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Carbohydrates

What are carbohydrates?

- Carbohydrates are polyhydroxy (have more than one hydroxyl group) aldehydes (terminal carbonyl) (C=O) or ketones (carbonyl group on the 2nd carbon).
- **Saccharide** is another name for a carbohydrate (simple or complex ones).

Functions: (structural and functional)

1-**major and first source of energy** (to produce energy the body will not break proteins, amino acids or fats if there is carbohydrates)

2-**structure** (like cellulose in plants which looks like threads, THESE are called cellulose fibers. Chitin which is a polysaccharide that forms the exoskeleton structure of insects or crustaceans like lobster)

3-**building blocks** of several important molecules contributing in their function, distinguishing an extracellular matrix from another one such as glycoproteins.

4-**cellular and immune recognition** (ex: immune cells can recognize the virus using the sugars on the surface of these viruses, same thing goes in cellular and blood groups recognition in cells)

side note: when a wrong blood group enters the body, the immune system is going to recognize **the sugar on the surface of the cells** and induce an immune response.

In addition, sugar molecules can be used in cell-cell recognition and communication.

Classification:

there are different ways by which we can classify carbohydrates:

classification I:

according to the number of sugars (monosaccharides) that constitute the molecule, to

1-**monosaccharides:** made of one sugar.

2-**disaccharides:** made of 2 sugars connected by a covalent bond.

3-**oligosaccharides:** made of (3-10) sugars.

4-**polysaccharides:** made of thousands or millions of sugars connected by covalent bonds.

Carbohydrates-natural forms:

Most carbohydrates are found naturally in bound form (connected to other molecules or similar molecules) rather than as simple sugars

1-Polysaccharides (starch, cellulose, inulin, gums, glycogen)

2-Glycoproteins and proteoglycans (hormones, blood group substances, antibodies)

amount of proteins is greater than sugars → glycoproteins

amount of sugars is greater than proteins → proteoglycans

3-Glycolipids (cerebrosides, gangliosides)

4-Glycosides: in which a sugar molecule interacts with another functional group via Covalent bonds

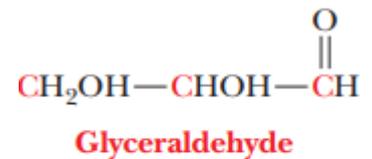
5-Mucopolysaccharides (hyaluronic acid)

6-Nucleic acids (DNA, RNA)

Monosaccharides:

Basic chemical formula: $C_n(H_2O)_n$

They contain two or more hydroxyl groups

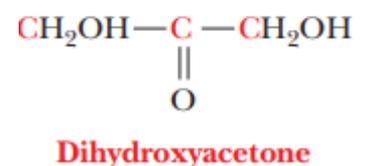


*the simplest aldehyde only has one carbon why does it have to be 3 here?

if we only have 1 carbon with the carbonyl group, we can't add a hydroxyl group,

and in the case of 2 carbons we can only add one

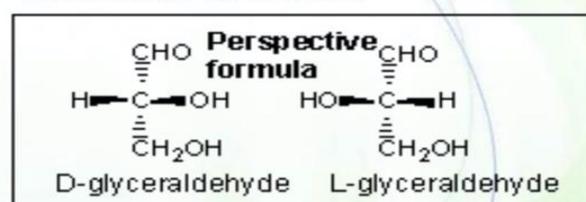
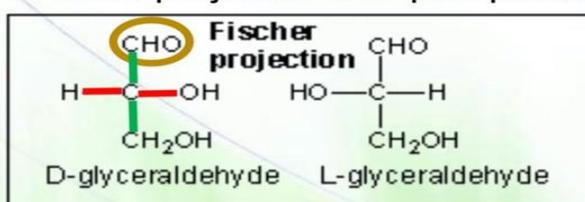
hydroxyl group while maintaining the aldehyde structure therefore it can't be polyhydroxy unless there is 3 carbons **at least**.



Also named **aldotriose**
 aldo :carbonyl group
 tri :3 carbons
 ose :sugar
 or **glyceraldehyde**

Also named
ketotriose or
dihydroxyacetone

Fisher projections or perspective structural formulas.



— Forward

█ Backward

○ Top (C1): Most highly oxidized C

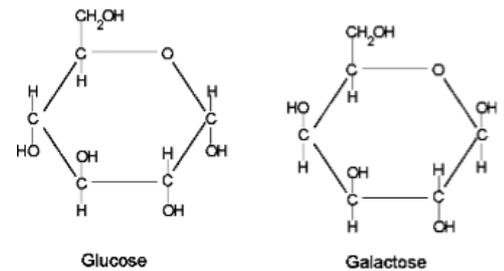
In glyceraldehyde, first carbon is achiral (not connected to 4 groups), third carbon is achiral (connected to two similar groups H), second carbon is chiral.

- if the hydroxyl group is on the left then it's an L - sugar and if it's oriented to the right then it's a D - sugar.

Common monosaccharides:

glucose: (aldohexose)

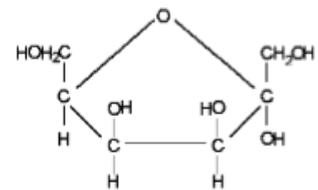
- main monosaccharide.
- mild sweet flavor.
- known as blood sugar.
- essential energy source (metabolism usually starts with glucose in terms of generation of energy).
- found in every disaccharide and polysaccharide.



galactose: (aldohexose)

- hardly tastes sweet & rarely found naturally as a single sugar (associated with other molecules like disaccharide or oligosaccharide)

*the difference between glucose and galactose is the orientation of the OH group on the 4th carbon (glucose downward and galactose upward) leading to a change in the orientation and the 3D space (isomers).

