Chem 452 - Lecture 7
Carbohydrates
111107

Carbohydrates are one of the four major classes of biomolecules, which include the proteins, lipids and nucleic acids. In terms of total mass, carbohydrates make up the largest fraction of biomolecules in the biosphere. Carbohydrates have the basic chemical formula $(CH_2O)_n$ and derive their diversity of structure from the the multiple stereoisomers that they can form. They play many important biological roles, including sources and storage forms of chemical energy, components of nucleic acids, and structural roles such as cell walls. The are also found covalently bonded to proteins and lipids, where they play important roles in cell-cell communication.

Introduction to Carbohydrates

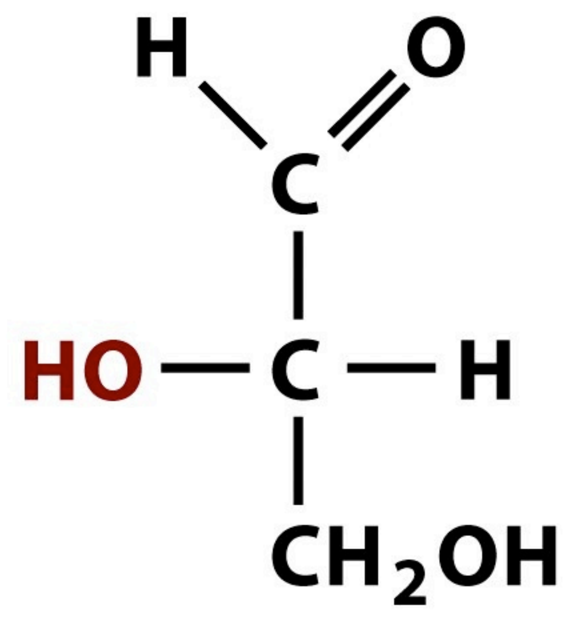
- $(CH_2O)_n$
- Chemically simple, structurally complex
- Nomenclature
  - monosaccharides
  - oligosaccharides
  - polysaccharides

Monosaccharides

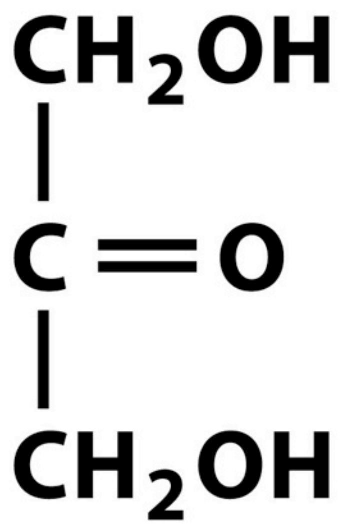
- Aldoses
  - polyhydroxyaldehydes
- Ketoses
  - polyhydroxyketones
- Number of carbons
  - triose
  - tetrose
  - pentose
  - hexose
  - heptose

Monosaccharides

- Trioses
  - Glyceraldehyde and Dihydroxyacetone



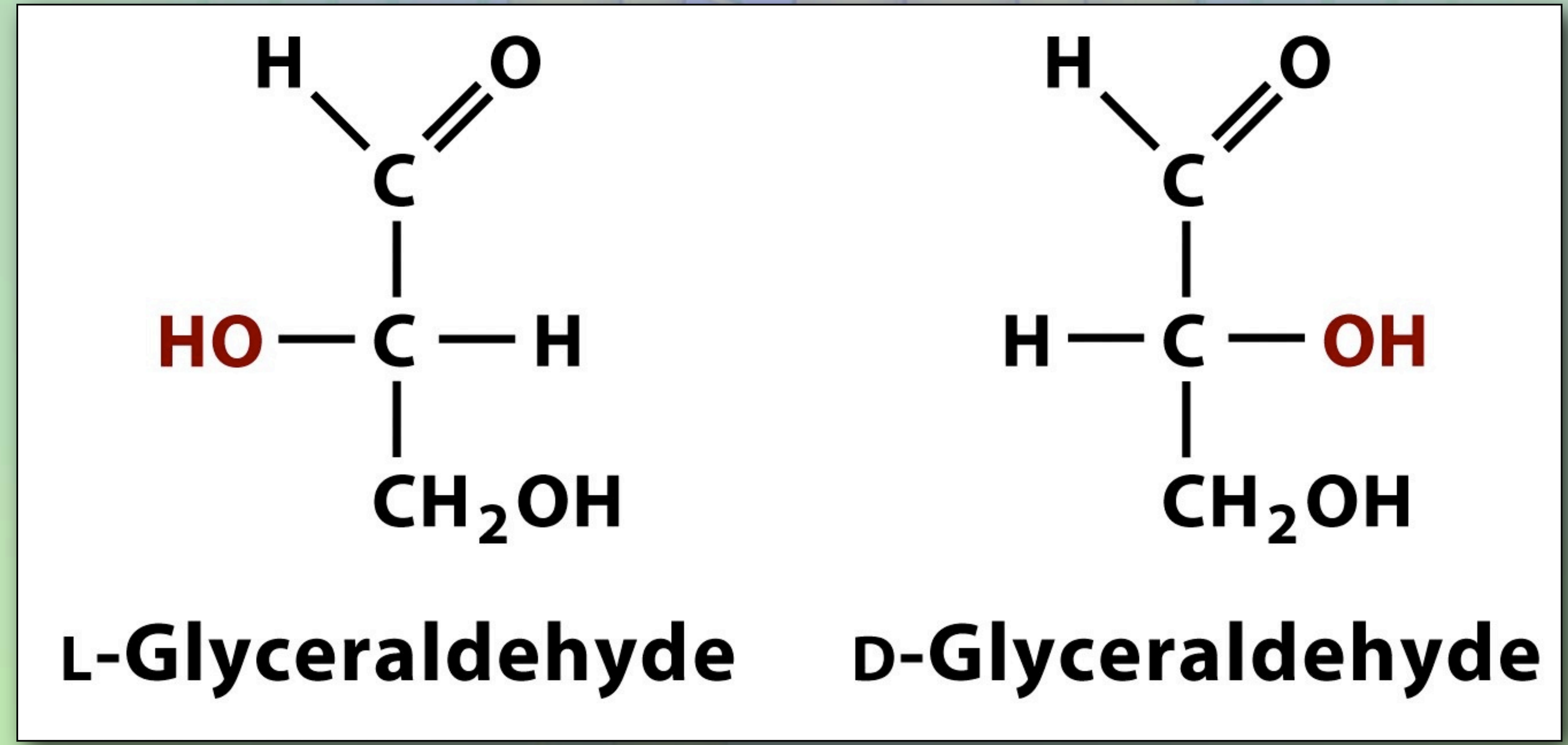
L-Glyceraldehyde



Dihydroxyacetone

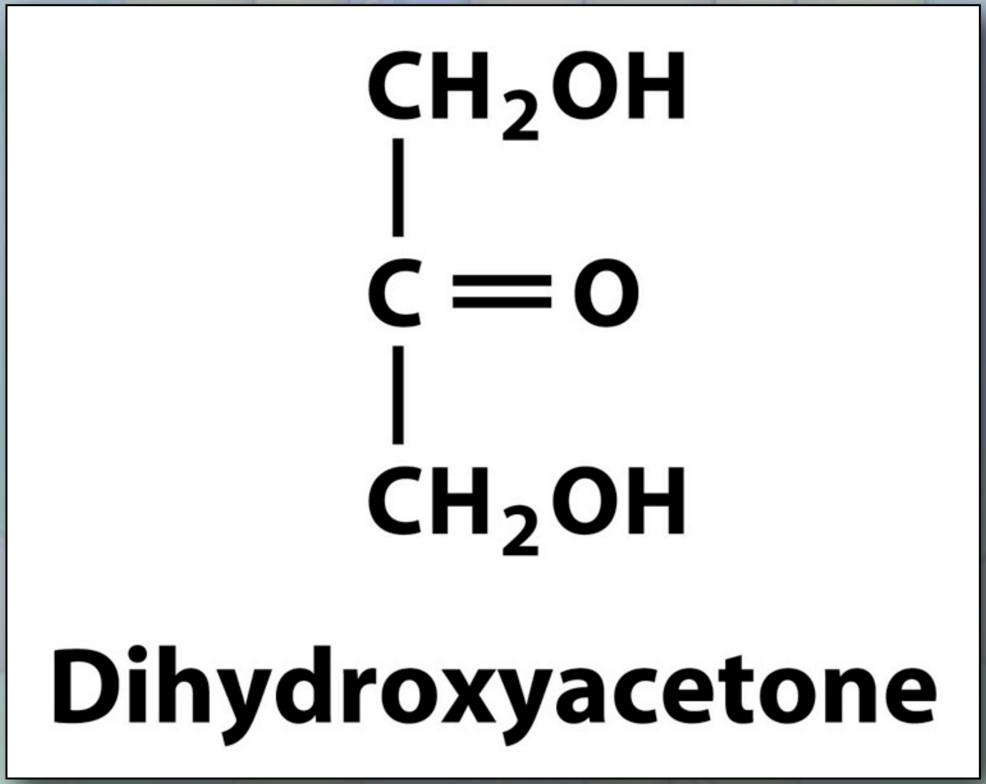
Monosaccharides

- Trioses
  - L and D Glyceraldehyde
    - Contains a chiral carbon
    - Fischer projections



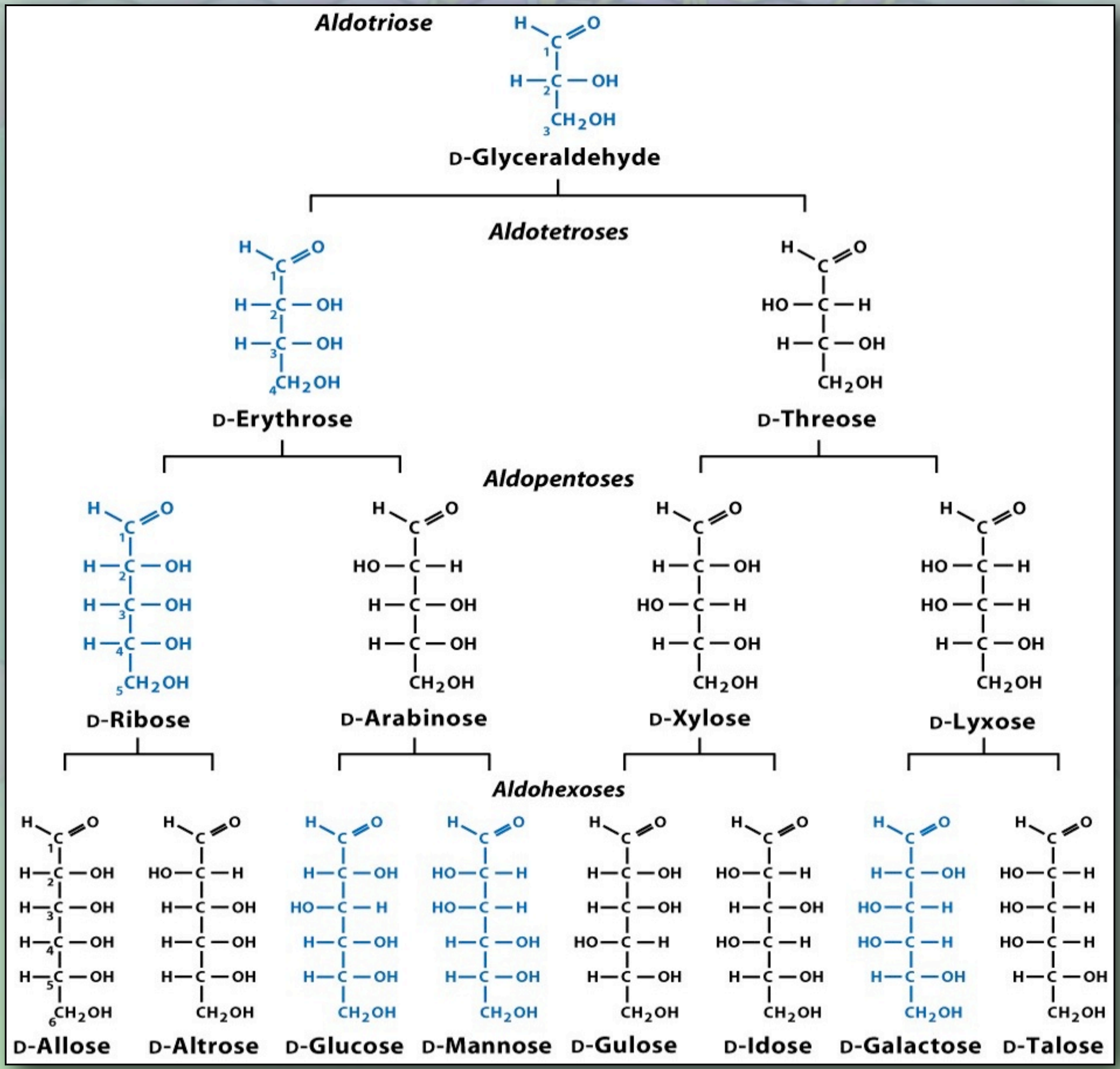
Monosaccharides

- Trioses
  - Dihydroxyacetone
    - Contains no chiral carbons



Monosaccharides

- Aldotriose through aldohexoses



Monosaccharides

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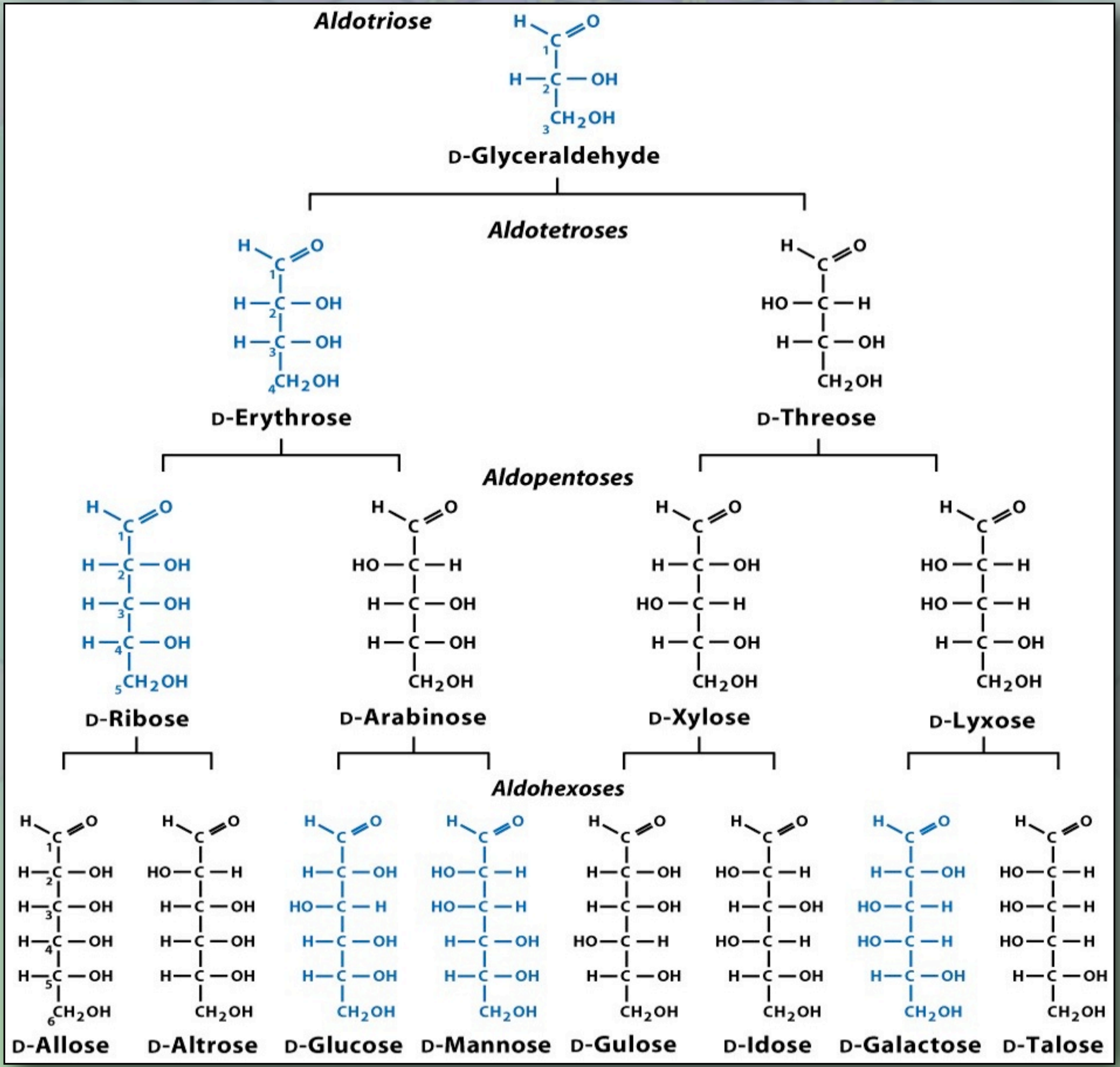
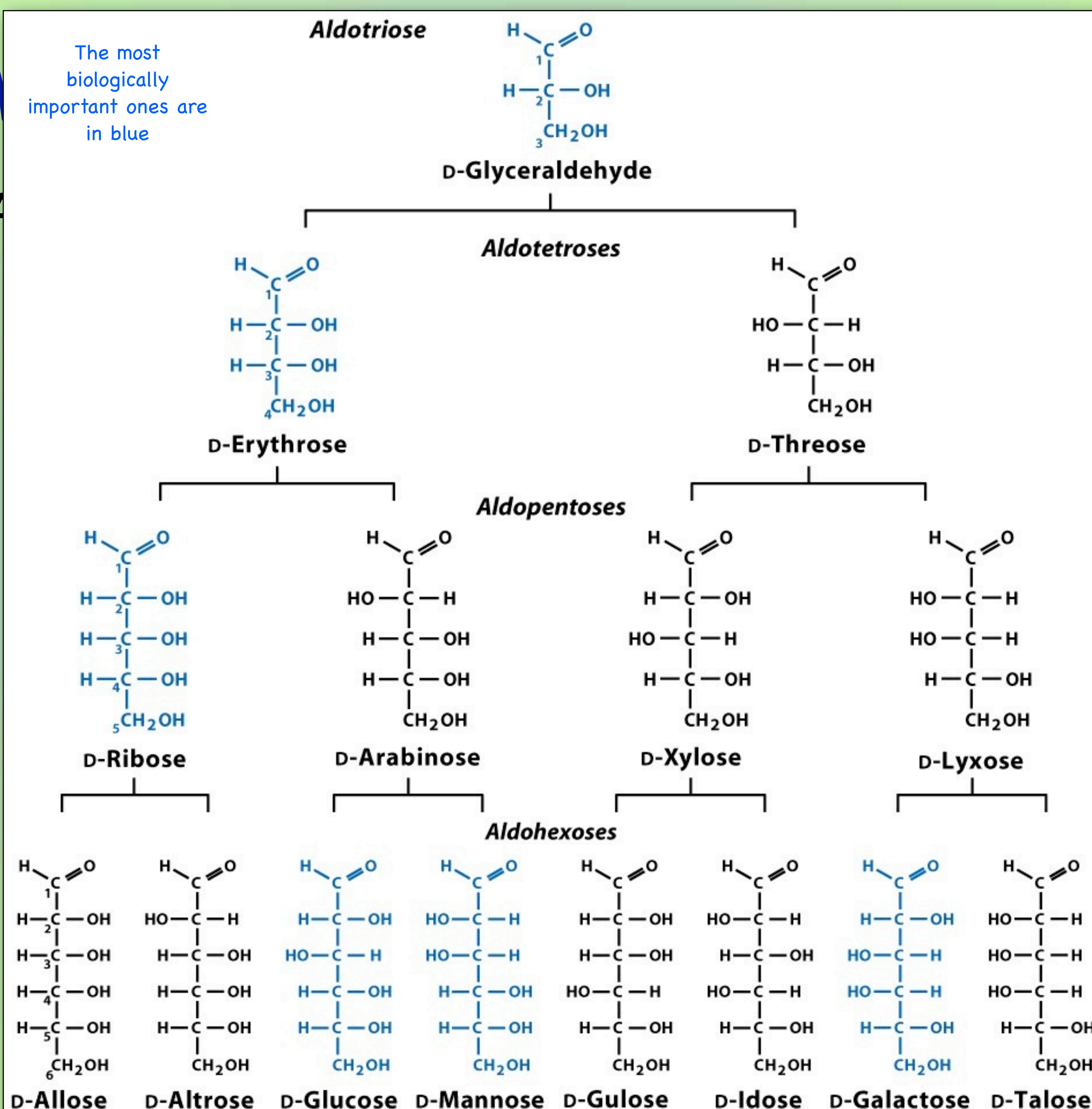


