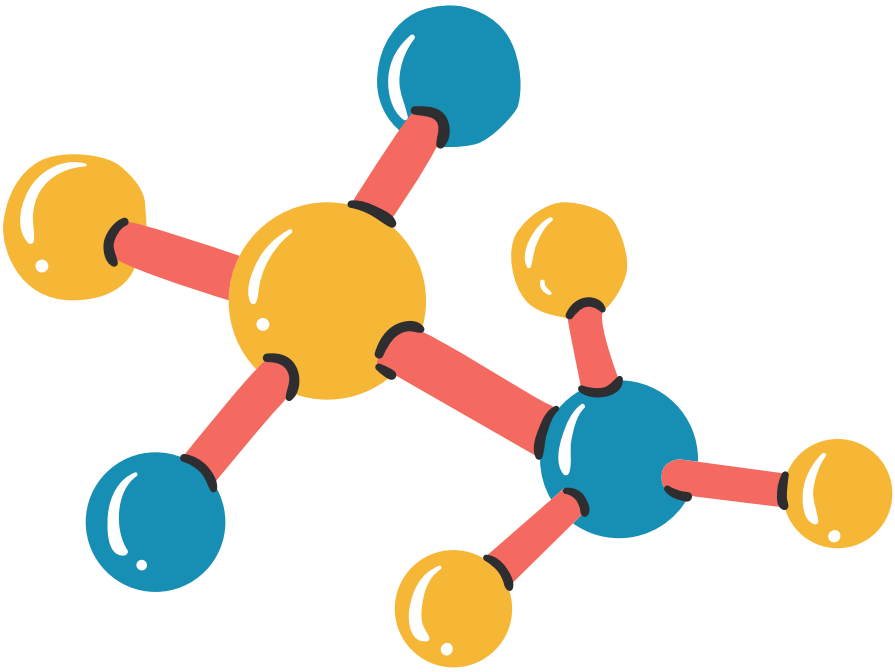
Sheet no.8

biochemistry



Summer 2022

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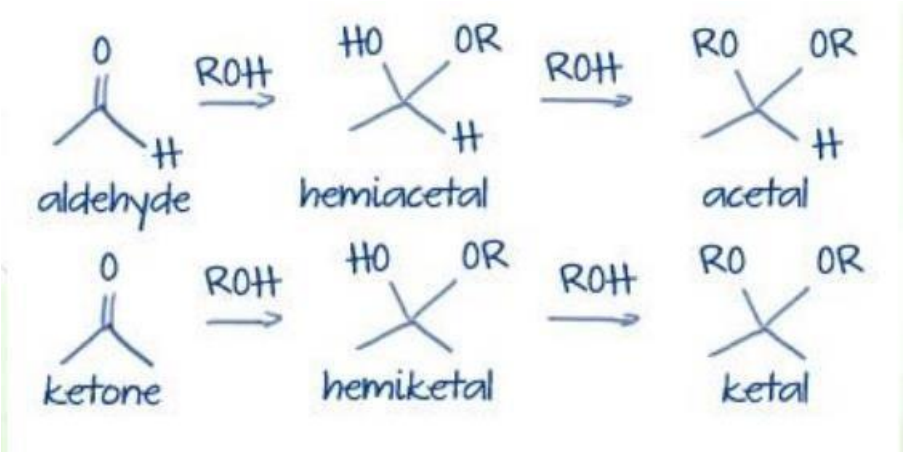
Acetal/ketal vs. hemiacetal/hemiketal

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?

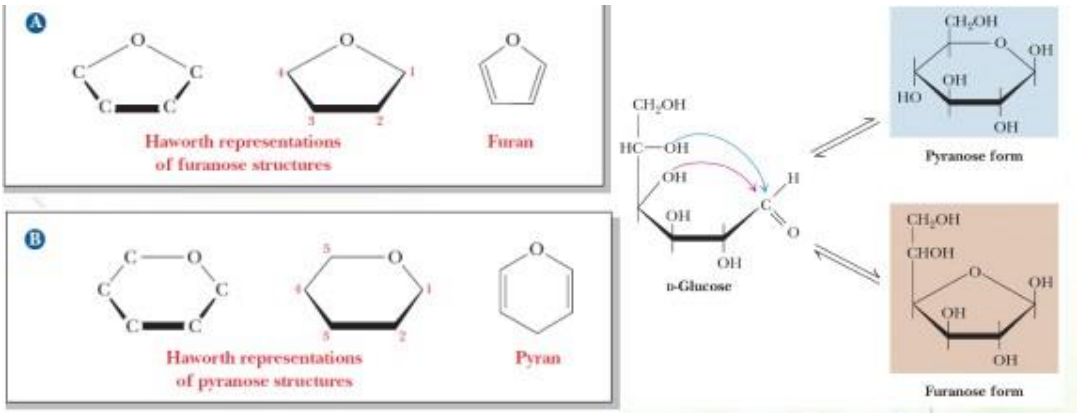
Hemiketal differs from hemiacetal only in hydrogen (hemiketal is bounded to OH , OR and two R groups while hemiacetal is bounded to OH ,OR ,H and R group)

For acetal and ketal it's the same difference but they have 2 OR groups instead of having one OH and one OR .

