Lecture : 9 section 1 , 2 , 3

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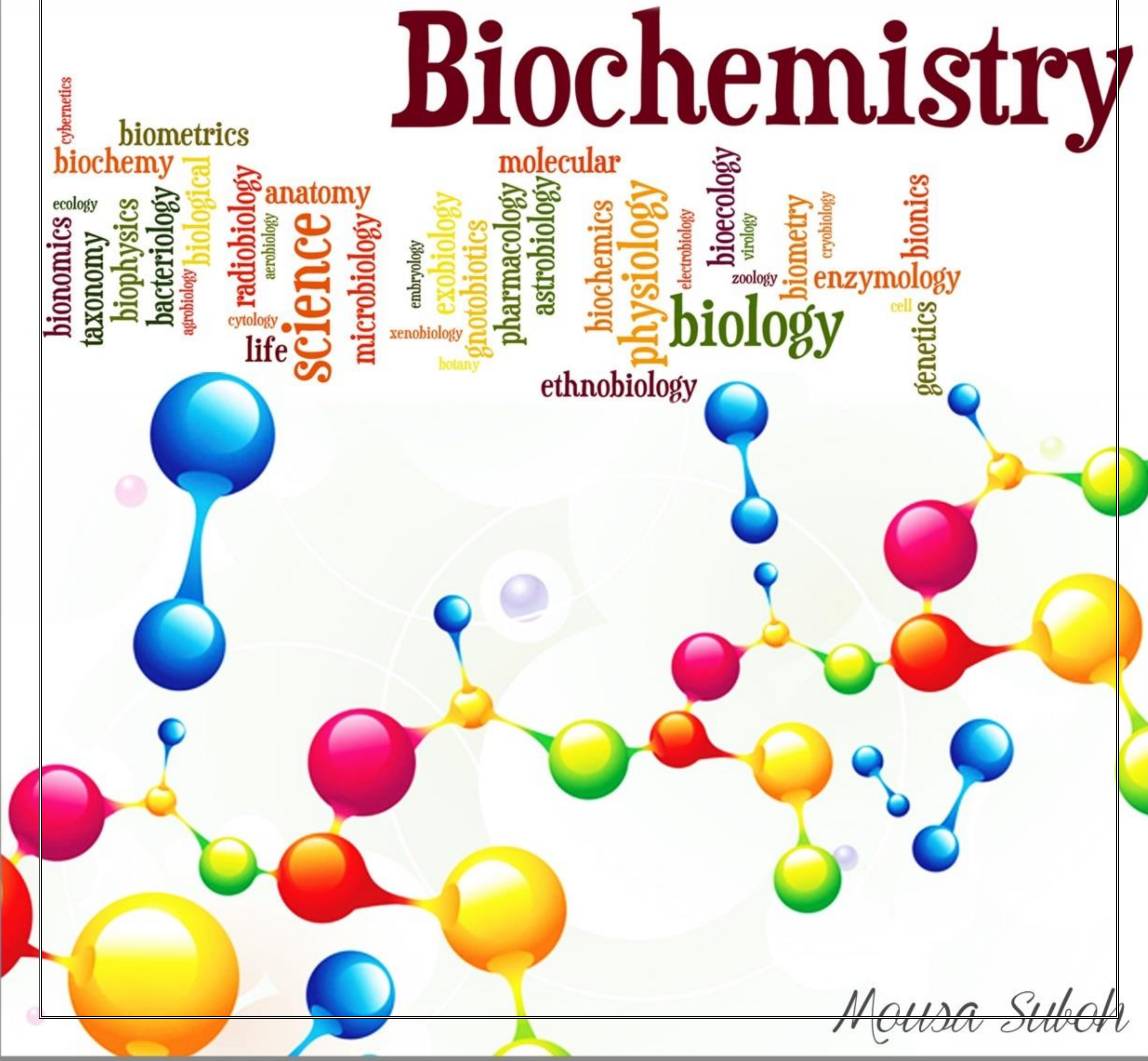
☐ Slide ■ Sheet

Medical Committee
The University of Jordan



Carbohydrates

Life is defined by its chemistry and every single class of molecules contributes to the defining features of it.Today we are going to talk about carbohydrates –a class of macromolecules- and by the end of this lecture you should be able to:

**Define carbohydrates and their classifications

**Explain their structures, functions and main features.

**To be acquainted with some definitions like: Acetals,hemiketals,anomers,epimers,alpha&beta sugars,anomeric carbons. ..etc.

What are carbohydrates?

Carbohydrates are polyhydroxy aldehydes or ketones that have multiple hydroxyl groups, and **Saccharide** is another name for them.

What are the main functions of carbohydrates?

