Lec. 6

· By: Rofida Awwad .

~ CARBOHYDRATES ~

Major types of macromolecules
- Carbohydrates
- Lipids
- Nucleic acids
- Proteins

CARBOHYDRATES 'Sugars' or 'saccharides'

'empirical formula' $(CH_2O)_n$ where $n \geq 3$ → simplest sugar is $C_3H_6O_3$

CARBOHYDRATES
- C
- H_2O

- Formulas
  - Empirical formula [the simplest ratio between each type of atoms found in molecules].
  - Molecular formula [exact number of each atoms found in molecules].
  - Structural formula [atomic connectivity - arrangements of the atoms. - types of bonds and functional groups].

~ MONOSACCHARIDES ~

- the basic units of CHO
- cannot be hydrolyzed into smaller sugars
- like: glucose ; galactose ; fructose.

~ DISACCHARIDES ~

- two monosaccharide covalently linked by [glycosidic bond]
- like: sucrose
  - glucose
  - fructose

~ POLYSACCHARIDES ~

- Polymeric molecules composed of long chains of monosaccharides linked together via [glycosidic bonds].
- like starch, cellulose, glycogen.

CamScanner

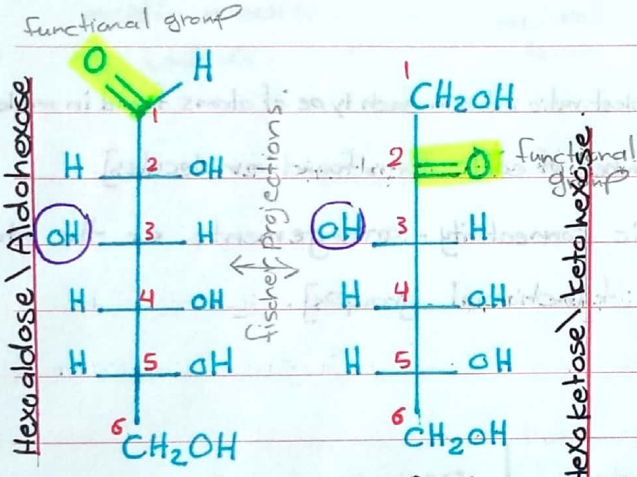
~ MONOSACCHARIDES ~

classified according to

- The number of carbon atoms: trioses, tetroses, Pentoses, hexoses ... etc.

- The chemical nature of the Carbonyl group [C=O].
  - ~ Aldoses ~ [the carbonyl group is an aldehyde].
  - ~ ketoses ~ [the carbonyl group is a ketone].

Hexose [$C_6H_{12}O_6$]



D-glucose

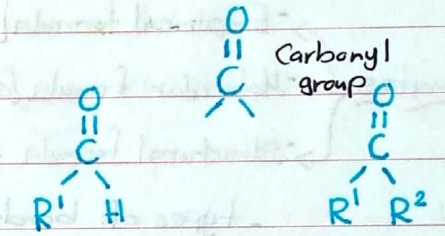
'grape or blood sugar'

Accumulation of the glucose leads to diabetus

D-fructose

'fruit sugar'

and in [honey], - it's the sweetest of all naturally occurring sugar.

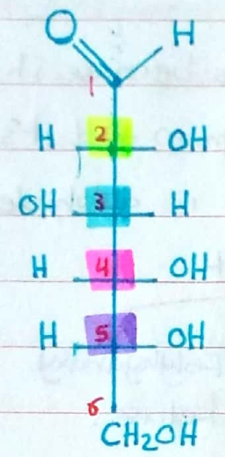


~ Aldehyde: R^1=H, alkyl or aryl

~ ketone: R^1 and R^2 = alkyl or aryl.

note} The number of stereoisomers for any given molecules = 2^n

where (n) represents the number of chiral centers.