Formation of a ring structure

monosaccharides have one carbonyl and many hydroxyl groups

So the hydroxyl groups behave as alcohol and the aldehydes and ketones behave as they are as a result the carbonyl and hydroxyl groups of the same molecule can react together forming the ring structure, and what determines which hydroxyl group to react with is the stability of the molecule (for example in glucose the carbonyl group on the first carbon reacts with the hydroxyl group on carbon number 5 because it's the most stable form with the least steric repulsion ,so glucose usually makes six atom rings .however, we can find small percentage of five membered rings). For fructose the most common is the 5 membered ring but we can find small percentage of six membered rings.



- If the carbonyl reacts with the hydroxyl group on the fourth carbon the result will be a five membered ring leaving two carbons outside the cycle (**furanose** form because it resembles the furan) and if it reacts with the hydroxyl on the fifth carbon a six membered ring will form leaving one carbon outside the cycle (**pyranose** form because it resembles the pyran).

NOTE: furan and pyran are reduced structures not related to sugars, its just for nomenclature

- When the hydroxyl group attacks the carbon in the carbonyl group the double bond between carbon number 1 (in case of aldehydes and carbon number 2in case of ketonesw) and the oxygen breaks and the carbon number 1 becomes chiral ,a new chiral center forms (it was achiral because of the double bond) and this will bring us to the next term (anomers).

Anomers

Before we talk about anomers we should know what **anomeric carbon** means It's the first carbon in aldoses and the second in ketoses and its important in determining whether the monosaccharide will react or not.

Anomers are molecules that differ only in their anomeric carbon

The hydroxyl group on carbon 1 could be above or below the ring but we don't describe it like this , we compare it to the carbon out of the cycle if the hydroxyl group on the anomeric carbon goes with the same orientation as the last carbon, we call it **beta configuration** . if it goes differently we call it **alpha configuration .** molecules responsible for support have beta bonds beta bond is diagonal see figure 2 (causes restriction of movement and the molecule is less useful in metabolism but more useful in support) and the bonds between molecules responsible for energy production are alpha see Figure 1

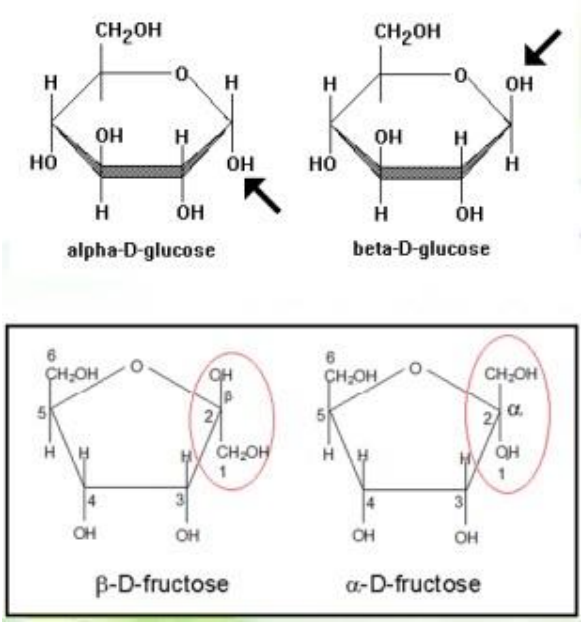


figure 1

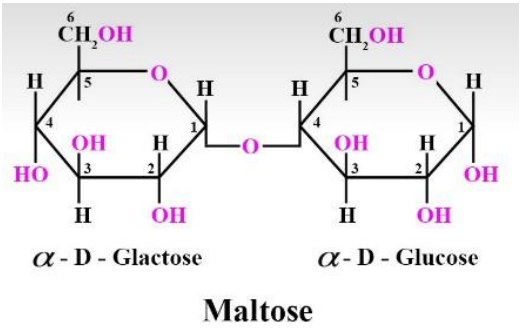
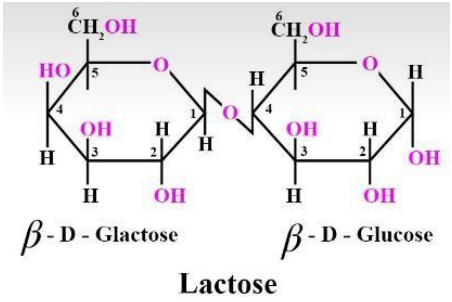
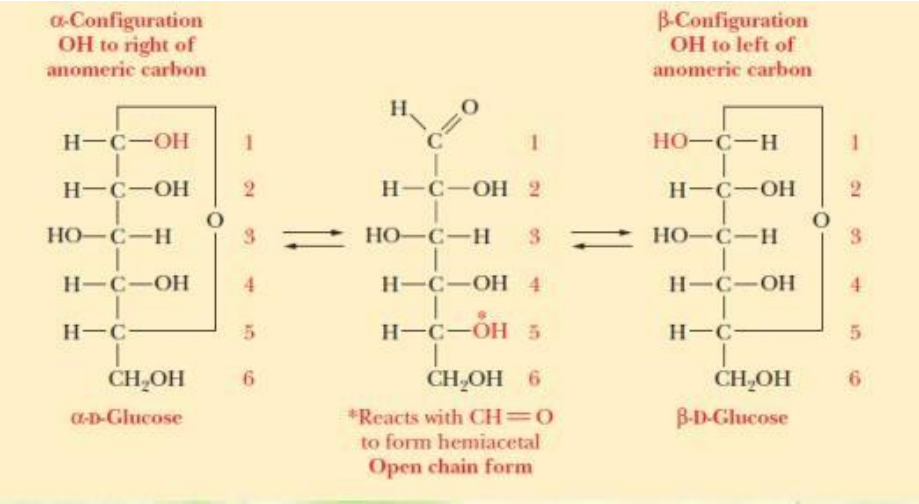