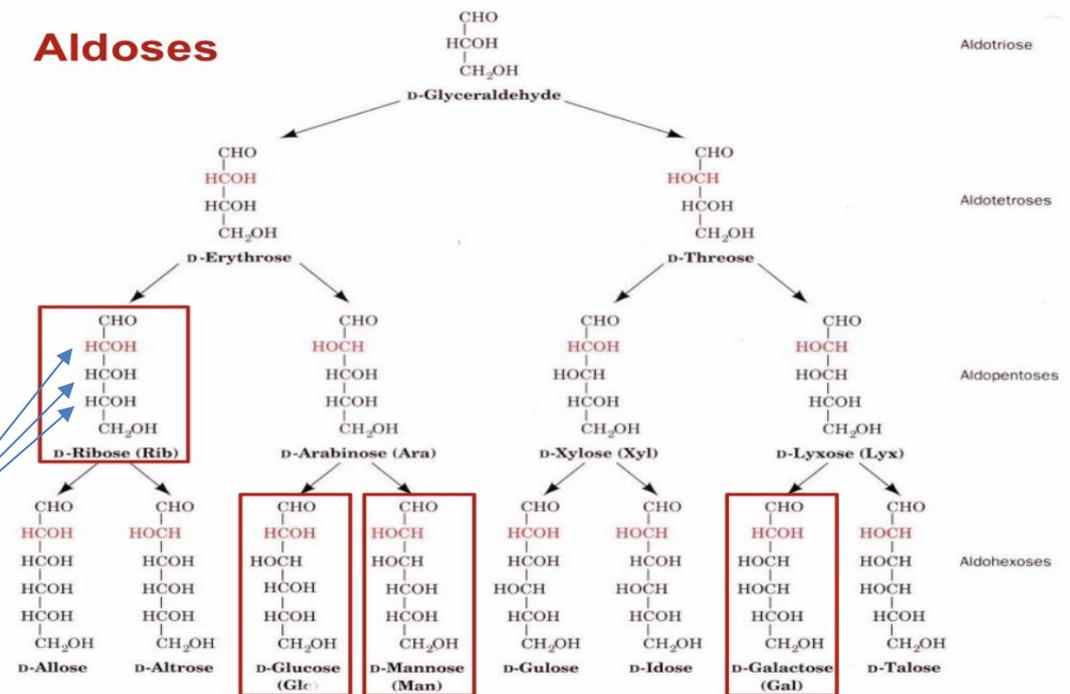


fructose: (ketohexose)

- sweetest sugar, found in fruits and honey.
- added to soft drinks, cereals, desserts.

*fructose is extracted from corn syrup as a replacement of sucrose which is extracted from sugar cane

Aldoses



Number of chiral centers= number of carbons-2

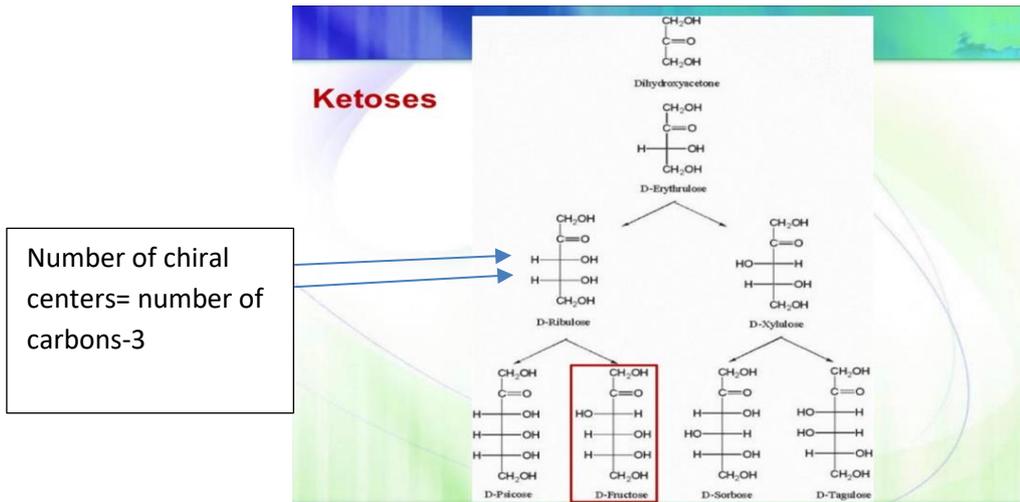
***Adding a carbon atom will increase the possibilities of the orientation of the OH groups around the carbons (chiral centers) leading to new compounds.**

side note: the sugars used in our bodies are D sugars.

L or D sugar?

this depends on the orientation of the hydroxyl group connected to the chiral carbon that is the farthest from the oxidized group

(if the hydroxyl group is on the left then it's an L - levo - sugar and if it's oriented to the right then it's a D -dexter- sugar)

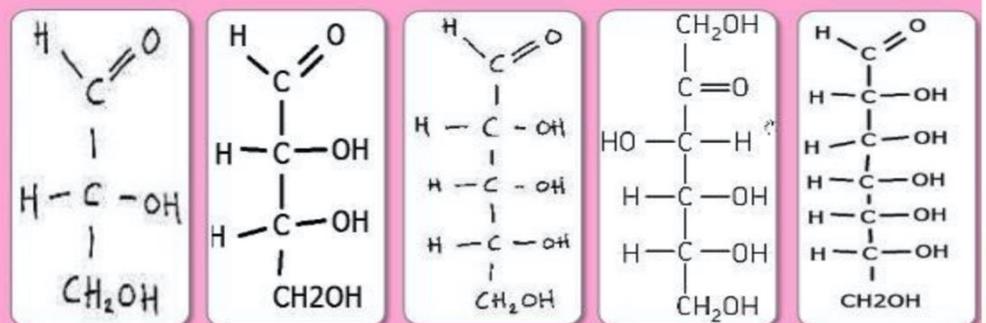


***we notice here less possibilities because there is less chiral centers**

Classification II:

By the number of carbon atoms they contain.

- Triose
- Tetrose
- Pentose
- Hexose
- Heptose
- ...



3 carbon atoms

- Triose
- $(\text{CH}_2\text{O})_3$

4 carbon atoms

- Tetrose
- $(\text{CH}_2\text{O})_4$

5 carbon atoms

- Pentose
- $(\text{CH}_2\text{O})_5$

6 carbon atoms

- Hexose
- $(\text{CH}_2\text{O})_6$

7 carbon atoms

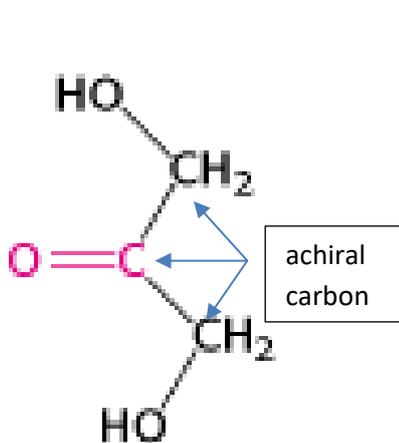
- Heptose
- $(\text{CH}_2\text{O})_7$

*hexoses and pentoses are the most common sugars.

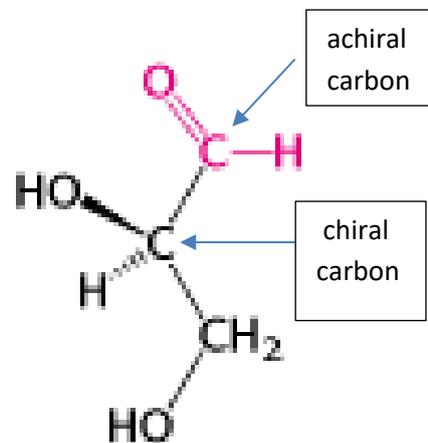
Trioses:

what is a chiral carbon?

:a carbon that is connected to four different groups and not atoms.