This figures only shows half of the aldoses

M

✦ A

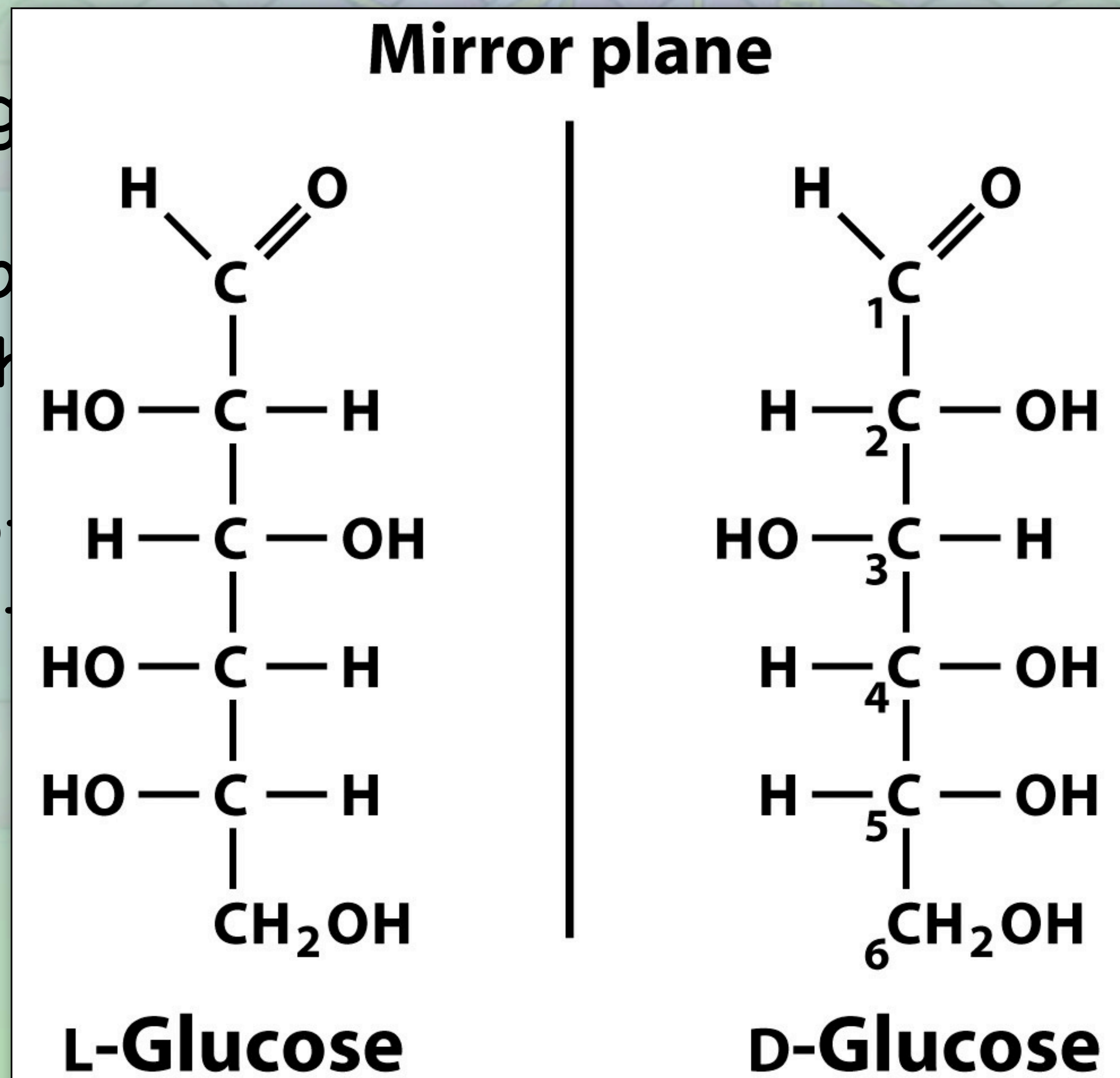

The most biologically important ones are in blue
Aldotriose
D-Glyceraldehyde
Aldotetroses
D-Erythrose
D-Threose
Aldopentoses
D-Ribose
D-Arabinose
D-Xylose
D-Lyxose
Aldohexoses
D-Allose
D-Altrose
D-Glucose
D-Mannose
D-Gulose
D-Idose
D-Galactose
D-Talose

Monosaccharides

- Aldotrioses through aldohexoses
  - This figure shows only the D-**enantantiomers**
  - Enantiomers are named for the chirial carbon that is furthest from the carbonyl group.
  - Most of the monosaccharides that we will encounter are D-enatiomers.

Monosaccharides

- Aldotrioses through aldohexoses
  - This fig **ners**
  - Enantio rbon that is furth
  - Most o ll encount



Monosaccharides

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  - Enantiomers are named for the chirial carbon that is furthest from the carbonyl group.
  - Most of the monosaccharides that we will encounter are D-enatiomers.

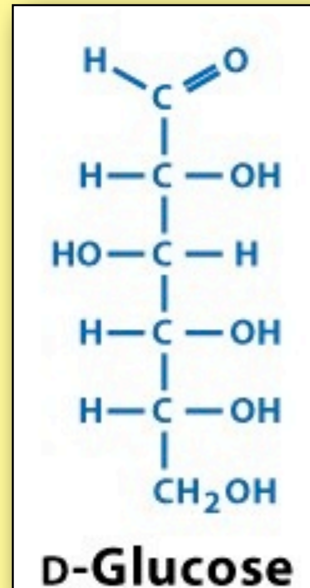
Monosaccharides

- Nomenclature for stereoisomers
  - **Enantiomers** are mirror images of one another
    - They share the same name and are distinguished using **D** and **L**.
  - **Diastereomers** are stereoisomers with multiple chiral centers that are not mirror images of one another.
  - **Epimers** are diastereomers that differ at only one chiral center.

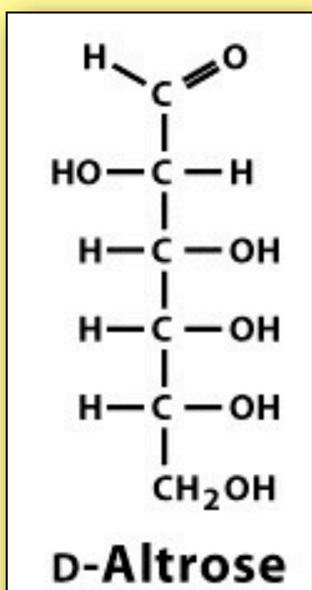
Monosaccharides

Question:

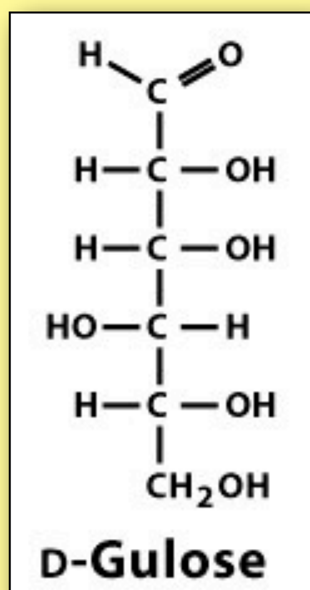
Which of following monosaccharides is an epimer of glucose:



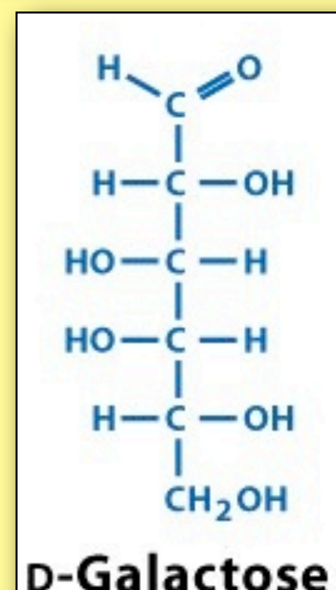
A.



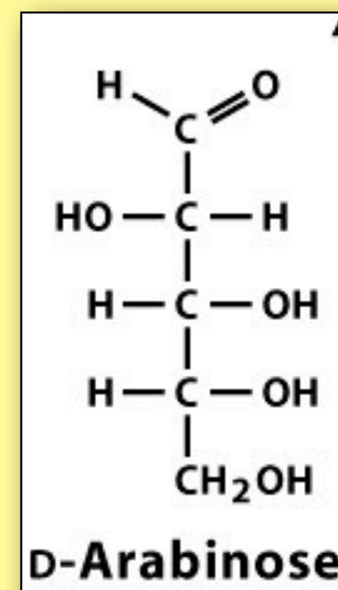
B.



C.

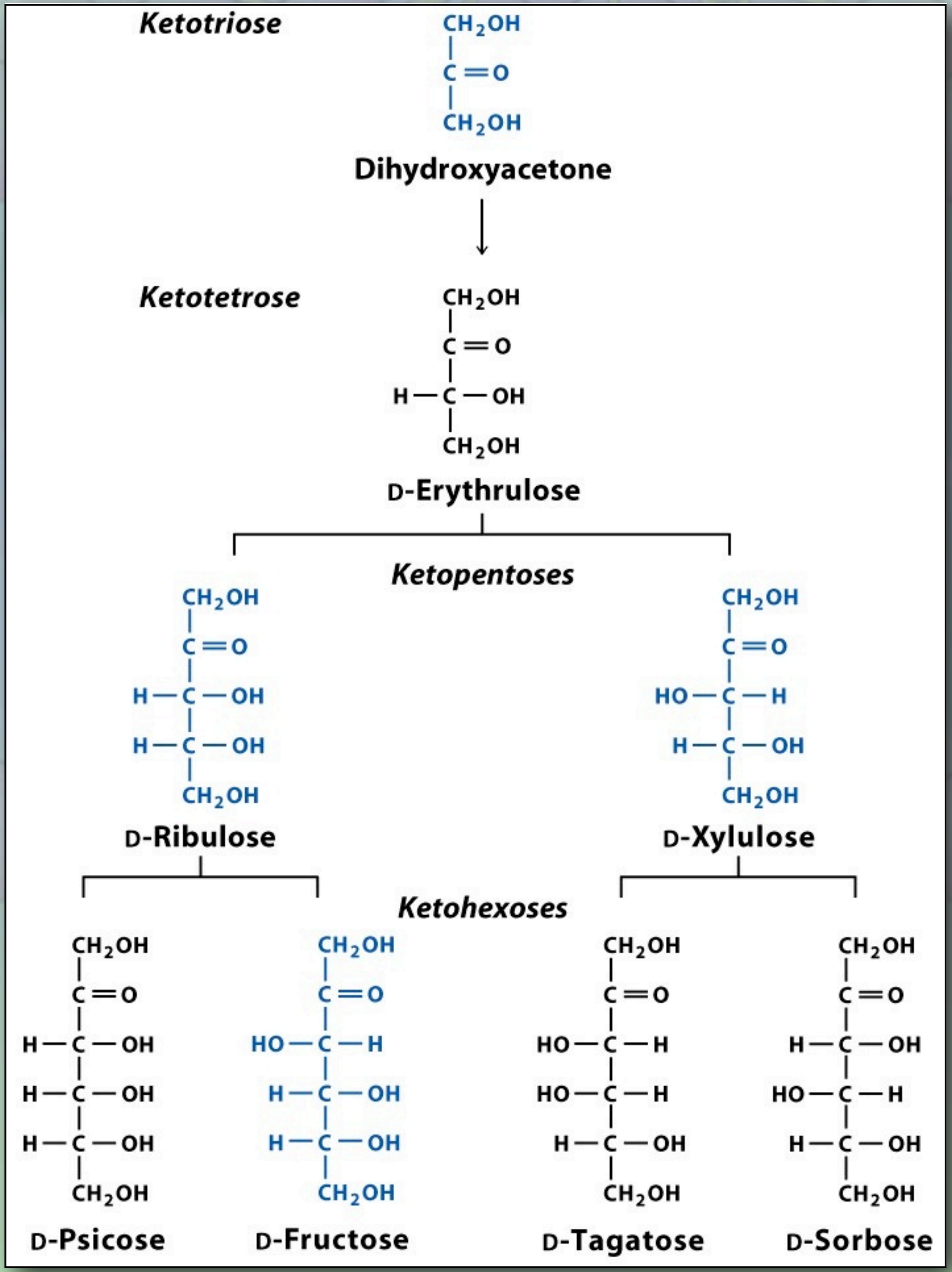


D.