figure 2



very important note :the two figures above are not required just to clarify what the doctor said

Anomers as fisher projection



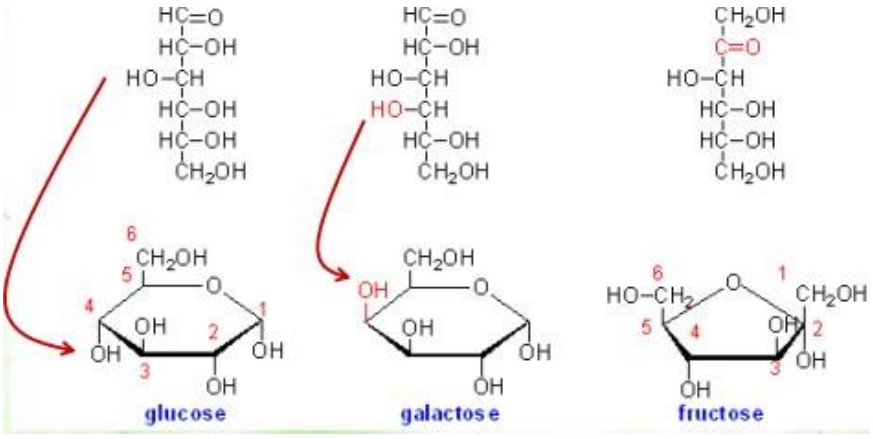
Some conventions

- We read it From up (carbon number 1) to down
- The carbon on the right in the open chain becomes below the ring while the left one becomes above it
- The penultimate (before the last chiral center) determines whether the molecule is L or D (if its hydroxyl group is on the right then its D , if its on the left then its L) .

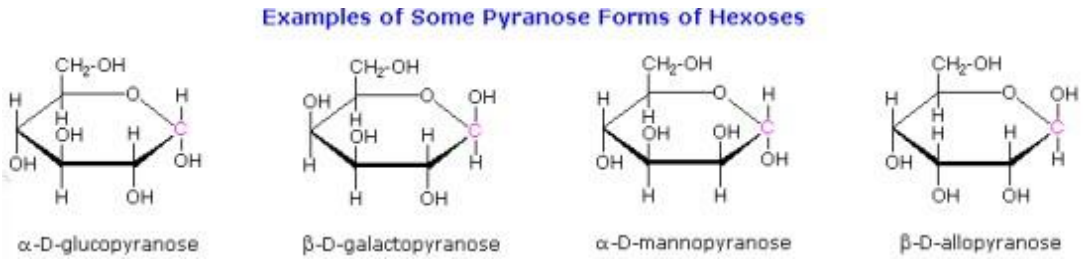
As for the open chain , we have **conventions for the cyclic chains** :
Always you draw the cyclic chain having the oxygen on the top and to the right side of the oxygen (your right side) is the anomeric carbon .finally, the carbon outside the ring is the last one(could be two outside the ring).

