Chem 352 - Lecture 5
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?

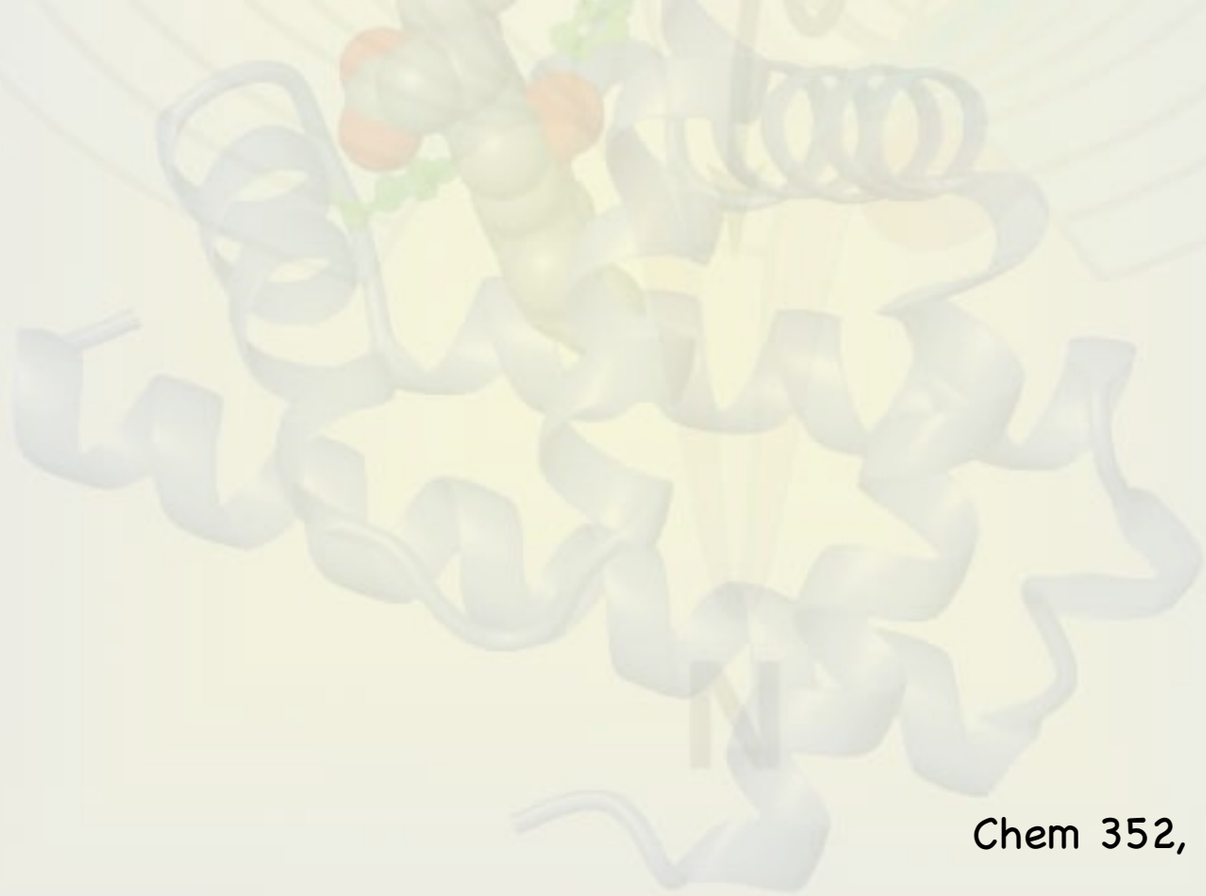
Introduction to Carbohydrates

Carbohydrates are included as one of the major classes of biological molecules:

- Proteins
- Nucleic acids
- Carbohydrates
- Lipids

Introduction to Carbohydrates

- Carbohydrates provide a major source of energy for living organisms.
- They also play major structural, protective and communication roles.



