

Chem 352 - Lecture 7 Carbohydrates

Question for the Day: Unlike amino acids, which owe their diversity to a diverse array of functional groups, monosaccharides feature primarily two functional groups, hydroxyl groups and either a ketone or aldehyde group. What, then, do monosaccharides owe their diversity to?

1

Introduction to Carbohydrates

Carbohydrates are one of the four major classes of biological molecules, which include,

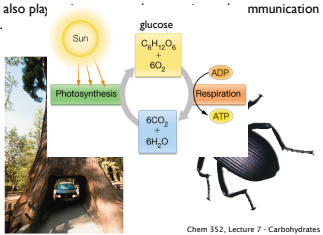
- Proteins
- Nucleic acids
- Carbohydrates
- Lipids

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Introduction to Carbohydrates

- Carbohydrates represent a major source of energy for living organisms.
- They also play communication roles.



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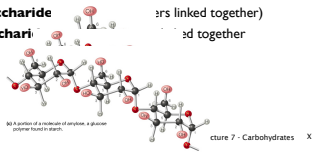
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Introduction to Carbohydrates

Carbohydrates are chemically simple, but can be structurally complex

- The simple sugars have the basic stoichiometric empirical formula $(\text{CH}_2\text{O})_n$, where $n = 3$ to 7
- Like amino acid, simple sugars (monosaccharides) can combine to form polymers.

- **monosaccharides** (monomer)
- **oligosaccharide** (sugars linked together)
- **polysaccharide** (sugars linked together)



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9.1 Monosaccharides

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Monosaccharides

Monosaccharides are

- either **Aldoses**
 - polyhydroxylaldehydes
- or **Ketoses**
 - polyhydroxylketones

Classes based on number of carbons:

- triose (3)
- tetrose (4)
- pentose (5)
- hexose (6)
- heptose (7)

Question:

What is the name ending that is typically used to designate a carbohydrate?

A. -ase
B. -ose
C. -ose
D. -al
E. -amine

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Monosaccharides

Trioses

- L and D Glycerinaldehyde
- Contains a chiral carbon
- Fischer projections
- Dihydroxyacetone

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{C}=\text{O} \\
 | \\
 \text{CH}_2\text{OH} \\
 | \\
 \text{C}=\text{O} \\
 | \\
 \text{CH}_2\text{OH} \\
 \text{L-Dihydroxyacetone}
 \end{array}$$

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{C}=\text{O} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{CH}_2\text{OH} \\
 \text{D-Glyceraldehyde}
 \end{array}$$

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Monosaccharides

There are different ways to designate the stereochemistry of a chiral center:

- **R vs S**
 - Rectus versus sinister - based on the atomic mass of the substituents
- **d (+) vs l (-)**
 - dextro or levorotatory - based on the bending of plane polarized light
- **D vs L**
 - Based on how glyceraldehyde bends plane polarized light

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Monosaccharides

Trioses

- L and D Glycerinaldehyde enantiomers
- Contains a chiral carbon
- Fischer projections
- Dihydroxyacetone

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H} \\
 \text{L-Glycerinaldehyde}
 \end{array}$$

$$\begin{array}{c}
 \text{CH}_2\text{OH} \\
 | \\
 \text{C}=\text{O} \\
 | \\
 \text{CH}_2\text{OH} \\
 \text{Dihydroxyacetone}
 \end{array}$$

$$\begin{array}{c}
 \text{O} \\
 || \\
 \text{C}-\text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{H}_2\text{OH} \\
 \text{D-Glyceraldehyde}
 \end{array}$$

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Monosaccharides

These are Fischer projections:

Trioses

L-Glyceraldehyde

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H} \\
 \text{L-Glyceraldehyde}
 \end{array}$$

D-Glyceraldehyde

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{H} \\
 \text{D-Glyceraldehyde}
 \end{array}$$

Tetroses

D-Threose

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{H} \\
 \text{D-Threose}
 \end{array}$$

D-Erythrose

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H} \\
 \text{D-Erythrose}
 \end{array}$$

Therefore, how many stereoisomers of this group of tetroses are there?