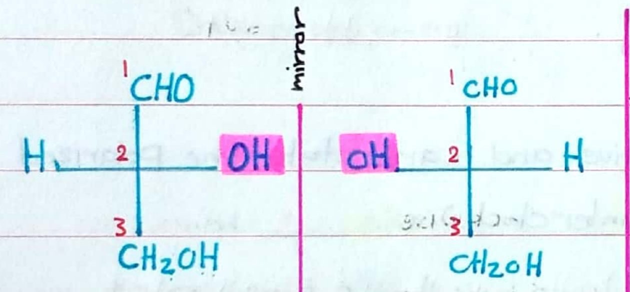


D-glucose

- Number of stereoisomers $= 2^4 = 16$

* طيب أحد chiral center ؟! بطلّع على ذرة الكربون الأولى مرتبطة مع H
واثنين O [A chiral center] ، اطلّع على C_6 فيها two H راحت
شو ظل عندي؟! C_2 ، C_3 ، C_4 ، C_5 وهم chiral center
وعددهم 4.

{-glyceraldehyde : is the simplest sugar}.

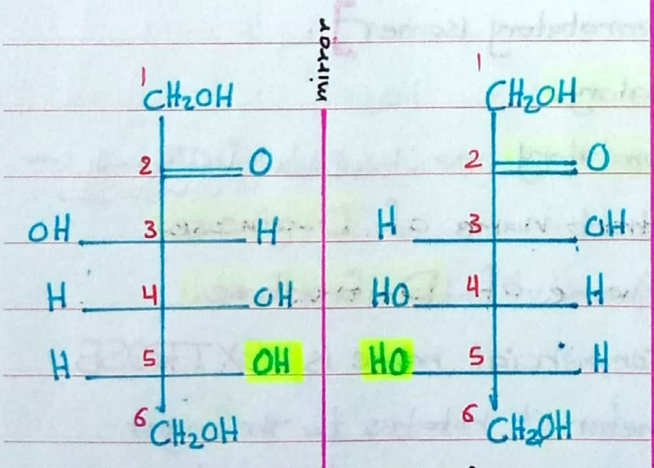


D-glyceraldehyde | L-glyceraldehyde

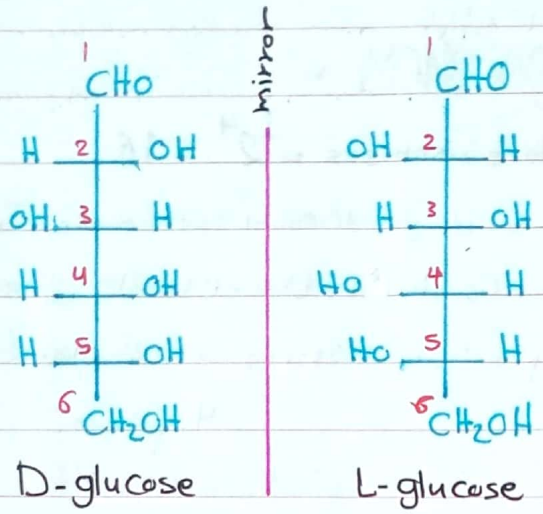
- If [OH] on the right it's [D].
- If [OH] on the left it's [L].
- General rule: we chose (D) or (L) according to the position of hydroxyl group [OH] located on the chiral center, [which is the farthest away from carbonyl carbon (functional group)], it has the highest oxidation number.
- If we want to make a mirror Images from [enantiomers] we have to change the position of (All) chiral centers.

تعريف

→ differ at the configuration of the fuction of groups at All chiral centers.



D-fructose | L-fructose



↳ Carbohydrates because it has multiple hydroxl group and it's functional group is aldehyde or ketone we call it

- Polyhydroxy Aldehyde
- Polyhydroxy ketone.

note: most naturally occurring sugars are D-isomers [bidlogically active form]. الموجود داخل جسمي

1- * Enantiomers are optically active and can rotate the polarized light plane either clockwise or counterclockwise.

* راجع الصورة في السلايد

↳ (+)D-glucose ≡ (d) D-glucose [جاية ال OH عند كربون رقم 5 على اليمين] ← Clockwise بلف / يمين

↳ D-glyceraldehyde [in fact the dextrorotatory isomer].

↳ D-fructose (laevulose) is levorotatory.

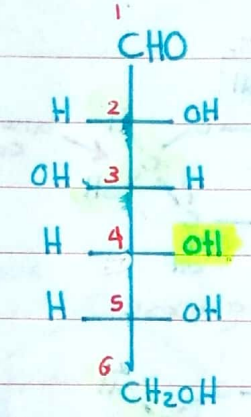
↳ D-glucose (dextrose) is dextrorotatory. ← سبب التسمية لانها اصلها في اليمين بتلف عاليمين

↳ Dextrose is the commercial / trade name of D-glucose.

