

Lecture : # 9 - sections 4 , 5 , 6

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Slide Sheet



Medical Committee
The University of Jordan

Biochemistry

cybernetics
biometrics
biochemistry
ecology
bionomics
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aerobiology
anatomy
cytology
life
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microbiology
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xenobiology
botany
exobiology
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astrobiology
molecular
biochemistry
physiology
ethnobiology
electrobiology
bioecology
virology
zoology
biometry
cryobiology
enzymology
cell
genetics
bionics



Mousa Suboh

Long time ago, people who sacrifice their sleep, family, food, laughter, and other joys of life were called SAINTS.
But now, they are called STUDENTS!

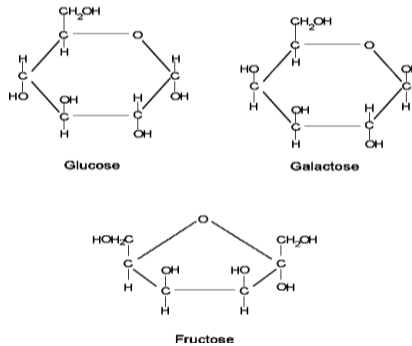
Monosaccharaides

Q. Can hydrolysis occur at anytime or any condition?

A. No. It needs special enzymes.

Q. What are the differences between glucose and galactose?

A. In glucose and at carbon atom #4 OH **projects downward**. While in galactose OH at carbon atom #4 **projects upward**.



***Kindly note that:**
EPIMERS at carbon #4.

- glucose and galactose are

Recall:

Epimers: differ only at one chiral center.

- Glucose at carbon #1 can project upward or downward depending on the form of the monosaccharide (alpha and beta glucose)

- Fructose sometimes has a 6 carbon atoms ring but mostly it has a 5 carbon atoms ring.

WHAT DO WE EXACTLY NEED TO KNOW?!!

((The doctor said that we have to distinguish between all the monosaccharaides that we have studied. When you look at the structure you should be able to tell which one of the monosaccharide is this one and if you have disaccharides you have to identify which monosaccharaides are forming these disaccharides.))

Monosaccharaides

- * Monosaccharaides are classified by their number of carbon atoms.
- * Monosaccharaides with 3 carbon atoms are called **TRIOSES**.
- * monosaccharaides with 4 carbon atoms are called **TETROSES**.
- * monosaccharaides with 5 carbon atoms are called **PENTOSES**.
- * monosaccharaides with 6 carbon atoms are called **HEXOSES**.
- * Trioses are the simplest sugars and they are divided into aldoses and ketoses. It's **aldoses** are called **Glyceraldehydes** (have a chiral center) and it's **ketoses** are called **Hydroxyacetone** (achiral).

Glyceraldehyde

- has 2 forms:
- D-Glyceraldehyde.
- L-Glyceraldehyde.

Hydroxy acetone

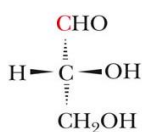
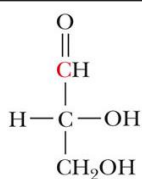
- Dihydroxy acetone
- Achiral

* D-Glyceraldehyde and L-Glyceraldehyde are **enantiomers** (they are mirror images to each other).

- 1 A comparison of glyceraldehyde (an aldotriose) and dihydroxyacetone (a ketotriose).



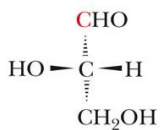
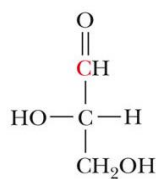
- 2 The structure of D-glyceraldehyde and a space-filling model of D-glyceraldehyde.



D-Glyceraldehyde



- 3 The structure of L-glyceraldehyde and a space-filling model of L-glyceraldehyde.



L-Glyceraldehyde



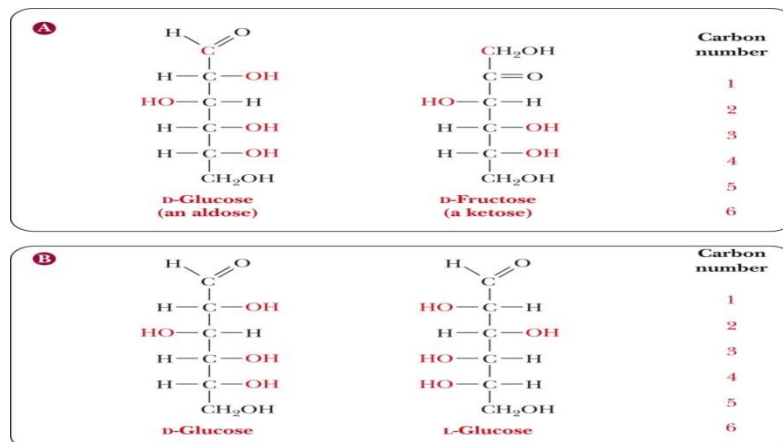
Fischer Projection

General notes on Fischer Projection:

- Bonds are written in a two dimensional representation showing the configuration of tetrahedral stereo centers.

