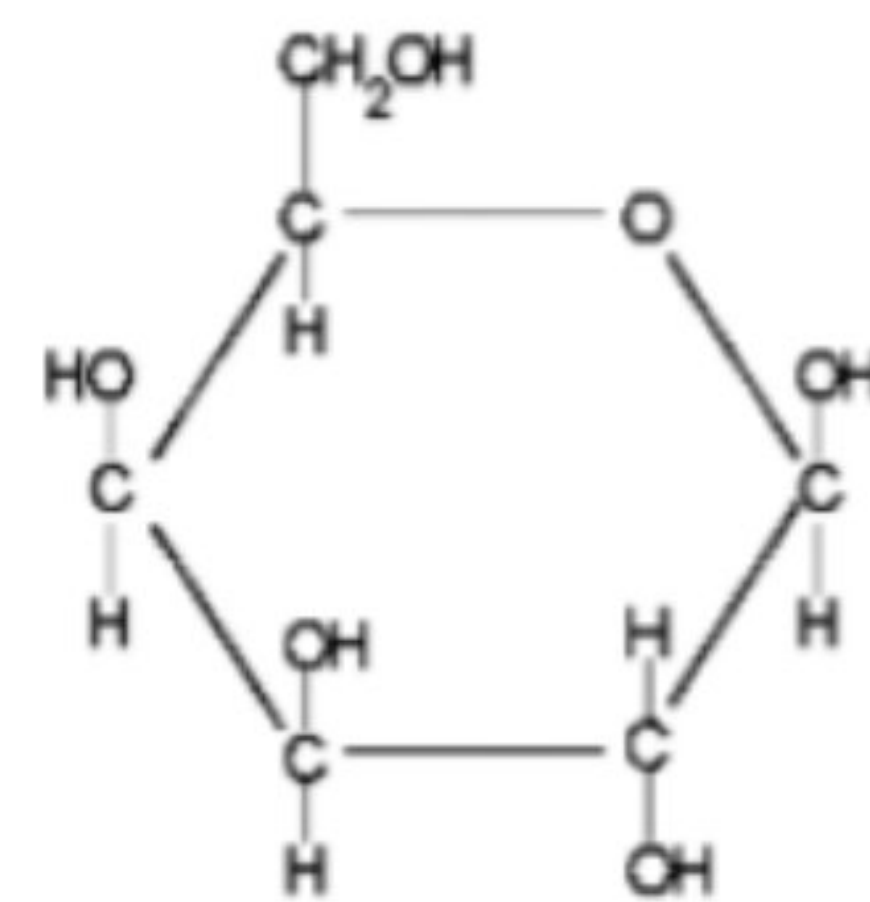
# Carbohydrates

## Monosaccharides



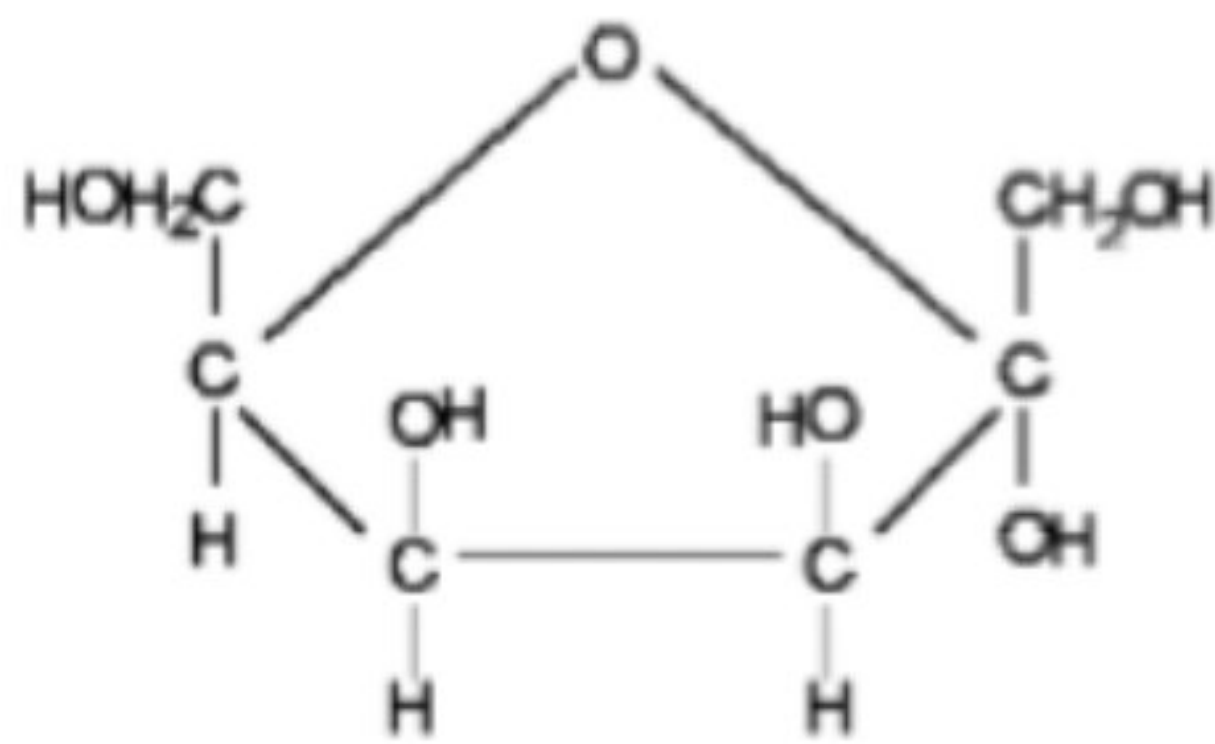
Glucose

aldohexose