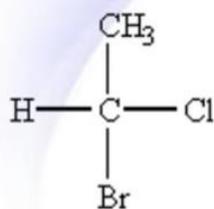


Dihydroxyacetone
(a ketose)



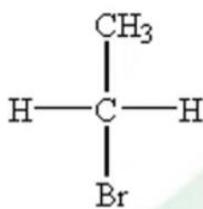
D-Glyceraldehyde
(an aldose)

Note what a chiral carbon is...



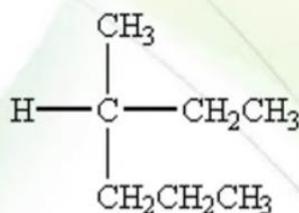
chiral

Has 4 different atoms bonded to the carbon



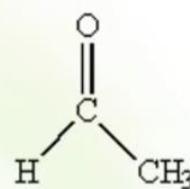
achiral

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



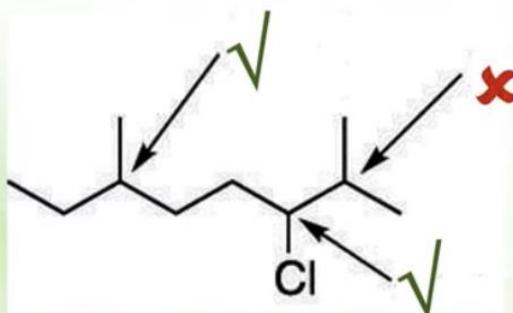
chiral

Has 4 different groups bonded to the carbon

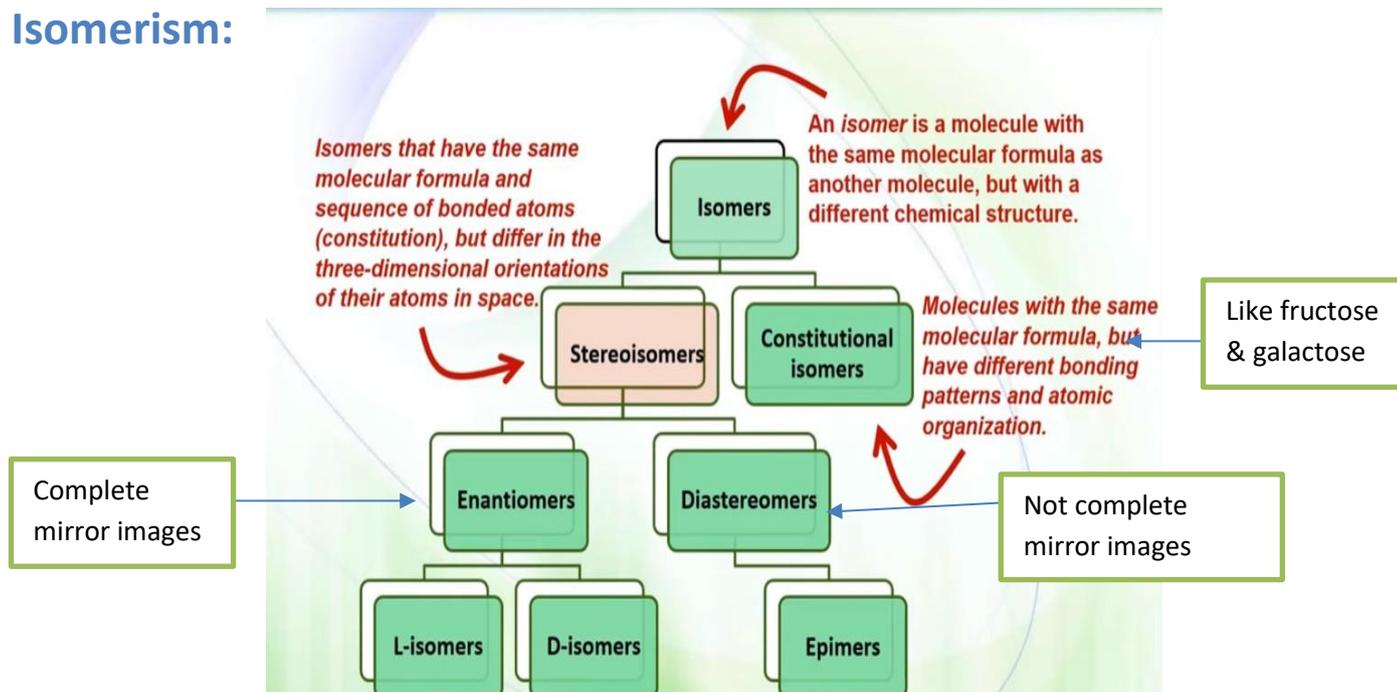


achiral

Only has 3 atoms bonded to the carbon.



Isomerism:



*Diastereomers that differ in the orientation of **one** chiral carbon are called epimers.

Isomers of glucose:

Glucose has 6 carbons, 4 chiral centers.

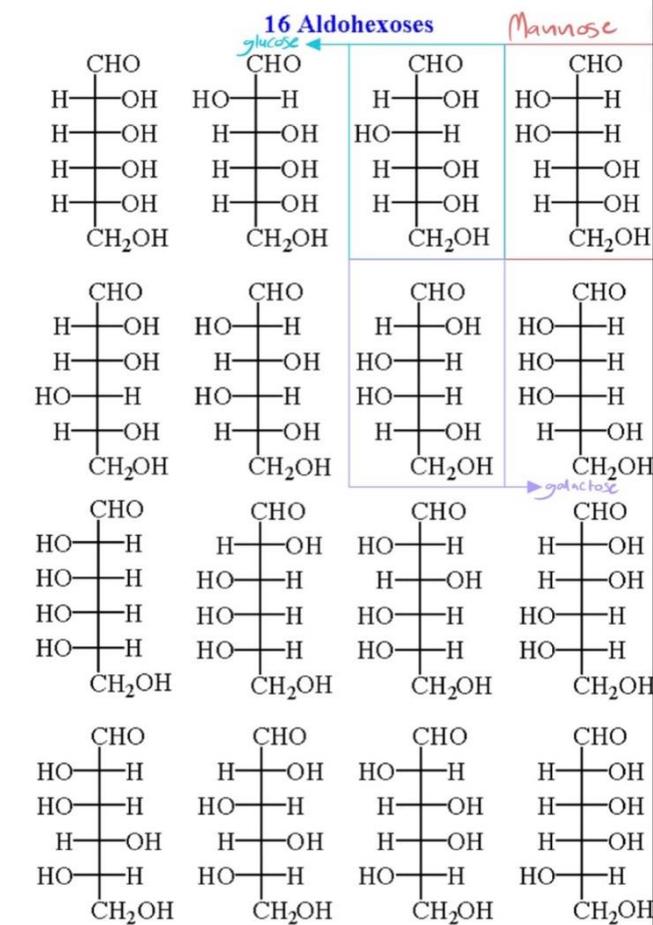
- it can be rearranged in space in different ways to form stereoisomers (not constitutional isomers)