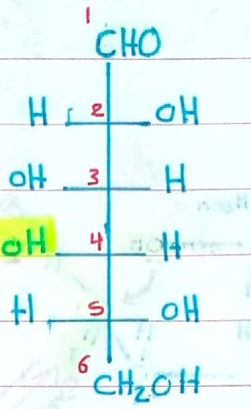
↳ Laevulose is the commercial name of D-fructose.

* The reason why GLUCOSE it's commercial name is DEXTROSE is when we put it in the polarimeter it rotates to the right while the FRUCTOSE it's commerical name is LAEVULOSE because it Rotates to the left when we put it in the pdarimeter.

2- Epimers: are stereoisomers that differ in the configurations of atoms at only one chiral center [i.e. chiral carbon in CHO]. They are not mirror image isomers.

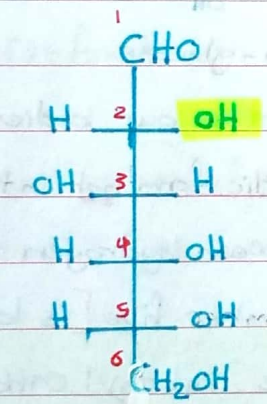


D-glucose

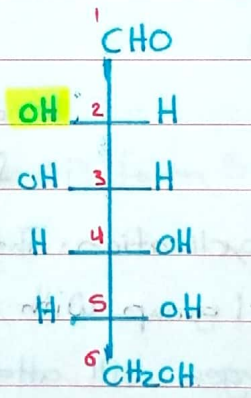


D-galactose

• glucose and galactose are (C4) epimers.



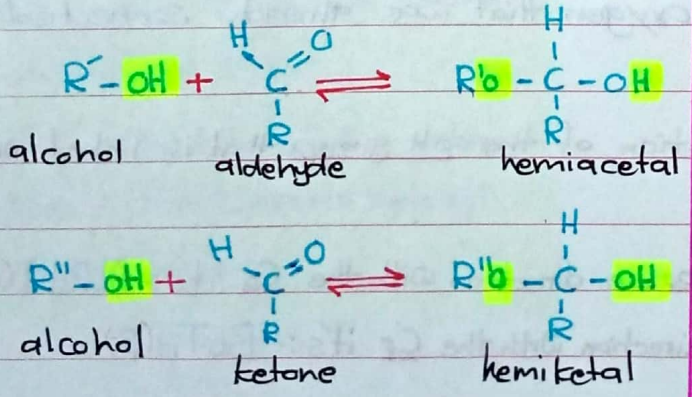
D-glucose



D-mannose

• glucose and mannose are (C2) epimers

~ Hemiacetal & Hemiketal ~



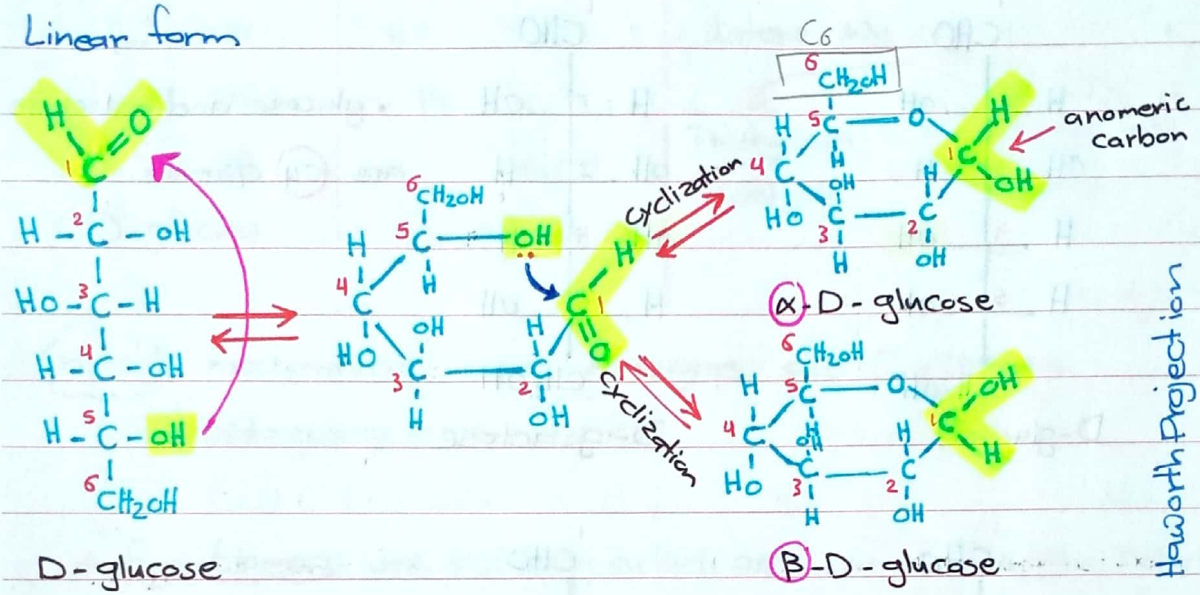
~ The mechanism of this reaction:

in the alcohol the bond between the O and H in the hydroxyl group will be broken, in the another hand the double bond on the aldehyde will also be broken to provide space for the coming visitors ↳

which are the hydrogen and oxygen with R so it will from something we call: Hemiacetal and Hemiketal.

Monosaccharide cyclization

Linear form



D-glucose

fisher projection.

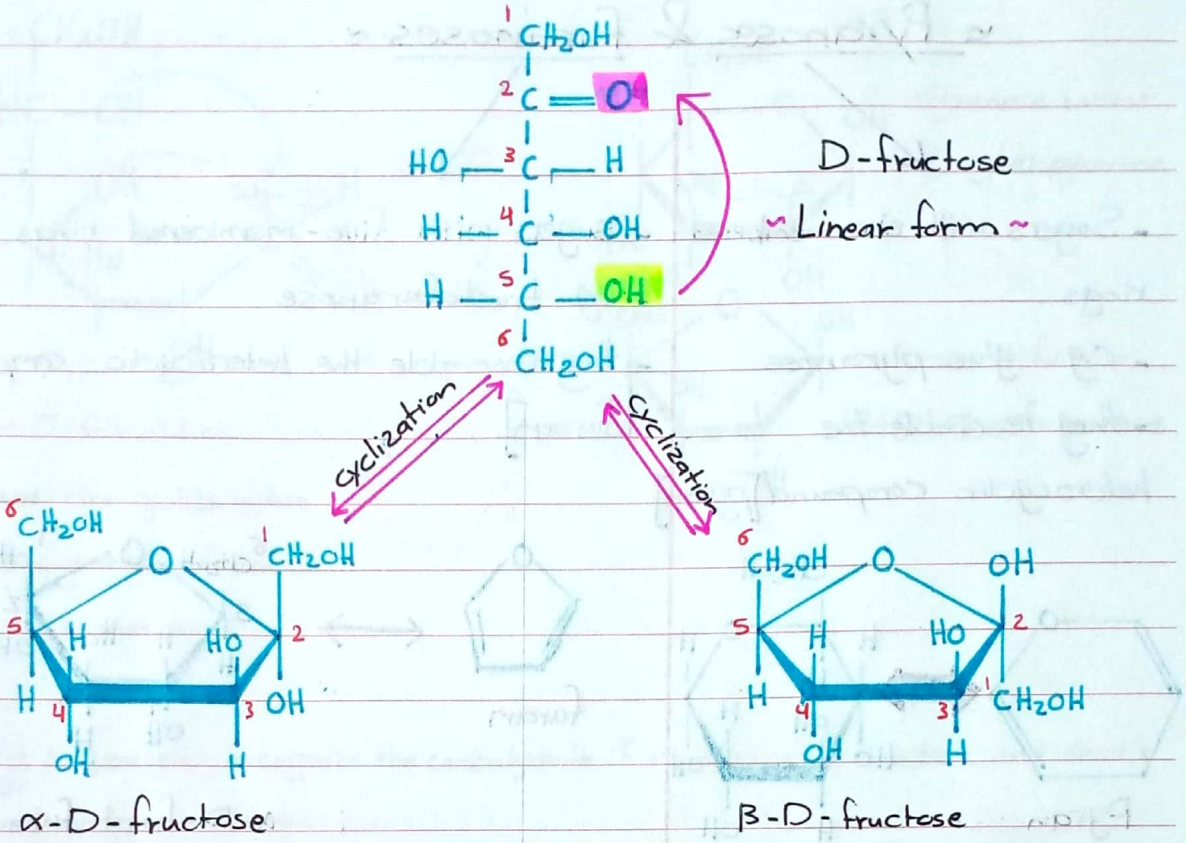
✓note: sugars in our bodies are found in cyclic form not in the linear form.