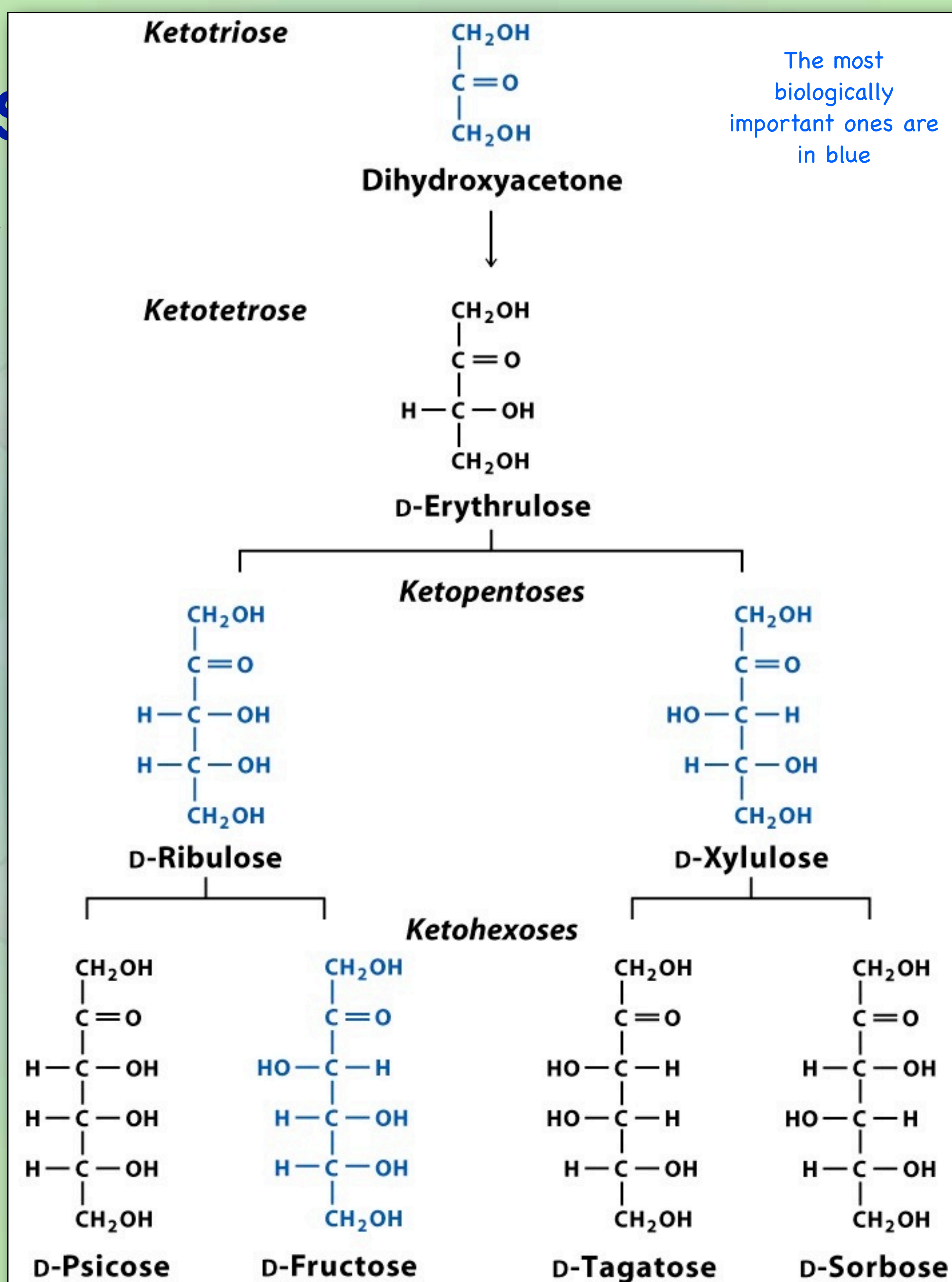
Monosaccharides

- Ketotrioses through ketohexoses



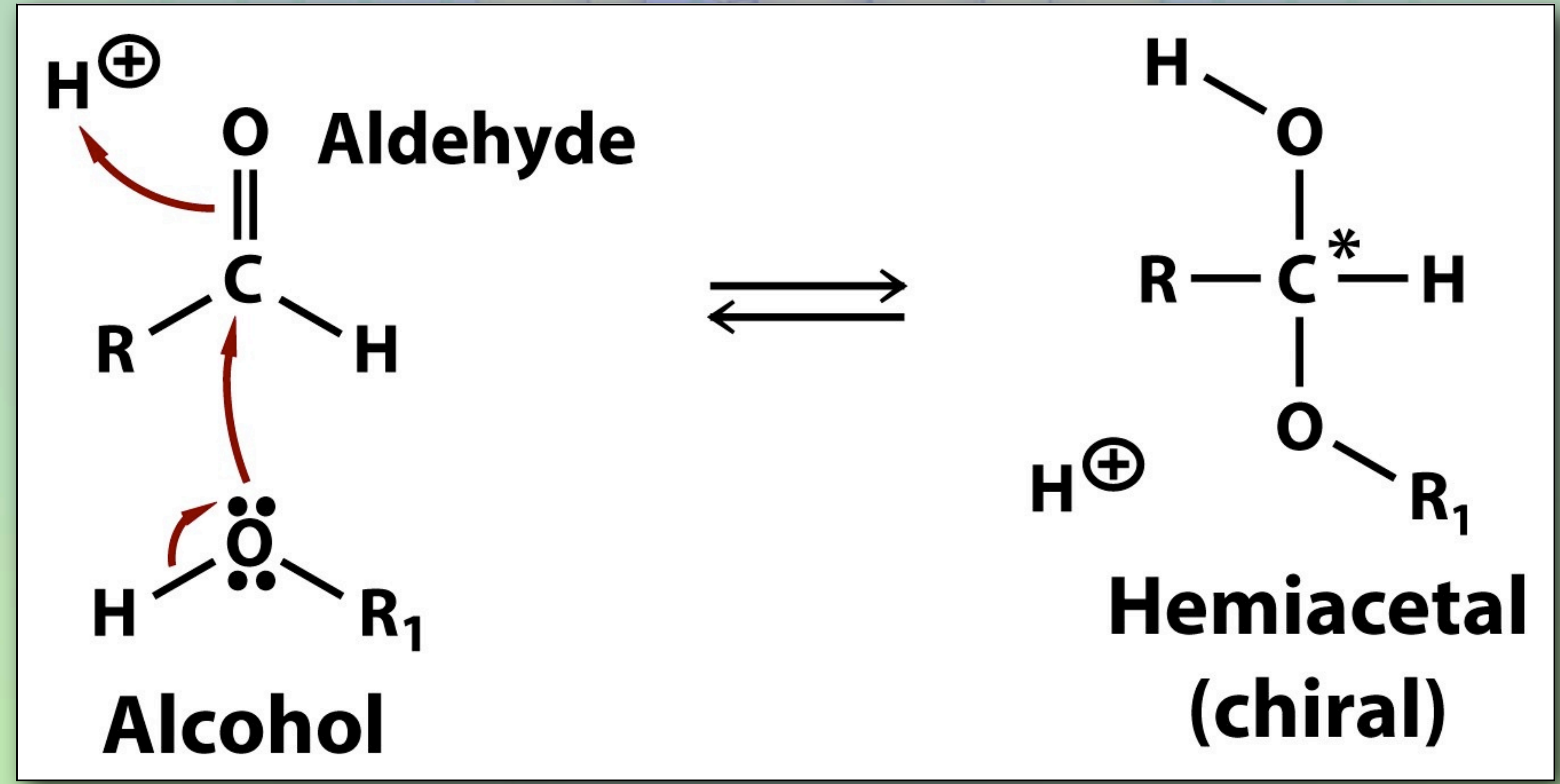
Monos

- Ketotri



Monosaccharides

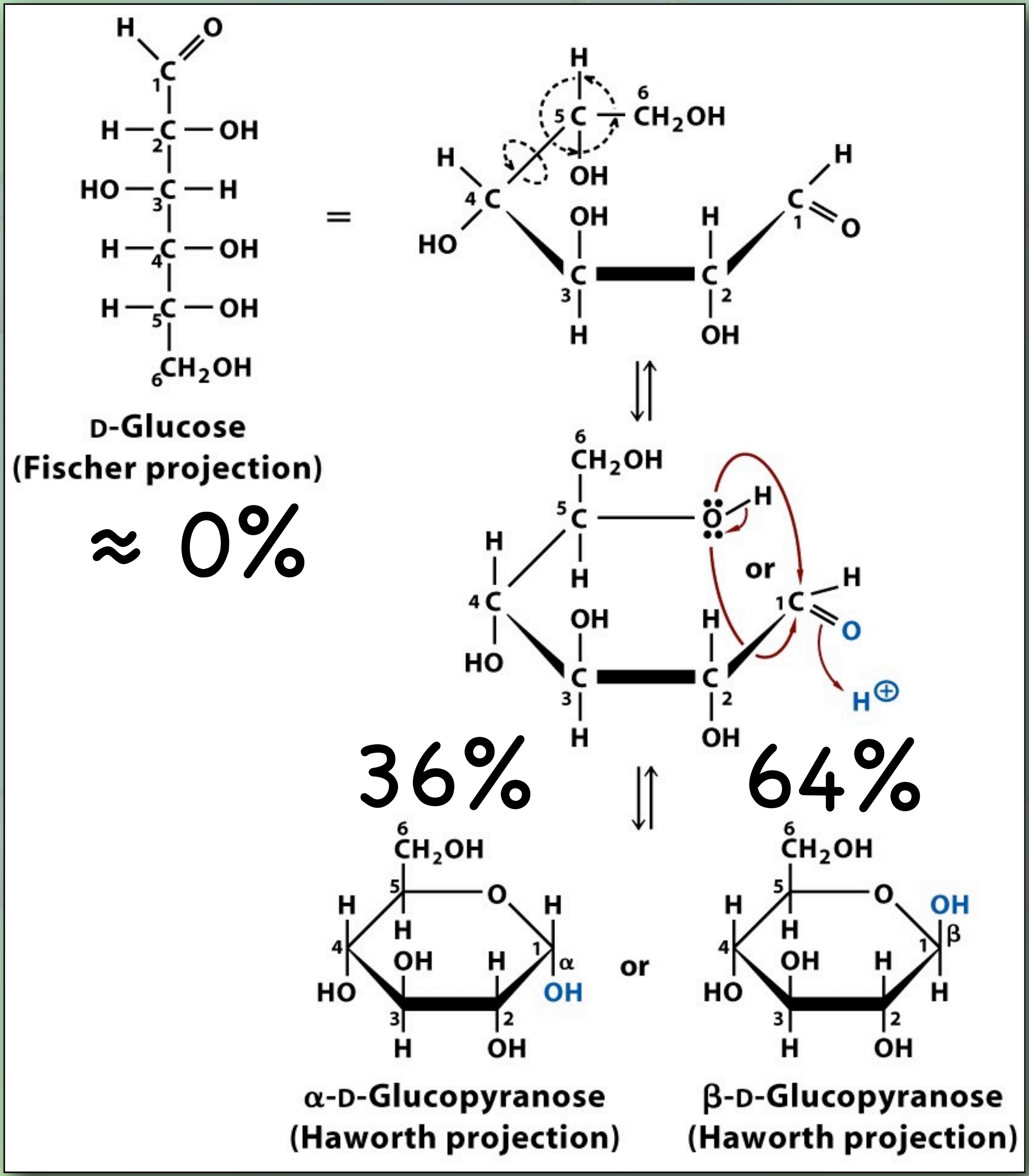
- The aldehyde and ketone groups are reactive.
  - The aldehyde or ketone group can react with a hydroxyl group to form a hemiacetal or hemiketal, respectively.



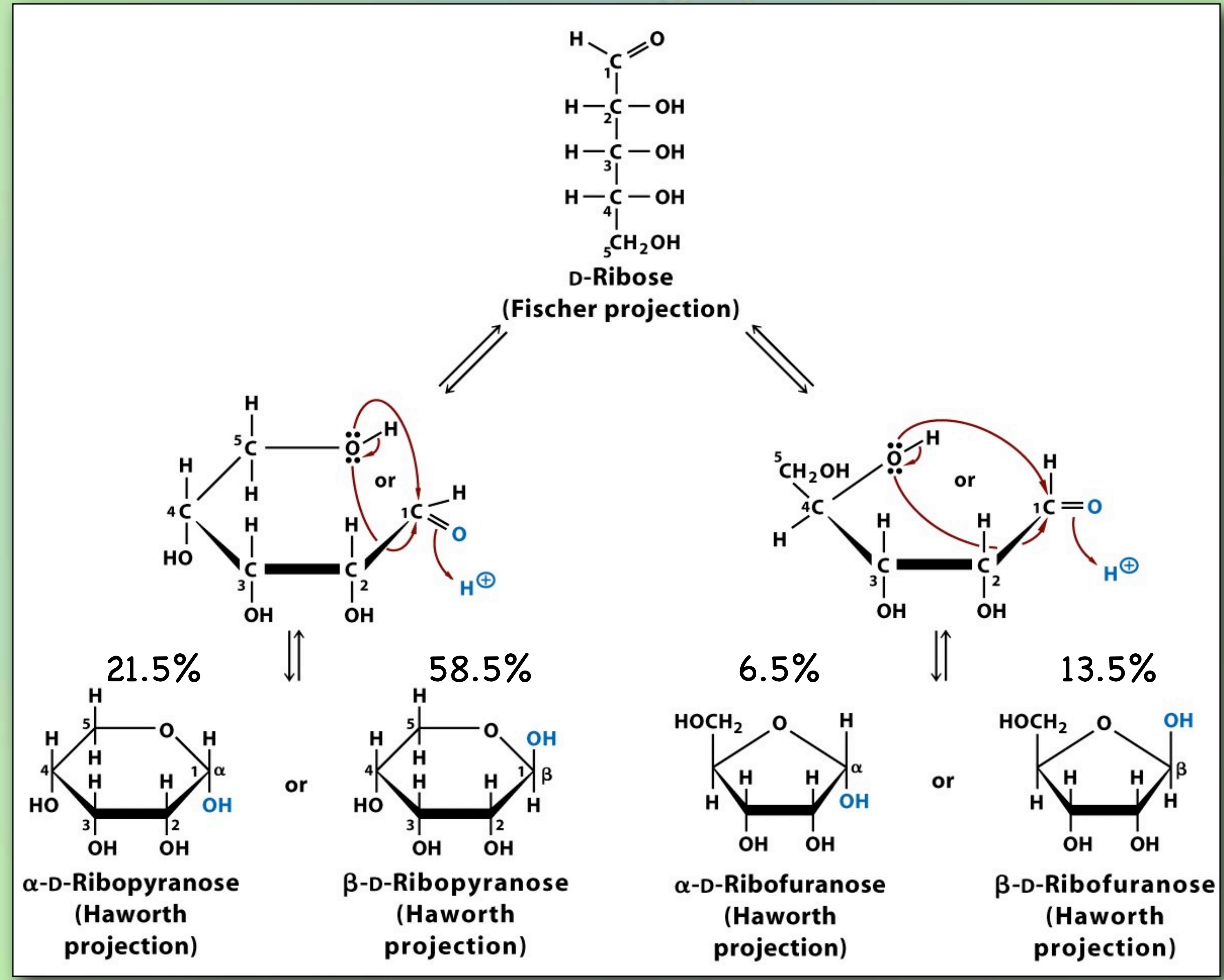
Monosaccharides

- Cyclization of aldoses and ketoses
  - The aldehyde or ketone react with one of the hydroxyl groups to form a hemiacetal or hemiketal, respectively.
  - This produces an additional chiral carbon.
    - The carbon is called the **anomeric carbon.**
    - The two new stereoisomers are referred to as the α and β anomers.

Monosaccharides



Monosaccharides



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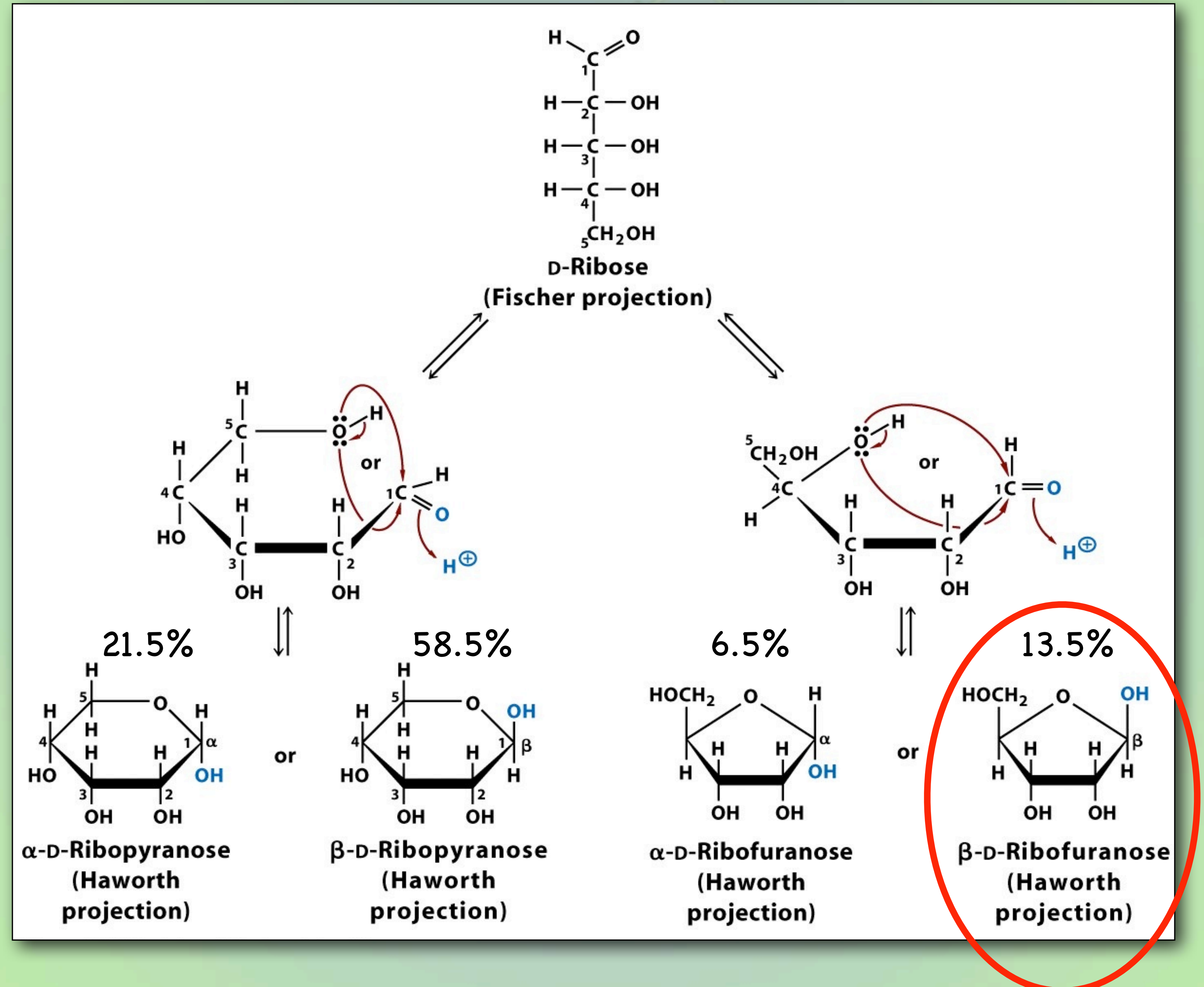
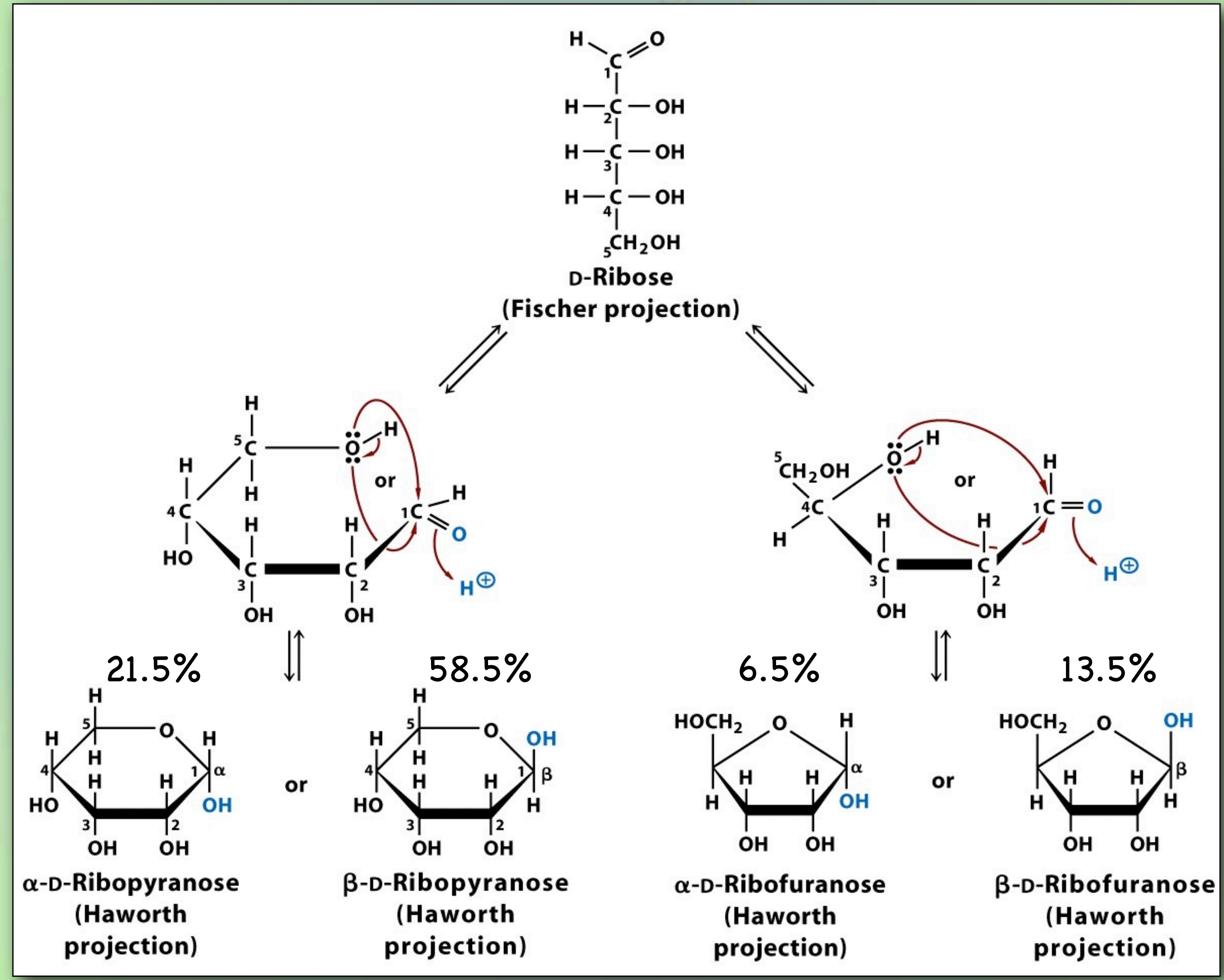
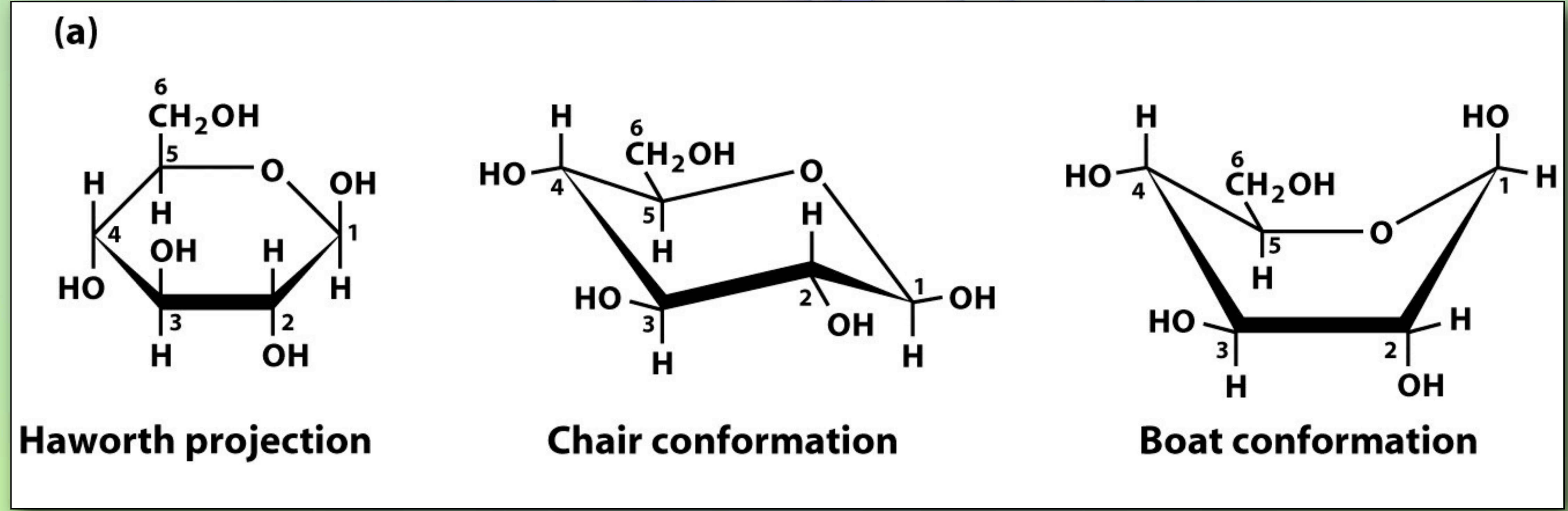


