بسم الله الرحمن الرحيم

BIOCHEMISTRY

DOPAMINE
SCIENTIFIC TEAM

Lecture 5

Carbohydrates

اللهم مكِّن لعبادك المؤمنين،
وانصرهم على من عاداهم يا عزيز

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THE SCIENTIFIC TEAM OF DOPAMINE
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What are they?

The functional group of sugars is the carbonyl group (so sugars are aldehydes or ketones) that give the chemical properties for the sugar molecules, and they have (OH) groups.

When we talk about naming molecules there is something called hierarchy (تراتبية)
the **carboxyl group** is the predominant (which makes the molecule an acid), the ketone, aldehyde and OH all of them are secondary
The main functional group is **carboxyl (COOH)**

- Carbohydrates are polyhydroxy aldehydes or ketones.
- Saccharide is another name for a carbohydrate

- Functions:
- Source of energy (glycogen and starch)
- Structure (cellulose and chitin)s
- Building blocks (glycosaminoglycans) Make larger molecules
- Cellular recognition (glycoproteins)

On the surface of any cell there are sugars, that are recognized by other cells like immune cells (like B cells, T cells..) by scanning the surface of the cell (scanning the sugar)

Carbohydrates – natural forms

- Most carbohydrates are found naturally in bound form rather than as simple sugars.
- Polysaccharides (starch, cellulose, inulin, gums)
- Glycoproteins and proteoglycans (hormones, blood group substances, antibodies)

-If the sugars connected to the proteins, we call them **Glycoproteins** [large proteins structures and little sugars]
-if the proteins connected to the sugars, we call them **Proteoglycan** [large sugar structure and some amino acids and peptides]

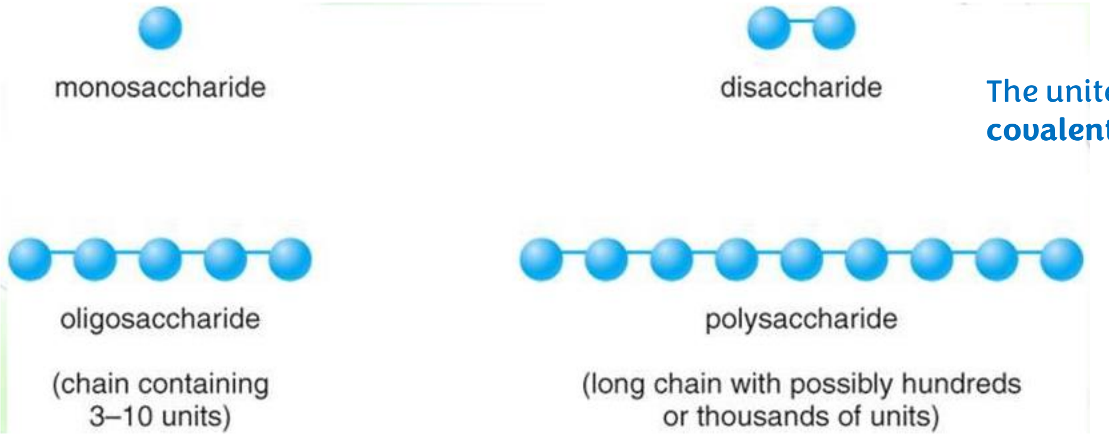
Lipid molecule with some sugars

- Glycolipids (cerebrosides, gangliosides)
- Glycosides (Sugar molecule reacted with alcohol molecule)
- Mucopolysaccharides (hyaluronic acid) Large molecules in ECM
- Nucleic acids (DNA, RNA)

Classification I

- By the number of sugars that constitute the molecule
- Monosaccharides, Disaccharides, Oligosaccharides, Polysaccharides

(3-10) UNITS



The unites are **covalently** bounded

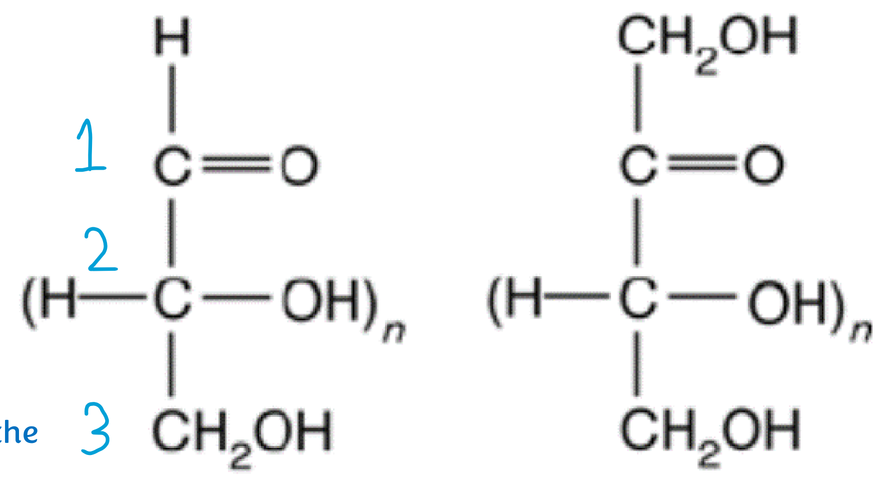
Monosaccharides

For every “C”, we have 2 “H” + 1 “O”, otherwise the molecule isn't considered a sugar.

- Basic chemical formula: $(CH_2O)n$
- They contain two or more hydroxyl groups.

Aldehyde should be on top

The ketone group should be the second C from the top.



An aldose

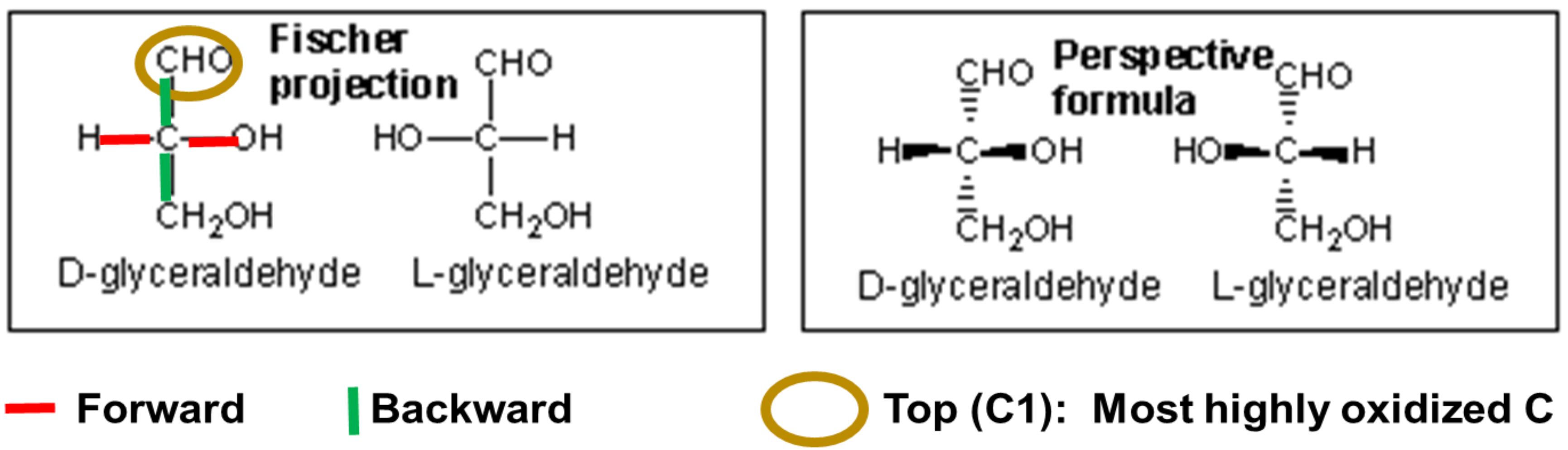
Ald: aldehyde

Ose: means sugar

A ketose

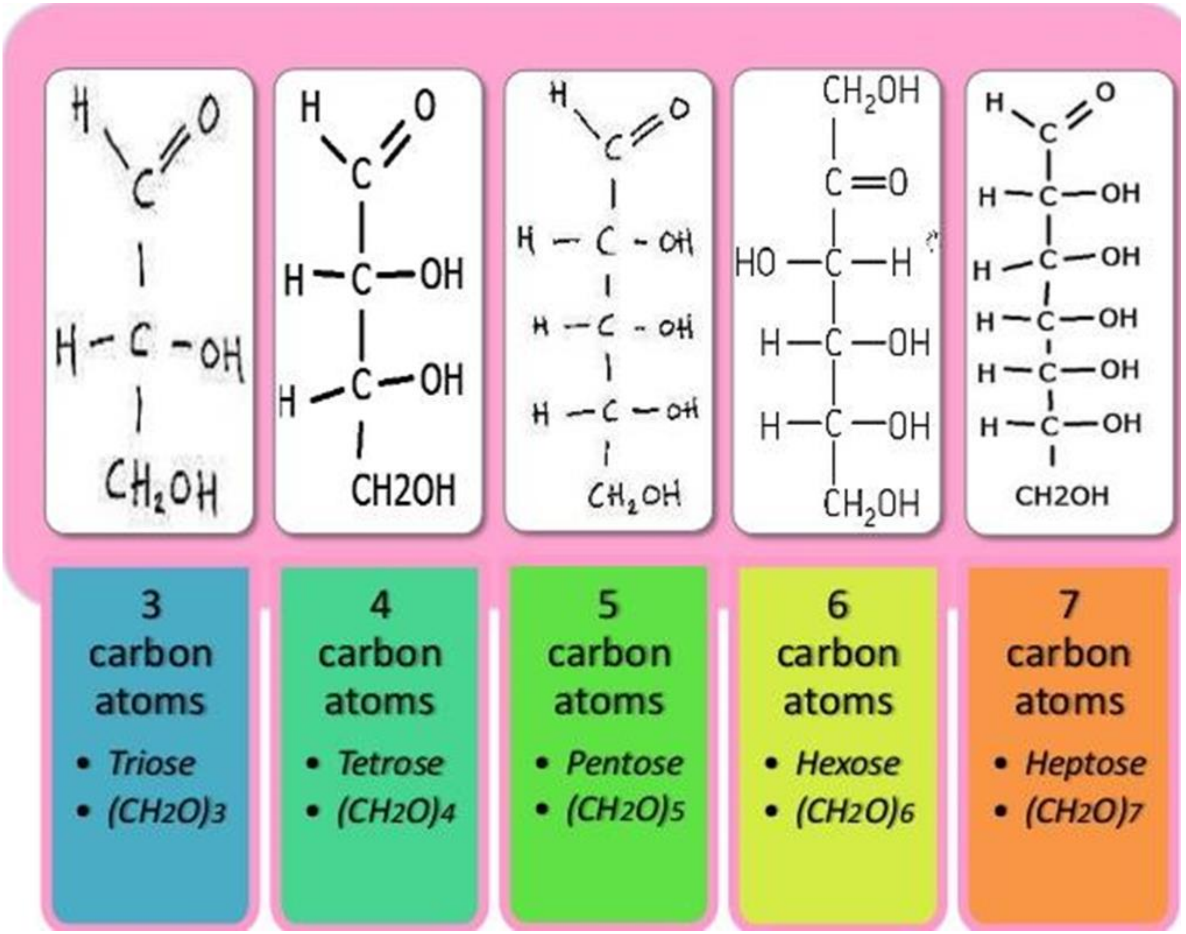
Ket: ketone

Fisher projections or perspective structural formulas.