1st- they are the main source of energy
2nd- they are involved in forming certain structures like cellulose and chitin
3rd- Structural polysaccharides are involved in the structure of organisms and tissues besides being building blocks which gives them the ability to form larger structures.
4th- They can be conjugated or linked so that they form special type of proteins known as glycolipds or glycoproteins
5th- Cellular recognition, a striking example of this is immune cells which are able to distinguish foreign bodies by looking at the sugar located on the surface of the body or the molecule,if

the sugar is different or considered to be abnormal to the body then the foreign body should be destroyed.

Classification of sugars (carbohydrates):

1st,**By the number of sugars that constitute the molecule;**

1. **Monosaccharide; one sugar molecule like glucose.**
2. **Disaccharides like lactose and sucrose**
3. **Oligosaccharides (3-10) of simple sugars**
4. **Polysaccharides like glycogen and starch**

Most carbohydrates are found naturally in bound form (conjugated or linked) rather than freely as simple sugars,conjugated like glycoproteins and proteoglycans (hormones, blood group substances, antibodies) and glycosides.

<u>Glycoprotein vs proteoglycans :</u>

A glycoprotein is a protein of some sugar while proteoglycans have sufficient amount of sugars with little aminoacids/peptides

** Mucopolysaccharides (hyaluronic acid):

Mucopolysaccharides, also called glycosaminoglycans, are long chains of building blocks called disaccharides made of two sugar molecules bonded together one example of them is heparin.

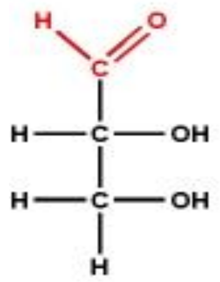
Refer to slide num5 to revise what you studied here about conjugated sugars examples ☺

<u>Monosacchrides</u>

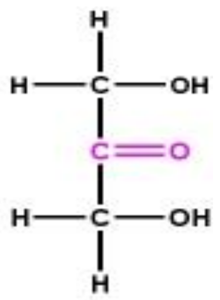
<u>*The basic formula :*</u> $(CH2O)n$, so a monosaccharide with 2 carbons is ? $C2H4O2$

Depending on the functional groups there are two types of monosaccharides:

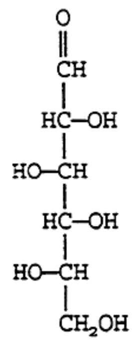
1- An aldose: a sugar that contains an aldehyde group
2- A ketose: a sugar that contains a ketone group.
   ** Recall that the OSE relates to sugars names (glucose,galactOSE)



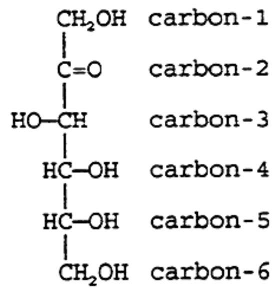
An Aldose



A Ketose



Glucose, an aldose

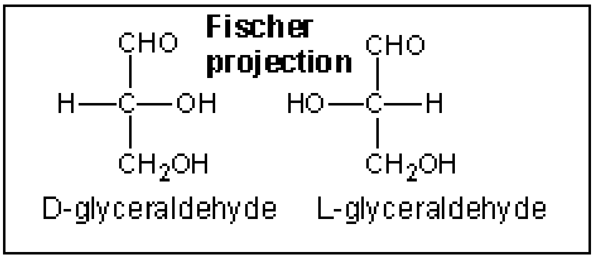


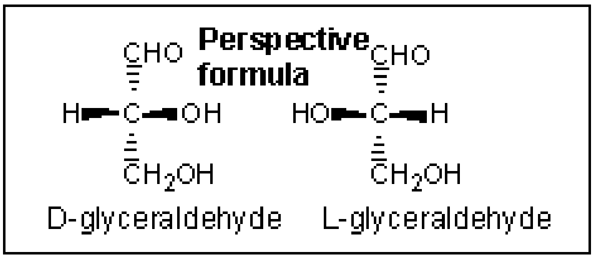
Fructose, a ketose

The simplest way to draw a sugar is Fisher Projection which indicates many features of a sugar by the horizontal and the vertical positions of atoms.

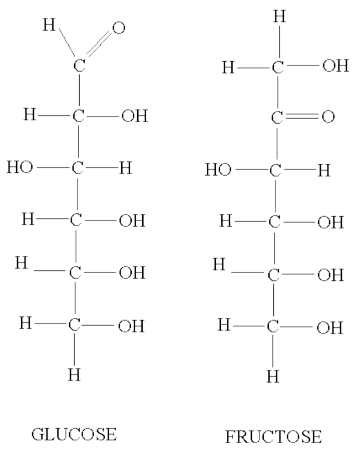
** Notice that the functional group whether a ketone or an aldehyde group should be positioned on the top, looking at the structures below we conclude that aldehyde group is always terminal and should be the first atom on the top,ketone group is mainly found on the second atom and should be also on the top and another atom below it.

Compare between Fisher projections and perspective structural formulas.