Monosaccharides



Monosaccharides

- Conformations of Monosaccharides
  - Monosaccharides can have different conformations.



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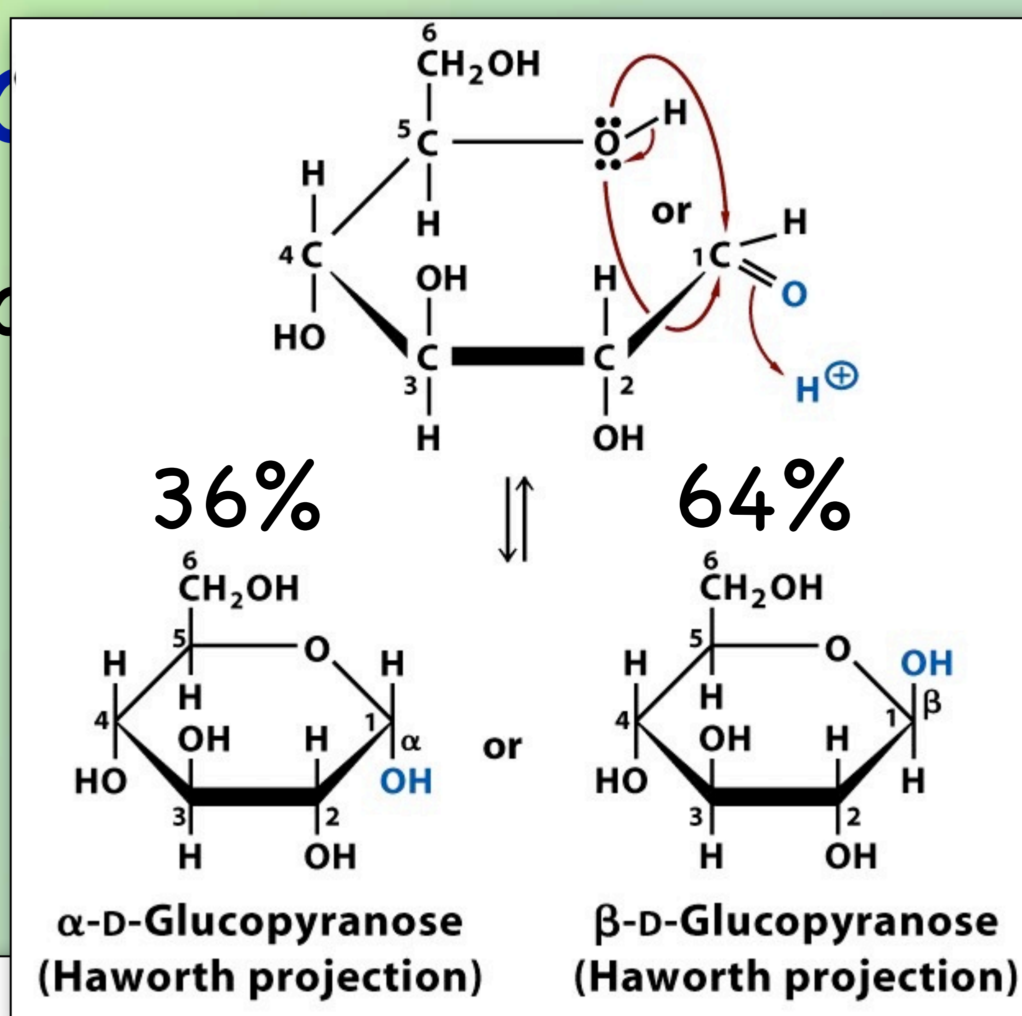

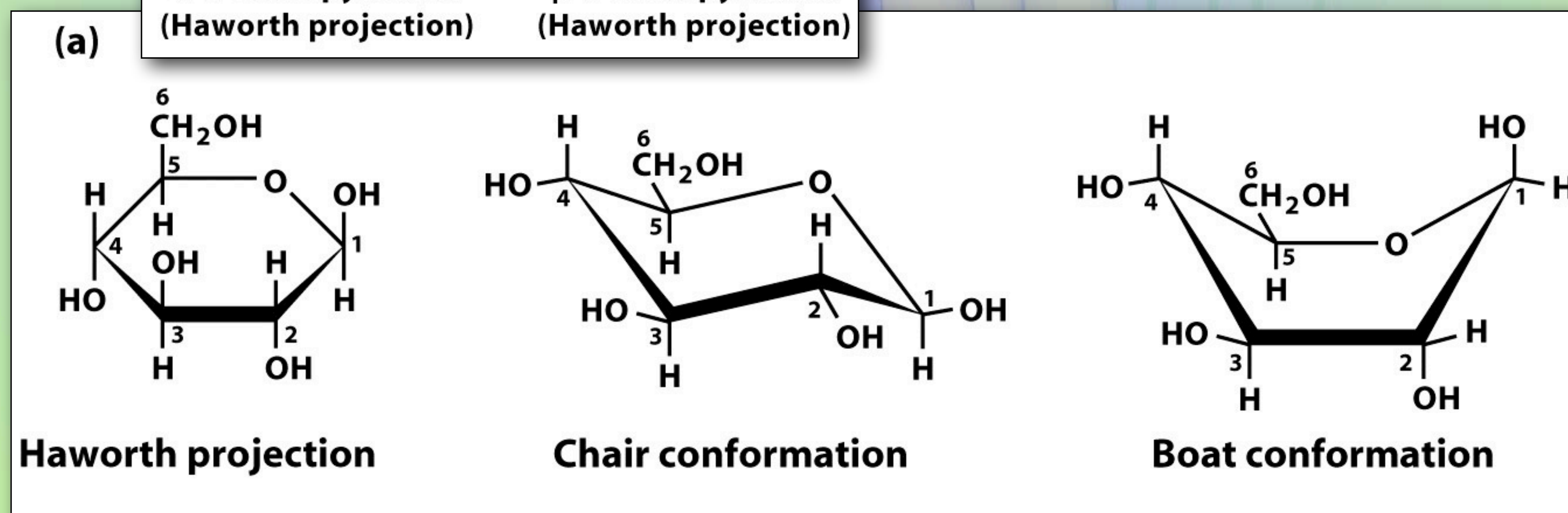

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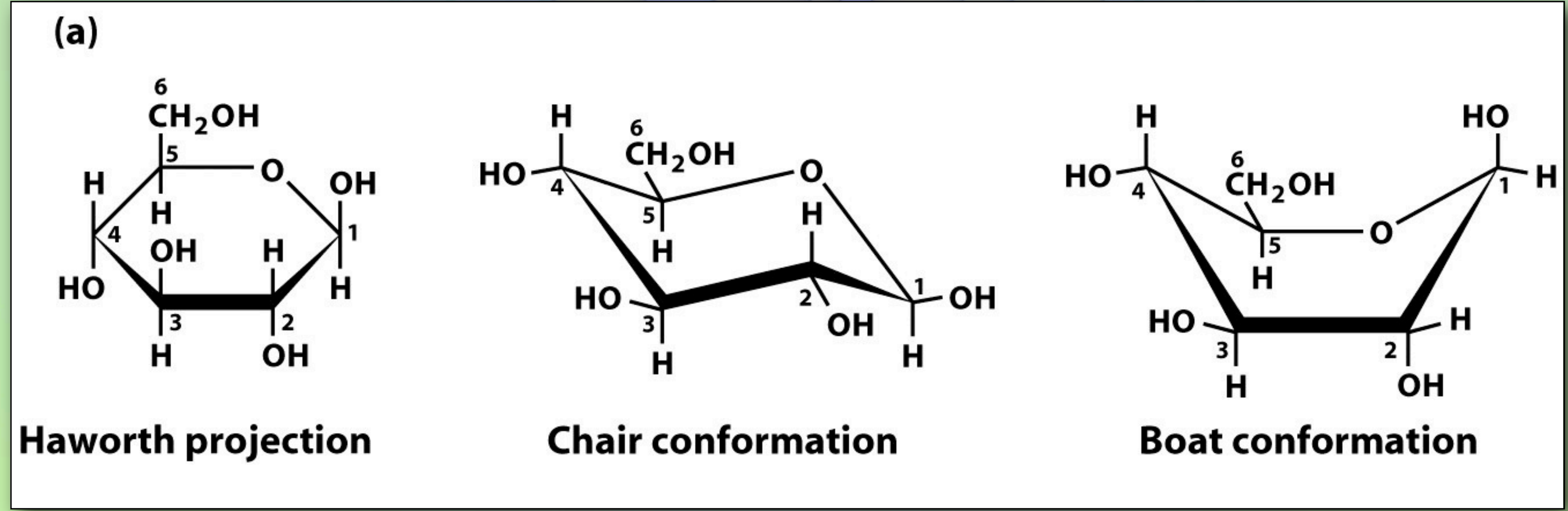

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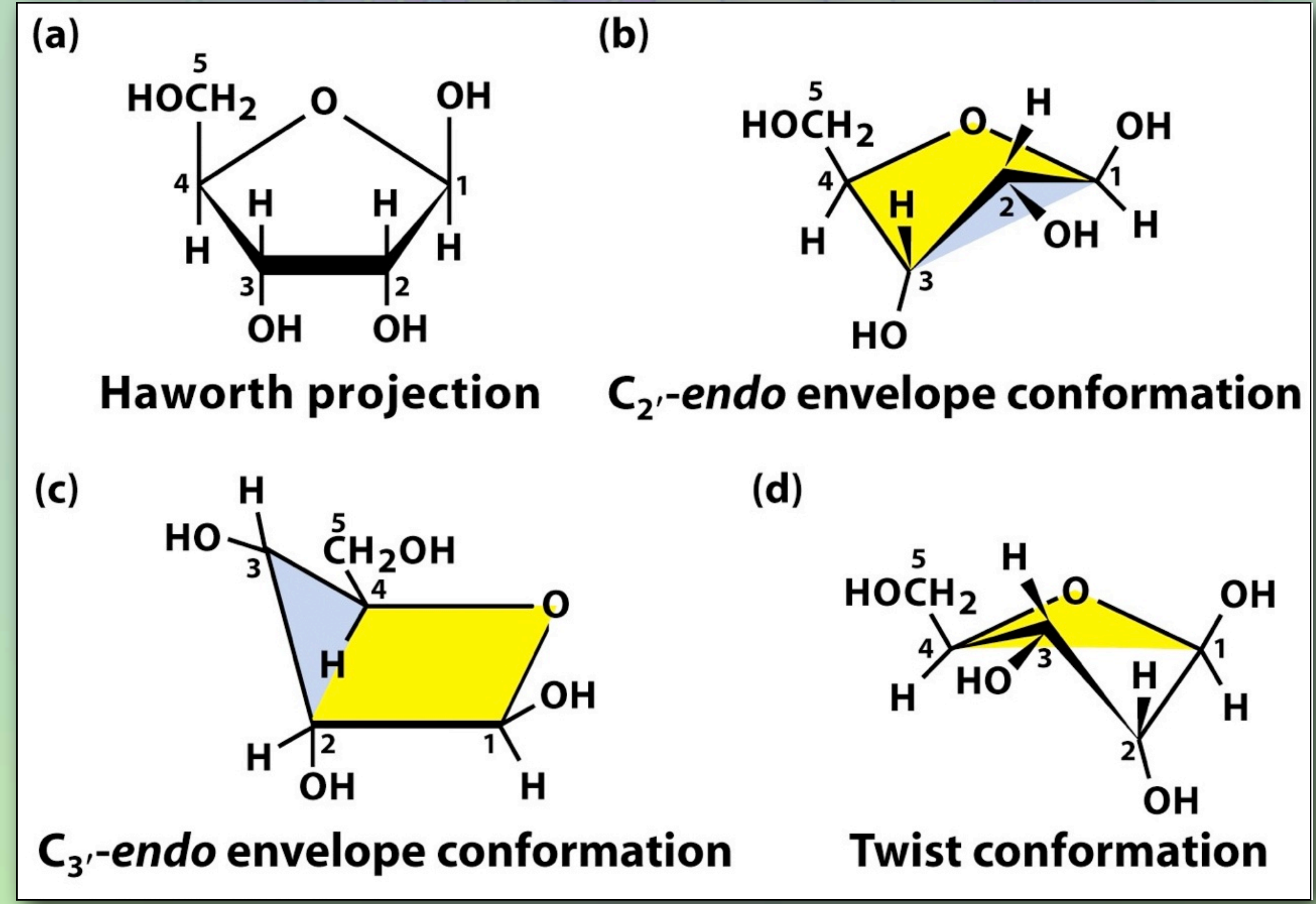


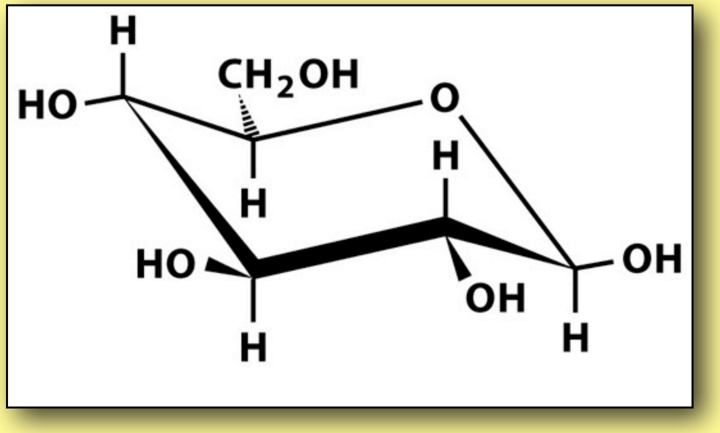
Monosaccharides

- Conformations of Monosaccharides

Question:

Which of following conformations for β-D-glucopyranose is predicted to be more stable:

A.