Classification 2

- By the number of carbon atoms they contain. (in monosaccharides)
  - Triose (is the smallest sugar that contain 3C)
  - Tetrose
  - Pentose
  - Hexose
  - Heptose
  - …

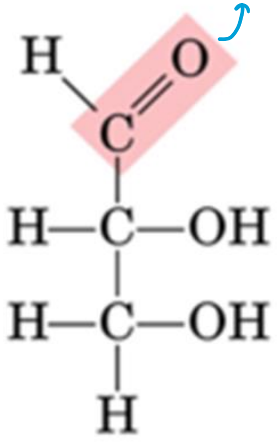


Every C should have OH group and H, Except the C that has the functional Group (aldehyde or ketone) and the last C.

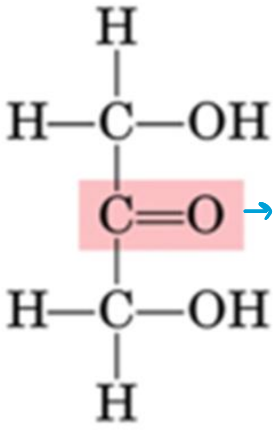
Classification III

- By the functional group

Aldehyde group should be in C no.1

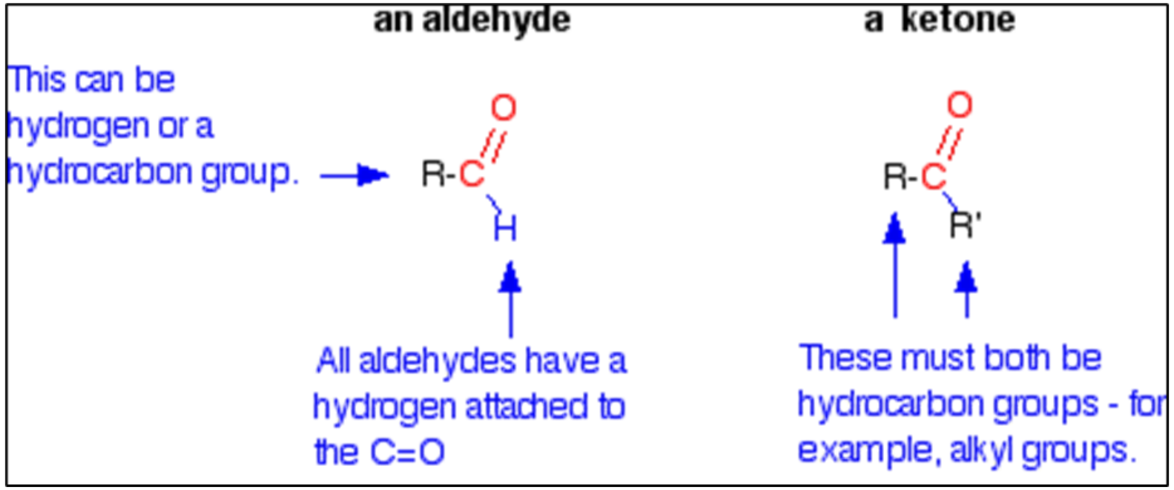


Aldose

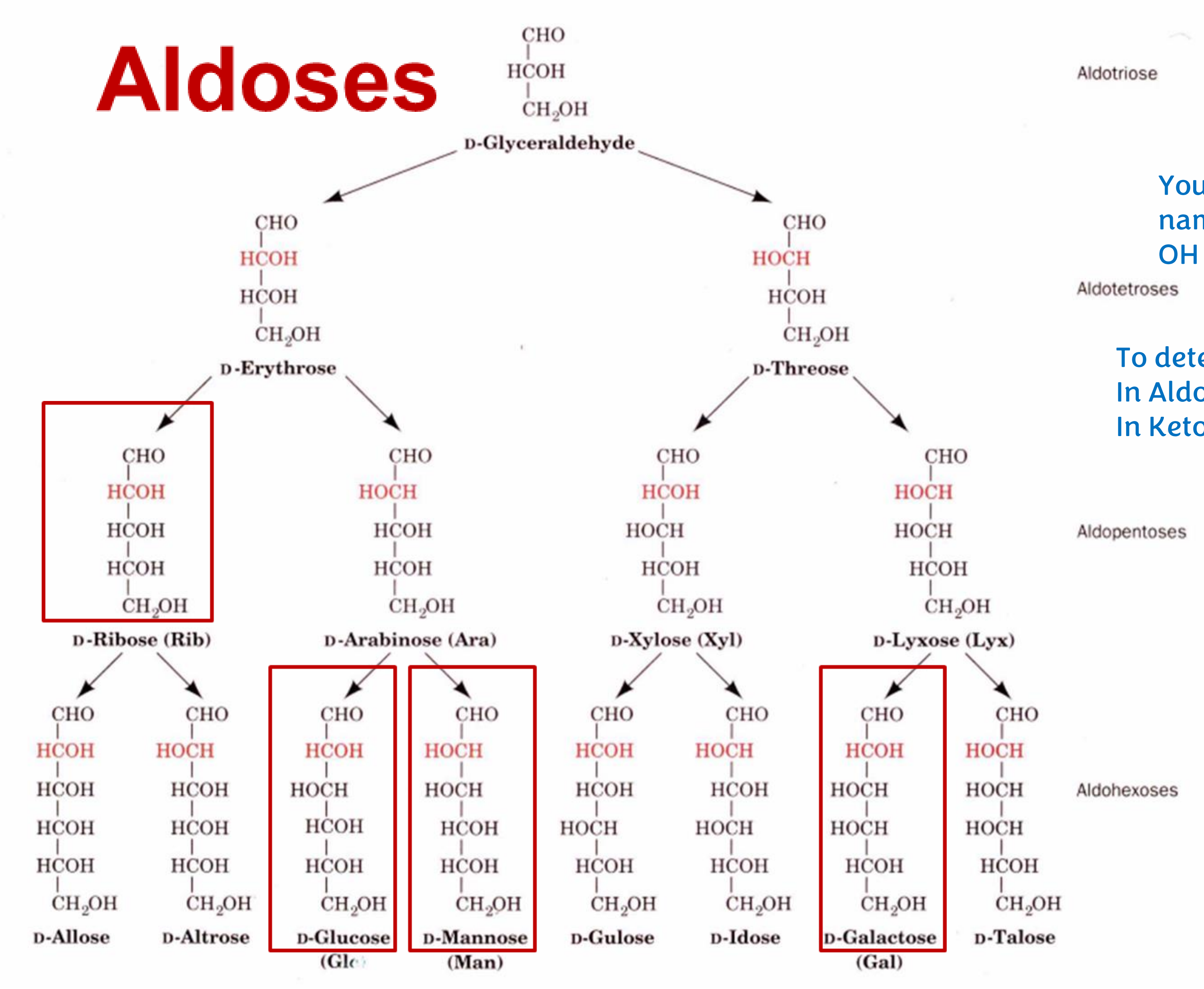


Ketose

Ketone group Should be in C no.2



Aldoses



Memorize the ones in boxes.

You should know: the structure, name, no. of C and the location of OH groups (left or right)

To determine the no. of chiral centers:-
In Aldoses: (no. of C – 2)
In Ketoses: (no. of C – 3)

Ketoses

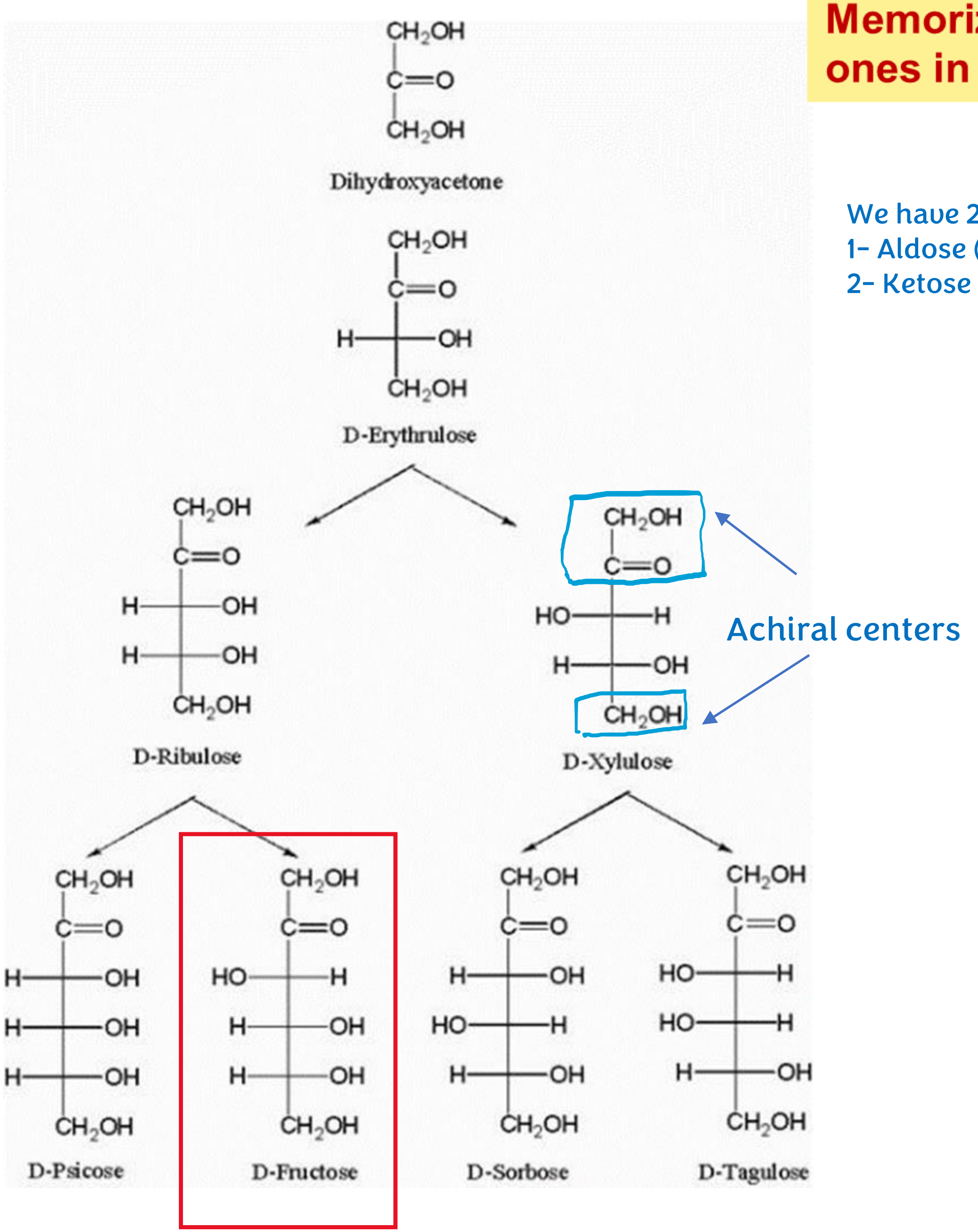
Memorize the ones in boxes.