Chain to ring

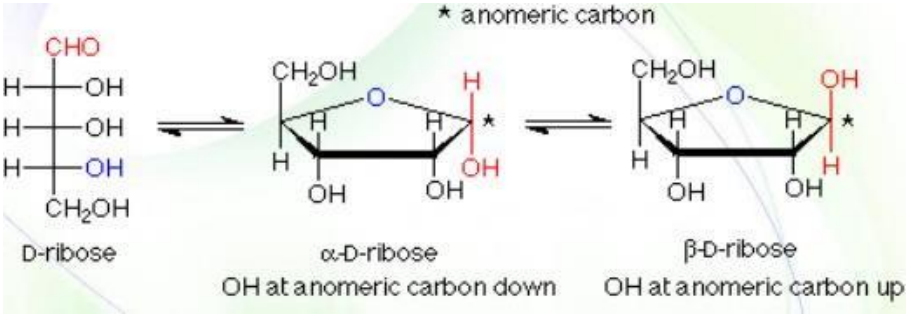
Left-right
vs. up-down



Cyclic aldohexoses



Cyclic ribofuranose

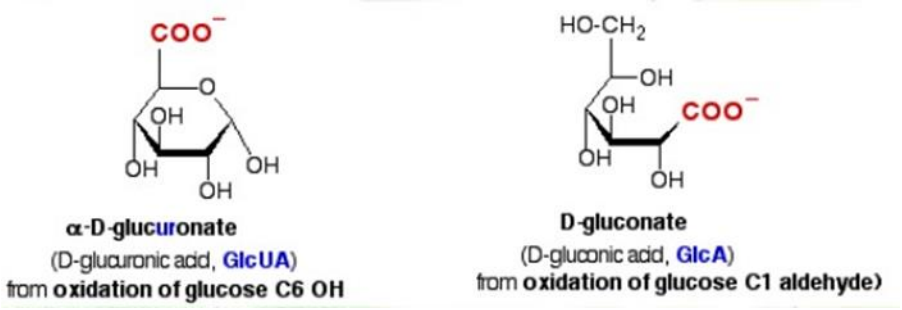


Modified sugars

Sugar acids(oxidation)

Where is it oxidized ? what does it form?

Oxidation : increase in the oxygen or decrease in the hydrogen



- Monosaccharides can be oxidized on the anomeric carbon (the most reactive one) if it is free (not bound to other than OH and H) the hydroxyl group on the anomeric carbon is reactive and can be oxidized , if the hydroxyl group lost its H and the oxygen is bound to other thing (sulfur nitrogen etc.) it can not be oxidized .
- As the monosaccharide is oxidized it reduces the other thing it reacts with ,that means it is a reducing sugar (all monosaccharides in their cyclic form are considered reducing sugars).
- Oxidation can occur in two positions the most reactive on the anomeric carbon and the other position is the last carbon (alcoholic in its nature) So we have two groups that can be oxidized but the aldehyde or keton is more reactive than the alcohol group (ketone is not reactive but it will be transformed into aldehyde)

- When its oxidized on its anomeric carbon we add the suffix onic (gluconic acid ,galactonic acid)
  If the last carbon is oxidized we add the suffix uronic (glucoronic acid….)

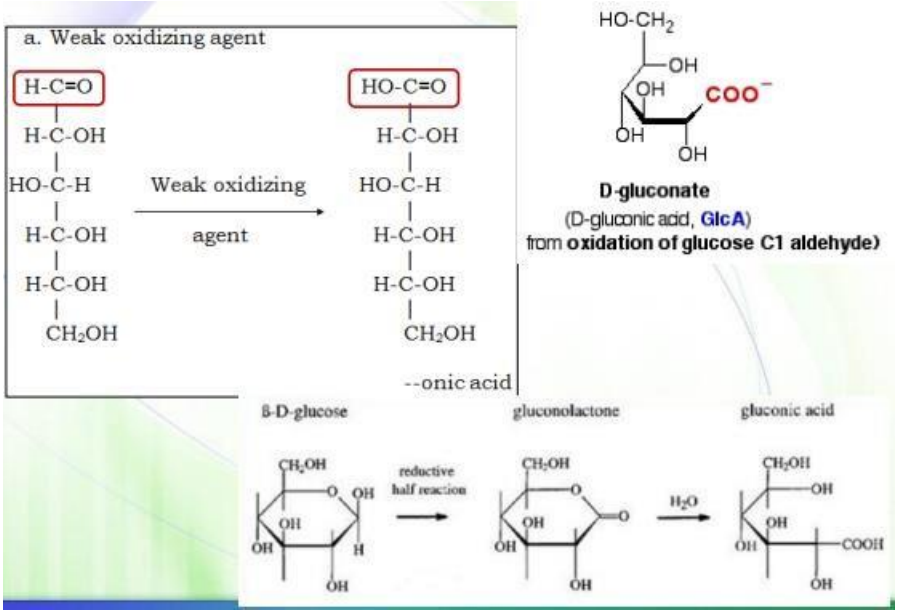
Now how can we determine which one would be oxidized (the anomeric or the last one)?

It depends on the oxidizing agent ,is it strong or weak (keep in mind that aldehyde on the anomeric carbon is more reactive than the hydroxyl group on the last one).