Some common monosacchrides:



1- Glucose
Common features of glucose:
** It’s a sweet sugar , known as the blood sugar and whenever we want test the blood sugar, the free glucose level of our blood is tested.

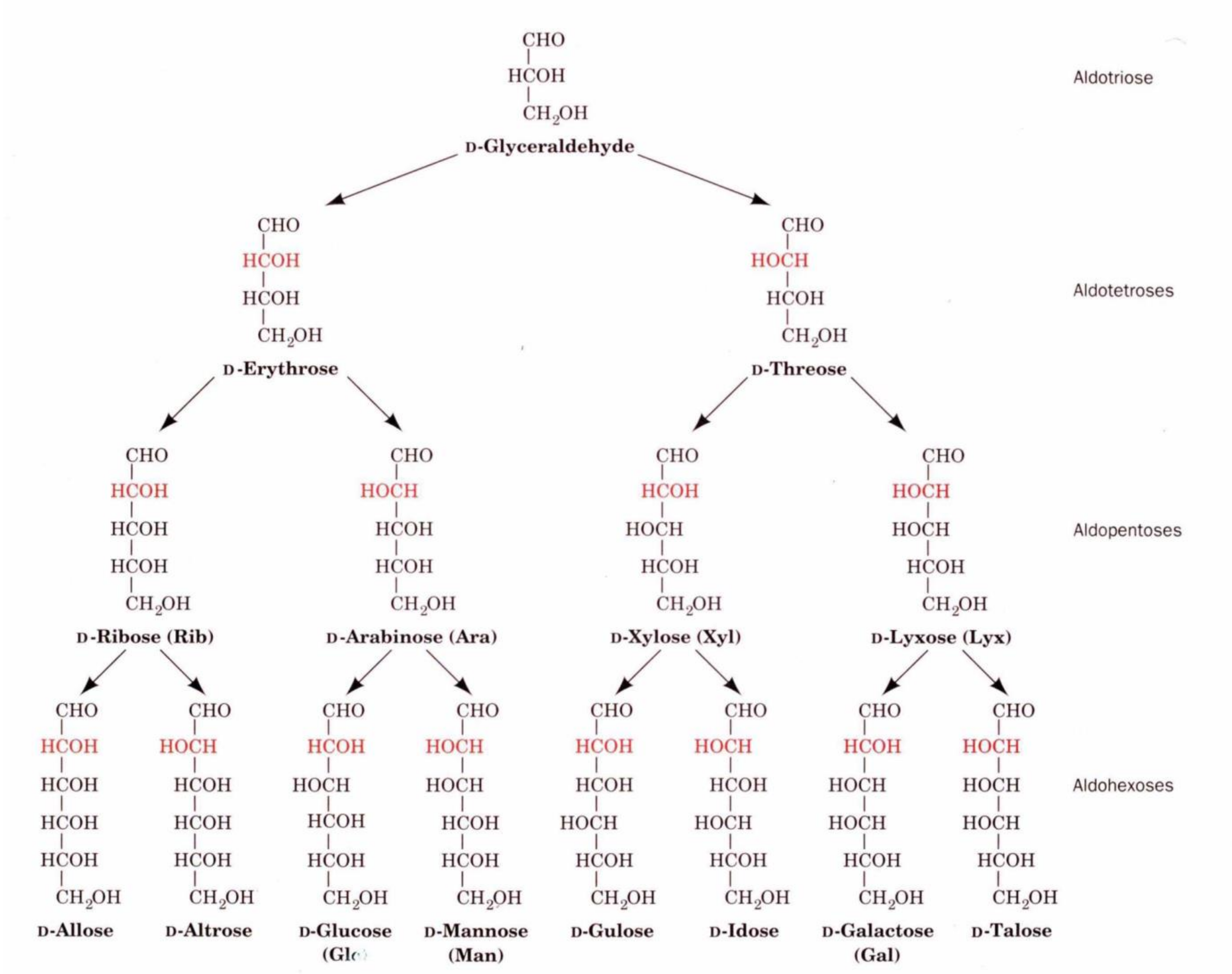
** The main source of energy
Whenever energy is needed, our cells immediately get their need of glucose directly or by certain metabolic pathways ,for example fructose –a monosaccharide - can be converted back via a glucose metabolic pathway.

