Chem 452 - Lecture 7
Carbohydrates
Part 1

Question of the Day: What characteristic of monosaccharides accounts for their large number of possible structures?

Introduction to Carbohydrates

- There is a similarity to other biomolecules
  - nucleotides -> oligonucleotides -> polynucleotides (DNA & RNA)
    - nucleic acids are chemically uniform and structurally uniform
  - amino acids -> oligopeptides -> polypeptides (proteins)
    - proteins are chemically diverse and structurally diverse
  - monosaccharides -> oligosaccharides -> polysaccharides (starch & glycogen)
    - saccharides are chemically uniform but structurally diverse!

Introduction to Carbohydrates

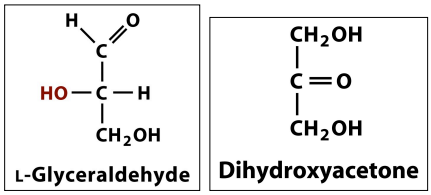
- $(CH_2O)_n$
- Chemically simple, structurally complex
- Nomenclature
  - monosaccharides
  - oligosaccharides
  - polysaccharides

Monosaccharides

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

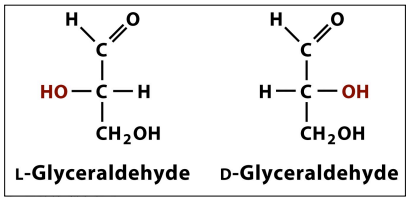
Monosaccharides

- Trioses
  - Glyceraldehyde and Dihydroxyacetone



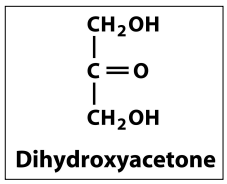
Monosaccharides

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



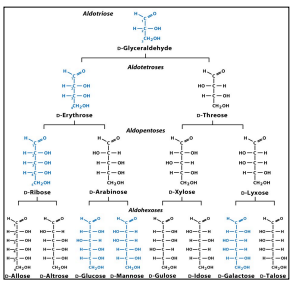
Monosaccharides

- Trioses
  - Dihydroxyacetone
    - Contains no chiral carbons



Monosaccharides

- Aldotriose through aldohexoses



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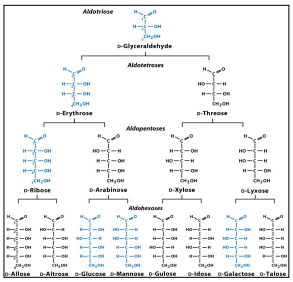

This figures only shows half of the aldoses

Monosaccharides

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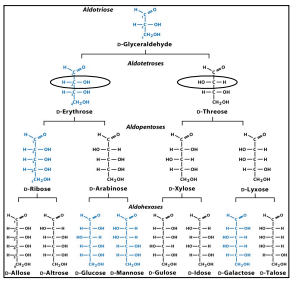

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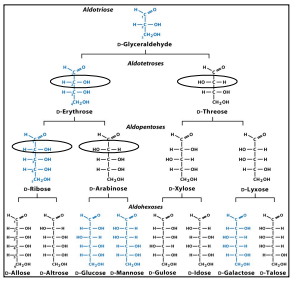

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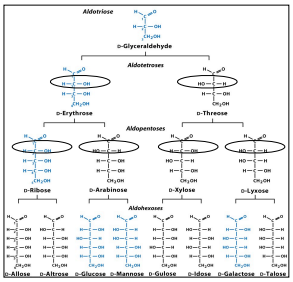

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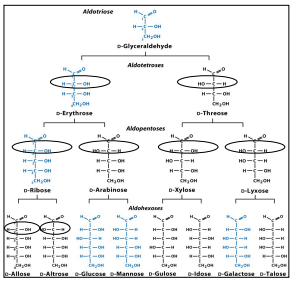

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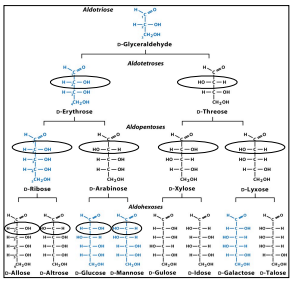