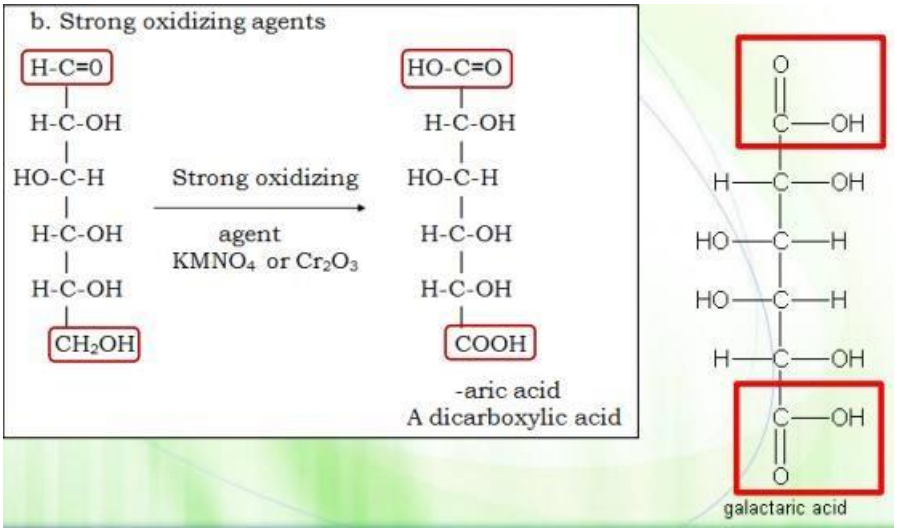
In the presence of weak oxidizing agent the anomeric carbon will be oxidized and the result will be –onic acid take a look for example 1
If we add a strong oxidizing agent both groups will be oxidized the resulting molecule will be -aric acid it has 2 carboxyl group (like glucaric acid) example 2

If we want to oxidize the last carbon without oxidizing the anomeric one in the presence of enzymes (they are selective) example 3
without enzymes the oxidizing agent will oxidize the more reactive one or both of them we cant oxidize the weak one without oxidizing the more reactive one.

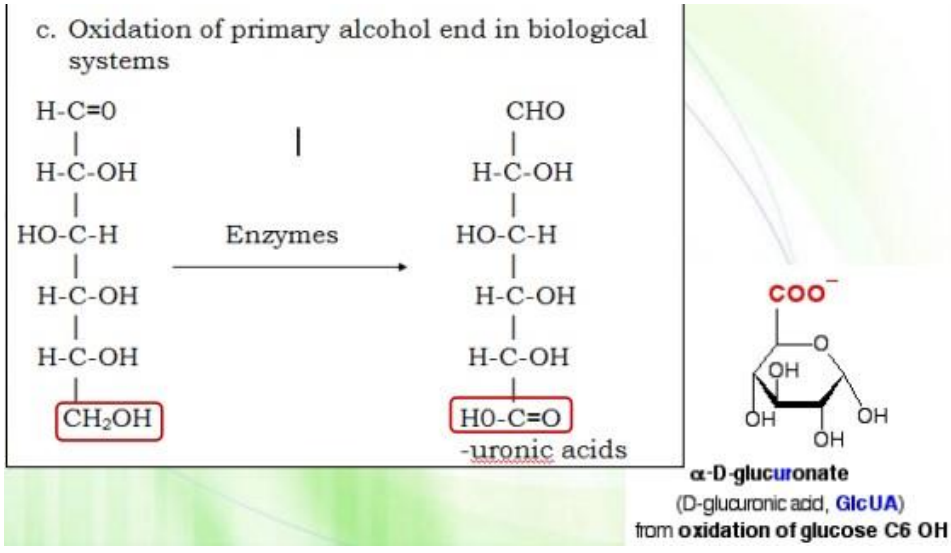
Example 1



Example 2



Example 3



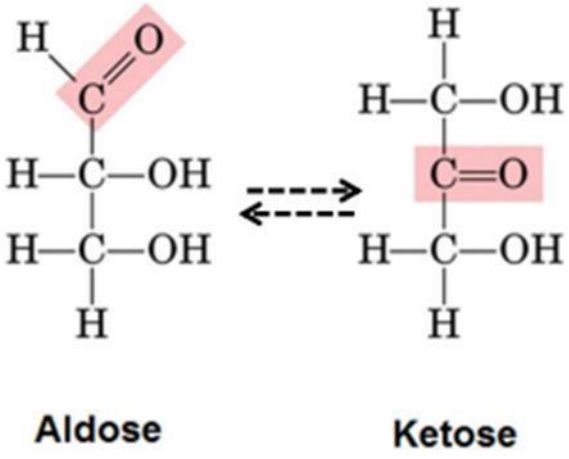
You can know which carbon has been oxidized from the suffix

For example if you see gluconic acid (the anomeric carbon is oxidized)

Note

- Oxidation of ketoses to carboxylic acids does not occur, but they can be oxidized because of formation of enediol form
  Ketoses are reactive but indirectly (through conversion into aldoses) the ketone is transformed into aldehyde and then the aldehyde reacts

- the enediol forms as intermediate in this conversion
  enediol is a compound that has double bond and two hydroxyl groups .