** Glucose is found in every disaccharide

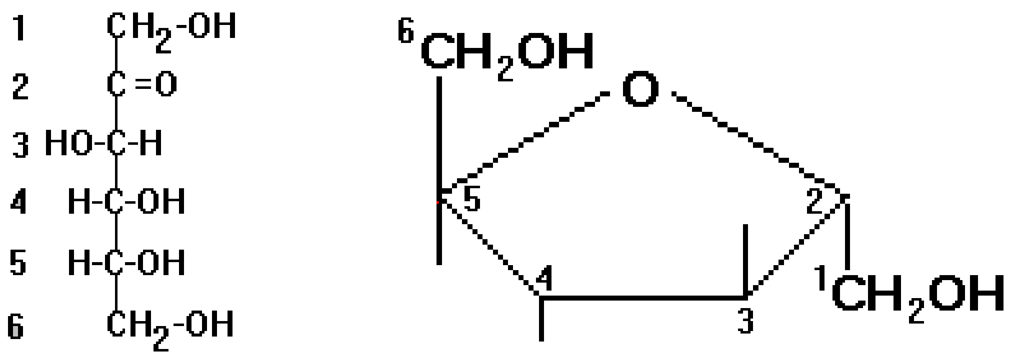
2-Galactose:
Hardly tastes sweet & rarely found naturally as a single sugar.

3-**fructose** which is the Sweetest sugar, found in fruits and honey and can be added to soft drinks, cereals, deserts.

Here is a picture of different sugar molecules:
Notice the aldoses, pentoses and hexsoses like glucose (6 carbons)



The sugars in boxes should be memorized (their structure),they are easily memorized notice their similarities and OH positions . (please refer to slide number 9 to see the boxes of the sugars you are required to memorize).The second group is known as ketoses the one you should know its structure is fructose.



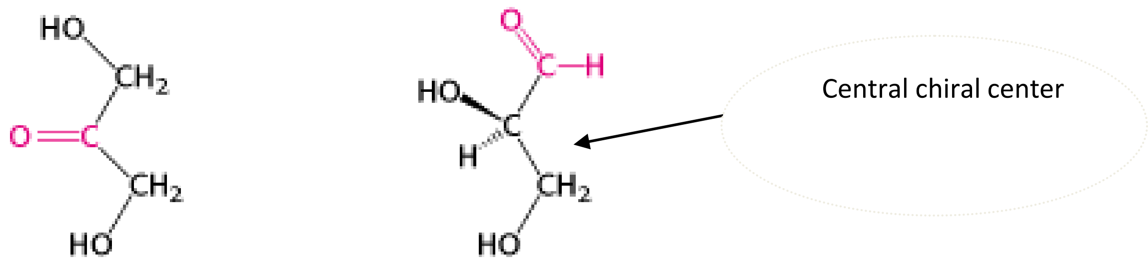
Fructose

Another classification for monosacchrides is by the number of carbon atoms they contain:
Trioses (the simplest),tetroses,pentoses….ext .

Note: Monosaccharide carbons start from 3 to 8 carbons.

Trioses:

Dihydroxyacetone and glyceraldehydes are examples of trioses,they have the same carbon,oxygen and hydrogen number but they differ in the functional group



Dihydroxyacetone (a ketose) **D-Glyceraldehyde** (an aldose)

Dihydroxy acetone is a ketose while glyceraldehydes is an aldose ,notice that glyceraldehydes has a chiral center which is connected to four different groups .

So far we talked about how are carbohydrates classified according to the number of molecules present and based on the functional groups,now we are going through the third classification which is based on their structures arrangements in the space.

If these molecules have the same number of oxygen,hydrogen and carbon then they are isomers.Isomers are either constitutional or sterioisomers. Constitutional isomers differ in the bond connectivity (the way they are connected together) while sterioisomers differ in the way they look in the space though they have the same bond connectivity.

For Glyceraldehyde there are two sterioisomers D & L sugars , D&L designate the position of the OH group that's connected to the chiral center.If the OH is going to the left it's called L molecule and if it's going to the right it's called D sugar.**All the sugars in our systems and the nature are necessarily of the D type.**

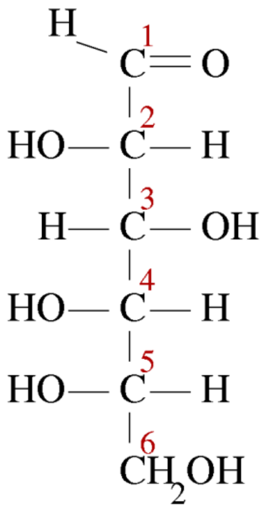
How can you determine the number of sterioisomers ?
A rule:
Number of sterioisomers = 2^n where n is the number of chiral centers

E.G 1:
For glyceraldehydes there are 2 sterioisomers.
2^1= 2

E.G 2:
For glucose sugar:

1- How many chiral carbon does it have?
2- How many possible sterioisomers?

It has 4 chiral carbons,sterioismomers are 2^4= 16



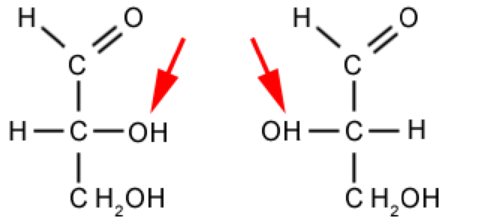
This number (16) represents the aldohexoses including glucose.

Refer to slide 14 to see all the isomers and try to find out glucose,mannose and galactose.