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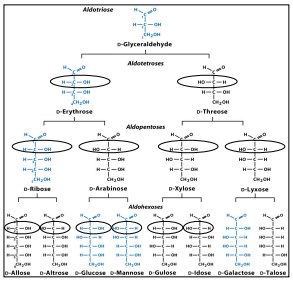

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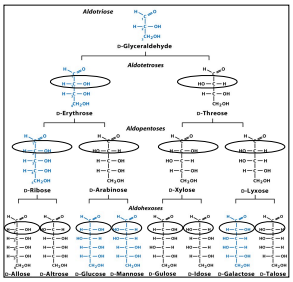

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Monosaccharides

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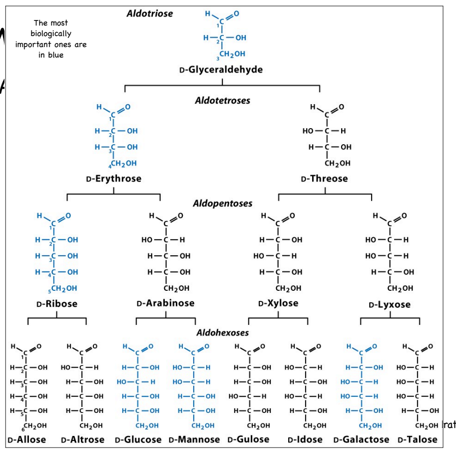

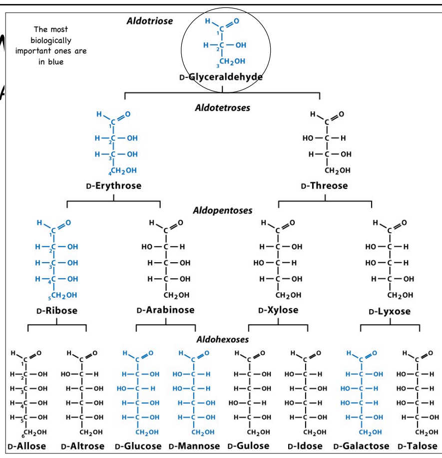

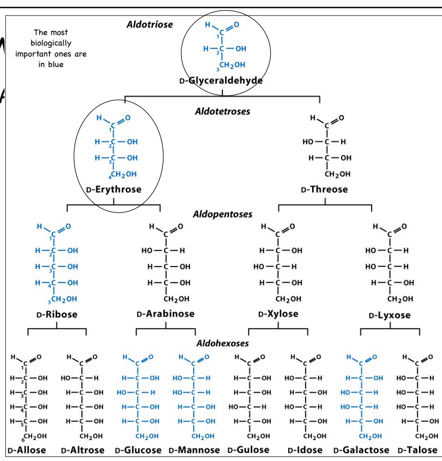

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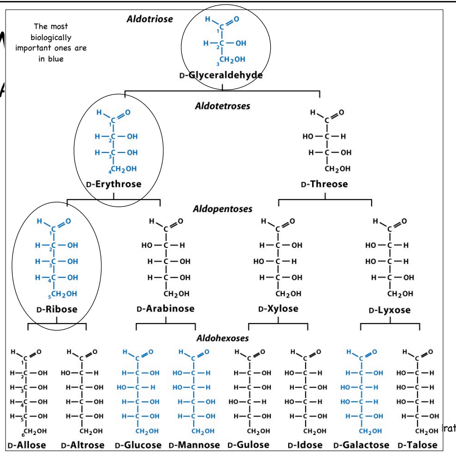

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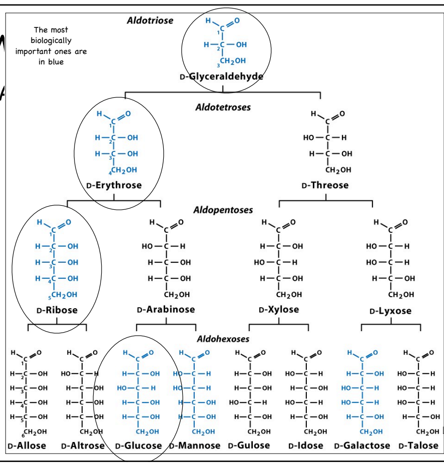