Pentoses

D-Xylose

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H} \\
 \text{D-Xylose}
 \end{array}$$

D-Ribose

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H} \\
 \text{D-Ribose}
 \end{array}$$

L-Xylose

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H} \\
 \text{L-Xylose}
 \end{array}$$

L-Ribose

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H} \\
 \text{L-Ribose}
 \end{array}$$

Hexoses

D-Glucose

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{CH}_2\text{OH} \\
 \text{D-Glucose}
 \end{array}$$

D-Fructose

$$\begin{array}{c}
 \text{O} \\
 || \\
 \text{C}-\text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{CH}_2\text{OH} \\
 \text{D-Fructose}
 \end{array}$$

D-Allose

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{CH}_2\text{OH} \\
 \text{D-Allose}
 \end{array}$$

D-Altrose

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H} \\
 \text{D-Altrose}
 \end{array}$$

D-Mannose

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{CH}_2\text{OH} \\
 \text{D-Mannose}
 \end{array}$$

D-Gulose

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H} \\
 \text{D-Gulose}
 \end{array}$$

D-Idose

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{CH}_2\text{OH} \\
 \text{D-Idose}
 \end{array}$$

D-Galactose

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{CH}_2\text{OH} \\
 \text{D-Galactose}
 \end{array}$$

D-Talose

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{H} \\
 \text{D-Talose}
 \end{array}$$

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L-enantiomers **Monosaccharides**

Trioses through hexoses

- This figure shows only the **D-enantiomers**
- The **L-enantiomers**
- Member the chiral centers are distinguished using the Fischer projection.
- Most of the D-enantiomers are the

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Monosaccharides

Question: Which of the following monosaccharides is an optical isomer of D-glucose?

Answer: **Enantiomers** are stereoisomers that are mirror images of each other.

A. **Enantiomer**

B. **Epimer** are stereoisomers that differ from each other at only one chiral carbon.

C. **Diastereomers** are stereoisomers that differ from each other at two or more chiral carbons.

D. **Not stereoisomers**

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Ketoses

- Trioses

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Aldoses

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Ketoses

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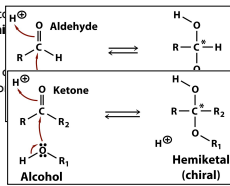
Monosaccharides

•Cyclization of aldoses and ketoses

• An aldehyde can react spontaneously with an alcohol to form a **hemiacetal**.

• A ketone can react with an alcohol to form a **hemiketal**.

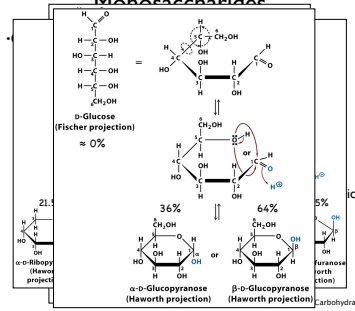
• Both the forward and reverse reactions are reversible.



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Monosaccharides



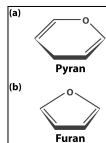
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Monosaccharides

•Cyclization of aldoses and ketoses

- The six-member rings are called **pyranose** rings
- The five-member rings are called **furanose** rings.



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Monosaccharides

•Cyclization of aldoses and ketoses

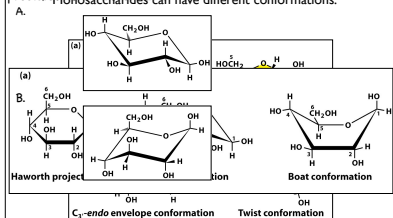
- **pyranose** rings
 - D-glucopyranose (aldohexose)
 - D-mannopyranose (aldohexose)
 - D-galactopyranose (aldohexose)
- **furanose** rings
 - D-fructofuranose (ketohexose)
 - D-ribofuranose (aldopentose)

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Monosaccharides

Clicker Question:
• Conformations of Monosaccharides
Which of the following conformations for β -D-glucopyranose is predicted to be more stable?
Monosaccharides can have different conformations.



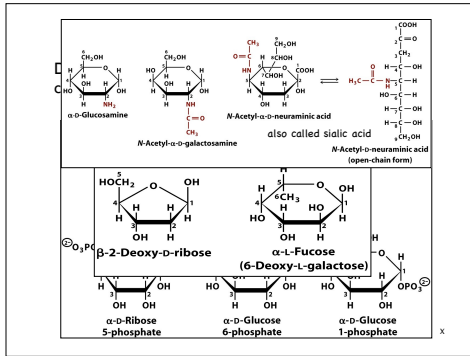
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9.2 Derivatives of the Monosaccharides

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Monosaccharides

Sugar alcohols

- The aldehyde or ketone group is reduced to an alcohol.
- Some are used as natural artificial sweeteners.



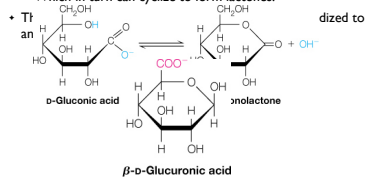
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Monosaccharides

Sugar acids

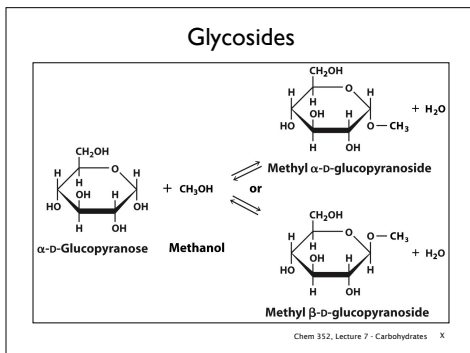
- The aldehyde can be oxidized to an acid to produce aldonic acids.
- Which in turn can cyclize to form lactones.