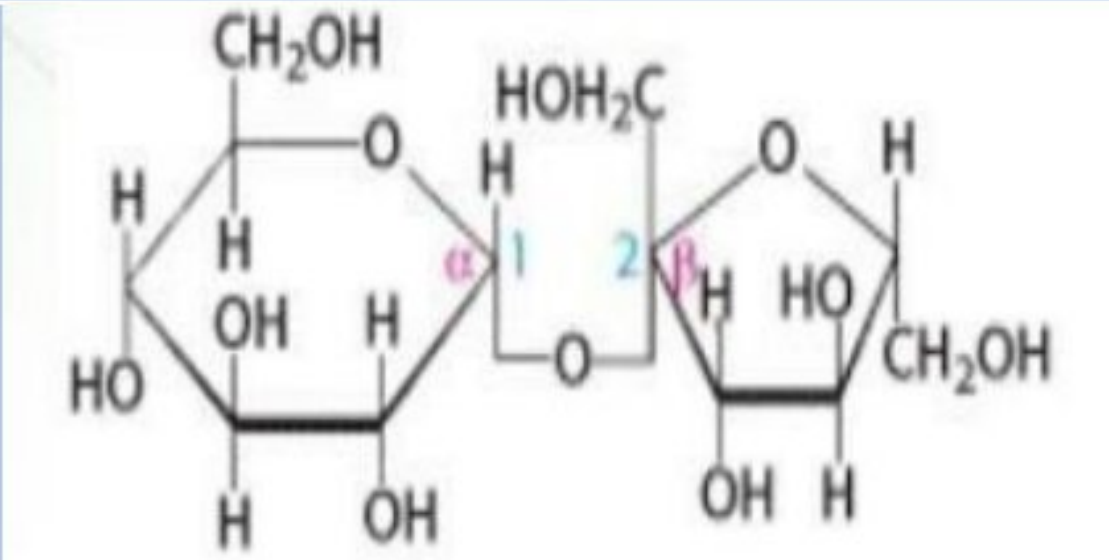
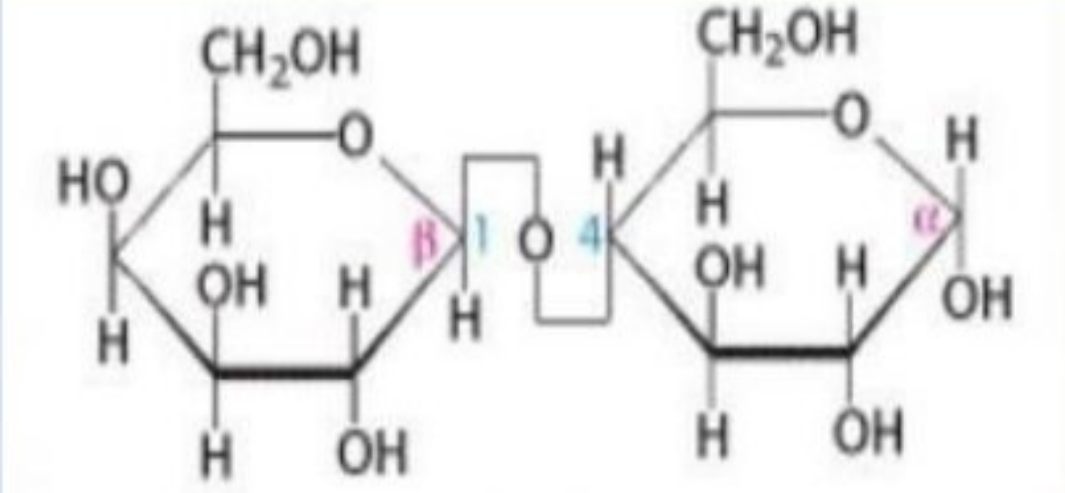
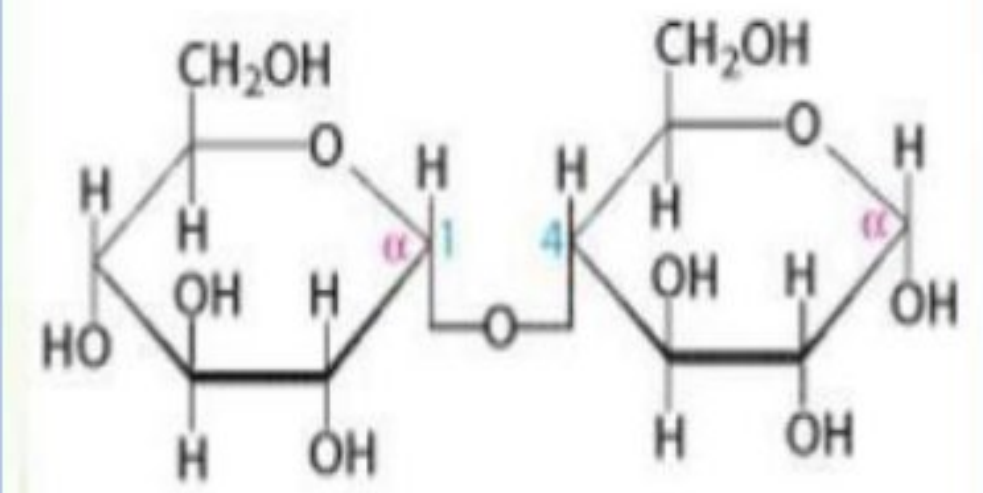
Galactose