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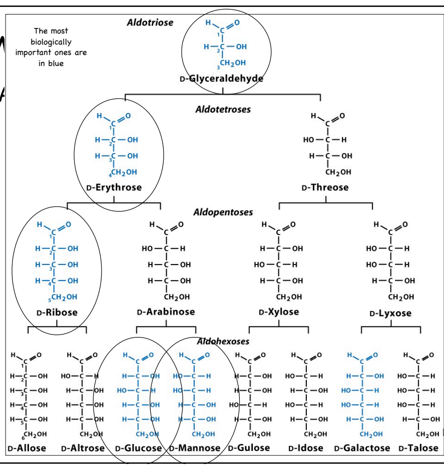

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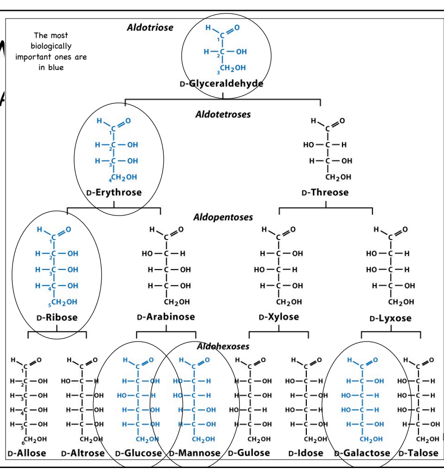

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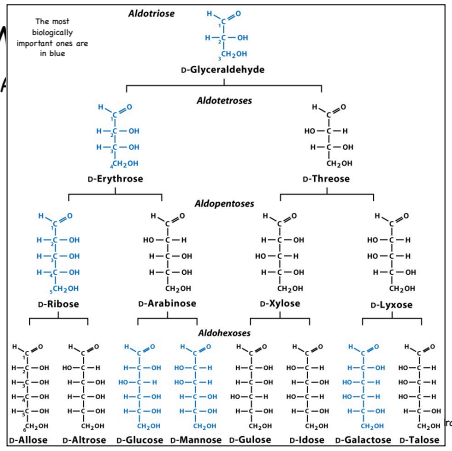
- A



rates 9

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

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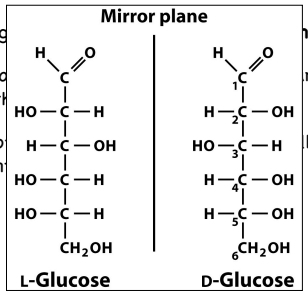
  - Enantio rbon that is furth
  - Most o l encoun



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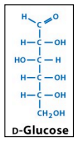
Monosaccharides

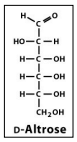
- Nomenclature for stereoisomers
  - **Enantiomers** are mirror images of one another
    - They share the same name and are distinguished using **D** and **L**.
  - **Diastereomers** are stereoisomers with multiple chiral centers that are not mirror images of one another.
  - **Epimers** are diastereomers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

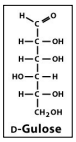
Monosaccharides

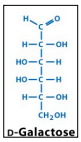
Question:

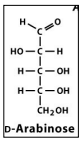
Which of following monosaccharides is an epimer of glucose:


D-Glucose

A. 
D-Altrose

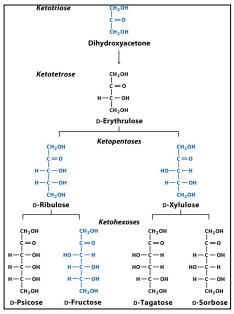
B. 
D-Gulose

C. 
D-Galactose

D. 
D-Arabinose

Monosaccharides

- Ketotrioses through ketohexoses

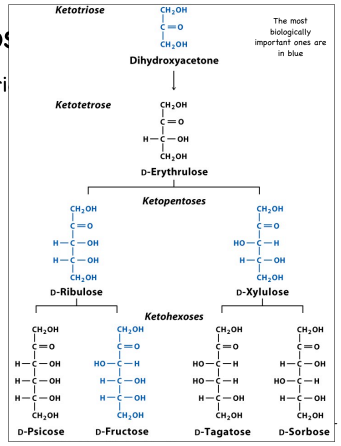


Monosaccharides

- Ketotrioses through ketohexoses

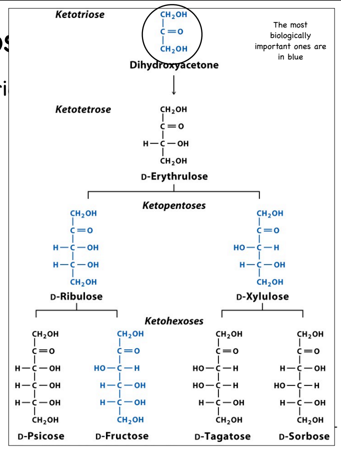
Monos

- Ketotri



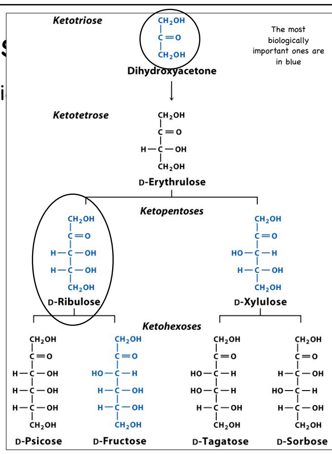
Monos

- Ketotri



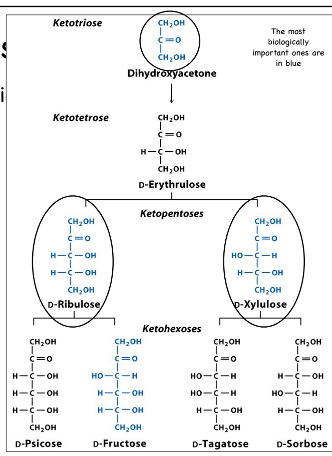
Monos

- Ketotri



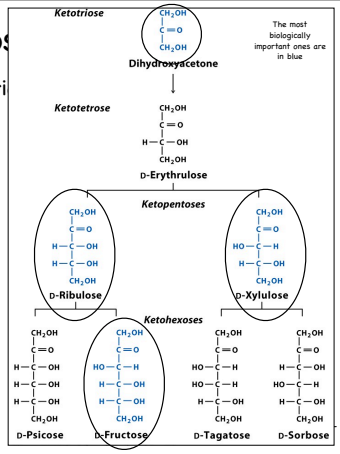
Monos

- Ketotri



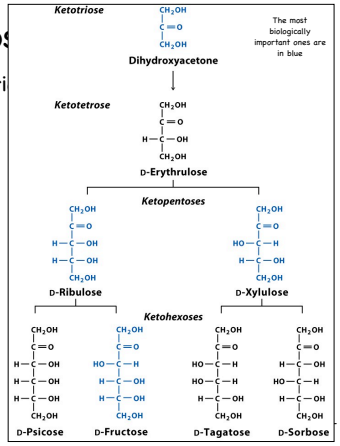
Monos

- Ketotri



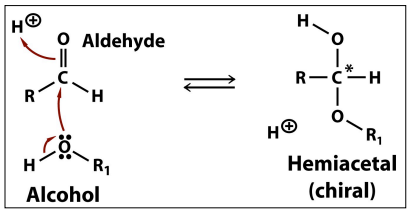
Monos

- Ketotri



Monosaccharides

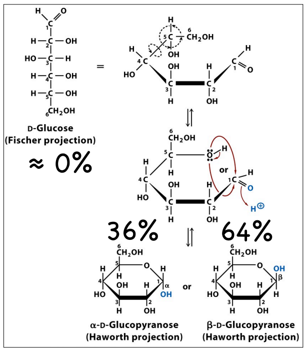
- The aldehyde and ketone groups are reactive.
  - The aldehyde or ketone group can react with a hydroxyl group to form a hemiacetal or hemiketal, respectively.



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



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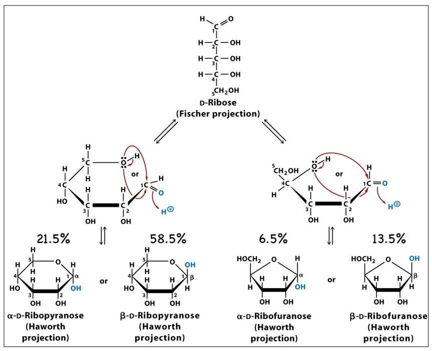