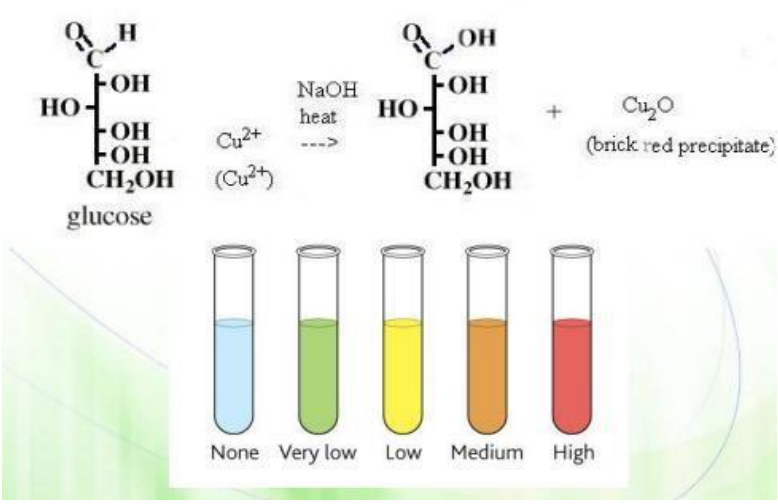


Aldose **Ketose**

Benedict’s test

It is used to know whether the solution contains reducing sugars or not and how much .

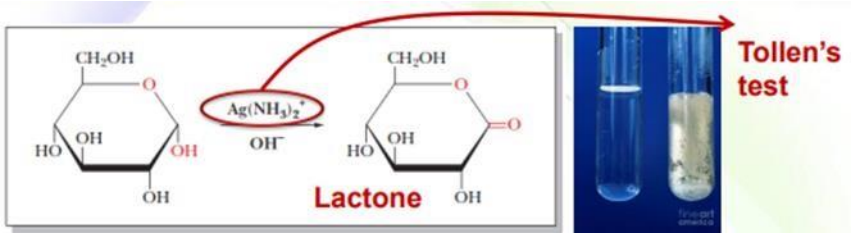
When reducing sugars (that can be oxidized) are mixed with Benedicts reagent (contains cupper which is the oxidizing agent) and heated, a reduction reaction causes the Benedicts reagent to change color ,the cupper oxide forms(it has red color). The color varies from green to dark red (brick) or rusty-brown, depending on the amount and type of sugar.



You can watch this video to see how does it happen

https://youtu.be/nlPHeqHOYpU

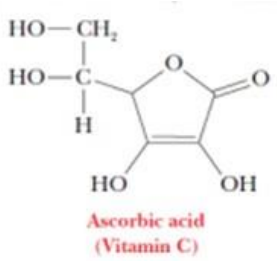
Oxidation of cyclic sugars (lactone)



- A more recent method for the detection of glucose, but not other reducing sugars, is based on the use of the enzyme glucose oxidase.
- The lactone is a ring structure whether sugar or something else containing ketone formation

- In the reaction above , when the anomeric carbon is free (not bounded to other molecules) it loses its H and forms a double bond with the oxygen and the lactone is formed.
- As a result of lactone formation the silver precipitate on the walls of the test tube as byproduct as an indication of the presence of sugar (and this is how mirrors are made).

•**Vitamin C** (ascorbic acid) is an unsaturated lactone.
•Air oxidation of ascorbic acid, followed by hydrolysis of the ester bond, leads to loss of activity as a vitamin. (عشان هيك بحكولنا اشرب عصير الليمون قبل ما تروح فايدته ,طلع معهم حق)
•A lack of fresh food can cause vitamin C deficiencies, which, in turn, can lead to **scurvy** ,it was discovered in the sailors because they don't have fresh source of vitamin C.
Vitamin C is important in making collagen so lack of it leads to weak collagen, spontaneous bleeding , pain in the limbs, fractures, and especially the legs and loss of teeth.(عشان هيك بالافلام بكون القرصان عنده خطاف بدل ايده واسنانه واقعة)



Ascorbic acid
(Vitamin C)

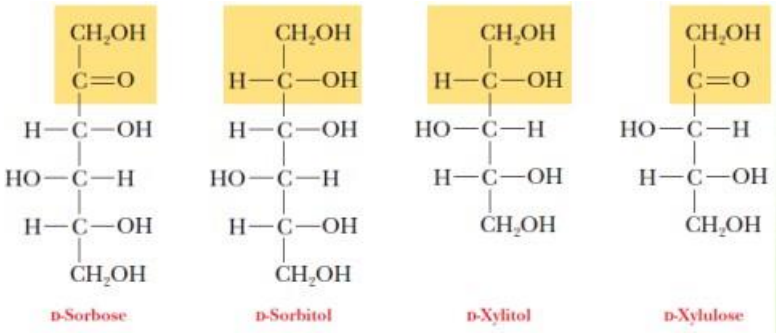
the principle of diabetic test :

In a recent test , an enzyme called glucose oxidase is used for the detection of glucose only. Diabetic test is based on this reaction , a drop of blood representing the whole blood (because glucose is soluble and not suspended) is taken by the chip through diffusion , the chip contains **glucose oxidase** (which oxidizes glucose only)producing hydrogen peroxide which is a colorless material , another enzyme (**peroxidase**) transforming it to a substance with color. Depending on the depth of that color , it should match how much glucose is in your blood .

sugar alcohol (reduction)