- 4 chiral centers, each chiral center has two possibilities (left and right)

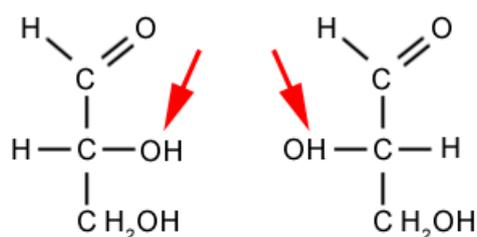
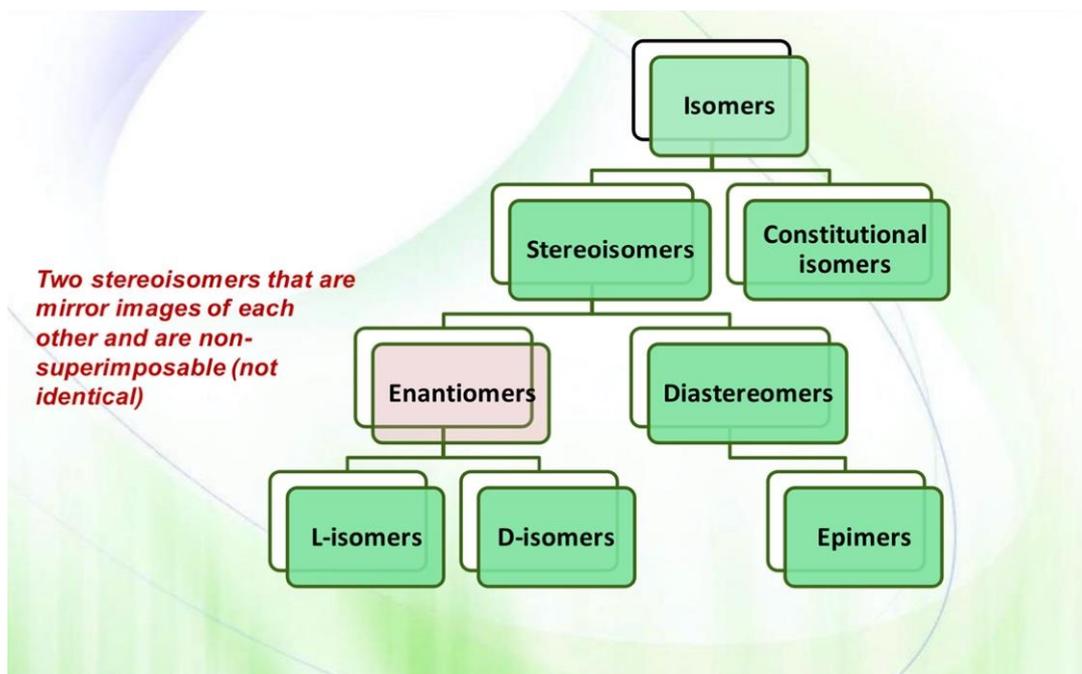
the number of these compounds =

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

*the more the carbons the larger the number of isomers of that molecule.

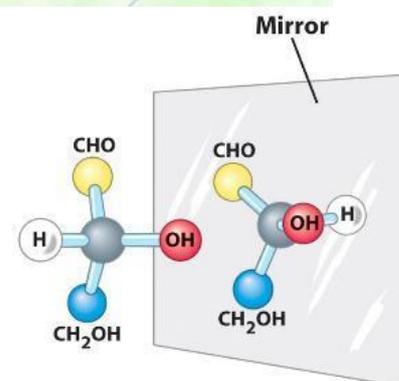


Enantiomerism:



D-Glyceraldehyde

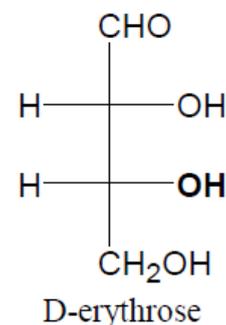
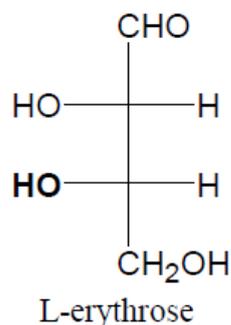
L-Glyceraldehyde



Ball-and-stick models

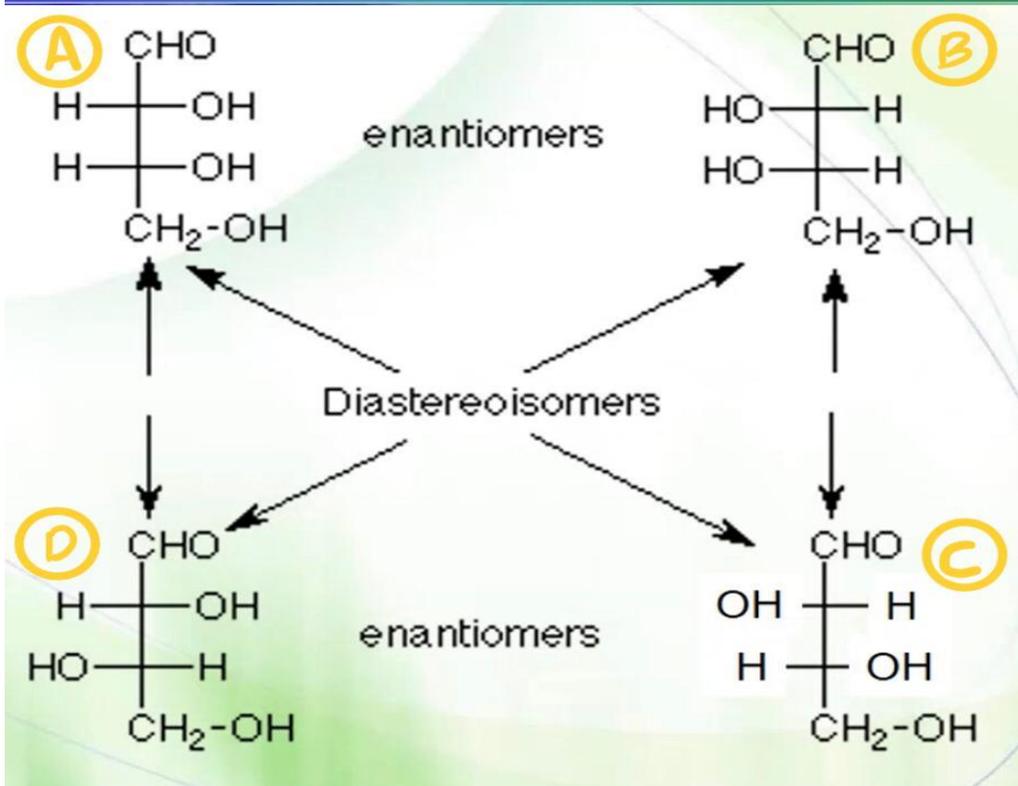
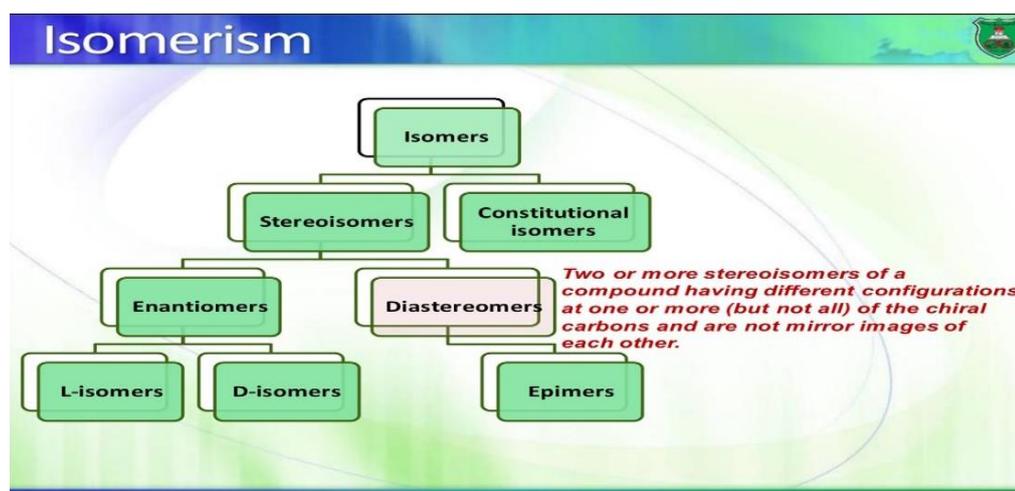
In the case of glyceraldehyde, there is only one chiral carbon. So, we have: **D**-glyceraldehyde and **L**-glyceraldehyde.