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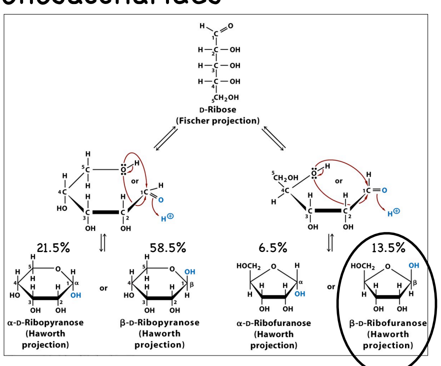

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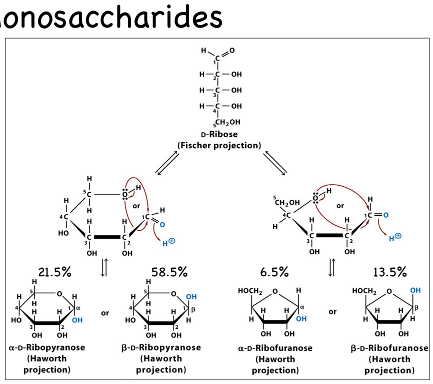
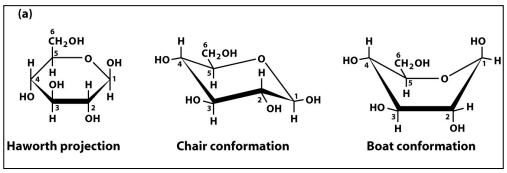


Monosaccharides

- Conformations of Monosaccharides
  - Monosaccharides can have different conformations.



Mo
- Co ccharides
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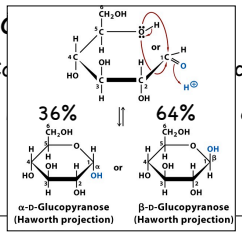

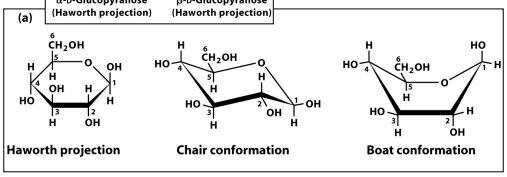

Chem 452, Lecture 7 – Carbohydrates 19

Monosaccharides

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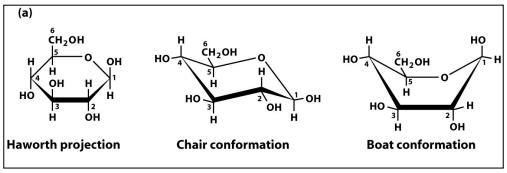

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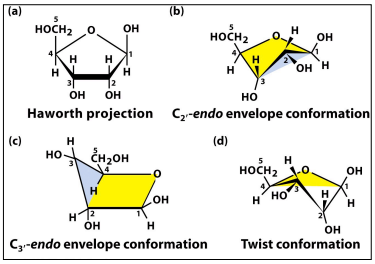

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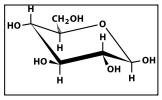
Monosaccharides

- Conformations of Monosaccharides

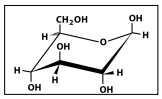
Question:

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

A.



B.



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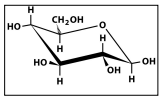

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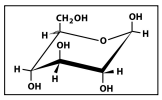

Monosaccharides

- 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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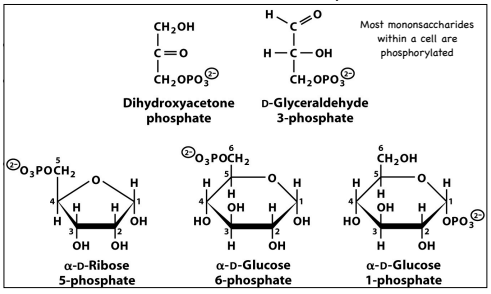

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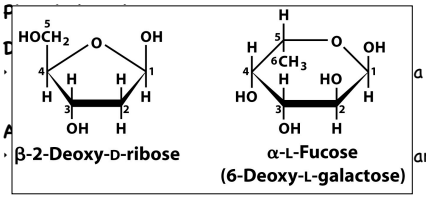
  - **D**
    - a
  - **A**
    - an