The mechanism of cyclization: The bond between hydrogen and oxygen in the hydroxyl group with carbon number five [is broken] then the hydroxyl oxygen will attack of [the carbonyl carbon] and [provide space] for the [new coming hydroxyl oxygen], the double bond will be broken [providing space] then the bond will form between [C1 with the oxygen and the hydrogen formed Hydroxyl group with the oxygen that was already connected to the C1].

- we look at the configuration of the OH group that is linked with the Anomeric carbon:

IF it points down with the opposite direction with the C6 it's:- ALPHA (α).

If it Points up with the same direction with the C6 it's:- BETA (β)

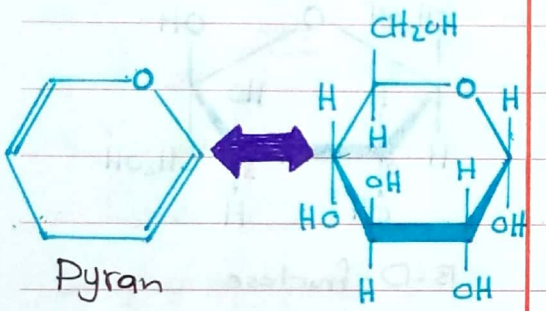


- Cyclization of the fructose will form 5 member rings while glucose will form 6 member rings.

- what is fate of the carbonyl carbon ?! It will become anomeric carboon (chiral center).
- what is fate of hydroxyl oxygen?! It will become ether.
- what is the fate of the carbonyl oxygen ?! It will become hydroxyl group (OH) alcohol

~ Pyranoses & furanoses ~

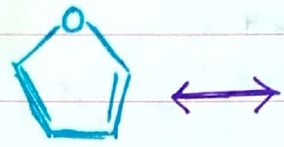
- Sugers with six-membered rings.
- e.g. glucopyranose
- they resemble the heterocyclic compound [pyran].



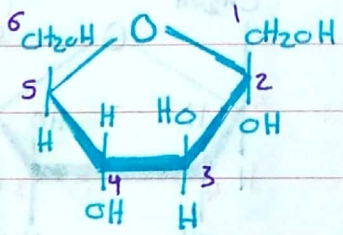
Pyran

α-D-glucopyranose

- sugers with five-membered rings
- e.g. fructofuranose
- they resemble the heterocyclic compound [furan].



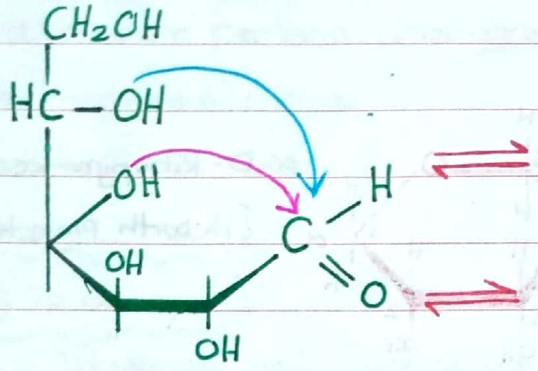
furan



α-D-fructofuranose

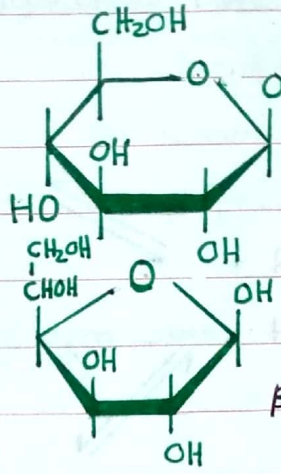
- we named it HETERO, Because it's mixture between carbon and oxygen. [غير متجانس]

- The most common type of carbohydrates in the human body is six-membered and five-membered rings.