-Here we have 4 carbons, 2 chiral centers.
 -in erythrocytes both OH groups are on the same side (when both are at the left side = L-erythrose, with the mirror image, both become at the right side = D-erythrose)



- If we have a compound that also have 4 carbons, 2 chiral centers, but the OH groups are on opposite sides (one on the left and the other on the right) it is called threose
 (L-threose = 1st OH on the right instead of left and the other OH on the left, once we mirror the sugar, it becomes D-threose) **“Whole different sugar.”**

Diastereomers:

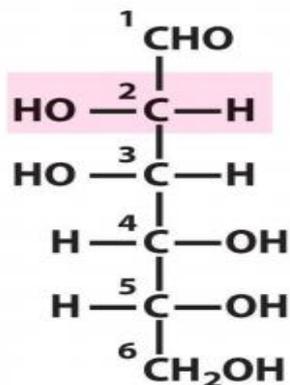


About the figure above:

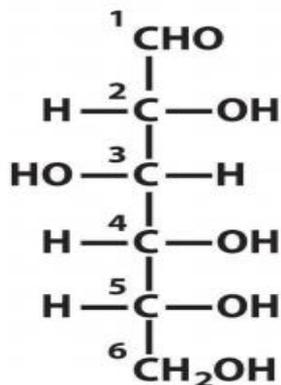
1. (A,B) are enantiomers because they are complete mirror image (both OH groups were on the right side then they became on the left) just like (C,D) .
2. (B,D) are diastereoisomers because not all the OH groups changed their orientation, (The orientation of the OH groups were left, left then they became left, right). which means that only one OH group changed its orientation, **"they are also epimers"**

(A,C),(A,D),(B,C) are also diastereoisomers and epimers

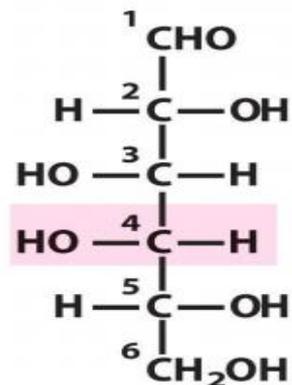
****note:** diastereomers are not the same compound (have different names).



D-Mannose
(epimer at C-2)



D-Glucose



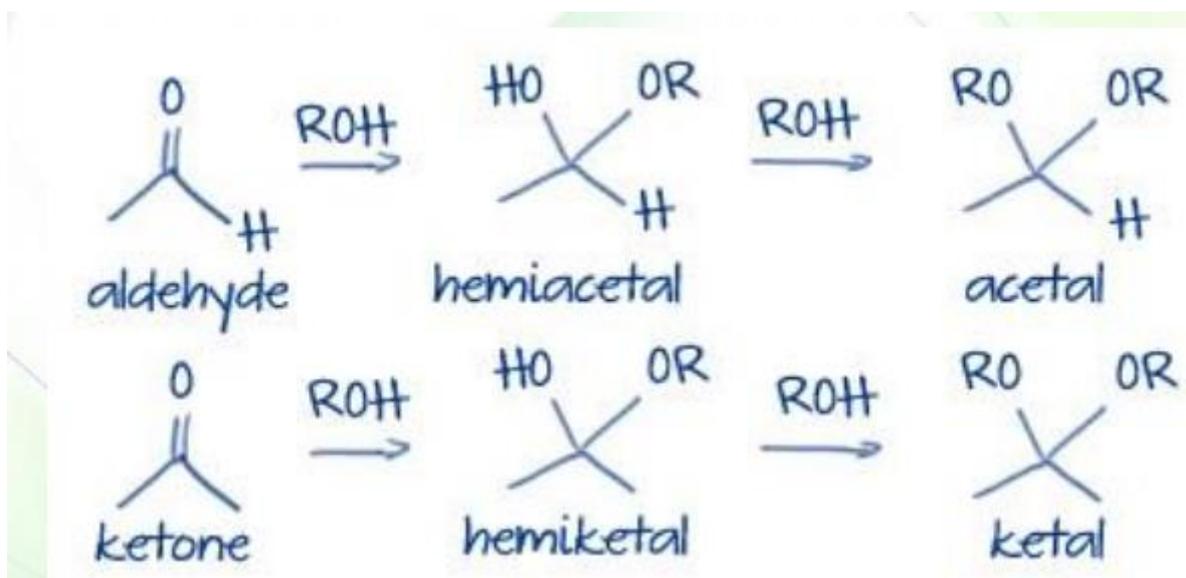
D-Galactose
(epimer at C-4)

Notice that D-Glucose and D-Mannose differ in the orientation of one hydroxyl group at number 2 so we say that they are epimers at carbon number 2 and they are diastereoisomers because they are not mirror image .