** **Horizontal** lines represent bonds projecting **forward**

** **Vertical** lines represent bonds projecting to the rear (**backward**)



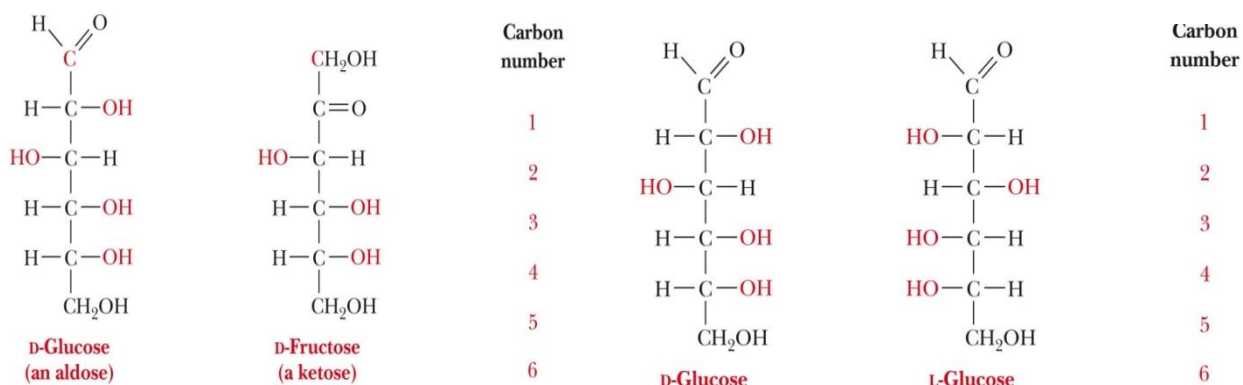
D, L-Monosaccharide

Q. How to distinguish whether a monosaccharide is D or L Monosaccharide?

A. By convention; D-monosaccharide: a monosaccharide that, when written as a Fischer projection, has the -OH on its penultimate (before the last) carbon on the **right**.

L-monosaccharide: a monosaccharide that, when written as a Fischer projection, has the -OH on its penultimate carbon on the **left**.

Try to guess whether these examples are D or L monosaccharides!



Note: Glyceraldehydes have D and L monosaccharaides.

Dihydroxyacetone has no chiral centers structure, so it's a triose with no stereoisomers.

Q. How many isomers are there for glucose?

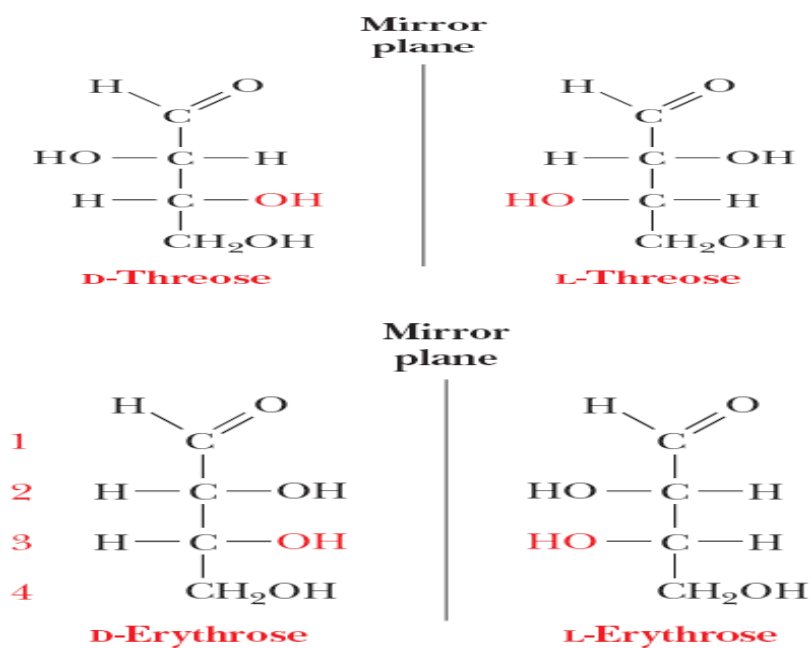
A. Glucose has 16 isomers since it has 4 chiral centers $\gg 2^4 = 16$

Aldotetroses

Tetroses: have 4 carbon units' carbohydrates.