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

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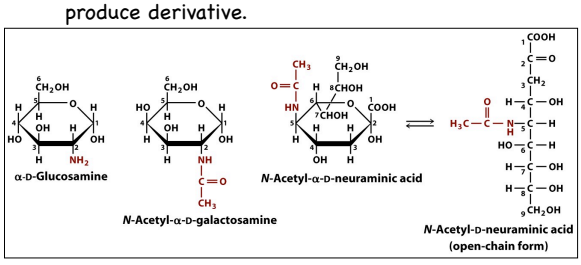
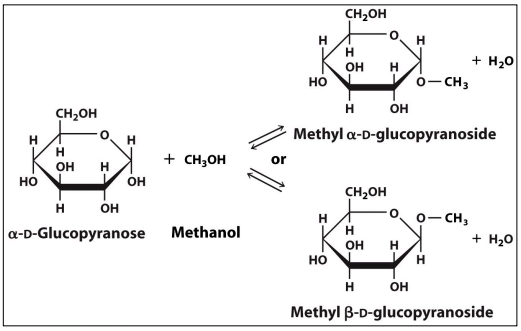


Glycosides

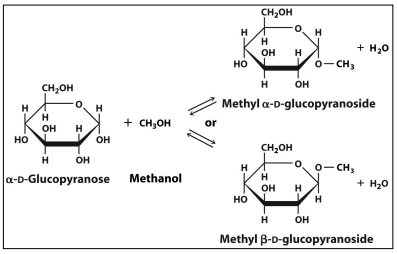
- The hemiacetal or hemiketal carbon (the anomeric carbon) can react with a hydroxyl group to form an **acetal** or **ketal**.
  - The bond formed is also called a **glycosidic bond**.

Glycosides



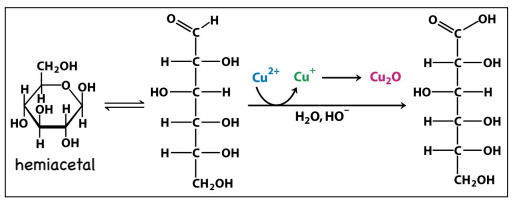
Glycosides

- 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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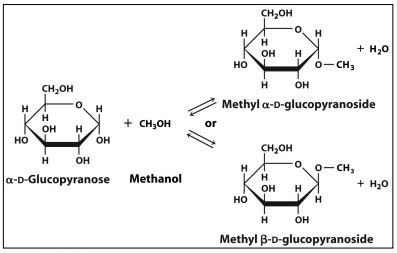

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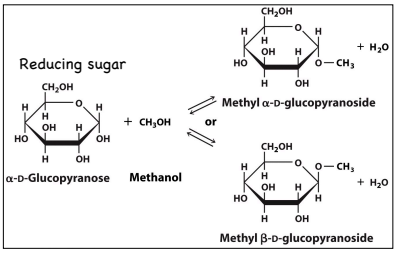

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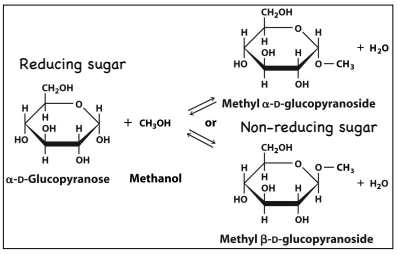

Complex Carbohydrates

- The glycosidic bond is used to connect two monosacchrides together to form a **complex carbohydrates**.
- monosaccharide + monosaccharide = **disaccharide** 33
- Important disaccharides include
  - Maltose (obtained from starch)
  - Cellobiose (obtained from cellulose)
  - Lactose (milk sugar)
  - Sucrose (table sugar)

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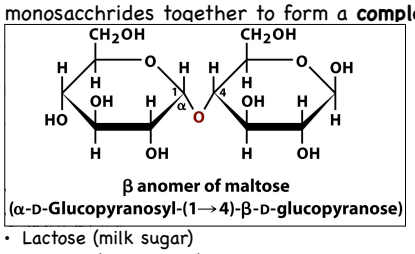
- 

- **β anomer of maltose**
(α-D-Glucopyranosyl-(1→4)-β-D-glucopyranose)
  - Lactose (milk sugar)
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Complex Carbohydrates