Ketotriose

Ketotetroses

Ketopentoses

Ketohexoses

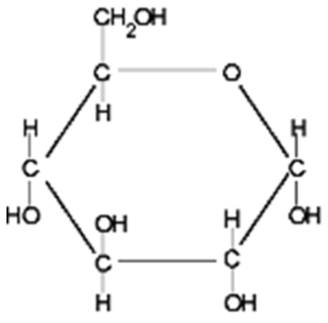


We have 2 trioses:
1- Aldose (glyceraldehyde), mainly D-.
2- Ketose (Dihydroxyacetone)

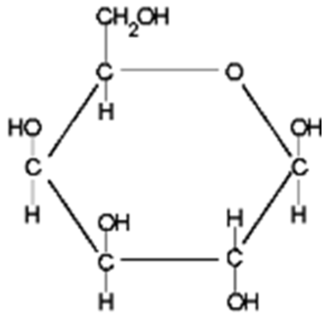
Common Monosaccharides

- Glucose: (The main source of energy in our bodies)
- Mild sweet flavor
- Known as blood sugar
- Essential energy source
- Found in every disaccharide and polysaccharide

It may be modified but it is the basis



Glucose



Galactose

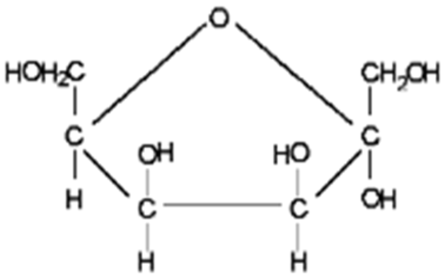
Galactose:

Hardly tastes sweet & rarely found naturally as a single sugar

Fructose:

Sweetest sugar, found in fruits and honey

Added to soft drinks, cereals, desserts

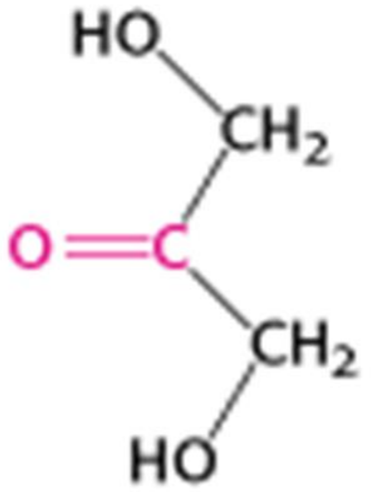


Fructose

Trioses

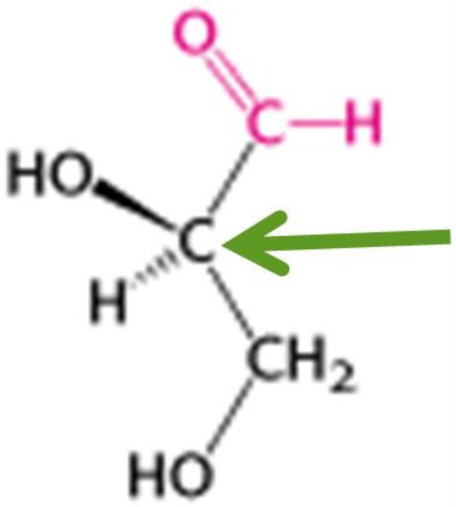
- **What is a chiral carbon?**

What is The Importance of chiral C ?
The molecule that contain chiral C with its mirror image can not superimposable [that's mean they are totally different, ex: There are molecules very sweet and their mirror image are very bitter (مر). DR. Ma'mon 2023]



Dihydroxyacetone
(a ketose)

Does not have any chiral C [the molecule with their mirror image are the same].



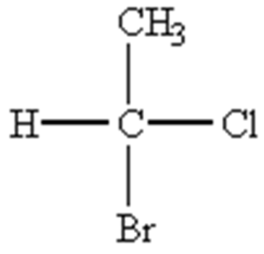
Chiral carbon

Make 4 covalent bonds with 4 different groups.

D-Glyceraldehyde
(an aldose)

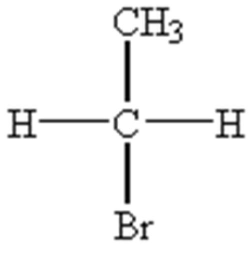
These are the only trioses(the simplest sugars)

Note what a chiral carbon is…



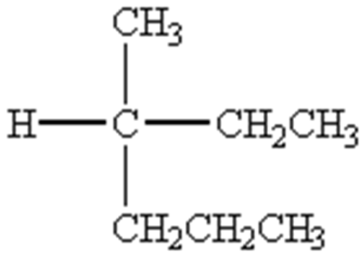
chiral

Has 4 differnt atoms bonded to the carbon



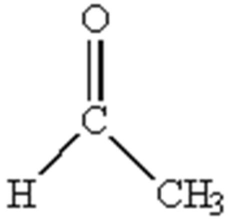
achiral

Does not have 4 different atoms or groups bonded to the carbon (2 hydrogens)



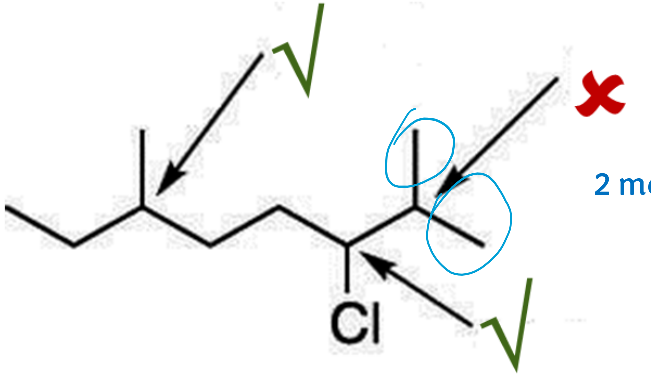
chiral

Has 4 differnt groups bonded to the carbon



achiral

Only has 3 atoms bonded to the carbon



2 methyl groups

A way to distinguish and designate sugars.

Isomerism

Simply, they're 2 molecules with the same atoms –C,H,O in this case– (molecular formula) , But these atoms have different arrangement (Structural formula)

An *isomer* is a molecule with the same molecular formula as another molecule, but with a different chemical structure.

Isomers that have the same molecular formula and sequence of bonded atoms (constitution) but differ in the three-dimensional orientations of their atoms in space.

have the same order of attachment but differ in arrangements of the atoms in space (3D STRUCTURE).

- **Isomers**
  - **Stereoisomers**
    - **Enantiomers**
      - **L-isomers**
      - **D-isomers**
    - **Diastereomers**
      - **Epimers**
  - **Constitutional isomers**

Molecules with the same molecular formula but have different bonding patterns and atomic organization.

Same atoms , but different attachments (atoms are connected differently).

L : Levo
D : Dextro

We'll talk about them later ; but they differ only in the attachments around a single chiral center (others are still the same).

Isomers of glucose

Glucose has 4 chiral centers, therefore 16 isomers.

Stereoisomers ; we can see that all of them have the same carbons attached to the hydroxyl groups and hydrogen BUT...