* D-Erythrose and L-Erythrose are **enantiomers** \rightarrow (non-superimposable mirror images). Also, They differ at 2 chiral centers, so they are NOT epimers.

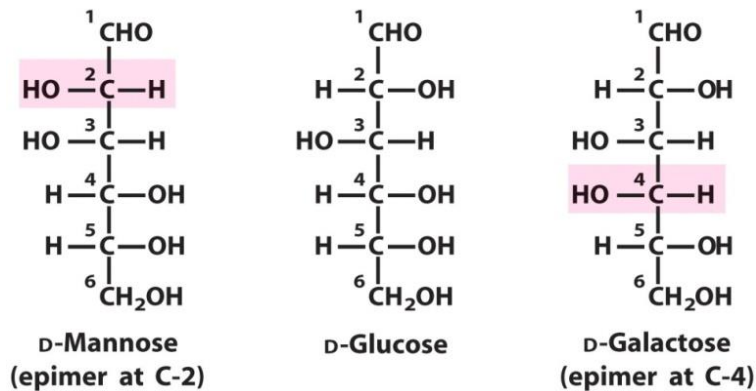
* D-Threose and L-Threose are **enantiomers**.



Pentoses and Hexoses

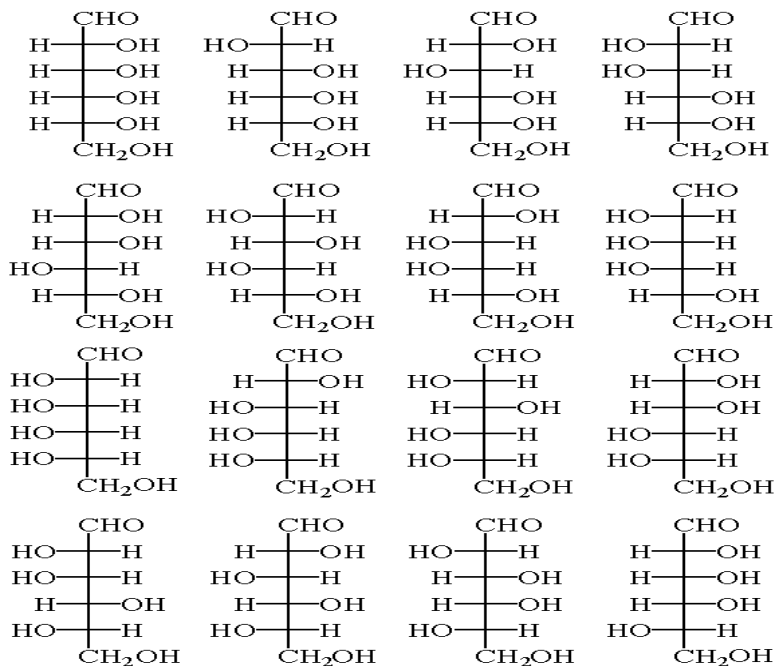
- Most common forms of monosaccharaides are pentoses and hexoses.
- Galactose is an epimer for glucose at carbon #4
- Mannose is an epimer for glucose at carbon #2
- There are 3 chiral centers in aldopentoses >> $2^3 = 8$ isomers.
- There are 4 chiral centers in aldohexoses >> $2^4 = 16$ isomers. e.g. glucose.

Rule: Always the number of chiral centers = the number of carbon atoms - 2.



Just take a quick look! :D

16 Aldohexoses



* Some stereoisomers are much more common in nature than others in carbohydrates. In amino acids, we have D- and L- amino acids but naturally occurring amino acids in protein are L- amino acids. In carbohydrates, D- sugars predominate in nature in comparison with L- ones.