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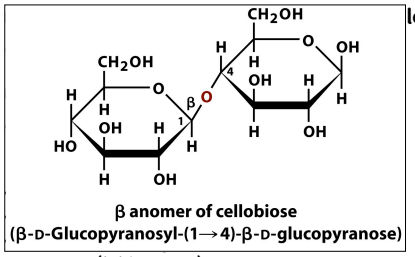
- **lex**
- 

- **β anomer of cellobiose**
(β-D-Glucopyranosyl-(1→4)-β-D-glucopyranose)
  - Sucrose (table sugar)

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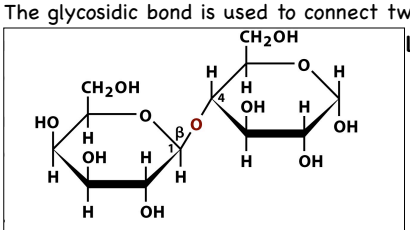

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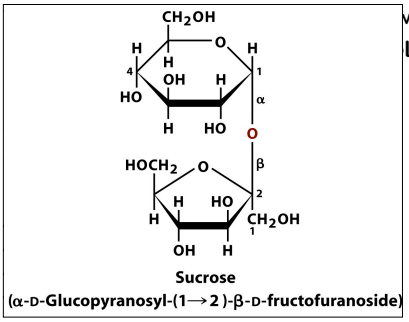

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Complex Carbohydrates

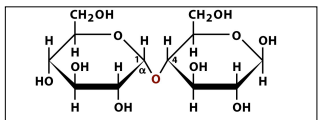
- Because a hemiacetal or hemiketal can open and expose an aldehyde or ketone, they can still serve as reducing agents.
  - This is used to distinguish the two monosaccharides in a disaccharide as the **reducing** and the **nonreducing** ends.

Complex Carbohydrates

- Question:

Which end of the disaccharide maltose is the reducing end?

A. B.



β anomer of maltose
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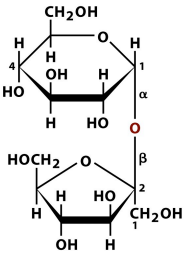
Complex Carbohydrates

- 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
(α-D-Glucopyranosyl-(1→2)-β-D-fructofuranoside)

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

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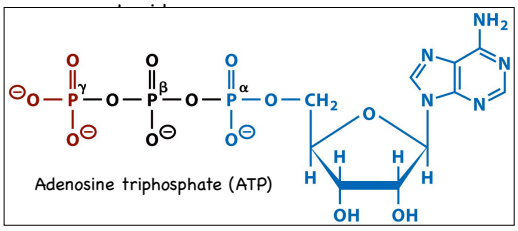

Adenosine triphosphate (ATP)

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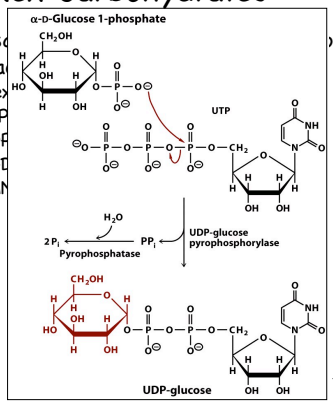

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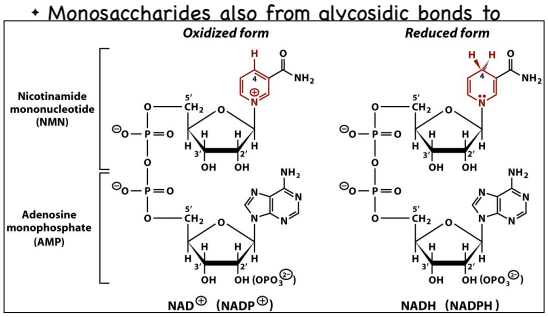

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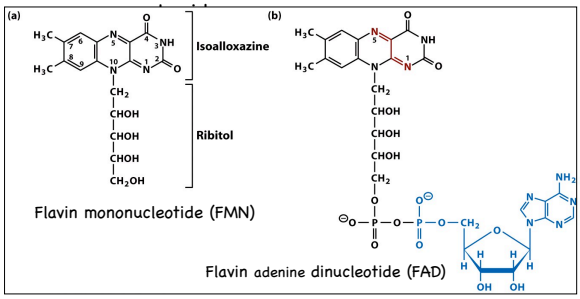

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Next up

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