Sterioisomers can be of 2 types enantiomers or diasteriomers.

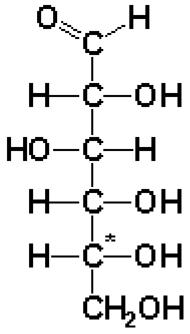
<u>Enantiomers:</u>

They have mirror images.For glyceraldehyde we have two enantiomers D and L.

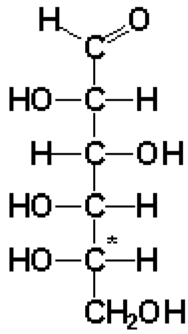


D-Glyceraldehyde L -Glyceraldehyde

How many enantiomers are present for glucose?(Remember that glucose got only 1 mirror image).So only 2 enantiomers D and L



D-glucose



L-glucose

So don't mix between how to get the sterioisomers number which is 16 and the enantiomers number which is 2,remember that enantiomers are part of sterioisomers.

Another important question is: How could you know the exact configuration (D or L) of a molecule if it has more than one chiral carbon?

1- Look at the last chiral carbon from the top or the furthest chiral carbon from the functional group (aldehyde or ketone)
2- Notice the OH position right or left then determine

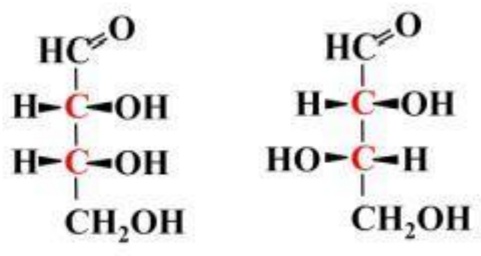
E.G:

In glucose molecule carbon number 5 is the furthest from the functional group ,it's position is right so this is a D sugar.if OH is on the left side then it's L sugar.

The doctor said: " In the exam you might be asked about a certain carbohydrates structures (you will be asked only about the ones you are supposed to memorize) or you might be asked about the number of sterioisomers or configurations "

Diasteriomers:

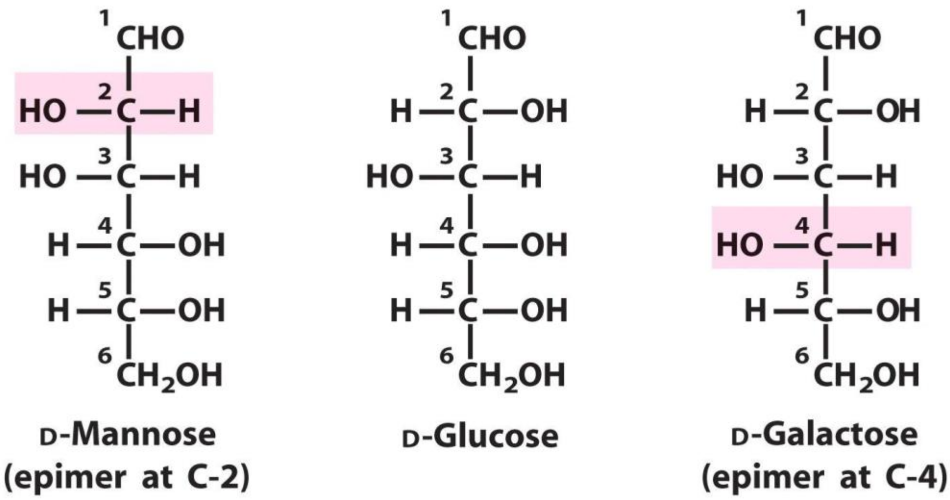
Are molecules with no mirror images and non-superimposable.*Refer to slide 19 to see more examples.*



Diastereomers

About slide num 19:
The enantiomers are on the top and they are mirror images while diasteriomers are those in the corners they are not superimposable

Some diasteriomers have higher classification,they are epimers. Epimers are diastereomers that differ in the orientation **of one chiral carbon.**



Look at the picture above,what is the difference between Mannose and Glucose?
They are actually the same but the 2nd chiral carbon of mannose, its OH group goes to the left while the one of glucose goes to the right.Now lets compare glucose and galactose,they are not mirror images but epimers at carbon number 4.

Now ☺ ! would you kindly notice the relationship between Mannose and Galactose? Are they epimers? The answer is no,although they differ in OH orientation but at different carbons 2 and 4 so they are diasteriomers .

Reactions of the functional groups
Acetal and Hemiacetal,ketal and hemi ketal.