Cyclization of sugars

- Cyclization of sugars takes place due to interaction between functional groups on distant carbons, C1 to C5, to make a cyclic hemiacetal

- Cyclization using C2 to C5 results in hemiketal formation

- In Aldoses, carbonyl group (C=O) is on C#1 ... while in ketoses; the carbonyl group is on C#2. so in order to make a cycle (ring), the carbon of the functional group (carbonyl carbon) either C#1 or C#2 attack C#5 which is the last chiral center in the molecule (it's the carbon before the last one). In aldoses one carbon atom is outside the cycle which is carbon #6 while in ketoses two carbon atoms are outside the cycle which are carbon #1 & #6.

Ketoses can make a 6 membered ring when C #2 attacks C #6 and here C #1 exists outside the ring.

** -OH ,that is attached to the carbonyl carbon, projects upward or downward:

=> If the projection of -OH of the carbonyl carbon & -CH₂OH (carbon #6) is on the **same side**
→ it's **cis** → **beta**

=> If the projection of -OH of the carbonyl carbon & -CH₂OH (carbon #6) is on **different sides**
→ it's **trans** → **alpha**

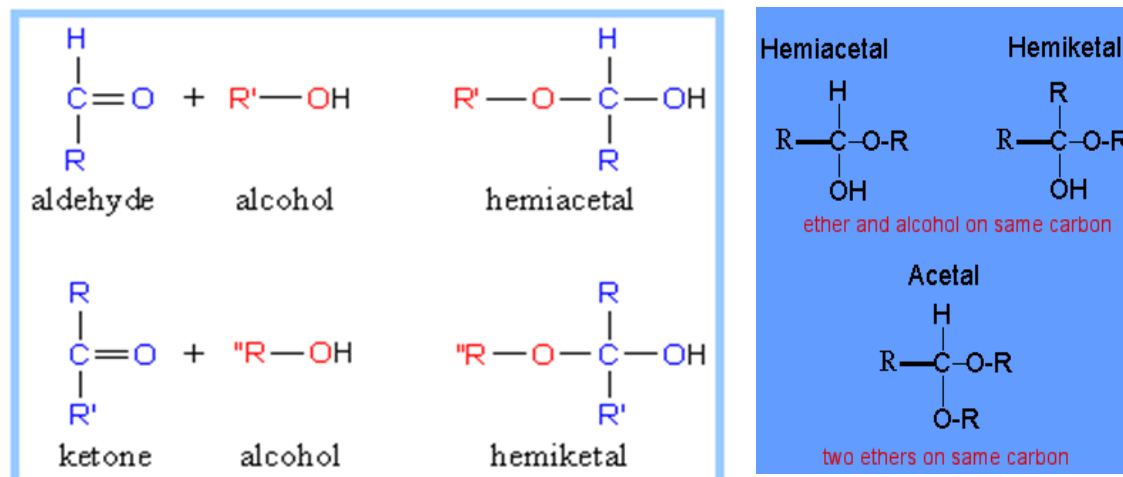
- If OH of C #1 projects to the same side>> then it's cis >> so it's beta.

- If OH of C #1 projects to two different sides>> then it's trans >> so it's alpha.

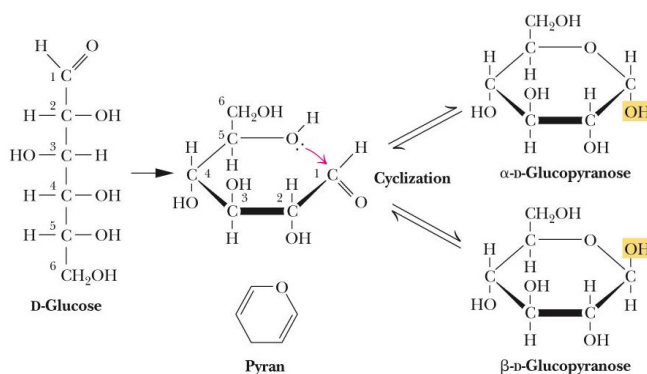
- In both cases, the carbonyl carbon is a new chiral center and becomes an anomeric carbon

- **Anomers:** differ only at their **anomeric carbon**, either α or β

* **Anomeric carbon:** is the one which determines if they are alpha or beta.

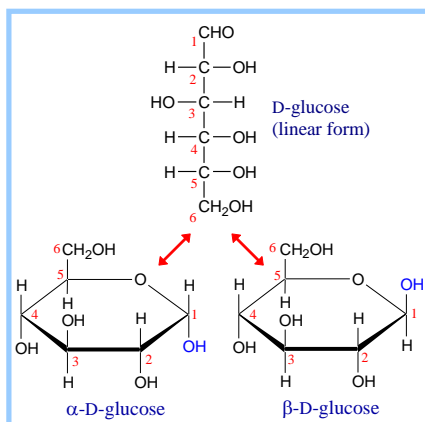


**Kindly note that by cyclization you offer a new chiral center from achiral one. (Because the carbonyl carbon was an achiral carbon and by the process of cyclization, it's becomes a chiral center).