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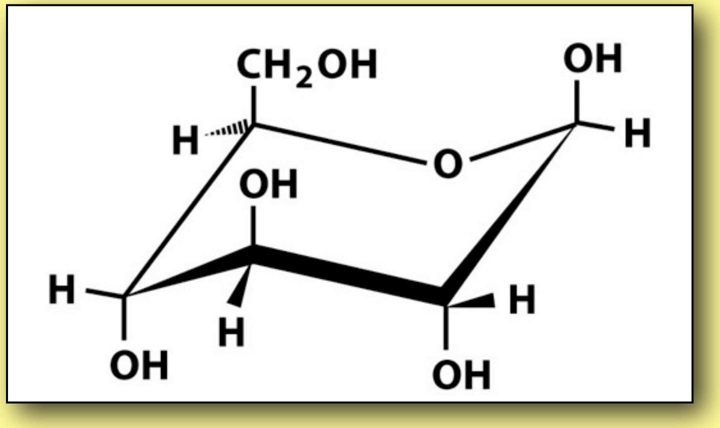

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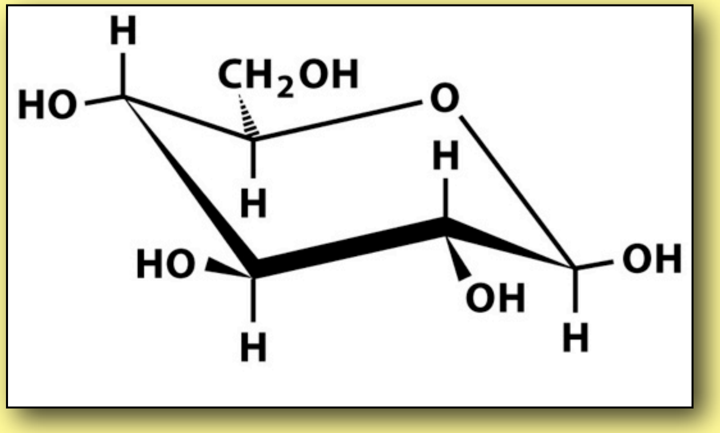

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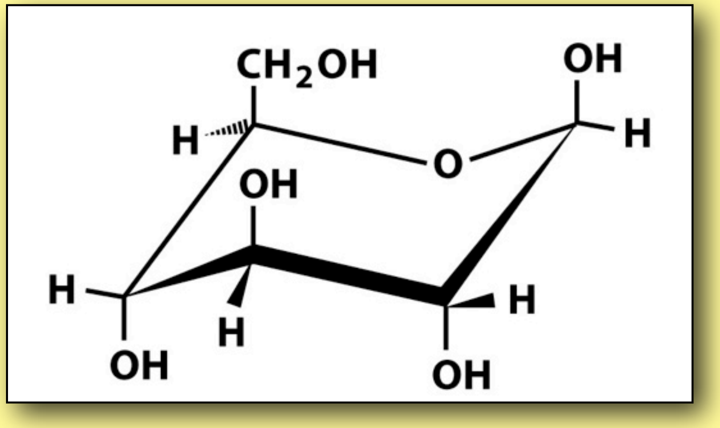

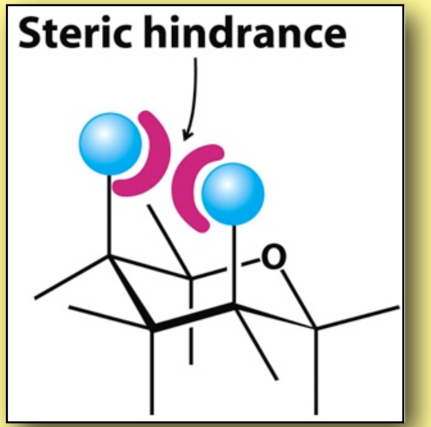

Monosaccharides

- Monosaccharides can be chemically modified to produce derivative.
  - **Phosphate esters**
  - **Deoxy sugars**
    - One of the hydroxyl groups is replaced with a hydrogen
  - **Amino sugars**
    - One of the hydroxyl groups is replaced with an amino group.

Monosaccharides

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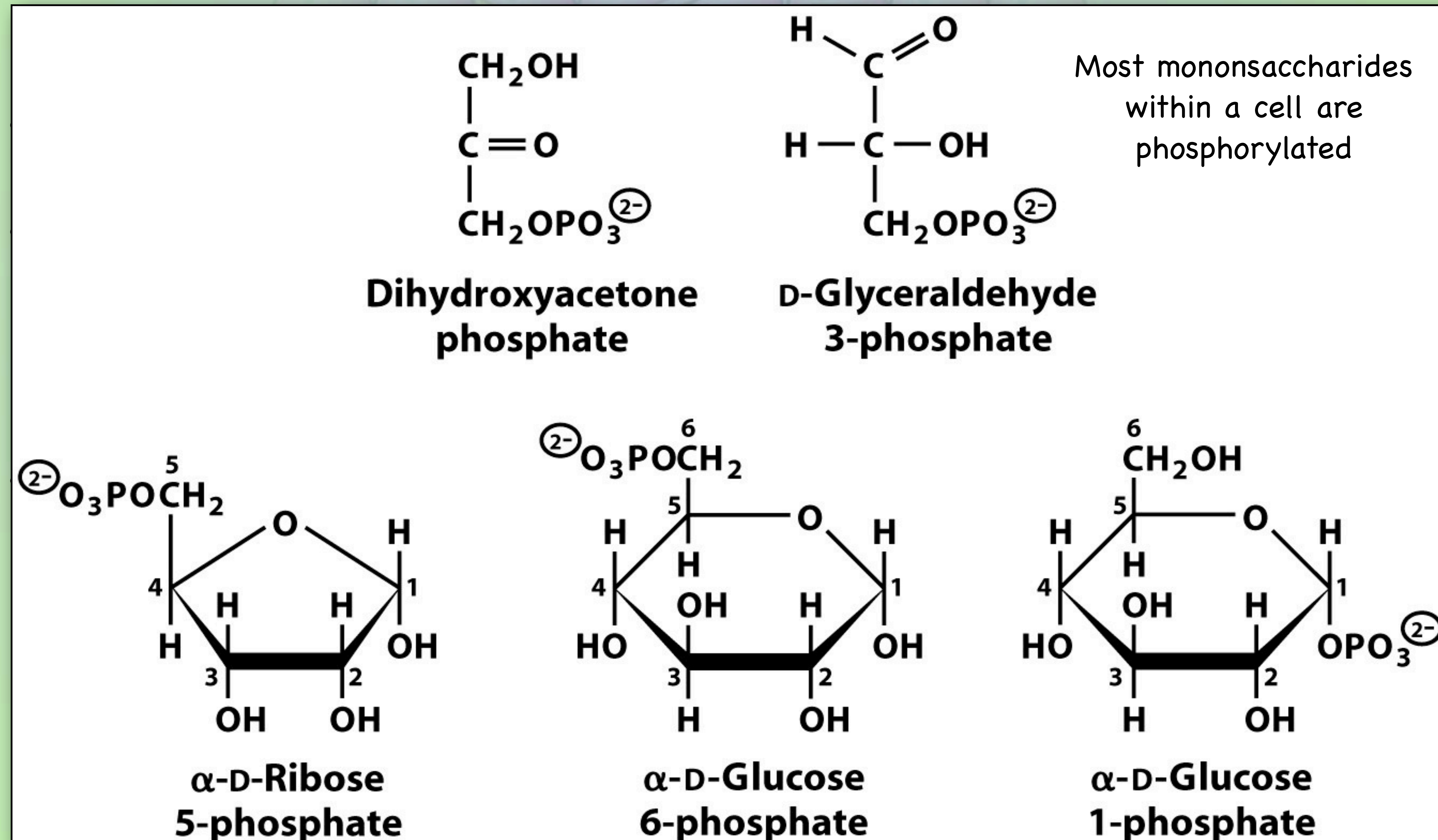

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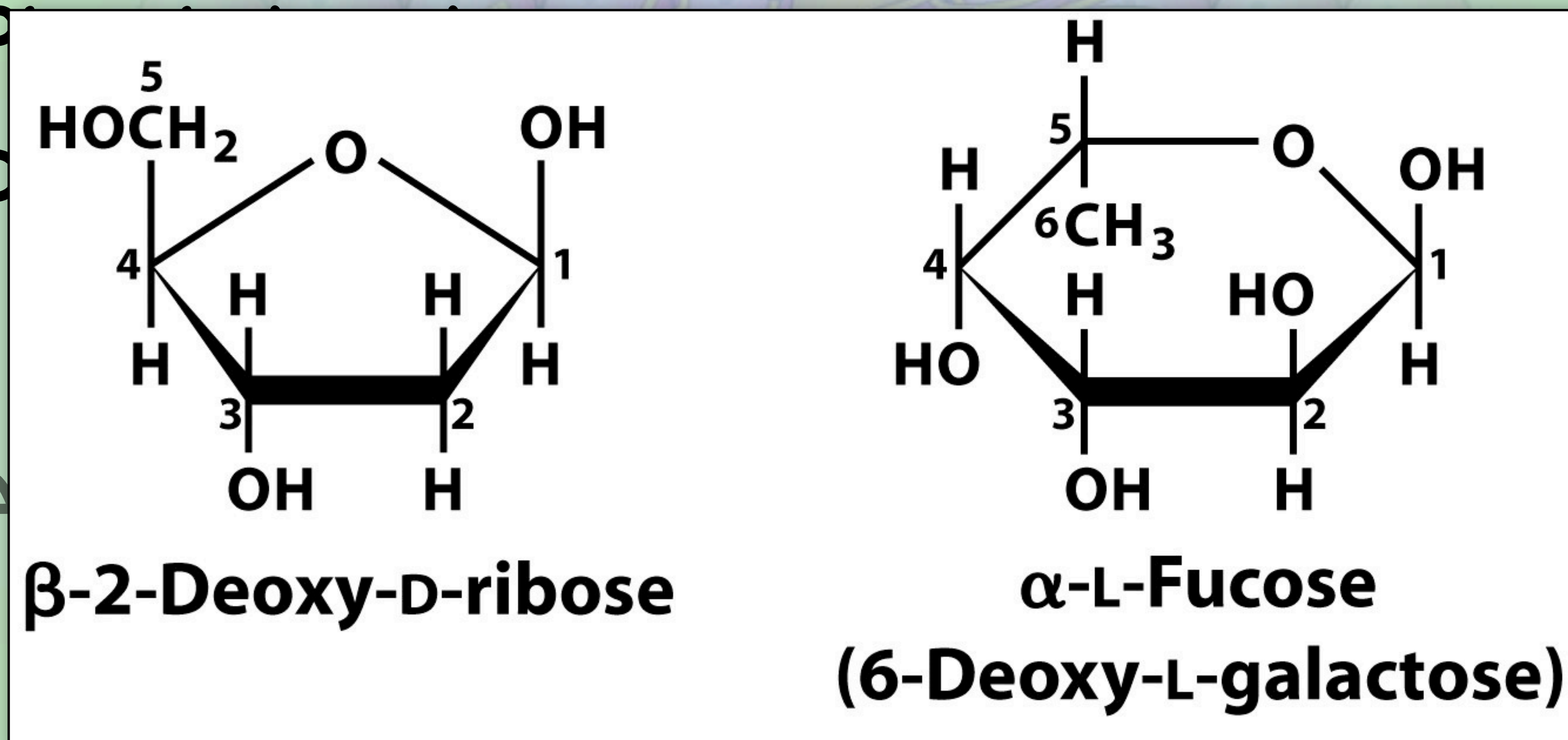

Monosaccharides

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  - **Phosphate esters**
  - **Deoxy sugars**
    - One of the hydroxyl groups is replaced with a hydrogen
  - **Amino sugars**
    - One of the hydroxyl groups is replaced with an amino group, which is often acetylated.

Monosaccharides

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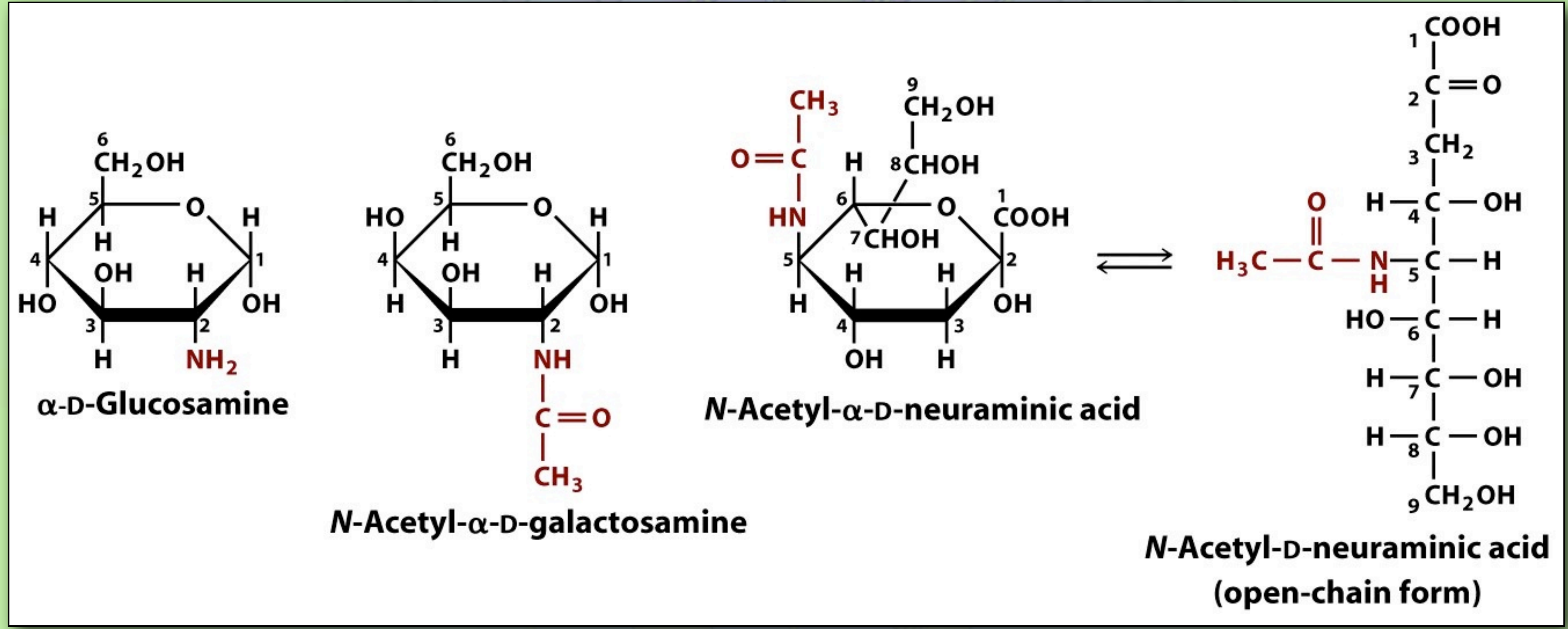
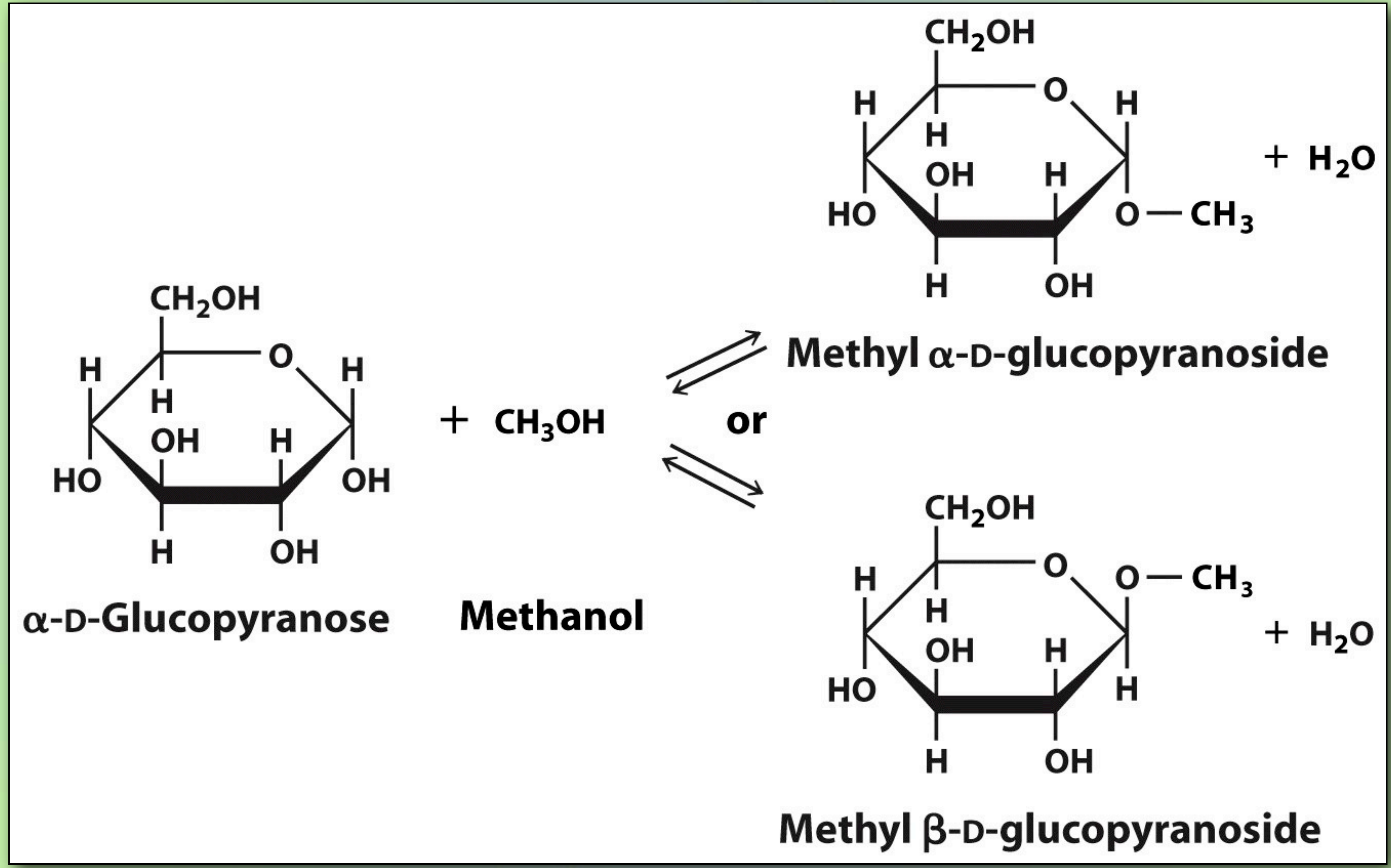