D-galactose and D-glucose are epimers and diastereoisomers at carbon no.4 because they are not mirror images and they are only different at one position only .

NOTE : All epimers are diastereoisomers .

L-glucose is a mirror image of D-glucose ,thus orientation of the OH groups on all C are different except one ,hence Diastereoisomers with D-mannose and D-galactose but is not epimer with them .



Hemiacetal: alcohol group(OH) + ether group(OR) + hydrogen

Acetal: two ether groups at the same carbon(OR) + Hydrogen.

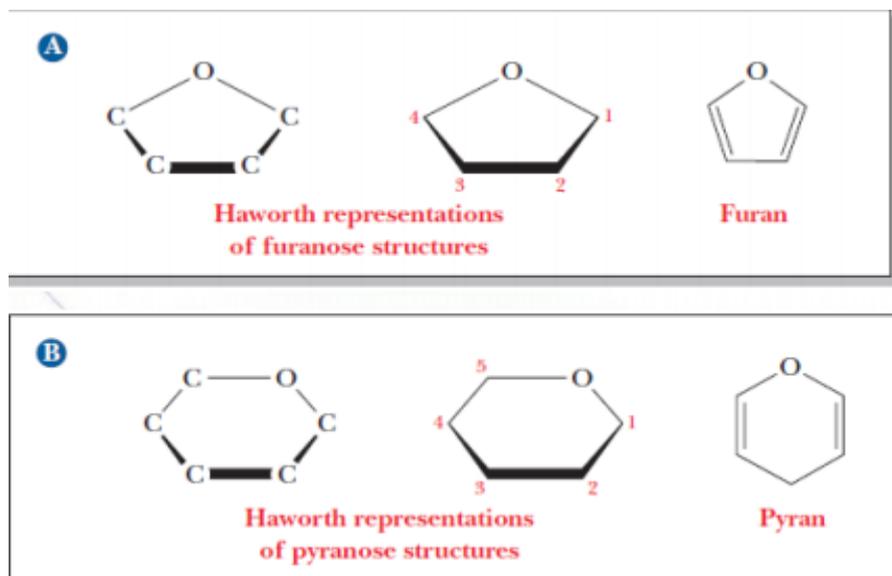
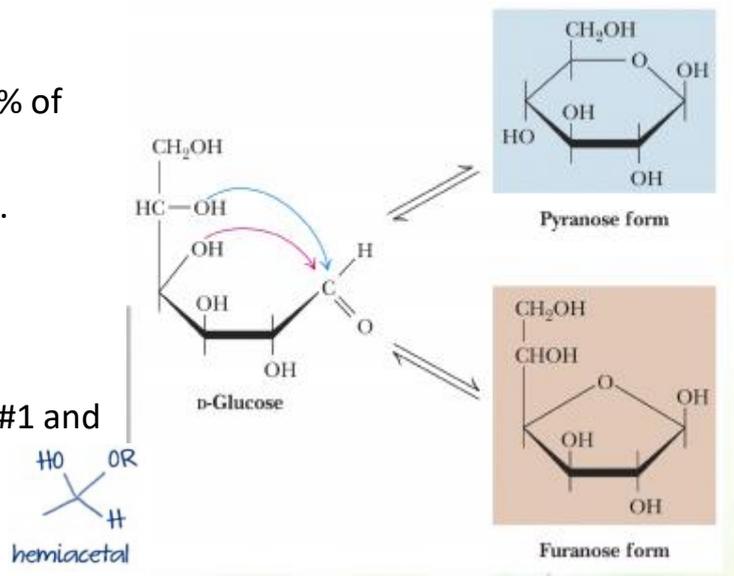
Hemiketal: differs from hemiacetal only in hydrogen. It bonds to OH group, ether, and two R groups.

Ketal: two ether groups and two R groups on the same carbon.

(Focus on the photo to understand the difference better)

Glucose is found in the ring structure 99% of the time, and 1% in the chain structure Because its more stable in ring structure.

A Chain is converted to ring by reaction between the aldehyde group on carbon #1 and the hydroxyl group on the last chiral carbon(carbon #4 or carbon #5) produces a **hemiacetal**.



There are two ring structures that glucose can form:

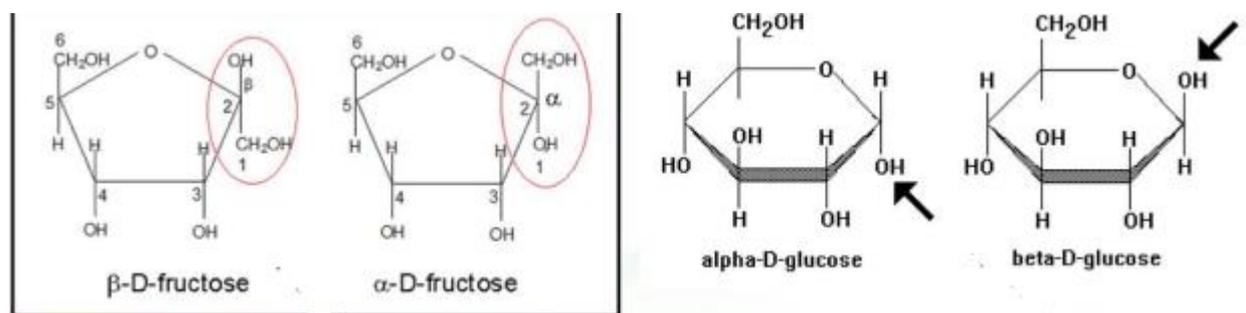
- 1) A Pyranose: as result of the reaction between carbon #1 and carbon #5.
- 2) A Furanose: as result of the reaction between carbon #1 and carbon #4.

both Pyranose and Furanose can be hemiacetal, if carbon #1 is connected to an ether group and a hydroxyl/alcohol group.

- ring structure is more stable in the Pyranose structure .

Important note : when forming the ring structure if the OH group is in the right side it will move downward , and if it is on the left side it will move upward. Except for the carbonyl carbon the can be upward or downward (alpha and beta) and shift between them .