# of isomers = 2^n (n is the number of chiral carbons in a sugar molecule)

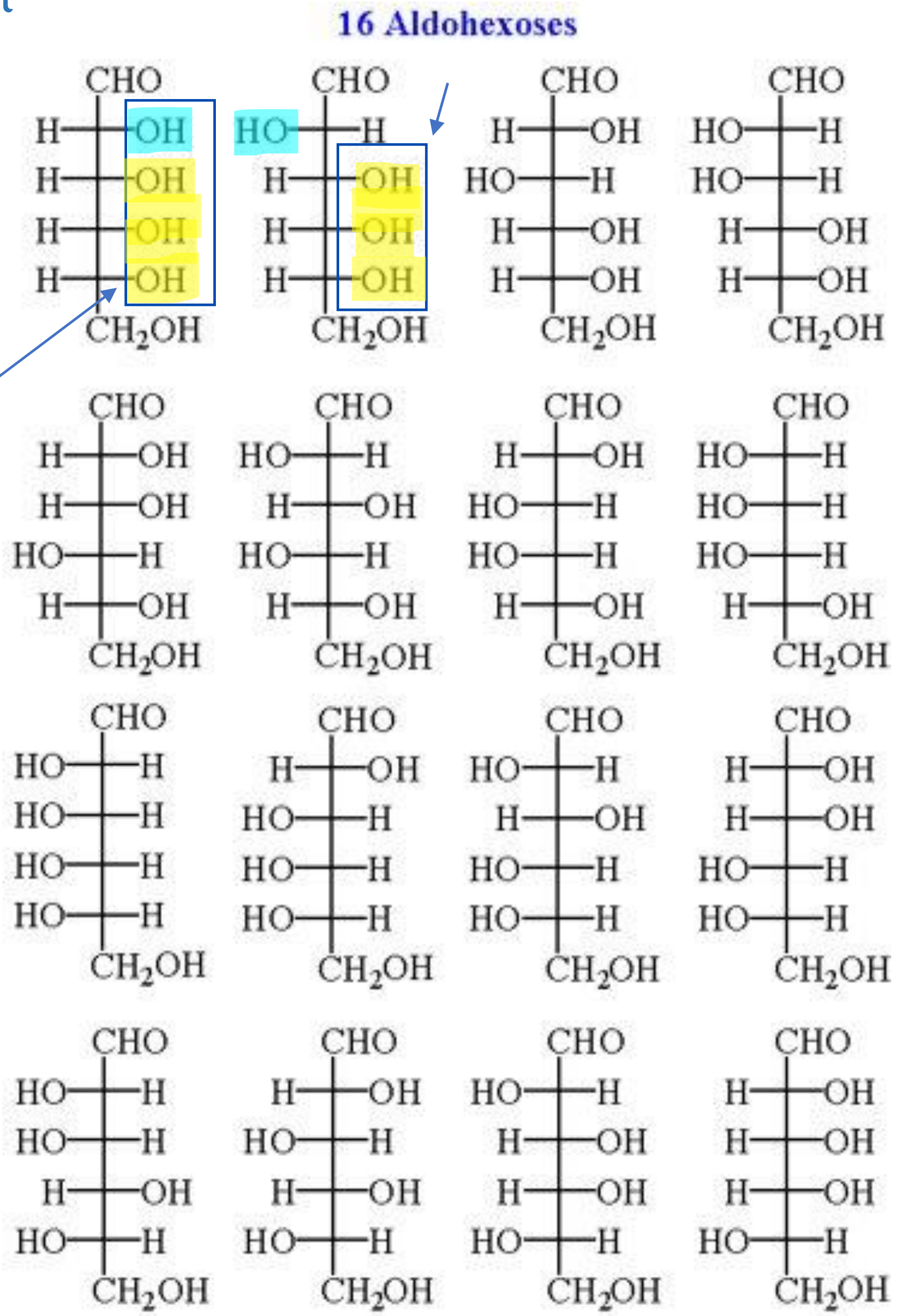
This isomer has 4 OH groups to the right , while the one next to it has 3 to the right. (apply your knowledge to differentiate between the other isomers.)

DR.Diala's way to calculate the # of chiral centers.

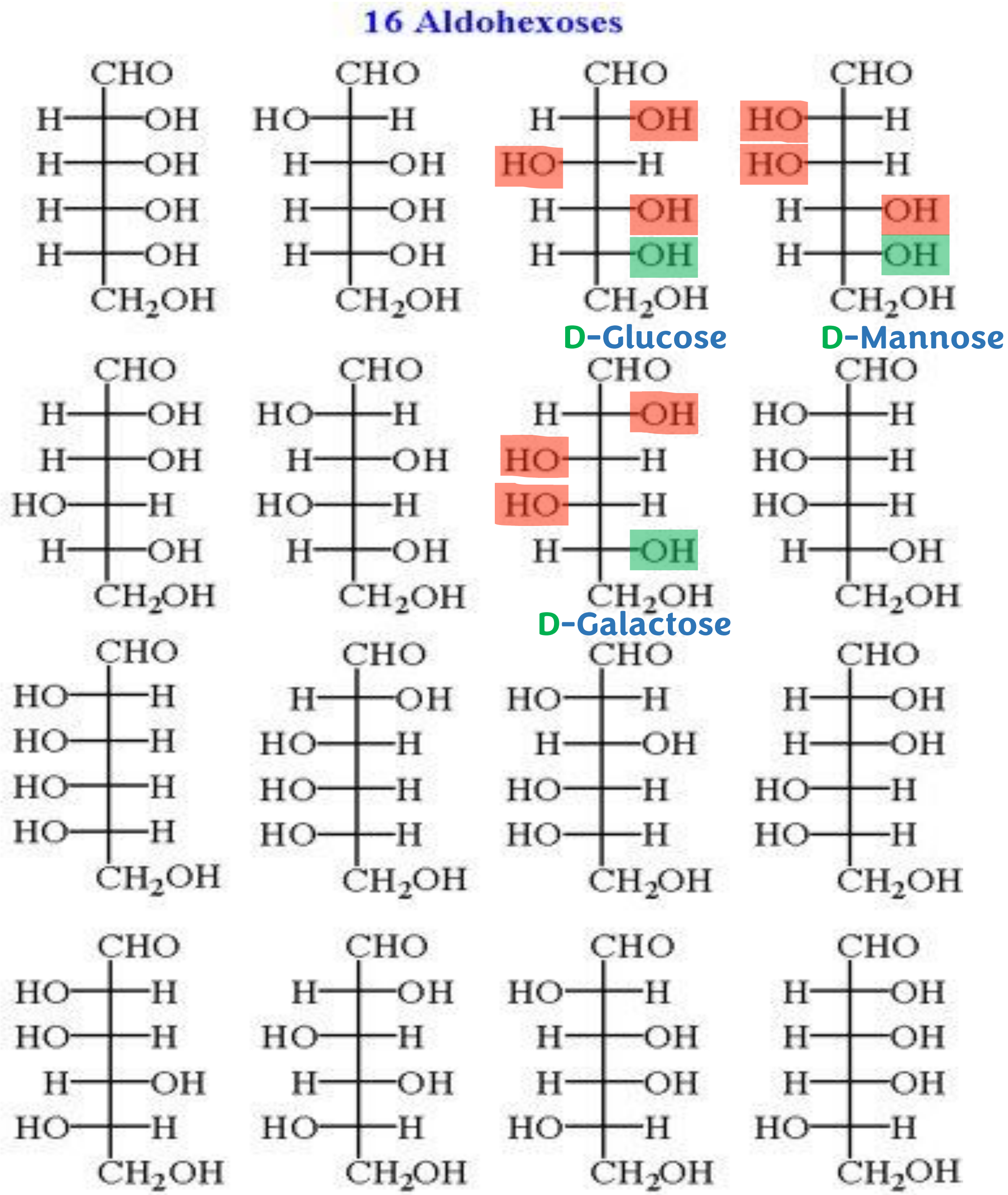
- If ketose (n-3)
- If aldose (n-2)
- Where n is the # of carbons

Search for:
Glucose,
Galactose
Mannose

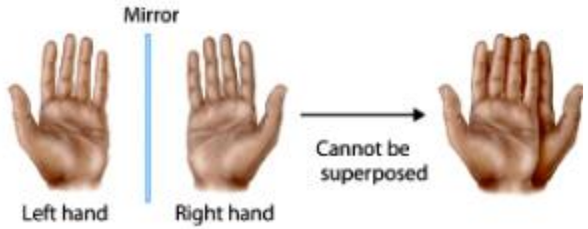
DO NOT forget to memorize the structures required. The answers for the question are colored in red. **(next slide)**



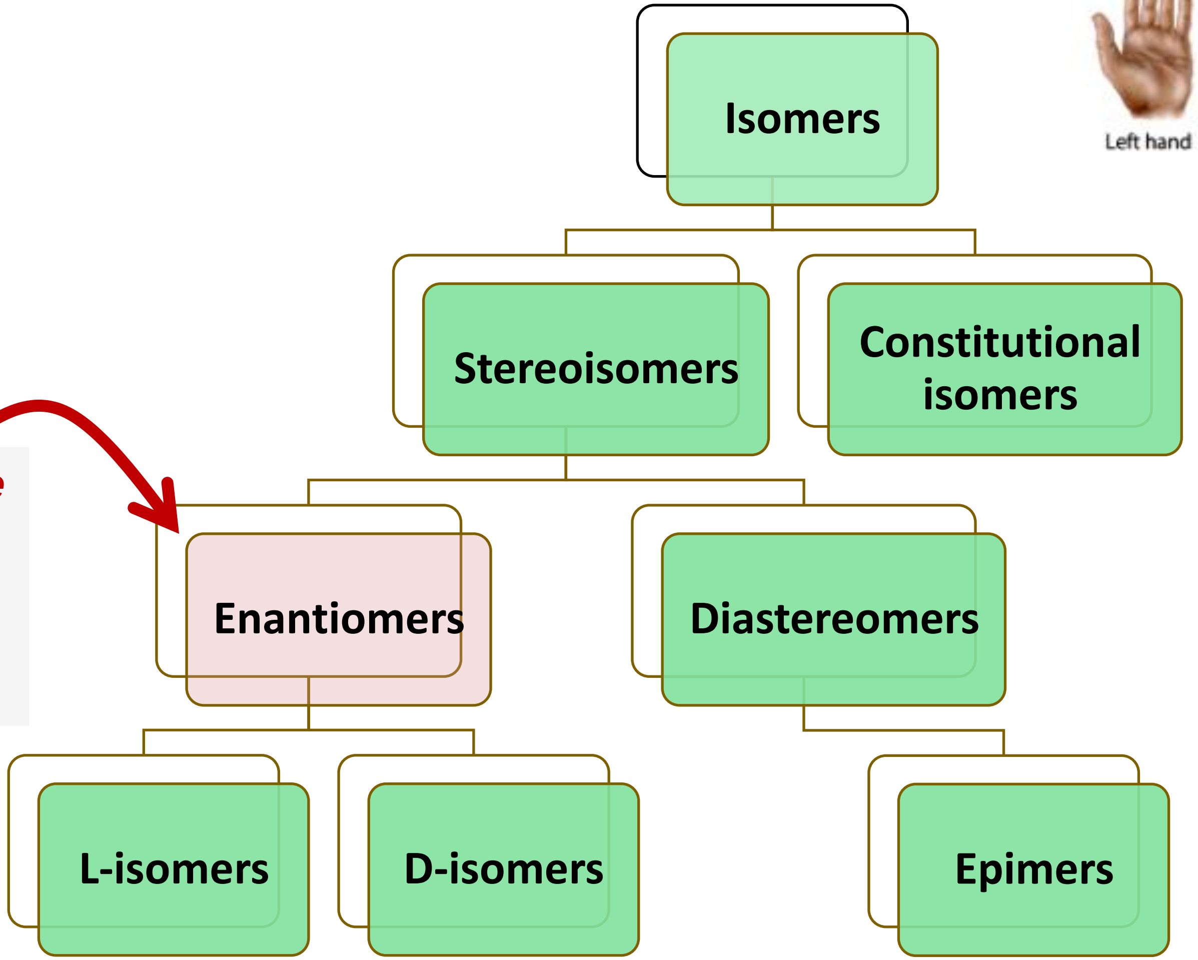
- Glucose: only 3 to the left.
- Galactose: 3 and 4.
- Mannose: 3 and 2.