~ D-Glucase ~

[D-glucose can cyclize in two ways forming either furanose or pyranose structures]



~ Pyranose form ~

β-D-glucopyranase

~ furanose form ~

β-D-glucofuranose

· Note: you can recognize the carbohydrate if it's glucose or fructose and that's done by :-

* in glucose the anomeric carbon number is 1 and it has hydrogen and hydroxyl group on it.

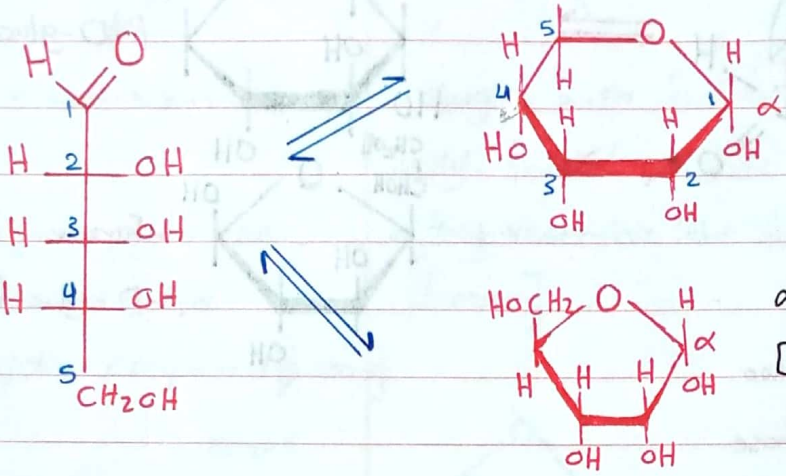
* While in fructose the anomeric carbon number is 2 and it has side chain looks like R-side chain but with hydroxyl group on it.

· Note: sugars can form both pyranase and furanose that depends on the number of the carbon atom, that is linked with hydoxyl group, which attacks the carbonyl carbon [the anomeric carbon].

~ If it's number was 5 it will make pyranose.

~ If it's number was 4 it will make furanose.

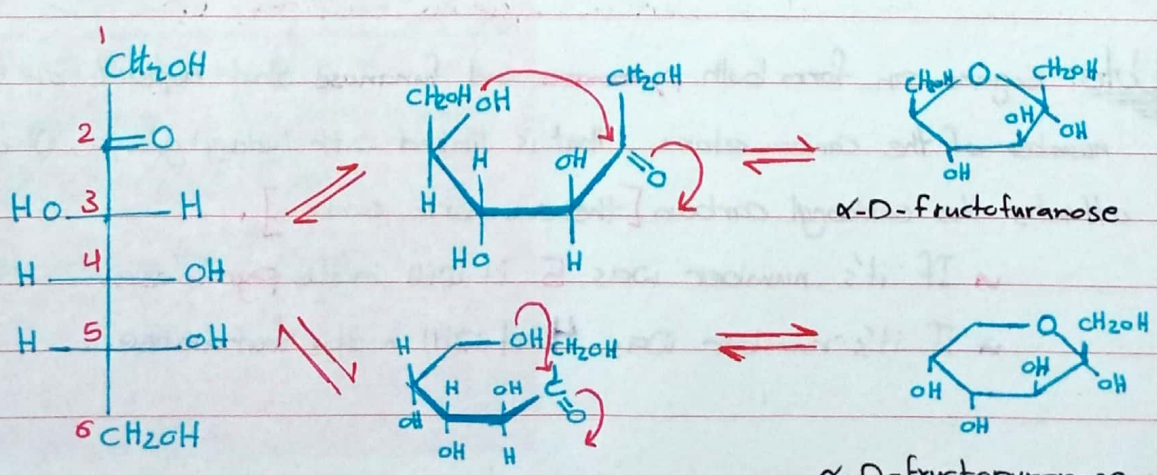
CamScanner



D-ribose
[fisher projection].