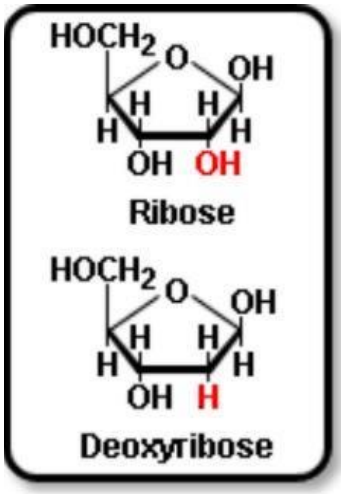
- reduction means gain of electrons , gain of hydrogen and loss of oxygen (aldehydes and ketones can be reduced into alcohols)

- What does it form?
- Examples include sorbitol, mannitol, and xylitol, which are used to sweeten food products
  in the figure below the sorbose is reduced into sorbitol and the xylulose into xylitol (simply by adding H to both carbon and oxygen and breaking the double bond between them)



Sorbitol and xylitol are not sugars instead they are modified sugars (aldehydes and ketones can be reduced to alcohols and still have a sweet taste. Cells recognize them as alcohols so they won't get into the pathway of sugar metabolism .)

Deoxy-sugars (reduced sugars)



One or more hydroxyl groups are replaced By hydrogens.

An example is 2- deoxyribose, which is a constituent of DNA.

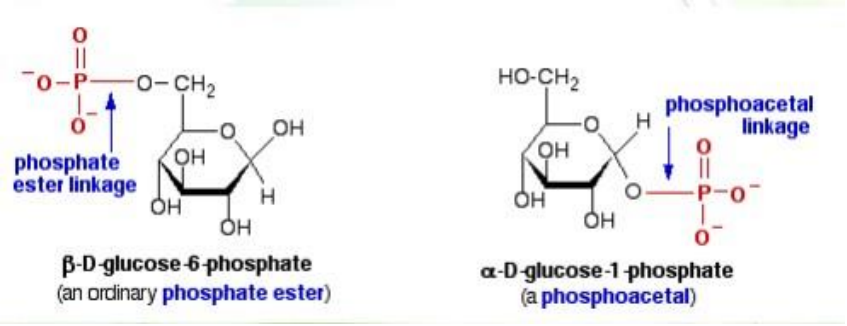
- Ribose in DNA loses its oxygen (which is reactive atom) on carbon number 2 making the DNA more stable and less reactive to prevent mutations.
- while RNA works momentarily and then will be degraded.

Sugar esters (esterification)

 What is the reacting functional group? Where does it react? What are the end products? Where are they used?

Esterification occurs on the anomeric or the last carbon .

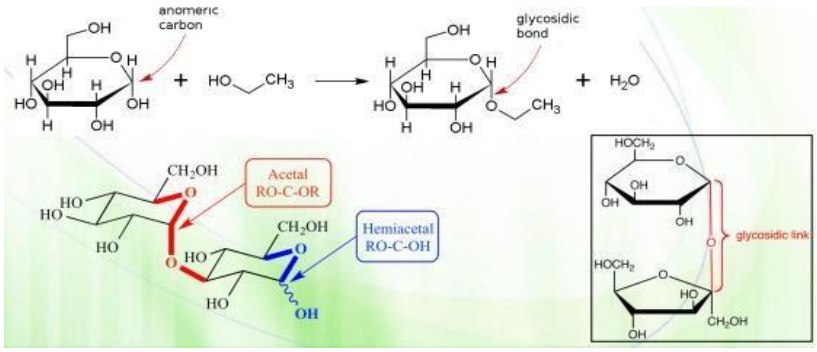
Sugar esters are products of sugar esterification; addition of phosphate groups to hydroxyl groups by phosphorylation.it's called esterification because the formula of the final product P=OOR is similar toesters' formula RC=OOR.



- anomeric carbon makes the glycosidic linkage , if it is with o then it is o-glycoside if it is with N then it is N-glycoside , if it is with C then it is C-glycoside and if it is with S it is thioglycoside . This is the bases of increasing the number of monosaccharide to make polymers.

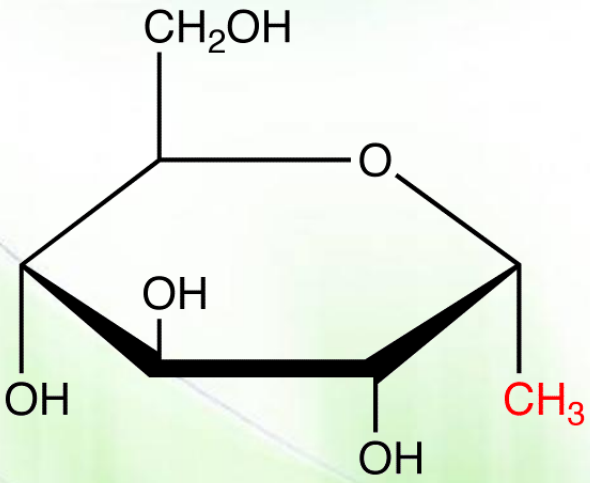
O-Glycosides

 What is the reacting functional group? Where does it react? What are the end products? Where are they used?