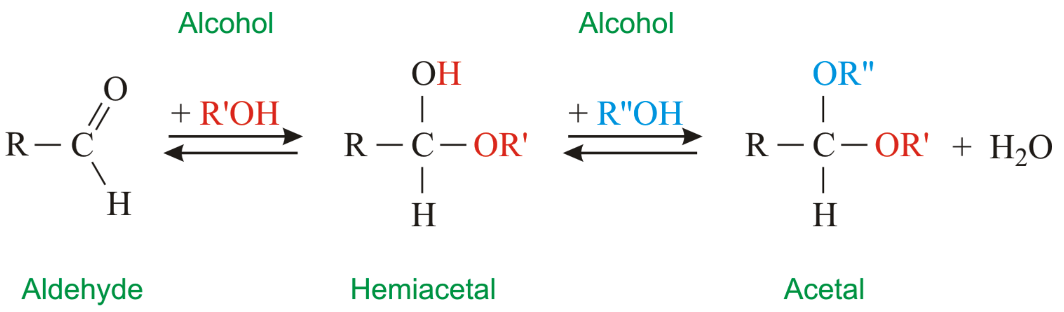
1- Aldehyde + Alcohol = Hemiacetal
2- Hemiacetal + another alcohol = Acetal

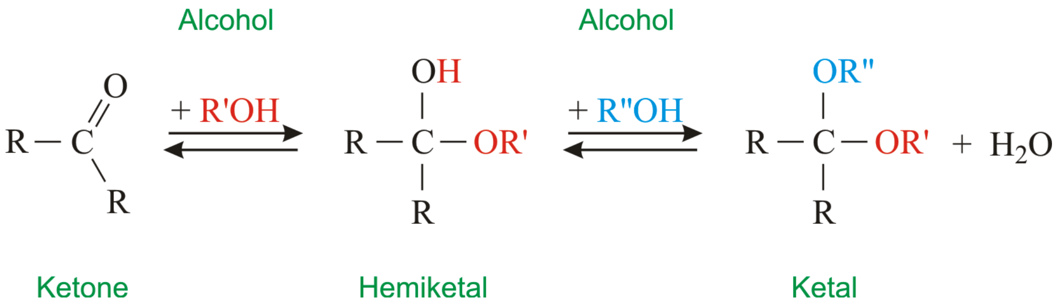
So 2 OR are present in an acetal while OH,OR are present in the hemiacetal.

In terms of ketone:

1- A ketone + alcohol = hemiketal
2- Hemiketal + another alcohol = Ketal

The conclusion :





Hemiketal Vs Hemi acetal:
Hemikital has 2R groups while hemiacetal has only one

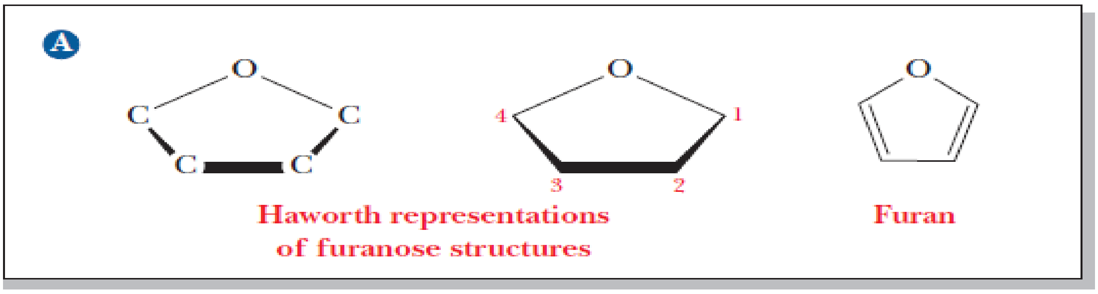
Ketal Vs Acetal:
A ketal has 2R 2OR groups while an acetal has 2OR 1R 1H

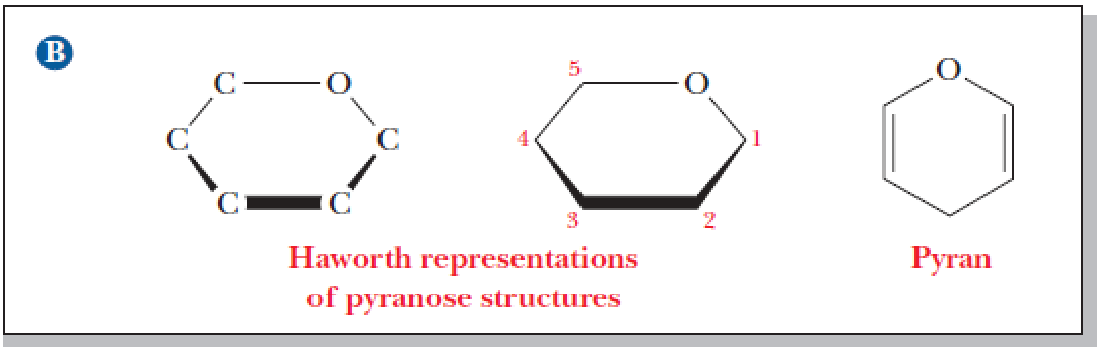
The question is! Why do we need to know all the previous details?
Sugars are reactive molecules due to the OH,aldehyde and ketone groups,that allow them to make a ring structure.Glucose when present in a solution it changes from a chain to the ring structure and this reaction is reversible.
Most sugars prefer to be in a ring structure because of its high stability.The OH present in a glucose molecule can be linked to carbon number 5 or 4 to make a ring structure,notice that carbon number 5 reacts with the aldehyde group.