Glycosides

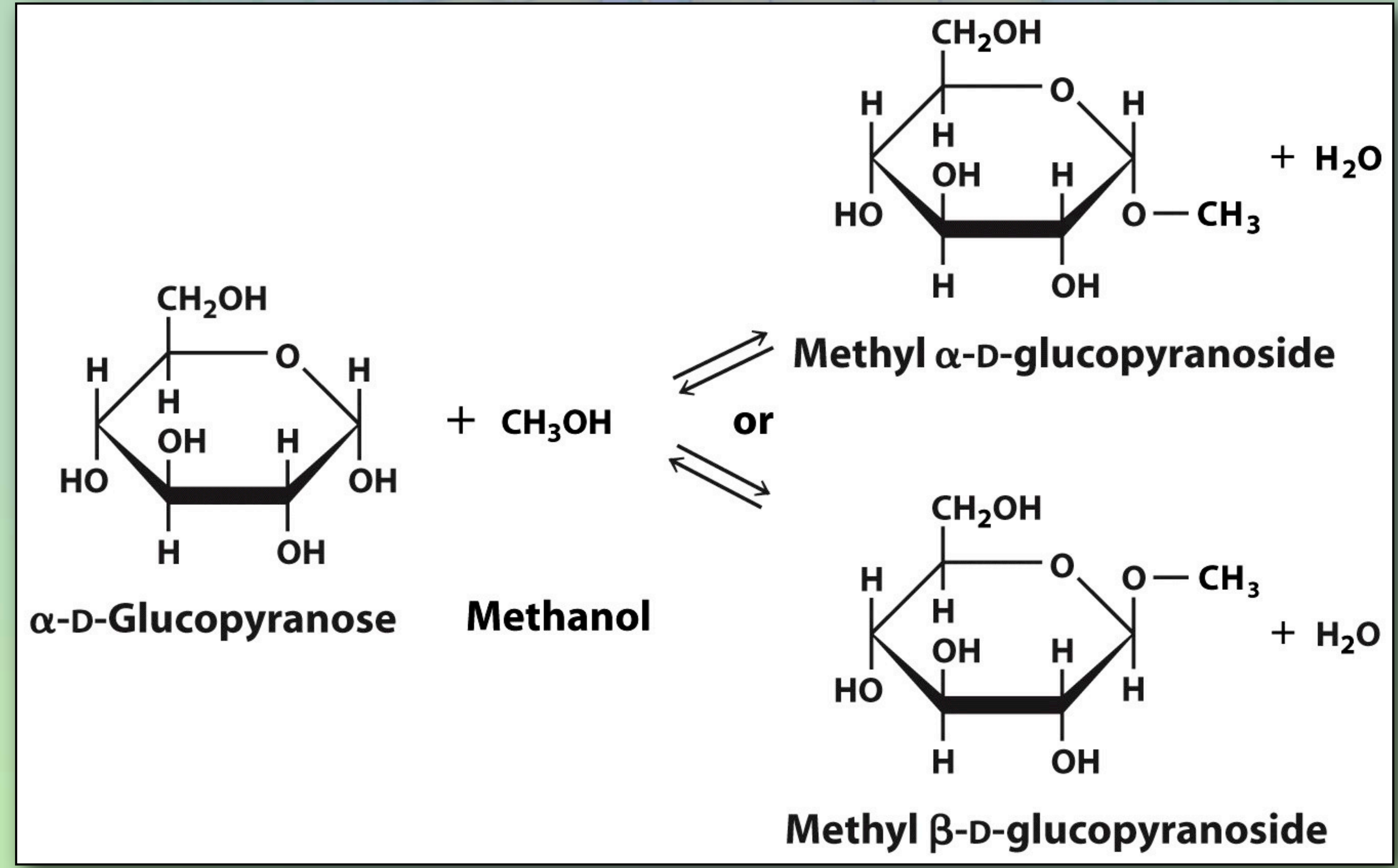
- The hemiacetal or hemiketal carbon (the anomeric carbon) can react with a hydroxyl group to form an **acetal** or **ketal**.
  - The bond formed is also called a **glycosidic bond**.

Glycosides


CH2OH
H
O
H
H
OH
H
HO
OH
H
OH
+ CH3OH
or
α-D-Glucopyranose
Methanol
Methyl α-D-glucopyranoside
+ H2O
O — CH3
Methyl β-D-glucopyranoside

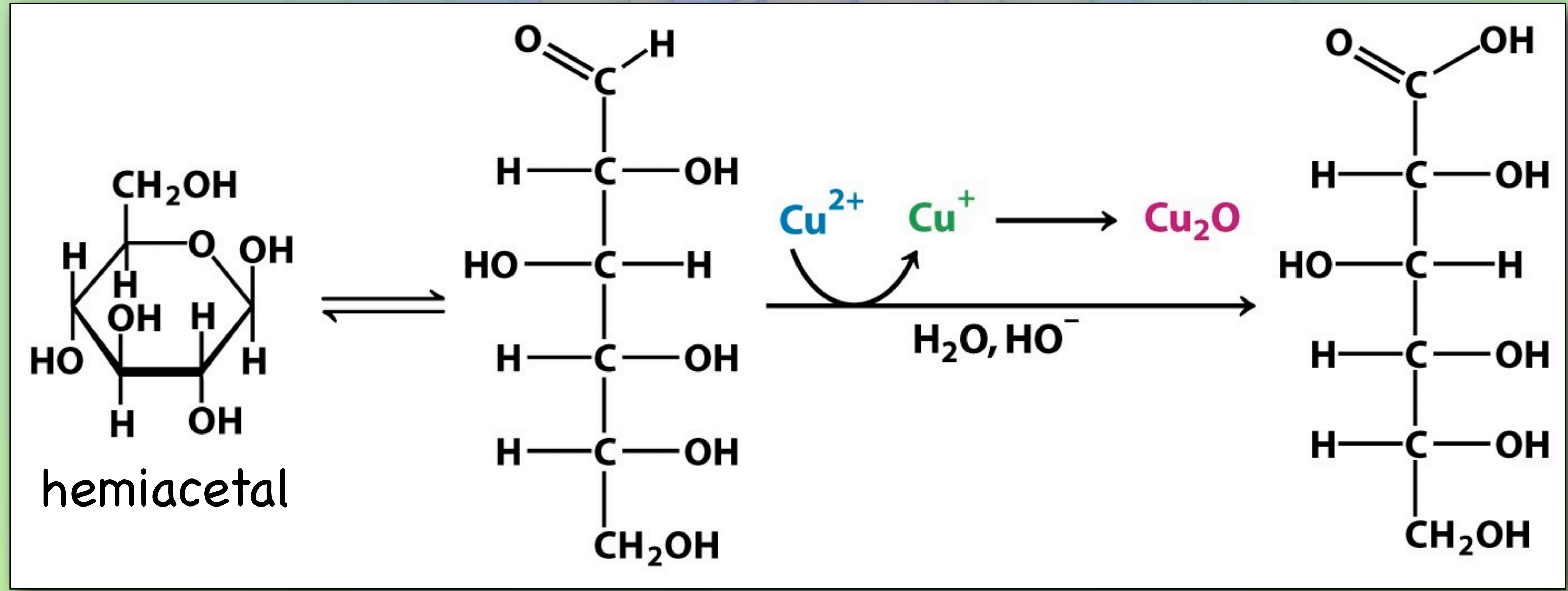
Glycosides

- Unlike hemiacetals and hemiketals, acetals and ketals prevent the pyranose or furanose ring from reopening.



Glycosides

- Cu^{2+} can be used to distinguish hemiacetals and hemiketals from acetals and ketals.
  - Sugars that contain hemiacetals or hemiketals can reduce Cu^{2+} to Cu^{+} and are called **reducing sugars**.



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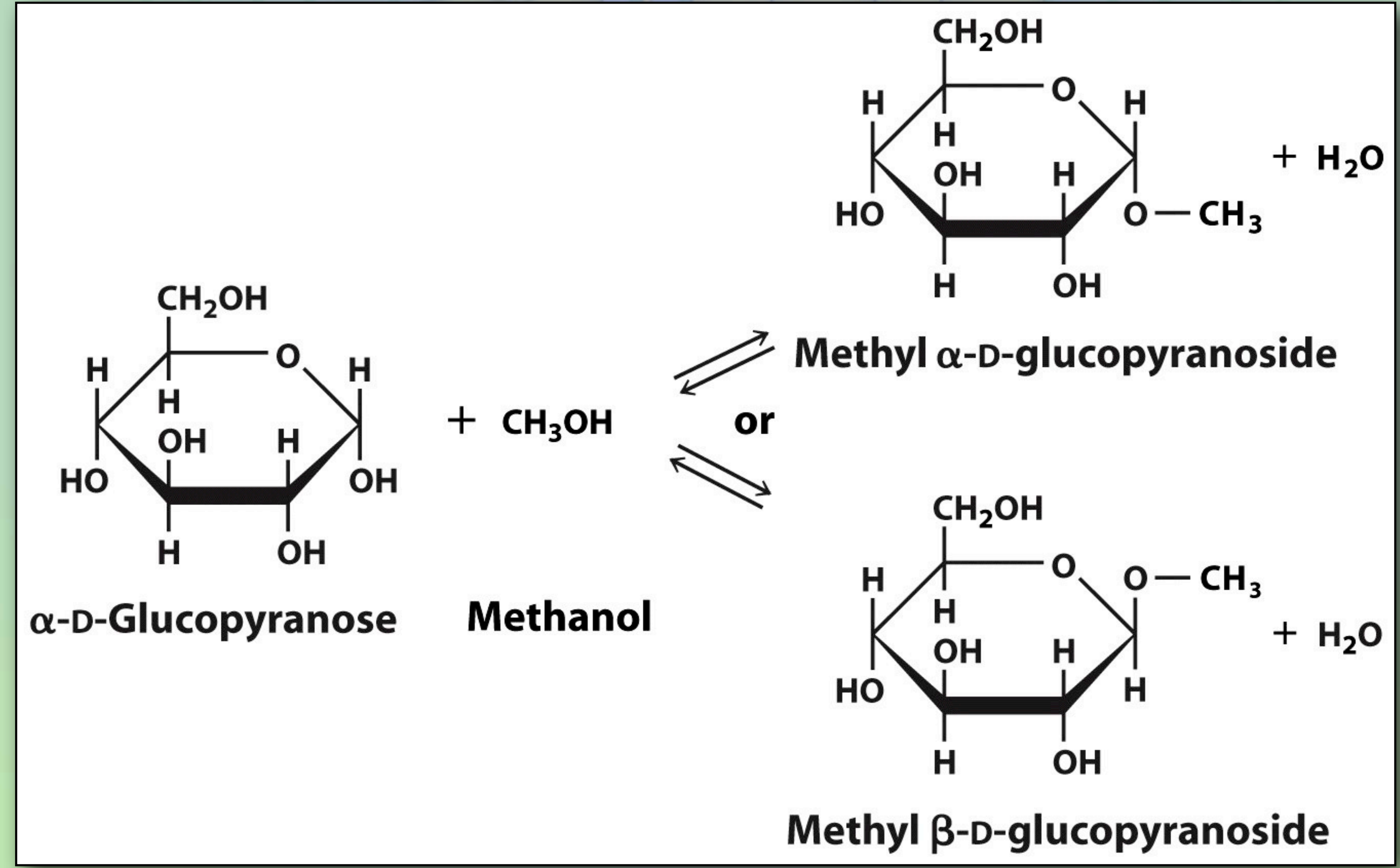

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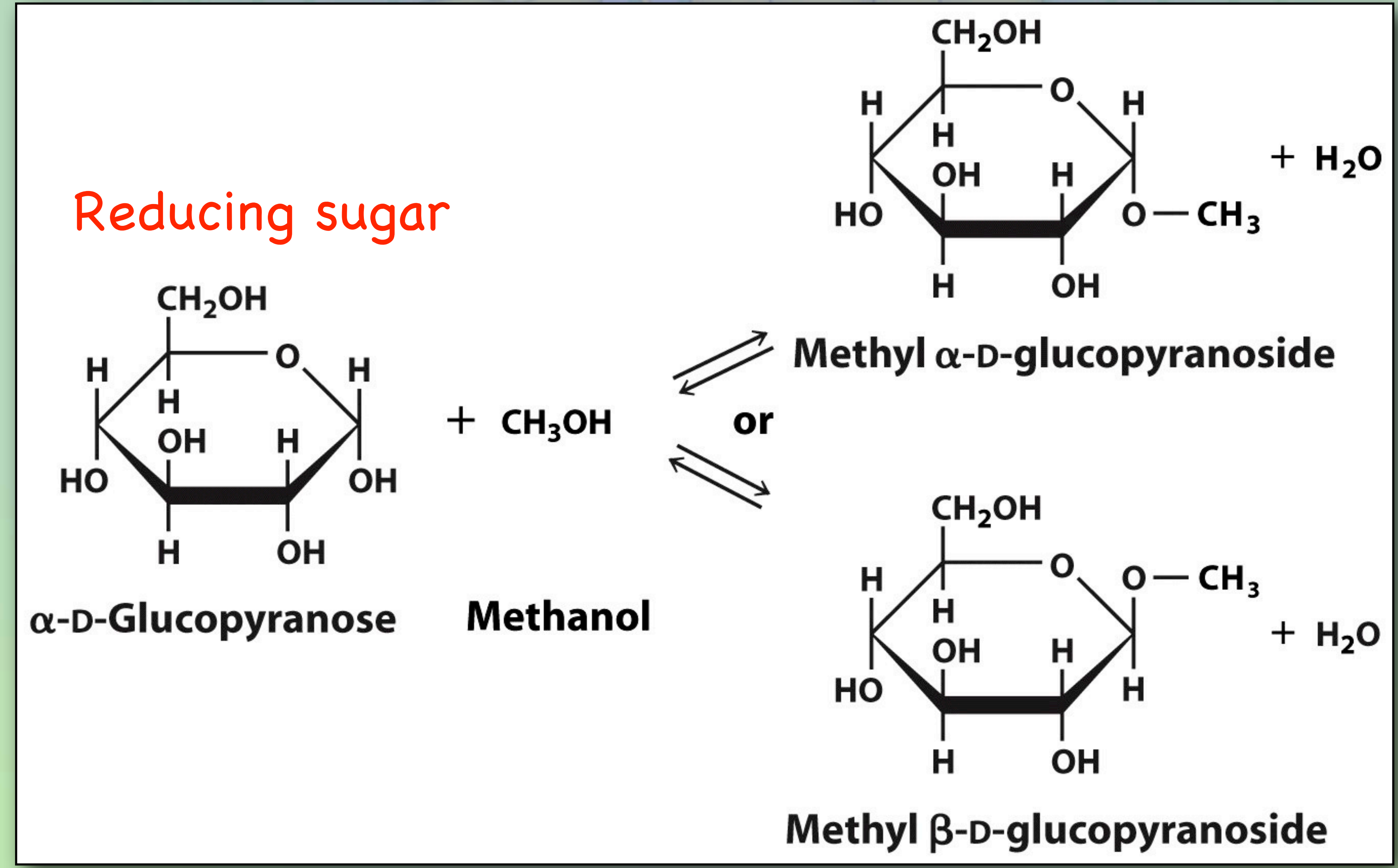

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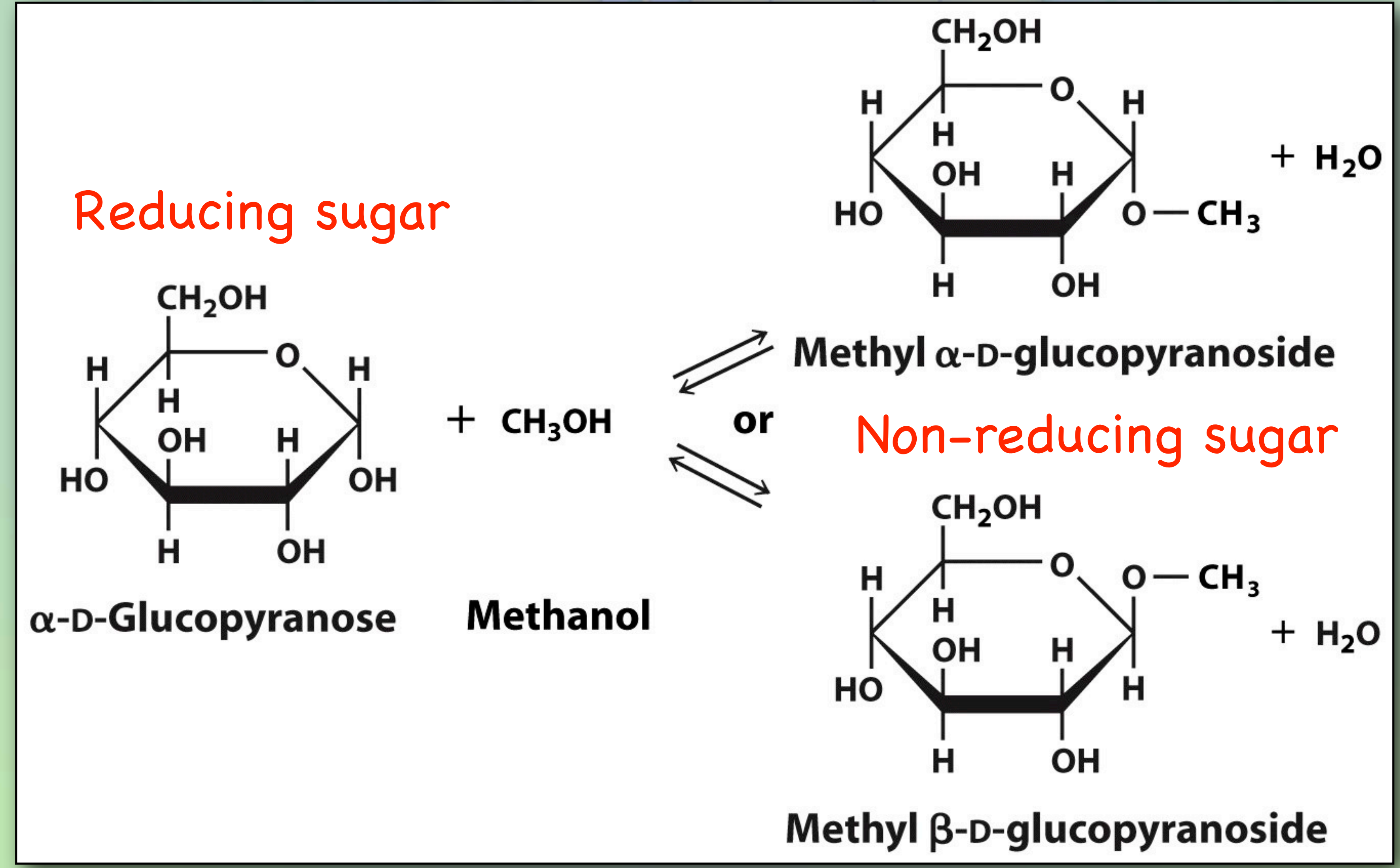