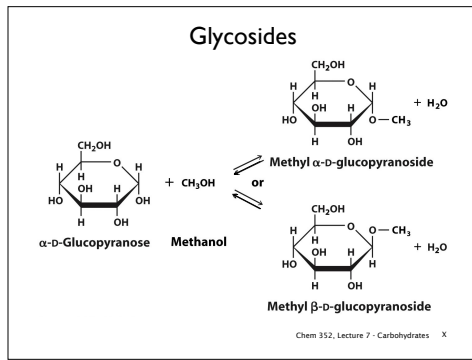
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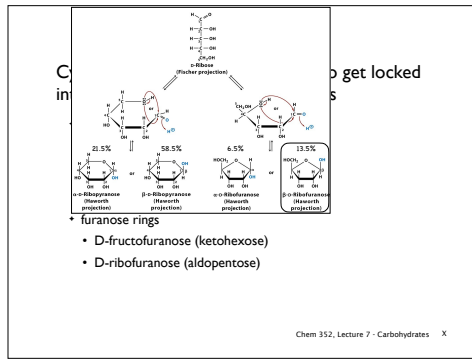
Glycosides



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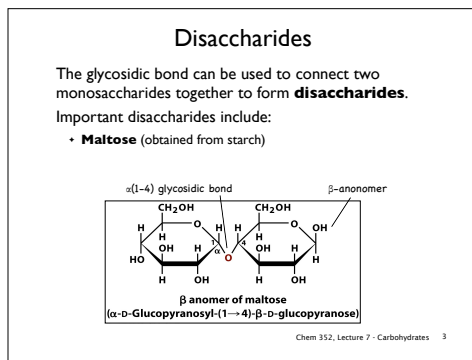
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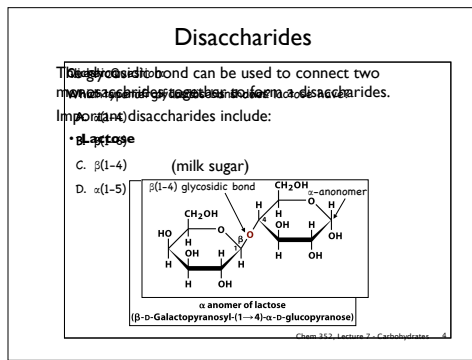
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9.3 Oligosaccharides

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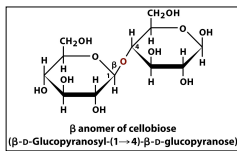
30

Disaccharides

The glycosidic bond can be used to connect two monosaccharides together to form **disaccharides**.

Important disaccharides include:

- **Cellobiose** (obtained from cellulose)



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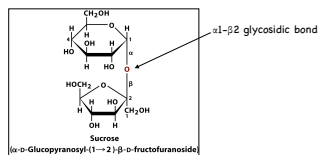
31

Disaccharides

The glycosidic bond can be used to connect two monosaccharides together to form **disaccharides**.

Important disaccharides include:

- **Sucrose** (table sugar)

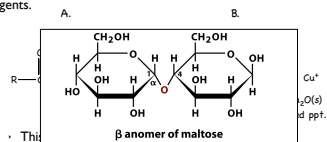


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Disaccharides

Question: Because a hemiacetal or hemiketal can easily open to expose either an aldehyde or a ketone, they can serve as reducing agents for the Cu^{2+} ions found in Fehling's and Benedict's reagents.



This molecule has **reducing ends** at the non-reducing ends.

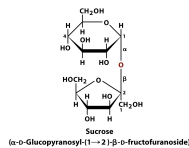
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Disaccharides

Not all disaccharides have a reducing end

- For example, the disaccharide sucrose contains both an acetal and a ketal, but no hemiacetal or hemiketal.



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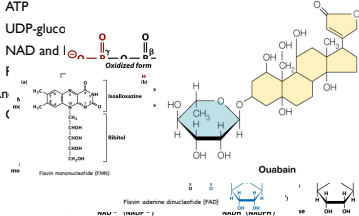
Glycosides

Monosaccharides also form glycosidic bonds to non-sugar.

- For example, nucleotides, such as

- ATP
- UDP-glucose
- NAD and its oxidized form
- Flavonoid glycosides
- An
- C

α-D-Glucose 1-phosphate



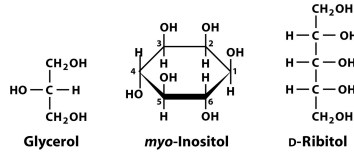
Flavin adenine dinucleotide (FAD)

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Glycosides

Ribitol is another example of a **sugar alcohol**.