Note: when the ring is already formed you can notice whether the molecule is acetal or hemiacetal according to the ROR numbers (ethers) for glucose ring it's a hemiacetal

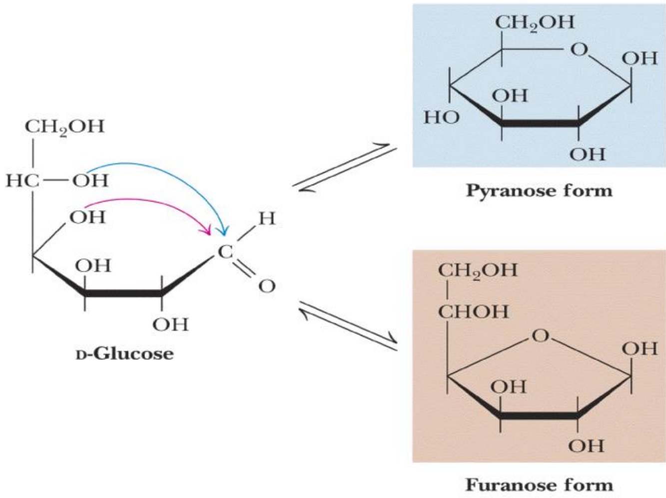
Haworth Projection:
For a chain structure we had Fisher projection and for a ring structure we have Haworth structure which allows you to look at the ring by angles.

The 2 ring structures of glucose have two different names, Furan and Pyran.
Pyran,a ring structure compsed of 1 oxygen and 5 carbons And it's a hexagonal ring.
Furan,pentagonal ring and one of them is oxygen.

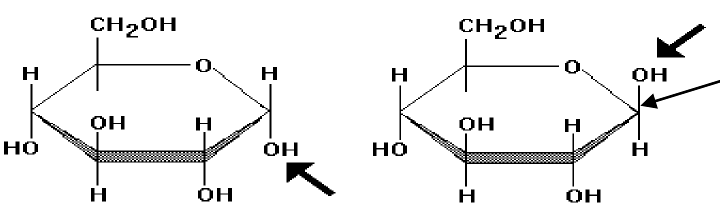




But which one of them is more stable and why?
Peranoze form is more stable with less steric hindrance and repulsion ,the van der wal are not strongly repulsive as much as those of Furan because of the enough space provided by the hexagonal ring



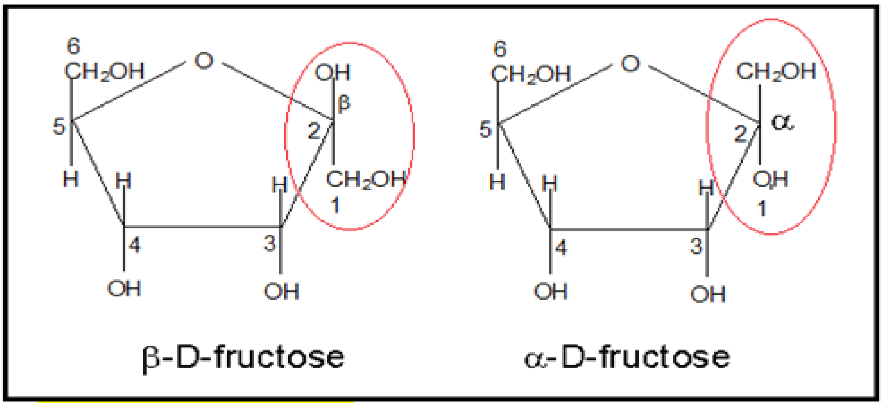
Considering the carbon in a ring that used to be the aldehyde carbon,it has been noticed that the groups that are attached to this aldehyde carbon are not fixed and they can move but any other groups like carbon number 2 or 3 are fixed,who is responsible for this?


alpha-D-glucose beta-D-glucose

المقصود ذرة الكربون هذه التي كانت متصلة بمجموعة الالدهايد .. تحمل مجموعة OH نشطة تسبب تغيرات على الحلقة