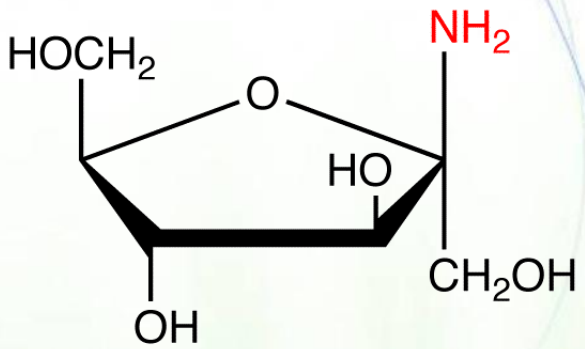


Note

- Glycosides derived from furanoses are called **furanosides**, and those derived from pyranoses are called **pyranosides,** regardless if they are N- or O-linkded.



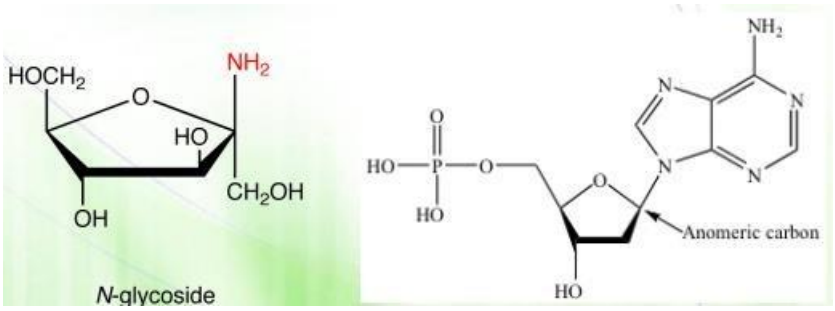
C-glycoside



N-glycoside

N-glycosides

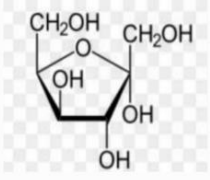
- What is the reacting functional group? Where does it react? What are the end products? Where are the used?
- Examples: nucleotides (DNA and RNA)



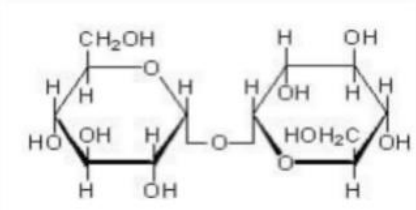
A side note : (معرفناش وين نحطها عشان هيك زتيناها هون) : all ring sugars in The slides are in the D form and we are not going to deal with L form .

Past papers :

1) The following figure represents D-sorbose.. which of the following statements is
wrong ?
A. It is a furanose.
B. It is an alpha sugar.
C. Carbon no.1 is the anomeric carbon.
D. It is a ketose.
E. It can re-open up into the chain form.



2) IS THAT
A) REDUCING SUGAR OR B) NON REDUCING SUGAR



Answer: B

3) Glycoside formation results in:
A. reaction of cyclic acetal with alcohol
B. reaction of cyclic acetal with another cyclic acetal
C. reaction of cyclic hemiacetal with alcohol

Answer: C

4) What is the wrong about D and L configuration:
A. D sugars Exist in abundance in nature
B. all of the amino acid in protein is L configuration
C. they don't deferent in anomeric carbon
D. they are deferent in only last chiral center
E. more than one of the above

Answer: B

5)How many chiral carbons are there in deoxyribose
A. 1
B. 2
C. 3
D. 4
E. none

6) Which of the following is not a reducing sugar?
A. glucose
B. Fructose
C. sucrose
D. galactose

Answer: C

7) Which is not correct about glucose?
A. It is an epimer of mannose
B. It is an epimer of galactose
C. Only D-isomer exist in mammalian cells
D. It mainly exists as open chain in solution

Answer: D

8) which of the following is the most found in nature ?
A. L-sugar
B. D-sugar
C. L-sugar and D-sugar in the same amount

Answer: B

9) D-glucose and D-galactose has all of the following except:
A. Hexoaldoses
B. They are Diastereoisomers
C. They are anomers
D. They are reducing sugars

Answer: C

10) which of these is aldo-pentose ?
A. glucose
B. fructose
C. maltose
D. ribose

Answer: D

11) Deoxy sugars are produced via
A. Reduction of a monosaccharide
B. Engaging anomeric carbons in a glycosidic bond
C. Conversion of sugar chain into cyclic form
D. Oxidation of a sugar acid
E. Hydrolysis of a disaccharide

Answer: A

12) Benedict's test is used to :
A. Confirm the presence of cyclic sugars
B. Confirm the presence of reducing sugars
C. Confirm the presence of sucrose
D. Confirm the presence of disaccharides
E. confirm the presence of sugar acids

Answer: B

Good luck

يا رب يخلص الصيفي بسرعة