Complex Carbohydrates

- The glycosidic bond is used to connect two monosacchrides together to form a **complex carbohydrates**.
- monosaccharide + monosaccharide = **disaccharide**

- Important disaccharides include
  - Maltose (obtained from starch)
  - Cellobiose (obtained from cellulose)
  - Lactose (milk sugar)
  - Sucrose (table sugar)

Complex Carbohydrates

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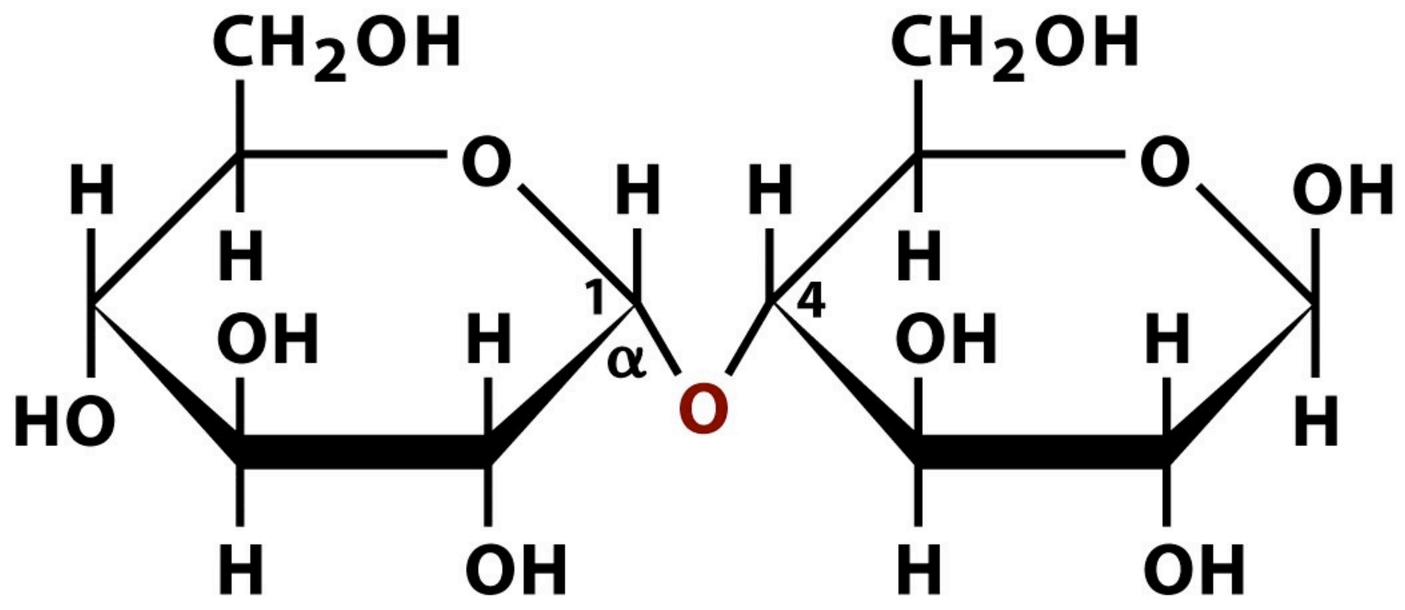

β anomer of maltose
(α-D-Glucopyranosyl-(1→4)-β-D-glucopyranose)

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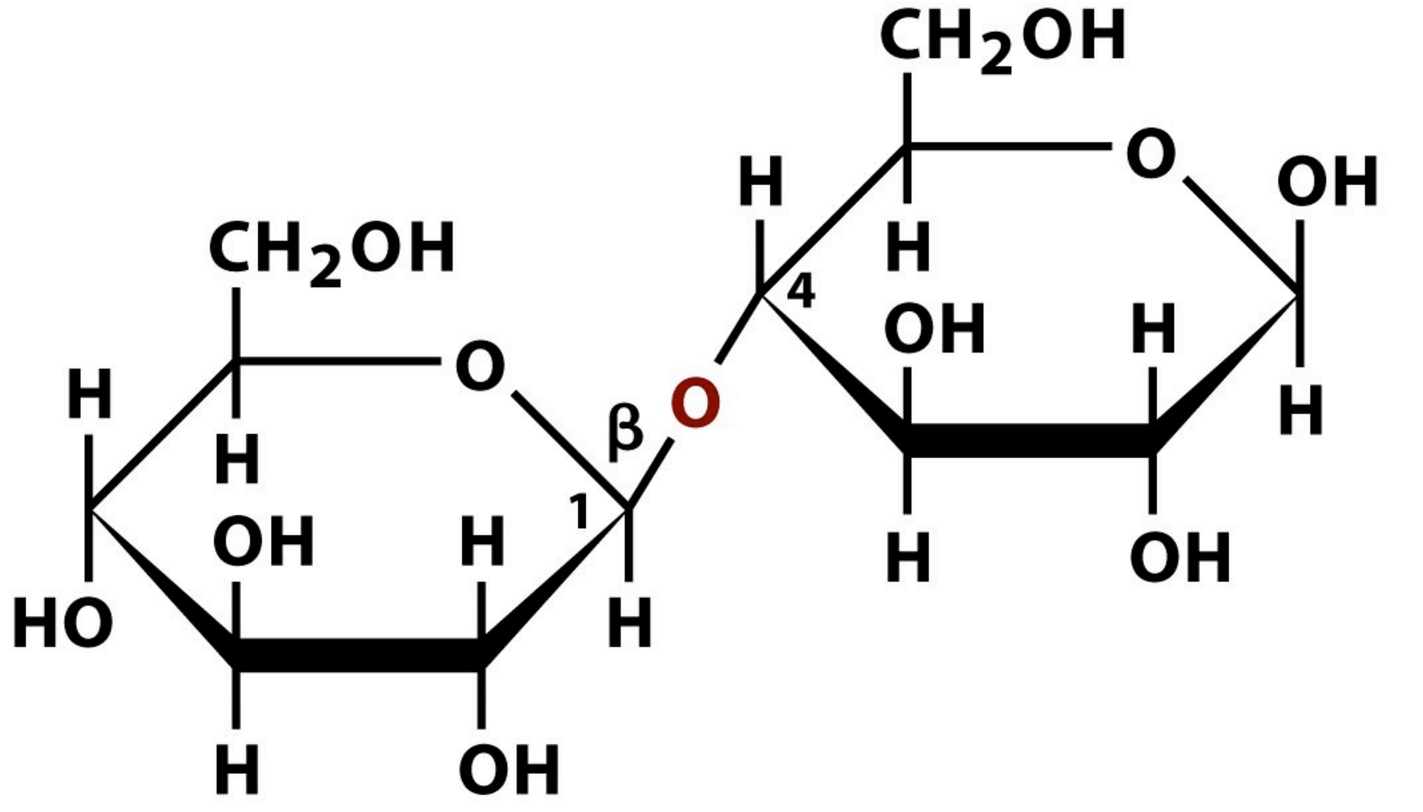
Complex Carbohydrates

- The glycosidic bond is used to connect two



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lex

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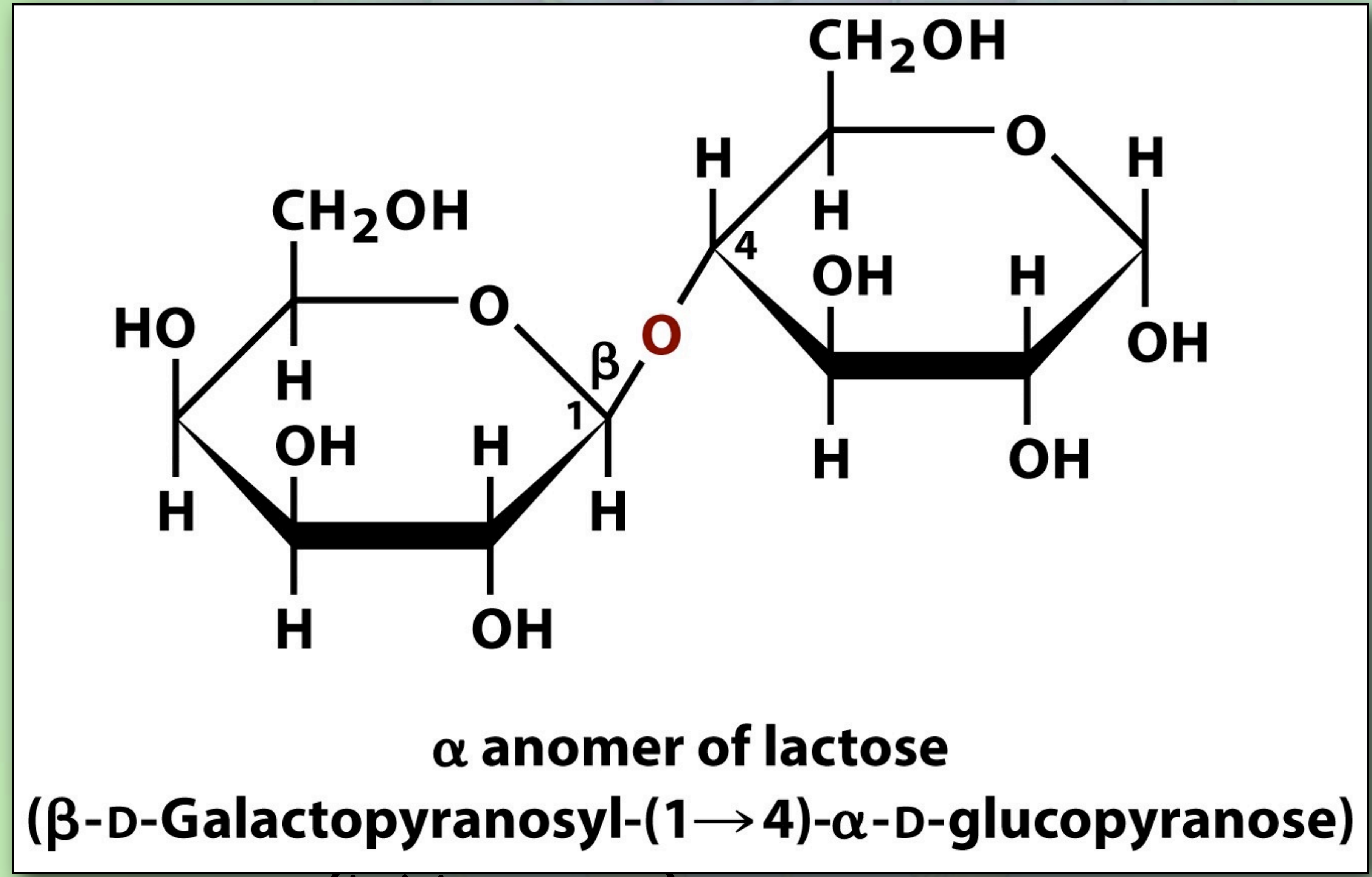

-
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Complex Carbohydrates

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  lex
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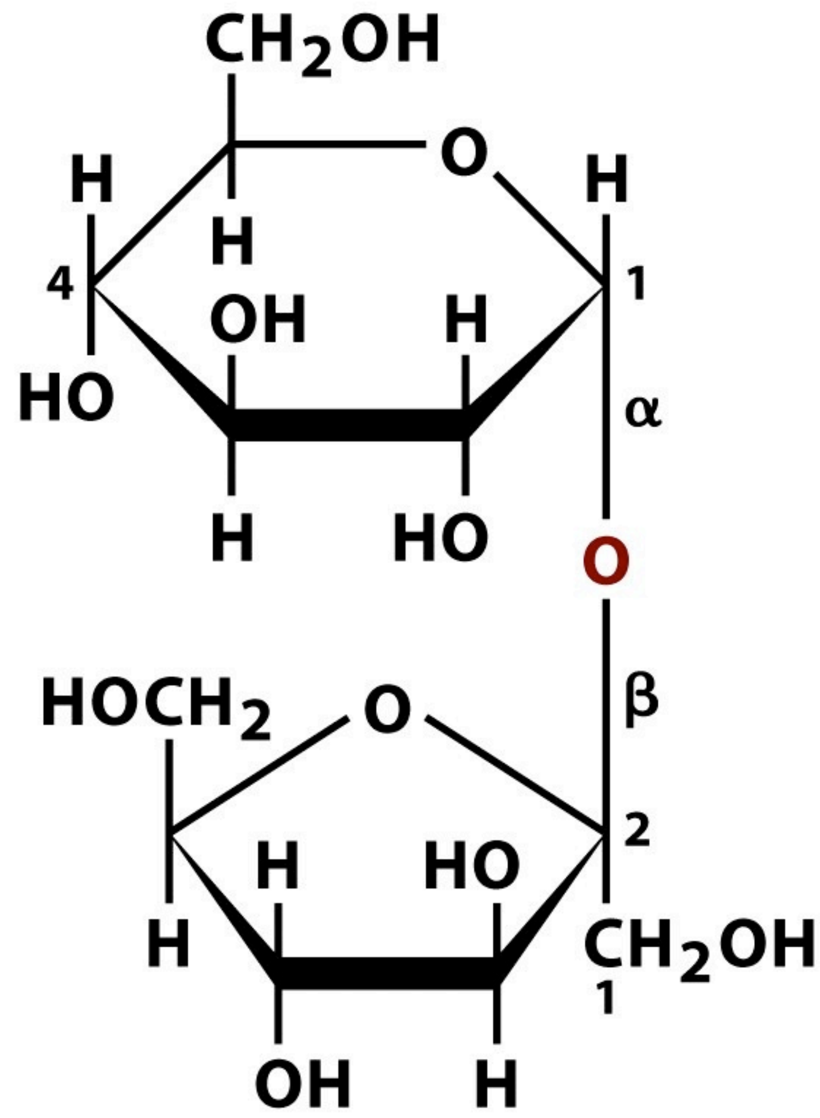

Sucrose

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Complex Carbohydrates

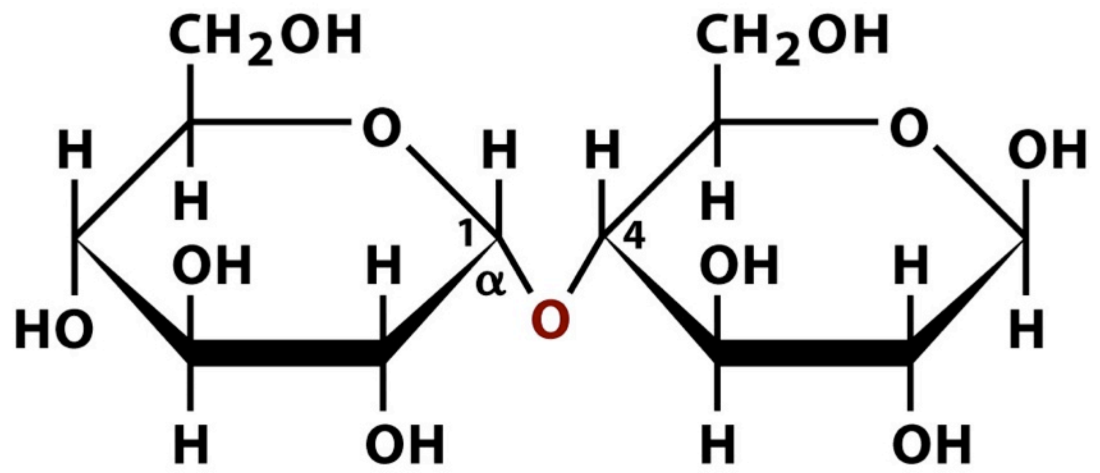
- Because a hemiacetal or hemiketal can open and expose an aldehyde or ketone, they can still serve as reducing agents.
  - This is used to distinguish the two monosaccharides in a disaccharide as the **reducing** and the **nonreducing** ends.

Complex Carbohydrates

Question:

Which end of the disaccharide maltose is the reducing end?