aldohexose



ketohexose

# Disaccarides

Name	monoers	linkage	structure
sucrose	Glucose+fructose	$\alpha(1 - 2)$	 <p>Sucrose (<math>\alpha</math>-D-Glucopyranosyl-(1 <math>\rightarrow</math> 2)-<math>\beta</math>-D-fructofuranose)</p>
latose	Galactose+glucose	$\beta(1 - 4)$	 <p>Lactose (<math>\beta</math>-D-Galactopyranosyl-(1 <math>\rightarrow</math> 4)-<math>\alpha</math>-D-glucopyranose)</p>
maltose	Glucose+glucose (homo-disaccharide)	$\alpha(1 - 4)$	 <p>Maltose (<math>\alpha</math>-D-Glucopyranosyl-(1 <math>\rightarrow</math> 4)-<math>\alpha</math>-D-glucopyranose)</p>

# Polysaccharides

name	monomers	branching	linkage	Branching point linkage	purpose
Glycogen	Glucose monomers	Highly branched	$\alpha(1 - 4)$	$\alpha(1 - 6)$	Storage poly saccharide
starch	Glucose monomers	Amylose → unbranched amylopectin → branched	Amylose → $\alpha(1 - 4)$ amylopectin → $\alpha(1 - 4)$	Amylopectin → $\alpha(1-6)$	Plant Storage poly saccharide
dextran	Glucose monomers	Highly branched	$\alpha(1-6)$	(1-2), (1-3) or (1-4)	Storage poly saccharide
cellulose	$\beta$ -glucose monomers	unbranched	$\beta(1 - 4)$	unbranched	plant structural polysaccharide
chitin	N-Acetyl- $\beta$ -Dglucosamine	_____	$\beta(1 - 4)$	_____	structural polysaccharide
pectin	two types of modified galactose (hetero-Polysaccharides)	_____	$\beta(1 - 4)$	_____	structural polysaccharide

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Thank you