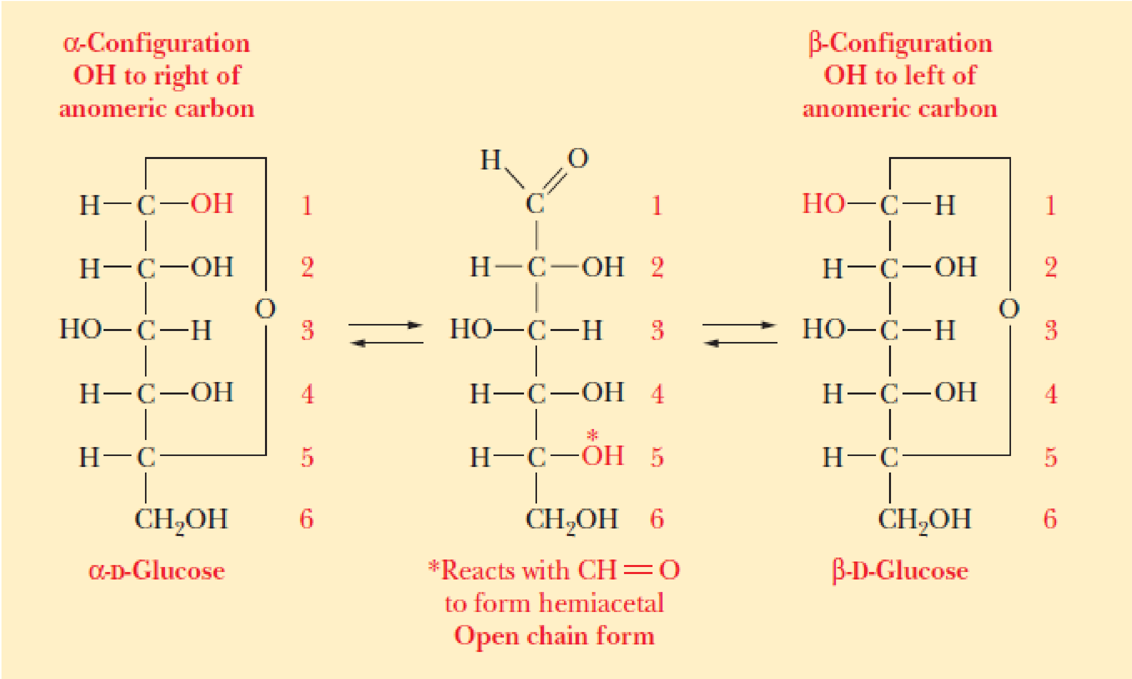
A smart student would accuse OH group ☺ attached to the first carbon which is reactive and can rotate up or down the ring. We designate these two structures by alpha and beta sugars if the OH is below the ring then it's Alpha ring and if it's up then the sugar is Beta sugar.

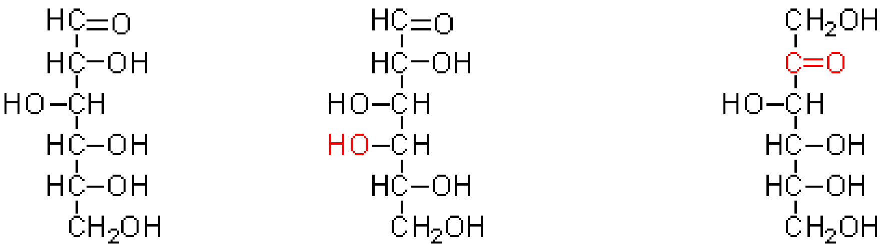
Alpha and beta rings are known as anomers.Anomers are sugar molecule in the ring structure they differ in the location of OH group attached to the anomeric carbon (carbon 1 of glucose)
Look at the coming picture and locate the anomeric carbon of fructose!

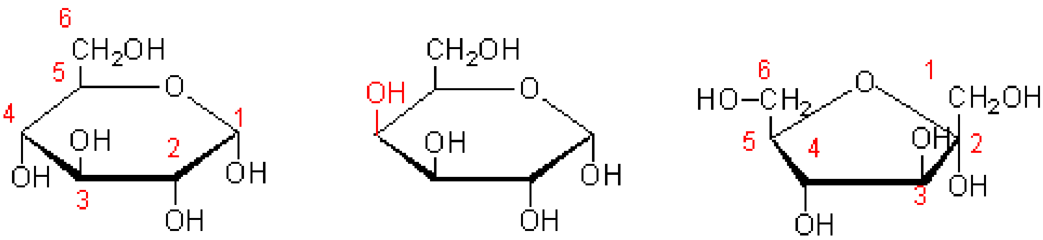


The anomeric carbon is number 2,it was basically linked to the ketone group. Anomeric is the one which was involved in this bond (C=O),so if you want to find the anomeric carbon you may look for the carbon attached to the oxygen in the ring but someone may ask where is the anomeric carbon is it the one attached to the right or the left of oxygen in Fructose ring??
The answer is look at the carbon that is attached to oxygen and attached to OH,check the OH position then name the sugar as an alpha or beta sugar.

The DR said "*finding out the anomeric carbon is about memorizing and experience mainly , in the coming lectures,we are going to take more details about this topic*"







glucose galactose fructose

No matter how far a person can go
the horizon is still way beyond
Best Wishes ☺