- Note:- Ribose is an example of [aldose] sugar because it has [aldehyde] group and it's also [pentoses] -5 carbon atoms- every hydroxyl group is on the right side.

~Isomeric forms of fructose~



D-fructose

~ Hexase (6 carbon atoms) or pentose (5 carbon atoms) can exist in pyranose and furanose forms (the more stable rings).

5 and 6 membered rings: is more stable and have the least energy.

e.g in solution :-

1. glucose and fructose are mostly pyranoses.
2. ribose is mostly furanose.

3- Anomers

- In cyclic sugars, the carbonyl carbon becomes a chiral center [asymmetric carbon] with two possible configurations: α and β. This new carbon is called [anomeric carbon].
- Anomers are pair of stereoisomers that differ in spatial arrangement of atoms at the anomeric carbon. In α-anomer, the (OH group) of the [anomeric carbon] is projecting down the plane of the ring and on the opposite side of the terminal CH_2OH group [in fisher projection] and visa versa in β-.
- The anomers freely interconvert in aqueous solution, e.g at equilibrium D-glucose is a mixture of β-anomer (63.6%), α-anomer (36.4%) and extremely tiny amounts of the straight chain.

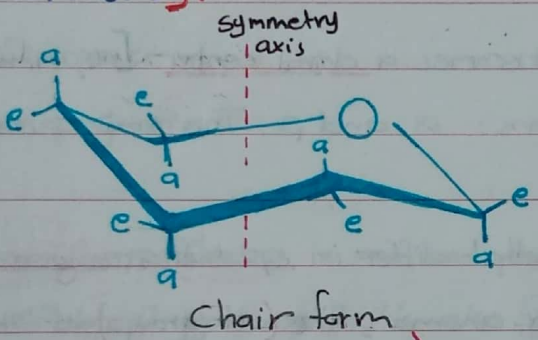
4- Conformers [cyclic form of sugar].

✓ The geometry of the carbon atoms of monosaccharide ring is tetrahedral (bond angles are close to 109.5°), so sugar rings are not actually planer. for example, Pyranoses take on either chair or Boat conformations [conformational isomers or Conformers].

note:- what causes the stereoisomers on conformes? - راجع المحدودة في المسلدين

It's caused by the rotation around single bonds either boat or chair. note chair is more stable than the boat, the reason why is the rotation. ← less energy

✓ The geometry of the carbon atoms of monosaccharide ring is tetrahedral (bond angles are close to 109.5°), So sugar rings are not actually planar. for example, Pyranoses take on either chair or Boat conformations [conformational isomers or conformers].



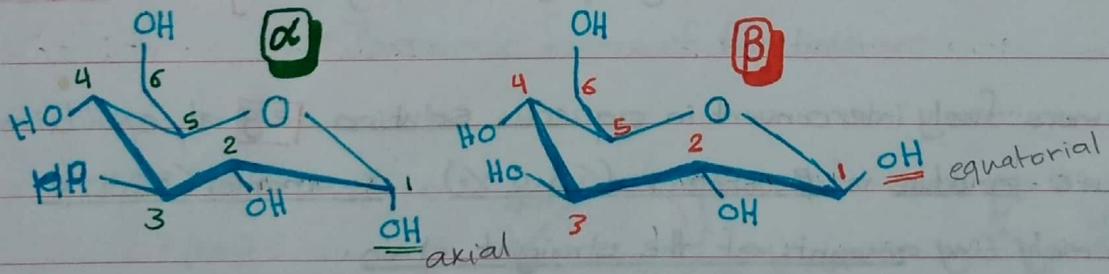
Chair form

[mean it points up or down the plan of the ring outer.]

~ a: axial ~

~ e: equatorial ~

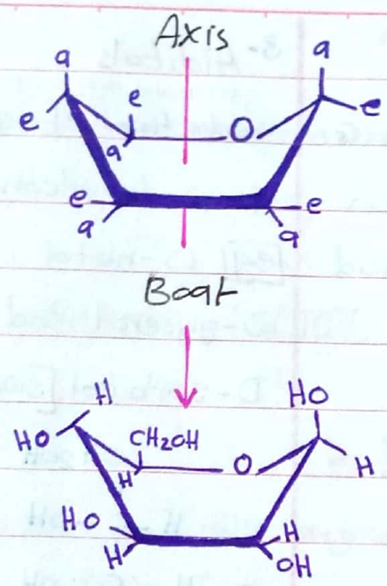
[means this bond goes with the same plan of the ring]



chair form of α-D-glucose chair form of β-D-glucose

✓ Steric repulsion:- is repulsion between electrons that are found on atom which are very closer to each other.