Anomers :



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-D-glucose – beta-D-fructose

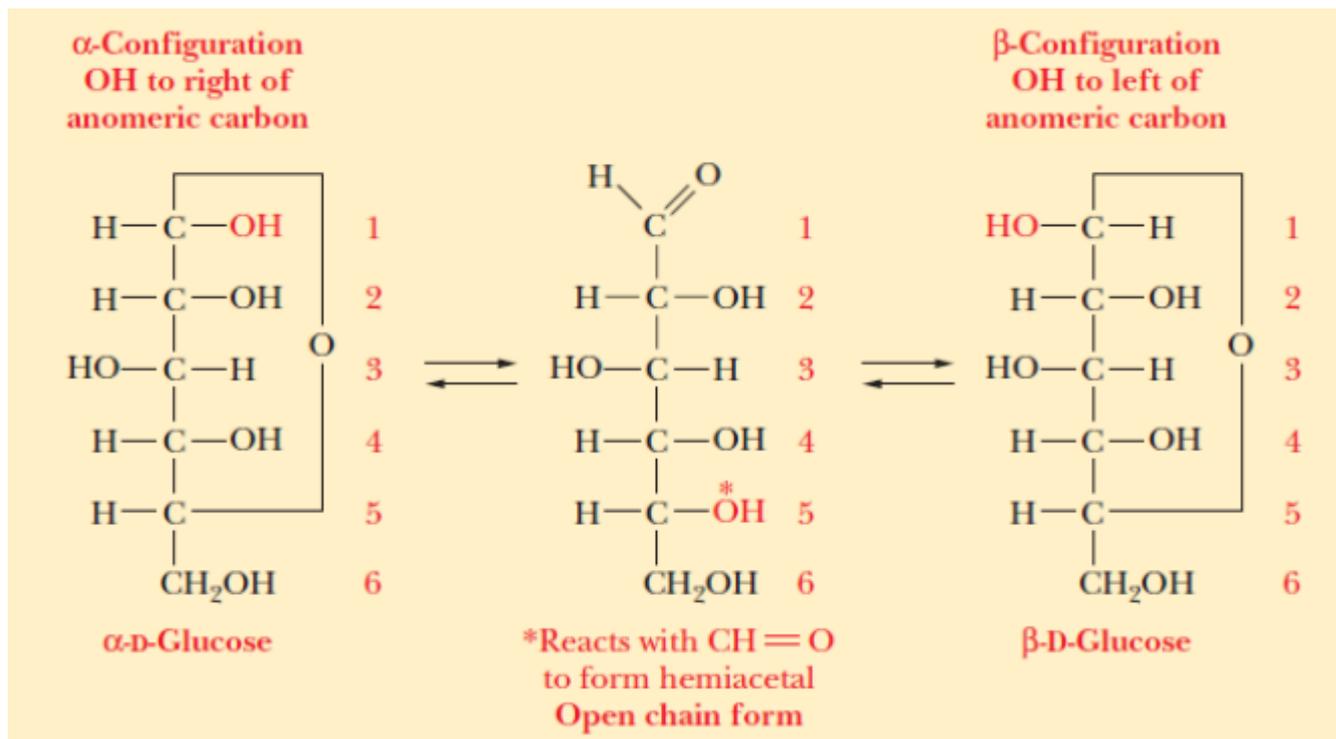
If the (OH) is facing downward: alpha-D-glucose alpha-D-fructose

-The structure that has the two large groups away from each other is more stable. So Glucose spend more time in beta form than alpha and fructose spend more time as alpha.

- but can the cells differentiate between alpha and beta forms?

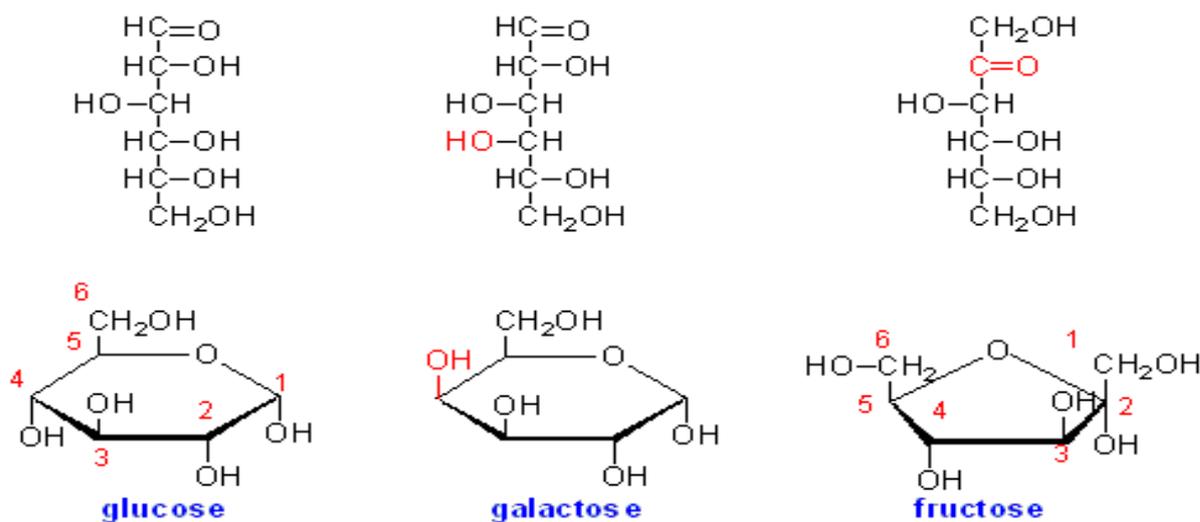
Actually it depends , if they are breaking it to extract energy they don't , but if they are using it to build DNA for example (that is need to be fold tightly)they will choose the stable form.

- We can draw sugars in ring structure as Fischer projection ,but it's not common(not used a lot in biochemistry)



Each molecule is alternating between these 3 structures (they are in equilibrium) but here it spends more time as beta , intermediate as alpha and the very least as linear structure.

The relation here is **anomers**.

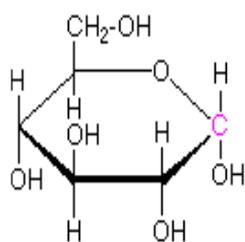


Again , if the OH group is on the right >> downward

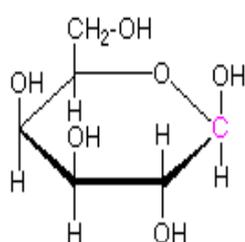
OH is on the left side >> upward

Cyclic Aldohexoses :

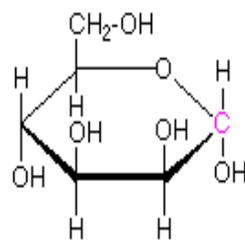
Examples of Some Pyranose Forms of Hexoses



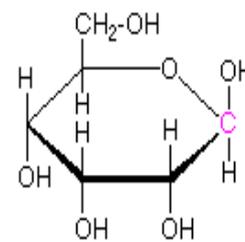
α -D-glucopyranose



β -D-galactopyranose



α -D-mannopyranose



β -D-allopyranose



This is called an alpha sugar because the anomeric carbon marked in PINK has the OH below the ring, it is also a D sugar

This is called a **beta sugar** because the anomeric carbon marked in PINK has the OH above the ring, it is also a D sugar