A. B.



β anomer of maltose

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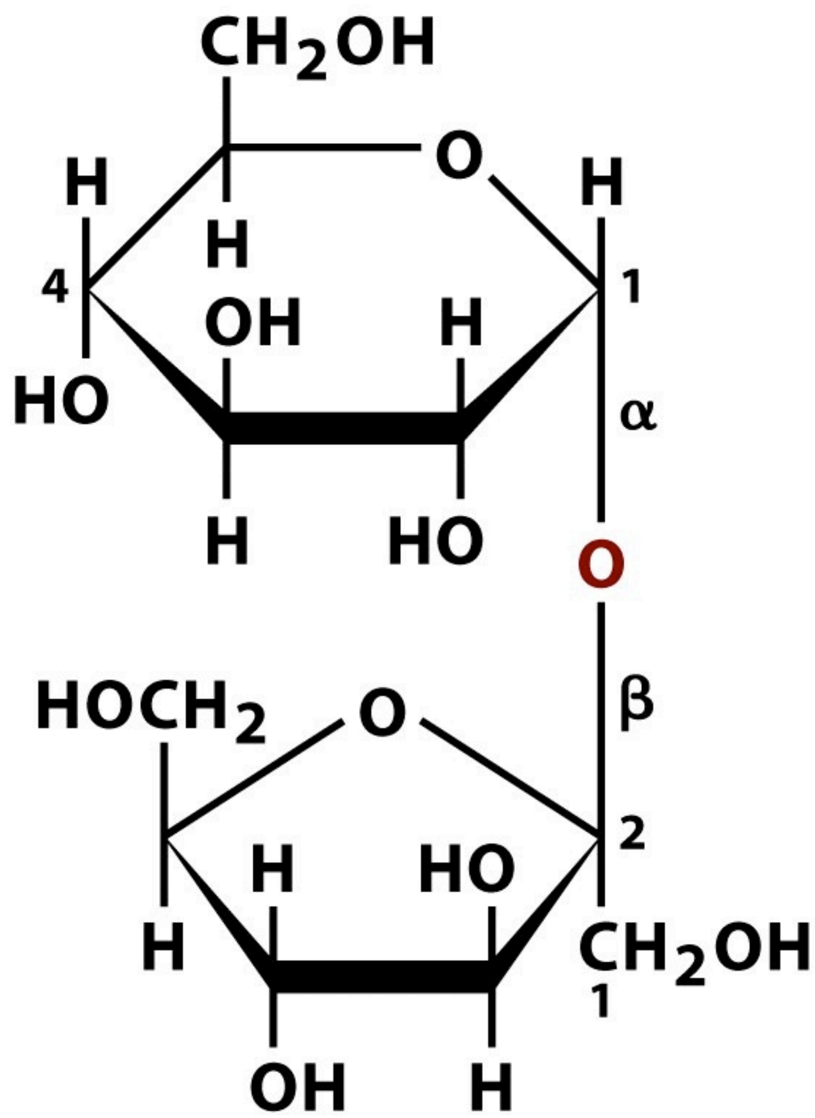
Complex Carbohydrates

- Not all disaccharides have a reducing end
  - For example, the disaccharide sucrose contains both and acetal and a ketal, but no hemiacetal or hemiketal.

Complex Carbohydrates

- No
  - F both
    a
    h



Sucrose

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Complex Carbohydrates

- Monosaccharides also from glycosidic bonds to non-saccharides.
  - For example, nucleotides.
    - ATP
    - UDP-glucose
    - NAD and NADP
    - FMN and FAD

Complex Carbohydrates

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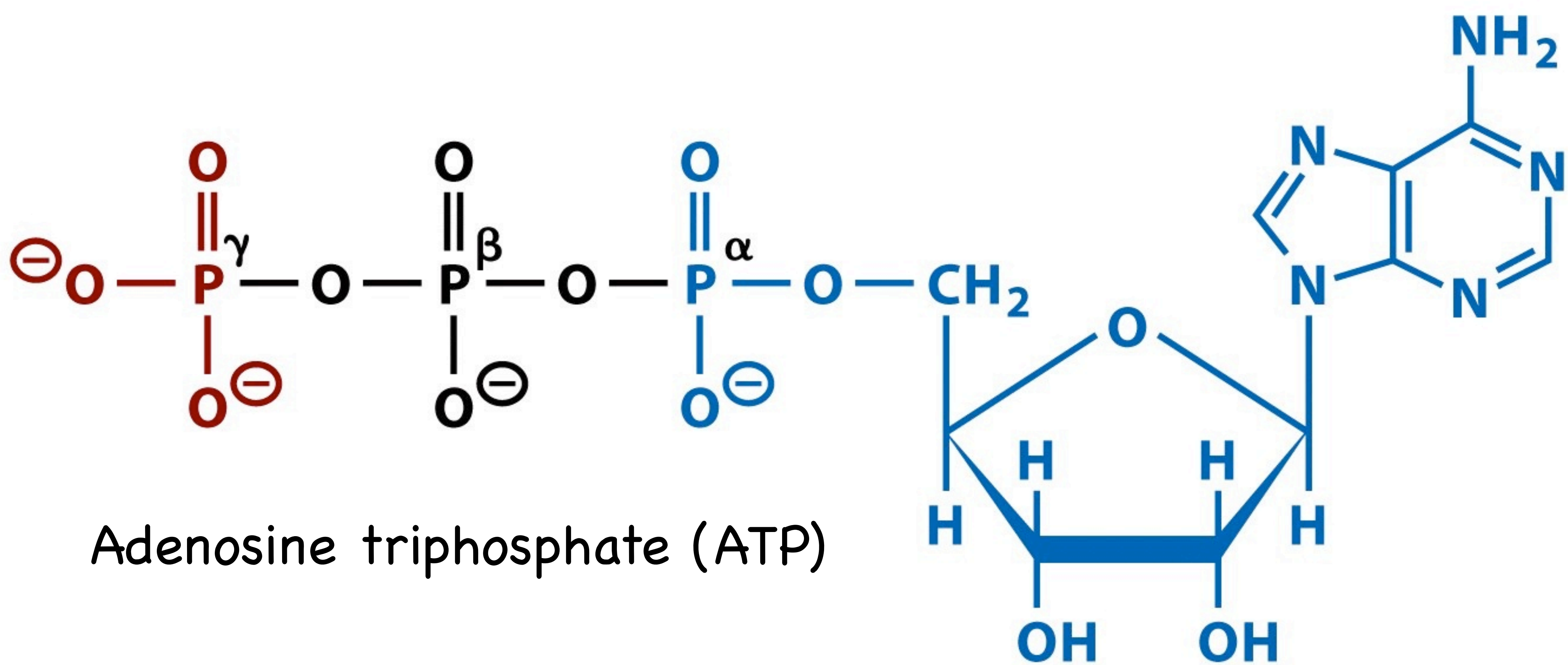

Adenosine triphosphate (ATP)

Complex Carbohydrates

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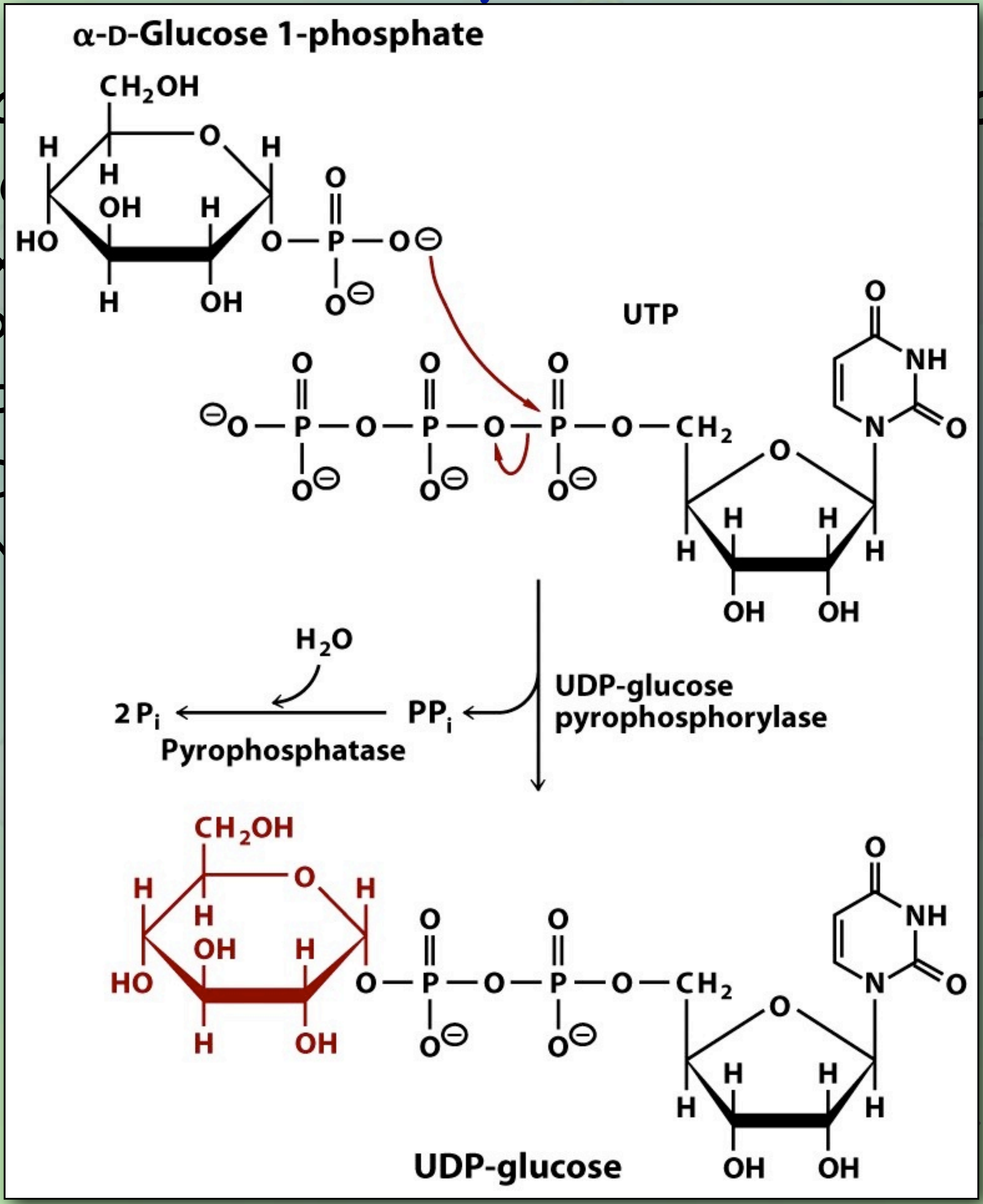
Complex Carbohydrates

- Monosa... onds to non-sa...
  - For ex...
    - ATP
    - UDP
    - NAD
    - FMN



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Complex Carbohydrates

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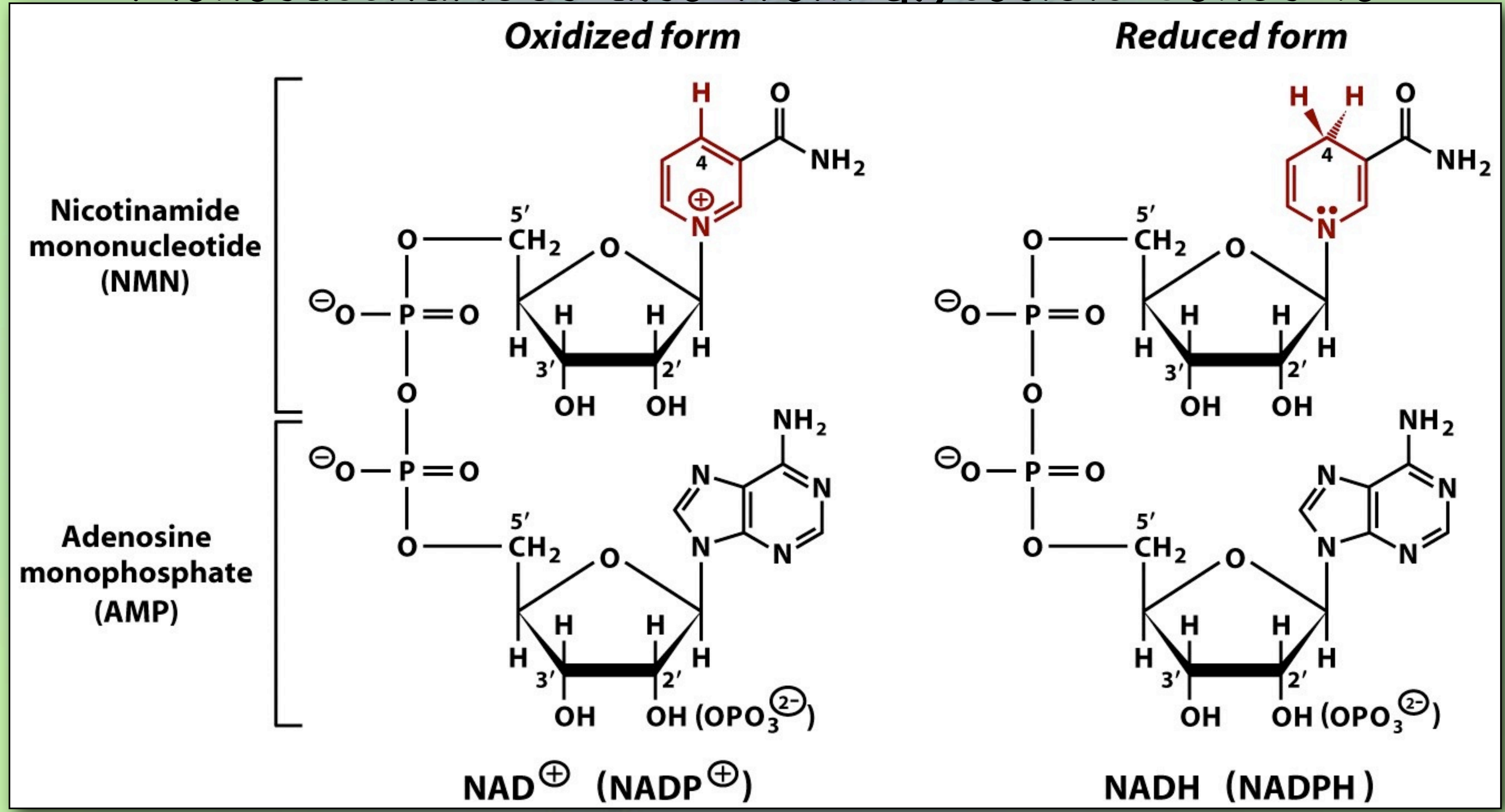
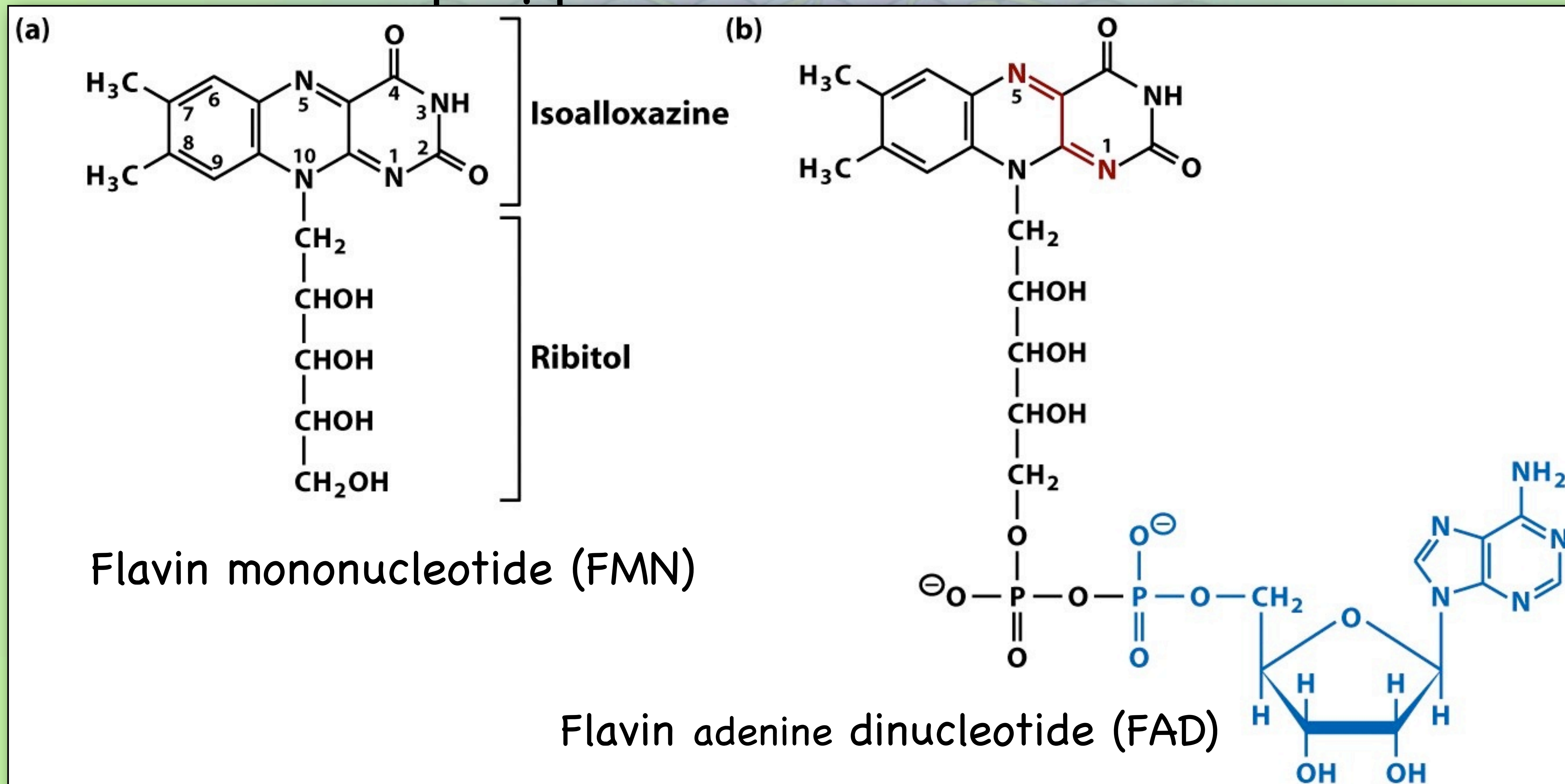


Complex Carbohydrates

- Monosaccharides also from glycosidic bonds to non-saccharides.
  - For example, nucleotides.
    - ATP
    - UDP-glucose
    - NAD and NADP
    - FMN and FAD

Complex Carbohydrates

- Monosaccharides also from glycosidic bonds to



Flavin mononucleotide (FMN)

Flavin adenine dinucleotide (FAD)

Complex Carbohydrates

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Next up

- Unit IV, Lecture 7 - Carbohydrates, con'd