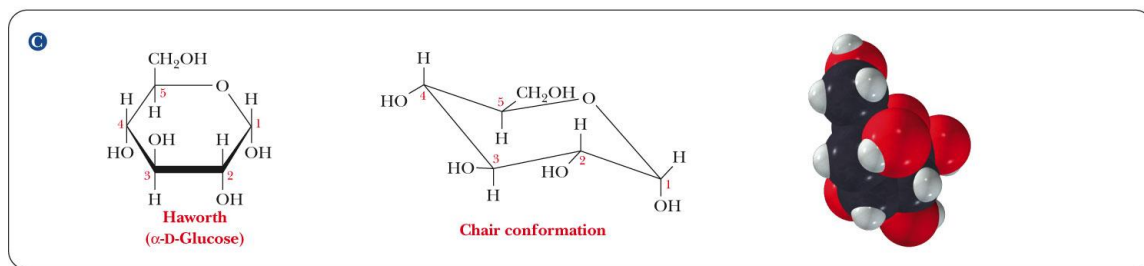
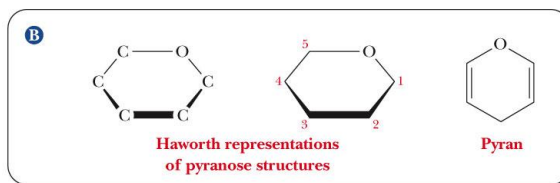
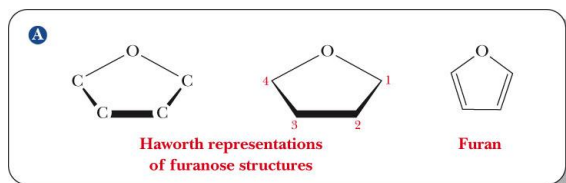


Haworth Projections

- Five- & six-membered hemiacetals are represented as planar pentagons or hexagons
- Most commonly written with the anomeric carbon on right & hemiacetal oxygen to the back right
- The designation **Beta** means that anomeric carbon -OH is cis to the terminal -CH₂OH; **Alpha** means that it is trans.



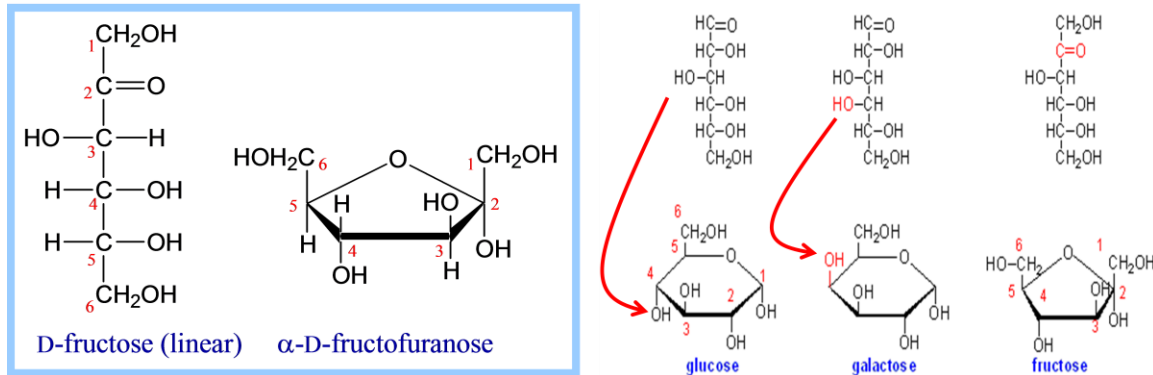
- A **six**-membered hemiacetal ring is called **pyranose**
- A **five**-membered hemiacetal ring is called **furanose**
- Five-membered rings are so close to being planar that Haworth projections are adequate to represent furanoses
- For pyranoses, the six-membered ring is more accurately represented as a strain-free chair conformation



- Fructose forms either:

- 1- A 6-member pyranose ring, by reaction of the C2 keto group with the OH on C6, or
- 2- A 5-member furanose ring, by reaction of the C2 keto group with the OH on C5

****Note:** Haworth Projections are good to be used in describing furanoses but they can't describe pyranose accurately because of strains.