- Where the aldehyde or ketone is reduced to an alcohol.



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9.4 Polysaccharides

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Polysaccharides

TABLE 8.2 Structures of some common polysaccharides

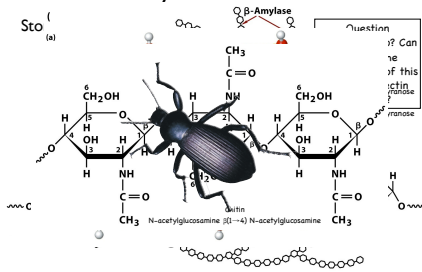
Polysaccharide ^a	Composition(s) ^b	Linkage(s)
Storage homopolysaccharides Starch Amylose Amylopectin Glycogen	What appears to distinguish the glycosidic bonds used in storage homopolysaccharides from the glycosidic bonds used in structural homopolysaccharides?	$\alpha(1 \rightarrow 4)$ $\alpha(1 \rightarrow 4), \alpha(1 \rightarrow 6)$ (branches) $\alpha(1 \rightarrow 4), \alpha(1 \rightarrow 6)$ (branches)
Structural homopolysaccharides Cellulose Chitin		$\beta(1 \rightarrow 4)$ $\beta(1 \rightarrow 4)$
Heteropolysaccharides Glycosaminoglycans Hyaluronic acid	Disaccharides (amino sugars, sugar acids) GlcUA and GlcNAc	Various $\beta(1 \rightarrow 3), \beta(1 \rightarrow 4)$

^aPolysaccharides are unbranched unless otherwise indicated.
^bGlc, Glucose; GlcNAc, N-acetylglucosamine; GlcUA, D-glucuronic acid.

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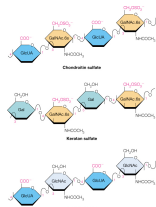
Polysaccharides



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Glycosaminoglycans

Are heteropolysaccharides which are also called mucopolysaccharides.



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Glycoconjugates

To lipids

- Glycolipids

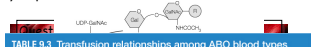


TABLE 9.3 Transfusion relationships among ABO blood types

Person Has Blood Type:	Makes Antibodies Against:	Can Safely Receive Blood from:	Can Safely Donate Blood to:
O	A, B	O	O, A, B, AB
A	B	O, A	A, AB
B	A	O, B	B, AB
AB	None	O, A, B, AB ^a	AB

^aIn principle, this relationship is true. However, ABs are not given donations from other types because the donor's antibodies could react with the recipient's antigens, unless the red blood cells are first separated from the plasma.

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Which Structures Do I Need to Know?

• Monosaccharide

- D-glucose
- D-galactose
- D-mannose
- D-fructose
- D-ribose

• Disaccharides

- D-lactose
- D-maltose
- D-cellobiose
- D-sucrose

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Which Structures Do I Need to Know?

• Monosaccharide Derivatives

- D-glucosamine
- N-acetyl-D-glucosamine
- D-gluconic acid
- D-glucuronic acid
- D-ribitol

• Polysaccharides

- amylose
- amylopectin
- glycogen
- cellulose
- chitin

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Questions

Question:

Indicate which of the following terms best describes the relationship between the following isomers:

D-glyceraldehyde and dihydroxyacetone

- A. anomers
- B. epimers
- C. diastereomers
- D. constitutional isomers

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Questions

Question:

Indicate which of the following terms best describes the relationship between the following isomers:

α -D-glucose and β -D-glucose

- A. anomers
- B. epimers
- C. diastereomers
- D. constitutional isomers

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Questions

Question:

Indicate which of the following terms best describes the relationship between the following isomers:

D-glucose and D-galactose

- A. anomers
- B. epimers
- C. diastereomers
- D. constitutional isomers

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Questions

Question:

D-Lactose comprises D-glucose and D-galactose connected to one another by a $\beta(1\rightarrow4)$ glycosidic bond. Draw the structural formula for the α -anomer of D-lactose.

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Questions

Question:

α -D-Lactose has how many stereoisomers?

- A. 2
- B. 32
- C. 256
- D. 512
- E. 1023

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Questions

Questions:

Raffinose is a trisaccharide that is found in beans and cabbage. When it passes undigested through the human digestive system to the upper intestine, where gas-producing bacteria break it down, the consequences of this physiological process have been immortalized in the movie "Blazing Saddles." The structure for raffinose is shown to the right.



Raffinose



- A. What three monosaccharides combine to form raffinose?
- B. What are the glycosidic linkages that connect the three monosaccharides?
- C. Is raffinose a reducing sugar?

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