✓ Bulk group:- is the atoms or functional groups or both that links with the carbon atom.



Boat form of β-D-glucose

* when it's equatorial the steric repulsion is less than when it's axial.
* When the stericrepulsion is high the energy between the molecules also will be high and that causes Instability.
* why the β-D-glucose is more stable than α-D-glucose ?! Because the hydroxyl group on beta on equatorial Position while in alpha it's on axial Position. (α) less stable than (β) due to Steric repulsion.

Sugar Modification

← اهم مشتقات وصول المشتقات ما بتنطبق عليهم التفاعلات اللي بتجري على carbohydrates لأنها اصبحت مركبات جديدة لها شكل آخر مختلف تماماً وبطلوا sugars.

- Aldonic acids: oxidation of aldehyde (C_1) to carboxylic acid; e.g D-gluconic acid. (from aldehyde to carboxylic acid).

· Uses:

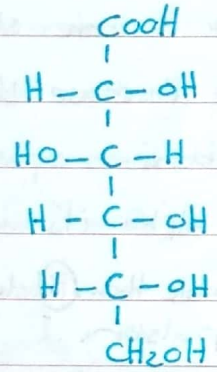
- Some drugs are injected (حقن) in the form of [gluconate] [the salt of gluconic acid].
- Calcium gluconate solution (I.V) as "cardioprotective agent in patients with high blood level of K^+.
  → use for people who had kidney failure; to reduce the high blood level of K^+.

sugars acids ← → sugars alcohol

1- Aldonic acids

oxidation of aldehyde (C1) to carboxylic acid;

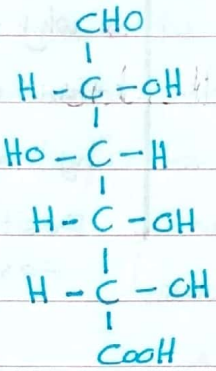
e.g. D-gluconic acid



2- Uronic acids

oxidation of OH at (C6) to carboxylic acid;

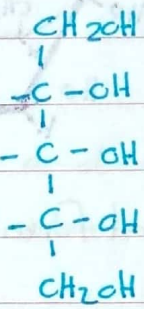
e.g. D-glucuronic acid



3- Alditols

reduction of carbonyl group to alcohol; (removal oxygen, gain hydrogen)

eg 1- D-ribitol,
2- D-glycerol and
3- D-sorbitol [sweetener].

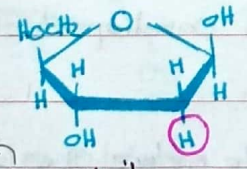


[D-ribitol]

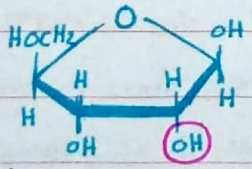
4- Deoxy sugars

OH group is replaced by H; e.g.

β-D-2-deoxyribose



DNA ← Deoxyribose

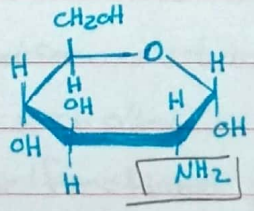


RNA ← Ribose

5- Amino sugars

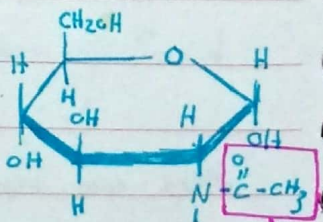
one or more OH groups are replaced by amino group which is often acetylated;

e.g. α-D-glucosamine (rebuild cartilage in osteo arthritis & osteoporosis) and α-D-N-acetylglucosamine (both are derivatives of α-D-glucose).



α-D-glucosamine

- uses in rebuilding of cartilage on osteoarthritis or osteoporosis.



α-D-N-acetyl glucosamine.

acetylated