Reaction of Monosaccharides \ Reducing Sugars - Oxidation

- Breaking of bonds → getting energy → oxidation
- Formation of bonds → storing energy → reduction (eg. Photosynthesis)
- Reduction reactions: energy metabolism vs. photosynthesis
- Reducing sugar (oxidation process): one that reduces an oxidizing agent

- In order of a monosaccharide to be oxidized, it should reduce the structure in front of it. And here the monosaccharide itself gets oxidized. Not all sugars can reduce other structures.

Sugars that can cause reduction of other molecules are: all monosaccharides + disaccharides except sucrose. Why?

* Oxidation of ketoses to carboxylic acids does not occur.

Ketone group can't be oxidized while aldehyde group can be oxidized into carboxylic acid.

However, all monosaccharides can be interconverted between the aldose form and ketose form by isomerization process.

Monosaccharides (ketoses) can be reducing sugars (i.e. can cause reduction of other molecules, or in other words can be oxidized), not because they can be oxidized but because they can get isomerized into aldoses which can be oxidized into carboxylic acid.

- Oxidation of a cyclic hemiacetal form gives a lactone.

So in order to know if the monosaccharaide is reducing or not, you should know its ability to be converted into a lactone. (In lactone the anomeric carbon has a double bond with an Oxygen atom).

- Reducing sugars are:

1) **All monosaccharaides** (aldoses and ketoses). {All Aldoses, because they can be oxidized directly .And all ketoses, because they can be isomerized into aldoses}.

2) **Disaccharides are reducing sugars EXCEPT sucrose.** In di- and oligo- saccharaides, Because we have more than one monosaccharaide attached to each other, we can't determine depending of the ability to be isomerized or not! However, we determine depending on the anomeric carbon; if the anomeric carbon is engaged in a bond then it can't be oxidized and the ring can't be opened so it's not a reducing sugar. But if it's not engaged in a bond, it can be oxidized and give the acid form of the structure and the ring can open, so it **IS** a reducing sugar! (Sucrose has 2 anomeric carbons engaged in an alpha 1-2 glycosidic bond so it's **NOT** a reducing sugar. It won't be oxidized using oxidizing agent).

Q. Why oxidation processes occurs for sugars?

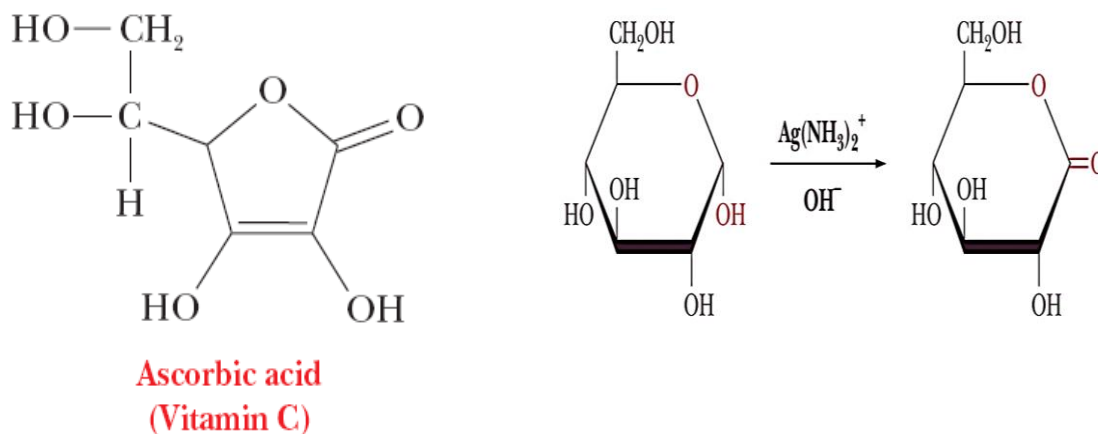
A. To break bonds, to get ENERGY.

General Notes:

1- Vitamin C structure is similar to Lactone's structure.

2- Vitamin C is an unsaturated Lactone. (Because it contains a double bond).

3- Vitamin C can be oxidized (the ester bond between carbon and oxygen is broken and the ring opens) when the molecule containing vitamin C is exposed to air.



Remember that you have chosen this road and you have to complete it till the end!

Sorry for any accidental mistakes

Best wishes

Marah Haddad