To understand the meaning of mirror images and non-superimposable, think of your hands they are mirror images of each other however when you put them on each other **facing the same way** they DON'T actually close on each other .



Enantiomers



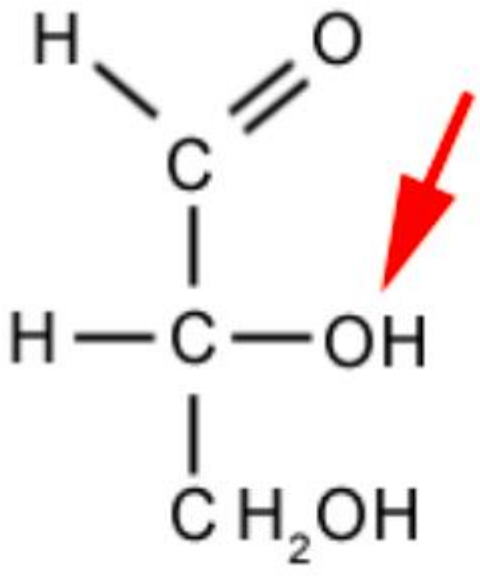
Two stereoisomers that are mirror images of each other and are non-superimposable (not identical)

So if they are mirror images , and they are non-superimposable ; they're enantiomers

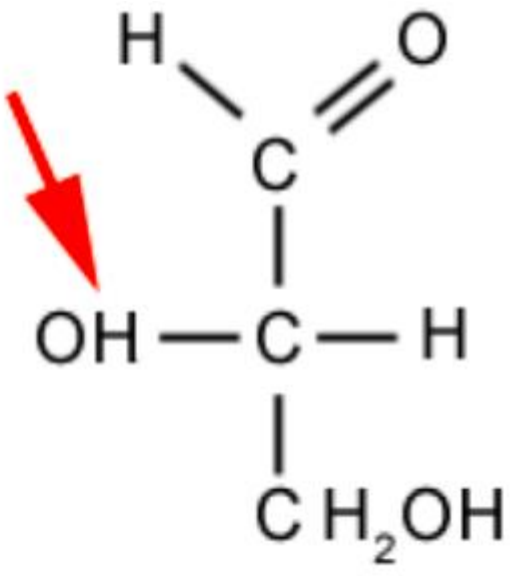
L for Left
D for Right

Sugar enantiomers (D- vs. L-)

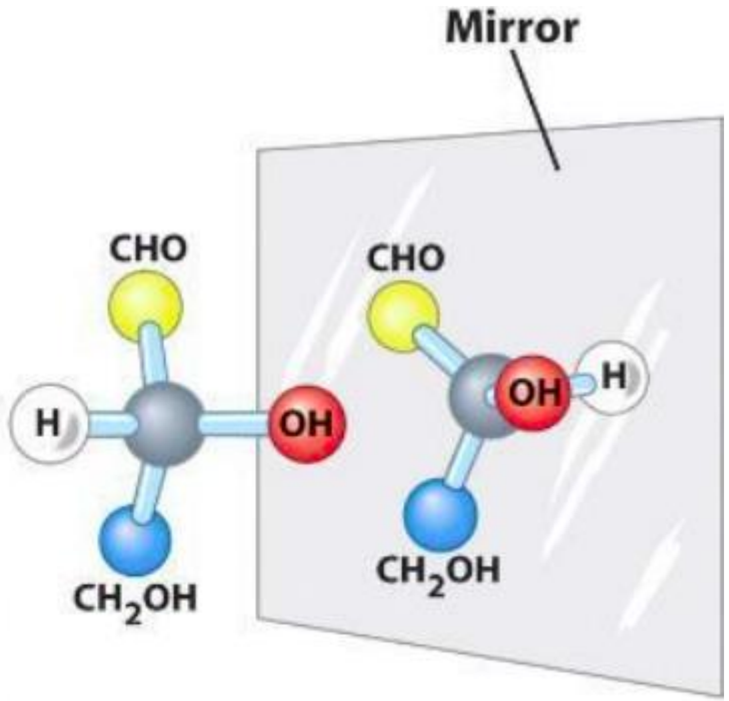
Glyceraldehyde has 2 enantiomers → L and D.
Each one of them is the enantiomer of the other.



D-Glyceraldehyde



L -Glyceraldehyde

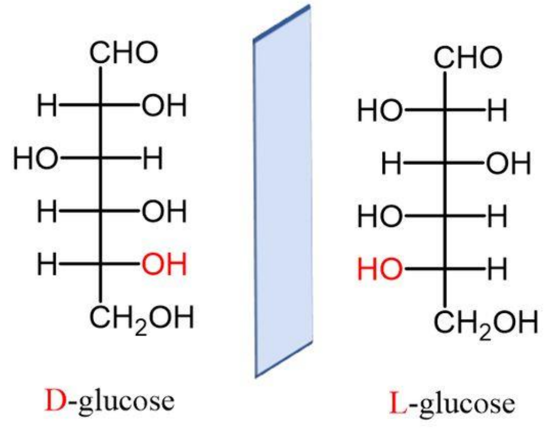


Ball-and-stick models

Here we have a triose with its enantiomers and they are given a designation (a letter). So, the glyceraldehyde will either be in the L structure or D structure.

What does the D- / L- designation depend on?

- 1- The hydroxyl (OH) group.
- 2- The hydroxyl (OH) group attached to the chiral carbon.
- 3- This chiral carbon is the furthest from the functional group.
- EXAMPLE...



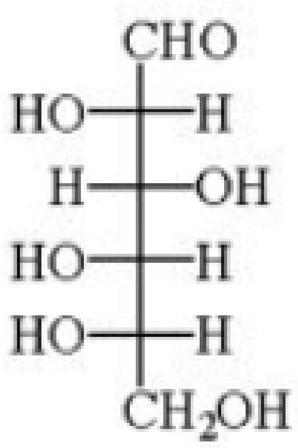
Enantiomers

We are looking at the OH group at the furthest carbon from the functional group (that is C#5) :
On the right the OH group is to the left therefore L- glucose.
AND on the left the OH is to the right therefore D – glucose.

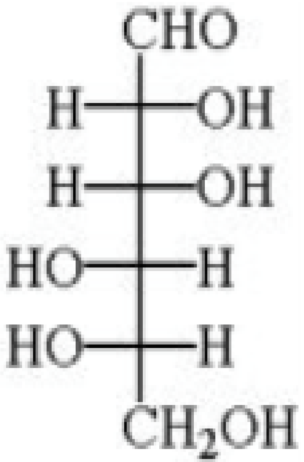
REMEMBER, the terminal carbon in monosaccharides is always Achiral.

NOW, after we knew what D- and L- means, go back to slide 14 and find the enantiomers of Glucose, Mannose ,and Galactose (and determine whether they're Levo or Dextro)

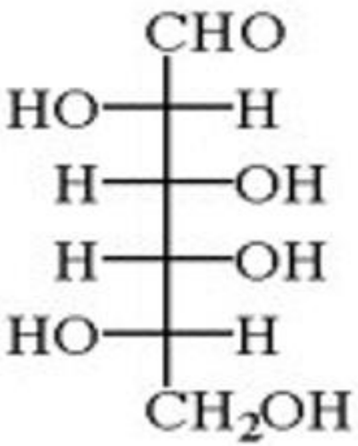
- ANSWER:



L- glucose



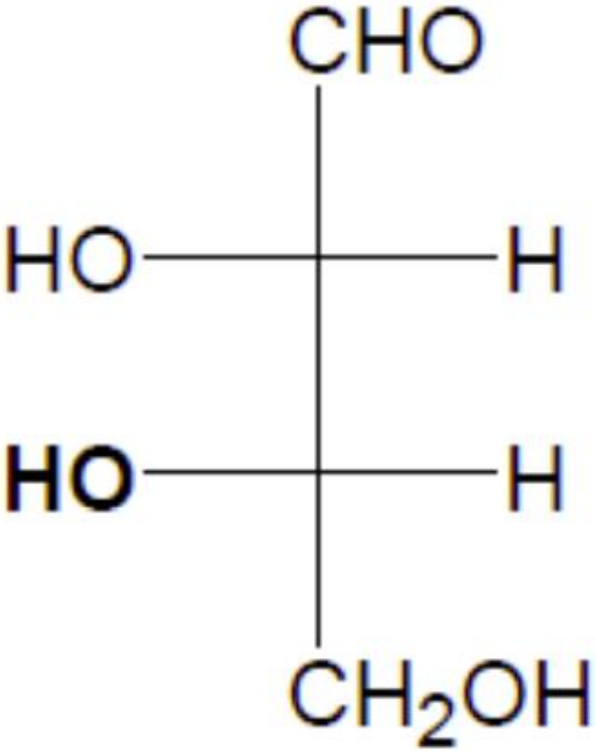
L- mannose



L- galactose

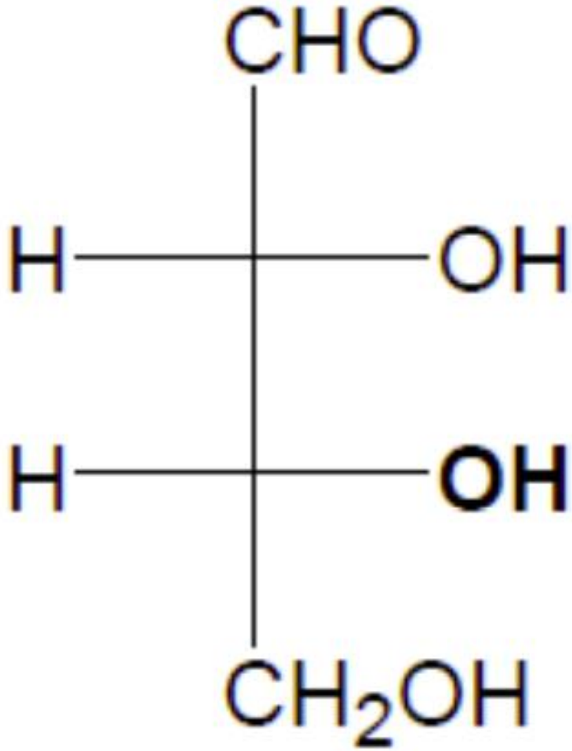
Which one(s) is a chiral carbon?

Organic key !!
If a molecule has
a specific configuration , its mirror
has the opposite configuration.
(and that is what we see here.)



L-erythrose

This is L ; because the OH group on the furthest carbon from the aldehyde group is to the left of that carbon



D-erythrose

To the right; D-erythrose

Do not memorize but study them.