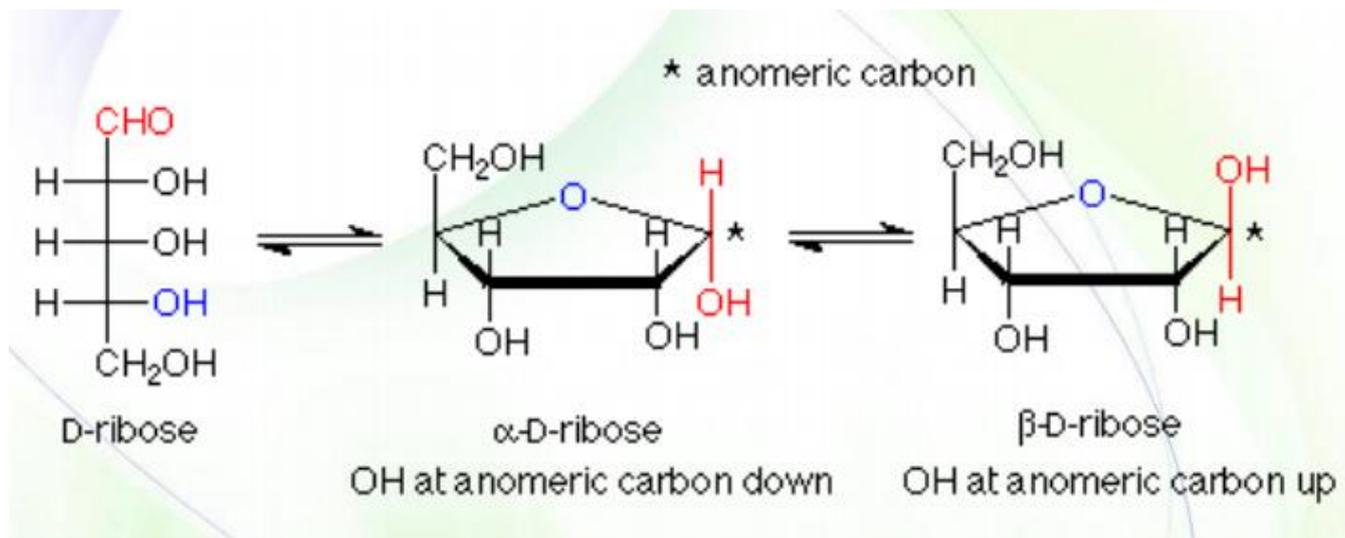
Pay attention to the difference in ring structure between glucose and mannose, remember that they are epimers at carbon #2. Glucose: since the OH at carbon #2 is oriented downward. Mannose: since the OH group at carbon #2 is oriented upward. Notice that both are the same at carbon #4.

This is called a beta sugar because the anomeric carbon marked in PINK has the OH above the ring, it is also a D sugar

How to know that it is glucose? Because the OH groups are above the ring at one carbon and below it at the next carbon. It is a hexose and a Pyran: because it consists of 6 carbons.

How to know that it is galactose? Because the orientation of all of the OH groups including the one on carbon #4 are above the ring. It's a hexose and a Pyran: because it consists of 6 carbons

Cyclic ribofuranose



This is a ribose that can only form a furanose as a ring structure. All of the hydroxyl groups in the ribose are oriented to the right, so if the sugar forms a ring it rotates to YOUR right, and all of the hydroxyl groups will become below the ring (as shown in the second structure). We can have two forms of the ribose (alpha or beta).

L-ribose \rightarrow the CH₂OH group will face downward **instead** of upward.

NOW A CUTE TEST BANK

1) Which of the following isn't a function of carbohydrates

- A) storage
- B) structure
- C) cell recognition
- D) catalytic function

ANSWER D

2) which monosaccharide is best describes as being : An aldose ... a hexoseand blood sugar ?

- A) fructose
- B) glucose
- C) mannose
- D) galactose

ANSWER B

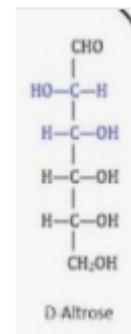
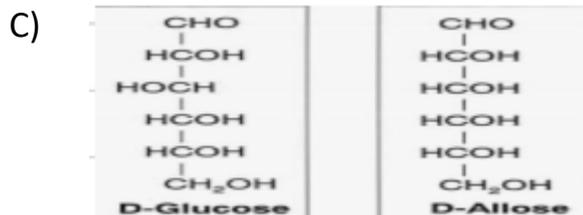
3) what is the main difference between hemiacetals and Hemiketals

- A) they are aldoses and ketoses that reacted with different Chemical group
- B) hemiacetal is bound to only one R group while hemiketals are bound to two
- C) hemiacetals are produced from ketoses while hemiketals come from aldoses

ANSWER B

4) what is the relationship between each of the following ?

- A) D - Glucose and D - Galactose
- B) D - Glucose and D - Fructose



D) D - Glucose and D – Altrose

Q4). A) epimers. B) constitutional isomers. C) epimers. D) Diastereomers

5) which of the following statements is accurate about :

1) D - Mannose. 2) D - Glucose. 3) D - Galactose

A) 1 and 2 are epimers while 2 and 3 are diastereomers

B) 2 and 3 are epimers and 1 and 3 are epimers

C) 1 and 3 are diastereomers while 1 and 2 are epimers

D) 1 and 2 are diastereomers and 2 and 3 are diastereomers

ANSWER C

6) the most stable ring structure for Glucose is Which forms between the and carbons :

A) pyranose / 1 / 5

B) furanose / 1 / 4

C) furanose / 1 / 5

D) pyranose / 1 / 4

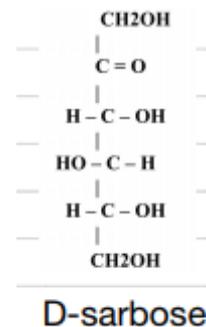
ANSWER A

7) It is said that in order to acquire a sugar diastereomer you have TO change the orientation of 2 atoms (switch them up) at at least one chiral carbon up to (all of them except one) but not all of them why is that ?

ANSWER if we flip all the chiral carbon we will turn the molecule into its enantiomer

A. The following structure is D-sorbose. D-sarbose

8) Which describes the relationship between D-sorbose and D-fructose?



- a) They are diastereomers that are also epimers.
- b) They are diastereomers but not epimers.
- c) They are epimers but not diastereomers.
- d) They are neither epimers nor diastereomers.

ANSWER B

9) The enantiomer of D-sorbose:

- a) is a D-sugar that has opposite configuration around one carbon.
- b) is a D-sugar that has opposite configuration around three carbons.
- c) is an L-sugar that has opposite configuration around one carbon.
- d) is an L-sugar that has opposite configuration around three carbons.

ANSWER D

10) When comparing D-sorbose with D-glucose

- a) they have the same number of equatorial substituents.
- b) they have the same number of epimers.
- c) they have the same chemical formula.
- d) they have the same osazone.

ANSWER C