Isomerism

Glucose obviously has 2 **enantiomers** (D- and L-)

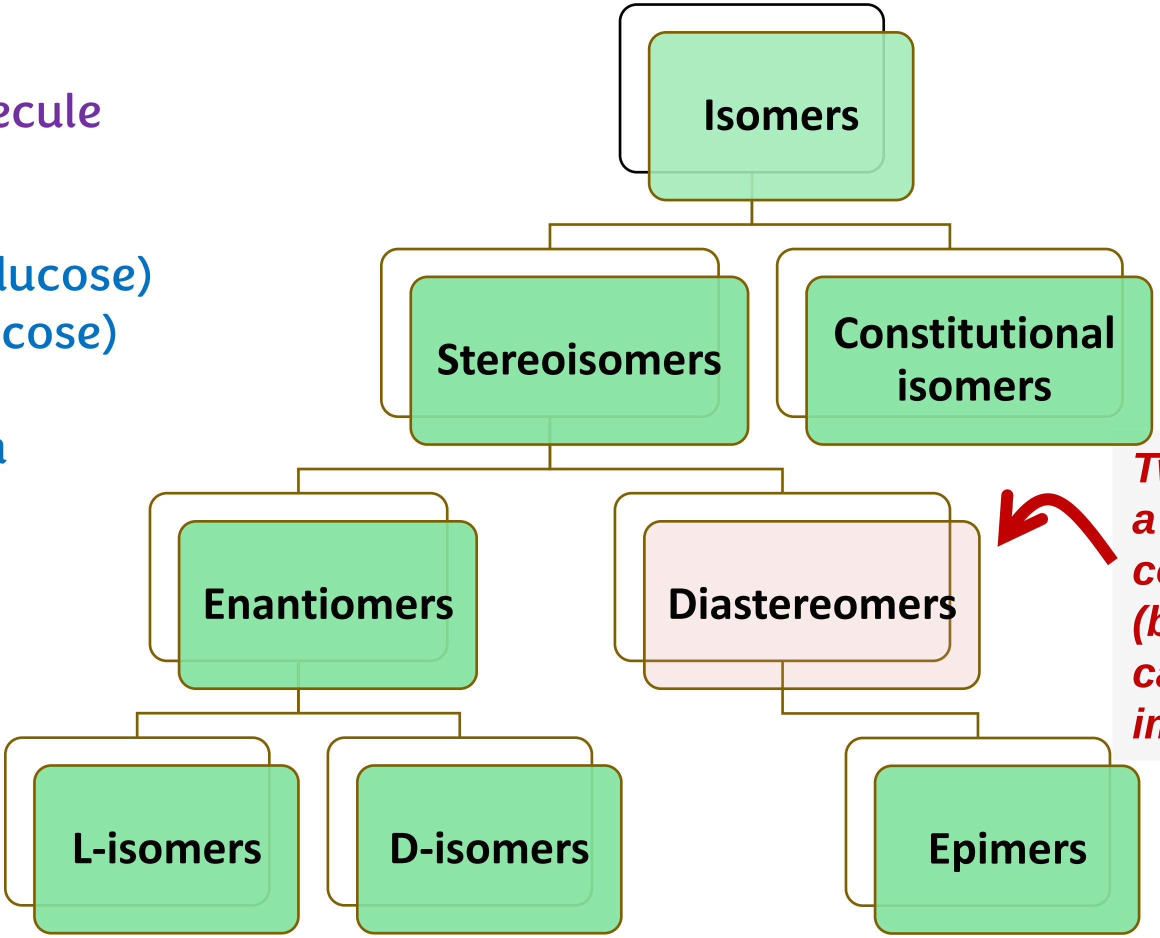
According to Dr. Mamoun:
Any molecule has 1 mirror image
(e.g., each glucose (D- or L-) molecule
essentially has 1 **mirror image**)

D-glucose has 1 mirror image (L-glucose)
D-glucose has 1 enantiomer (L-glucose)

The total # of stereoisomers for an aldohexose ($2^{6-2} = 16$)

The 16 is divided into:

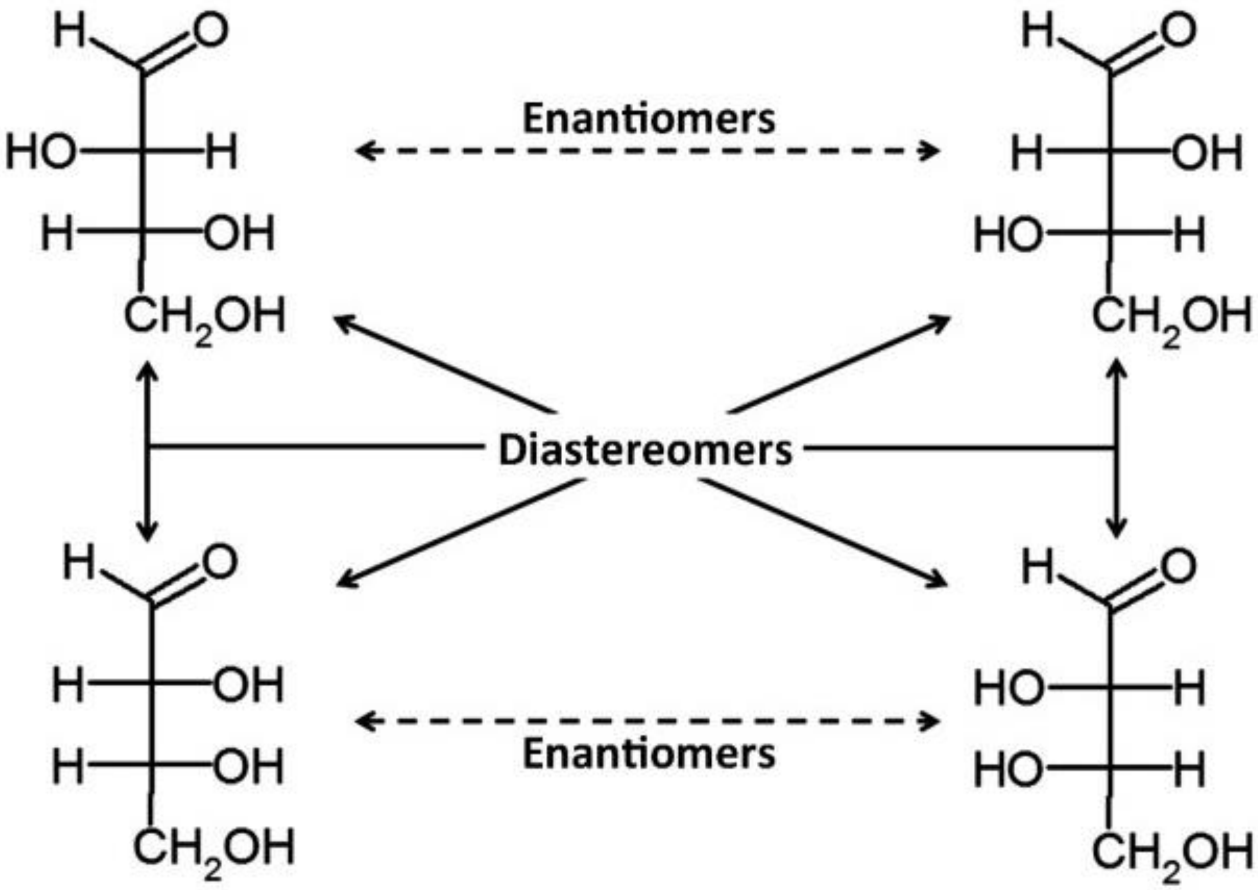
The molecule itself (1)
An Enantiomer (1)
Diasteriomers (14)



Two or more stereoisomers of a compound having different configurations at one or more (but not all) of the chiral carbons and are not mirror images of each other.

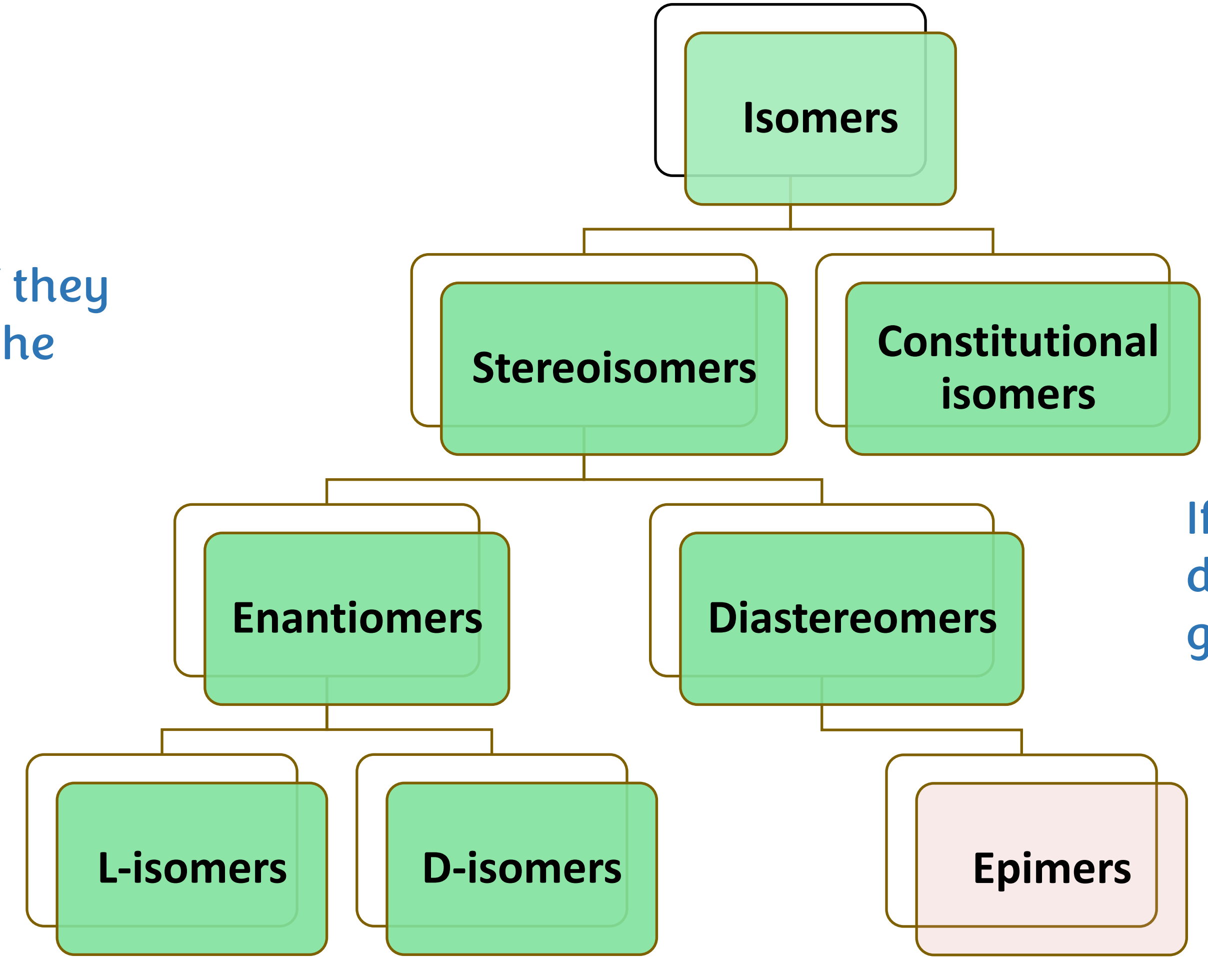
They're stereoisomers but not mirror images nor superimposable; one or more chiral centers got their configuration inverted BUT not all.

Stereoisomers, but non-mirror images and non-superimposable, then…diastereomers



Isomerism

"In other words, two molecules are epimers if they are identical except for the orientation around one specific carbon atom."



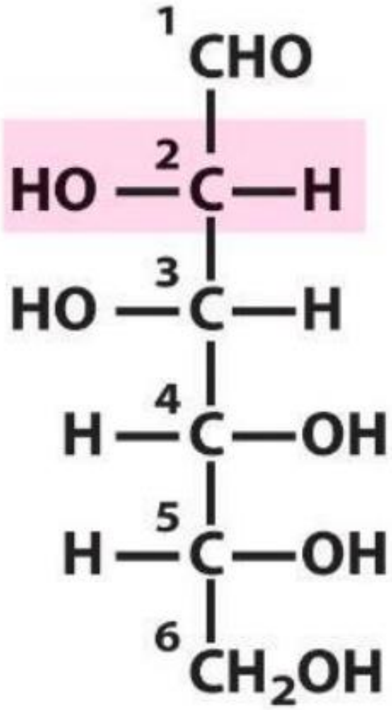
If they differ only in one hydroxyl group, they're Epimers

Epimer refers to one of a pair of stereoisomers whereby two isomers differ in configuration at only one chiral carbons.

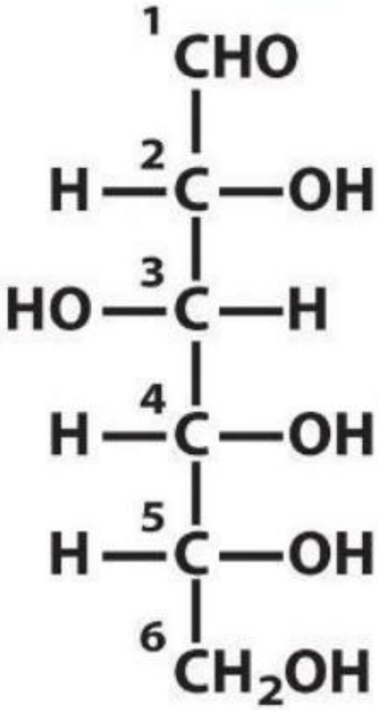
Diastereomers with different orientation of one chiral carbon, then… epimers

Memorize and study them.

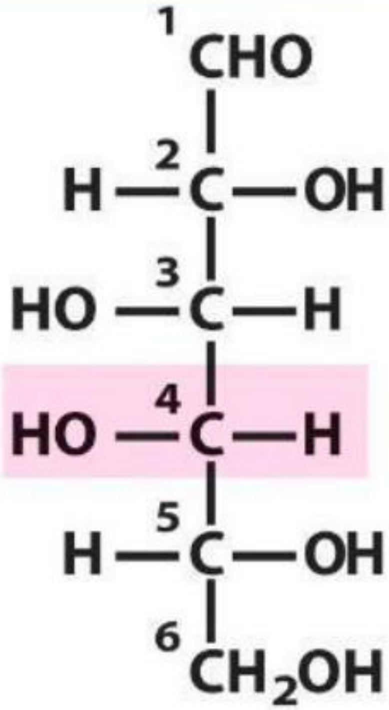
Notice how these are almost the same but at carbon # 2 mannose has the OH to the left , in contrary to glucose whose having it to the right. (And that is what makes them epimers)



D-Mannose
(epimer at C-2)



D-Glucose



D-Galactose
(epimer at C-4)

BOTH D-Galactose and D-Mannose are epimers to D-Glucose.

They're Diastereomers but more specifically Epimers

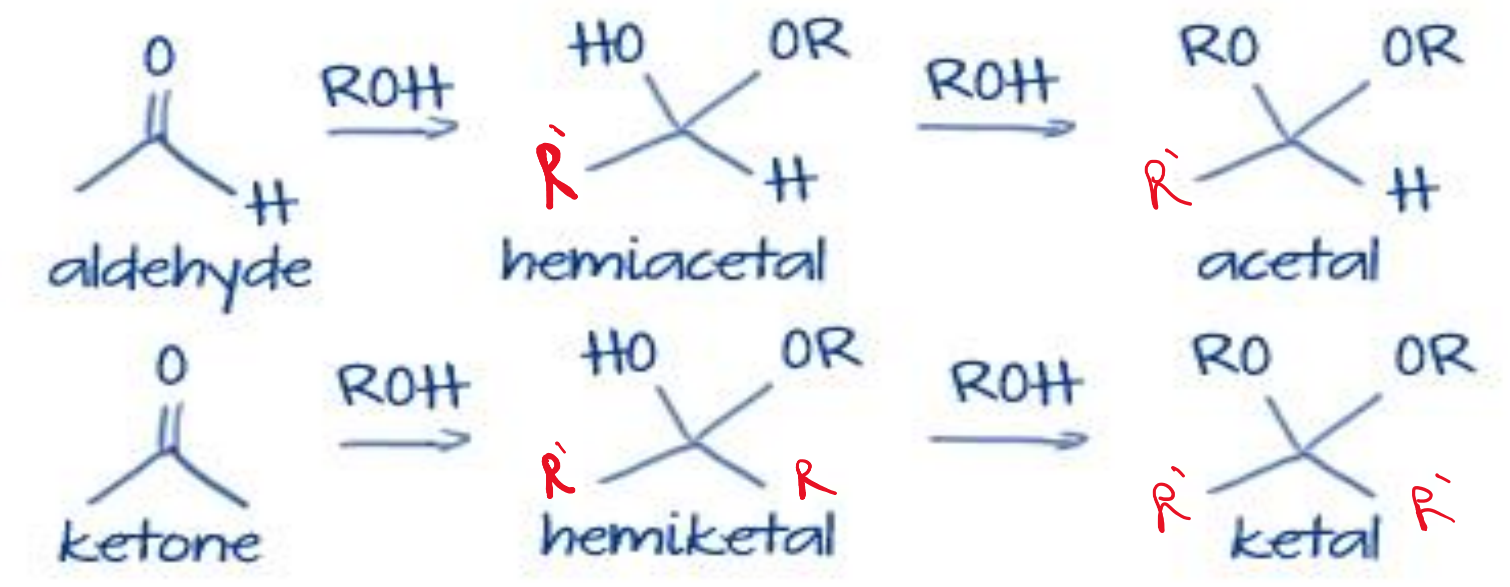
Is L-glucose an epimer with D-mannose and D-galactose?

NO, diastereomers but not epimers.

Carbonyl groups and hydroxyl groups are reactive making them more active toward reactions (they have oxygen) and this is one reaction.

Acetal/ketal vs. hemiacetal/hemiketal

- Hemiacetal and hemiketal: ether and alcohol on same carbon Acetal and ketal: two ethers on same carbon

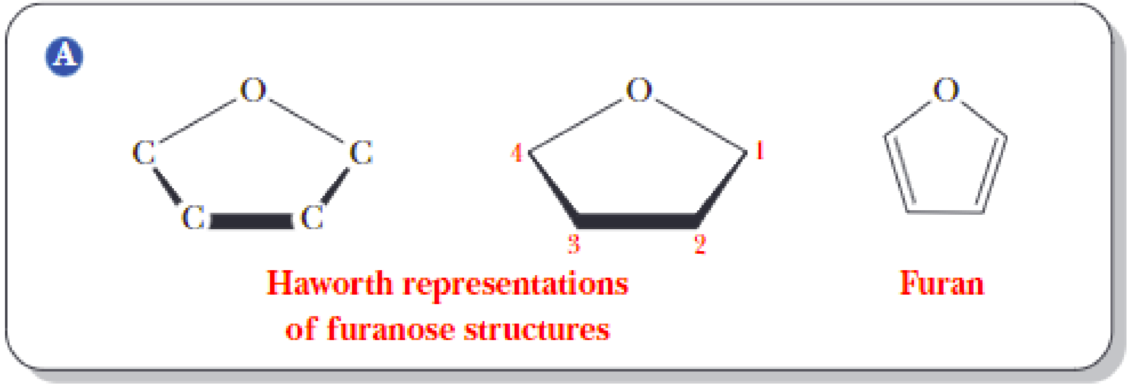


What is the difference between hemiacetal and hemiketal and the difference between acetal and ketal? They're same in concept , the only difference is the origin ; ketal and hemiketal result from the addition of an OH containing molecule (sugar for instance) to a ketone, while acetal and hemiacetal are from an aldehyde.

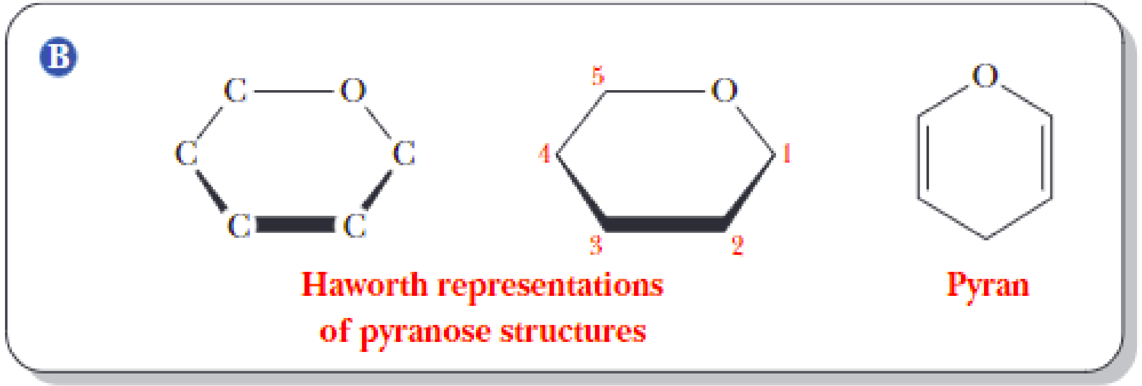
The presence of the carbonyl and the hydroxyl groups , gives the sugar molecule the ability to interconvert from the open chain form to the ring form.

Formation of a ring structure

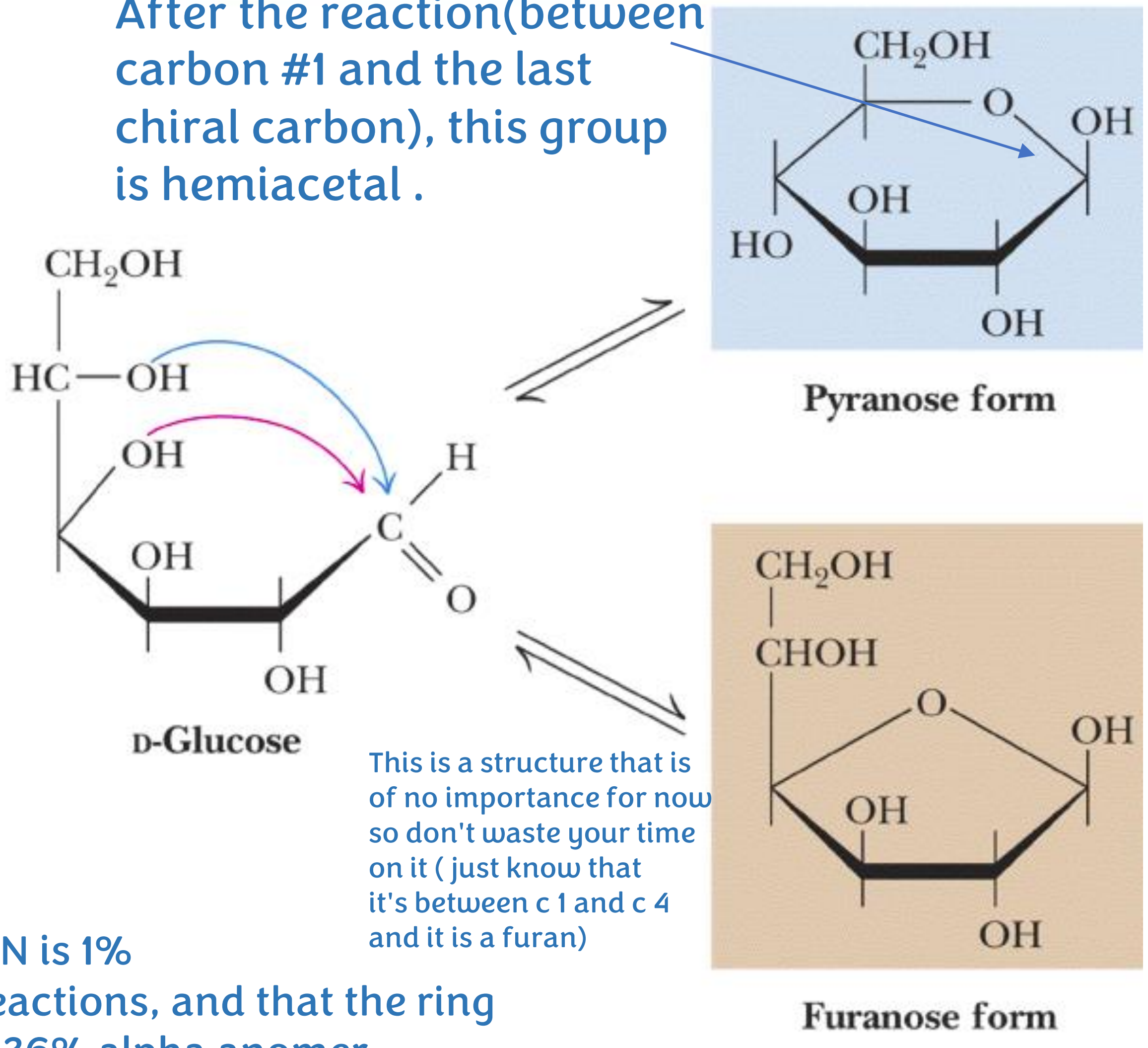
The ring is more stable than the open chain form. And pyranose is more stable than furanose which has more strain.



Rings have names ,a 5 membered ring with oxygen in it is furan and 6 membered rings with oxygen as a member are called pyran . So , glucopyranose is just a six membered glucose ring.



After the reaction(between carbon #1 and the last chiral carbon), this group is hemiacetal .

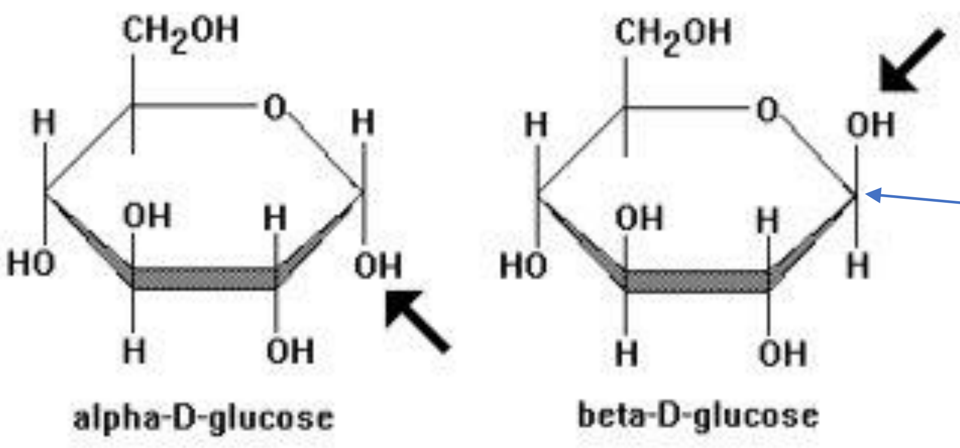


This is a structure that is of no importance for now so don't waste your time on it (just know that it's between c 1 and c 4 and it is a furan)

DR. Mamoun said that the RING is present 99% and the OPEN CHAIN is 1% while DR. Diala said that we mostly find open chains only during reactions, and that the ring structure is in 100% of the time divided into 64% beta anomer and 36% alpha anomer.

They're isomers that differ in the location of the OH group on the anomeric carbon relative to the plane.

Anomers



The ring is a plane (think of it as paper) and it has groups above it and below it .

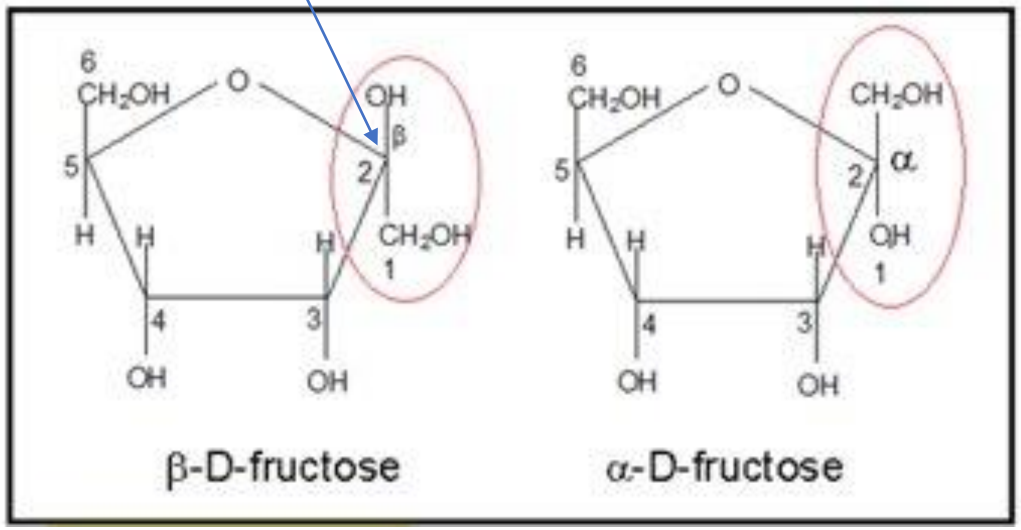
In the ring form all groups are stable (stay in their position) except for those at carbon #1 (former carbonyl group) the OH group moves up or down.

Making memorization easier...

Think of alpha as fish (due to its shape- **α**) and fish residue in water underground , so the alpha glucose has the OH group down in relative to the ring.
And think of beta as (بيت) which is overground.

Beta is more stable than alpha in glucose
Alpha is more stable than beta in fructose

Anomeric carbon



For any feedback, scan the code or click on it.

Corrections from previous versions:

Versions	Slide # and Place of Error	Before Correction	After Correction
V1 → V2 (1 change)	15, 19; Galactose Fisher projection	D-Galactose has OH at: C2 – left C3 – right C4 – left C5 – right *L-Galactose:* *is the complete opposite*	D-Galactose has OH at: C2 – right C3 – left C4 – left C5 – right *L-Galactose:* *is the complete opposite*
	27; Text about stability	*Original text in blue*	*Added the texts in light blue and purple*
V2 → V3	16; the text at the bottom	-	Removed
	21; text at the right	Glucose has 1 enantiomer	D-glucose has 1 enantiomer *Added the purple texts*
V3 → V4	17; text below the title	Glyceraldehyde has 1 enantiomer	*Modified to include the written now*

Additional Resources:

رسالة من الفريق العلمي:

1. https://chemistry.stackexchange.com
2. Campbell Textbook:
   sec. 16.1
   (Sugars: Their Structures and Stereochemistry)
3. Mark's Basic Medical Biochemistry
   sec. 2.5
   (Structures of the Major Compounds of the Body)

قال صلى الله عليه وسلم:من هالَه الليلُ أن يكابدَه ، أو بخِلَ بالمالِ أن يُنفِقَه ، أو جَبُنَ عن العدوِّ أن يقاتلَه ، فلْيُكثِر من (سبحان اللهِ وبحمدِه) ؛ فإنها أحبُّ إلى اللهِ من جبلِ ذهبٍ ينفقُه في سبيل اللهِ عزَّ وجلَّ.