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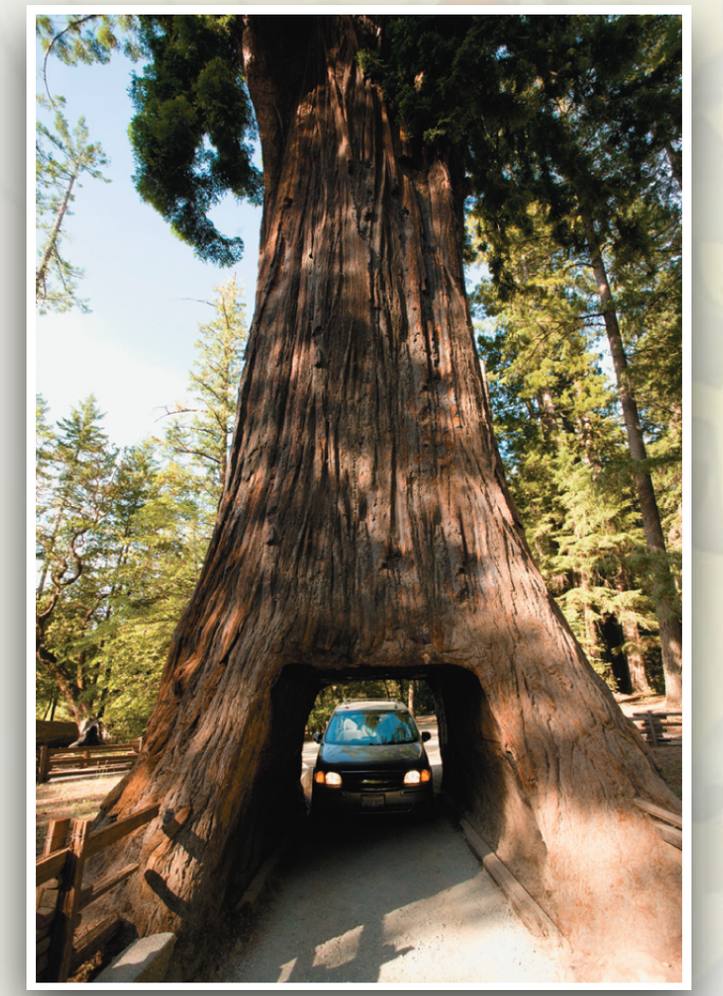

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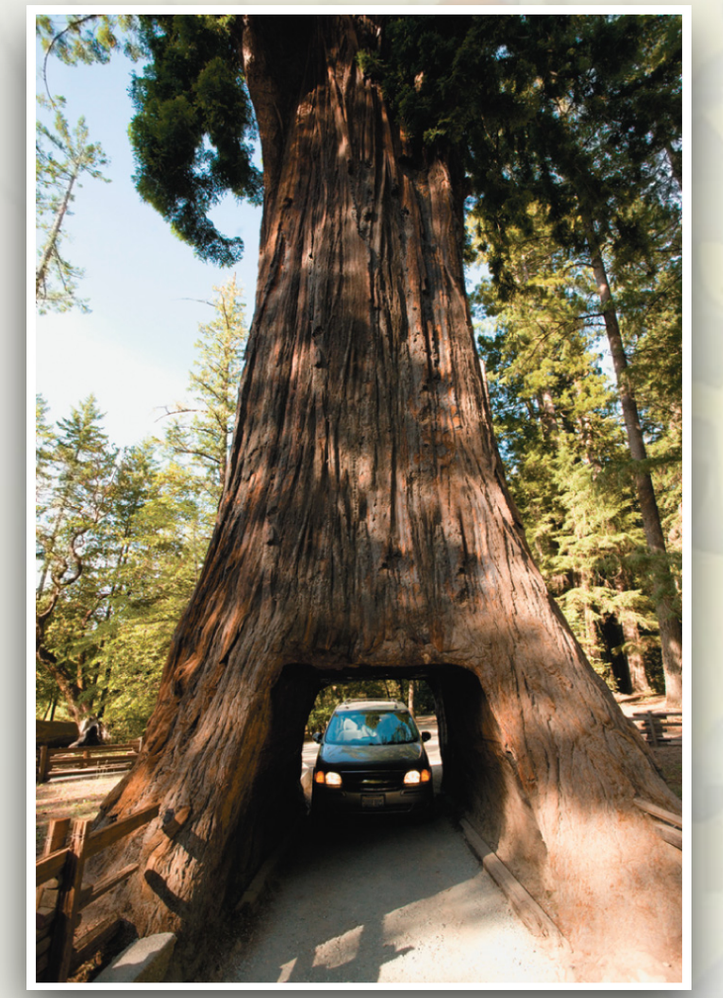

Introduction to Carbohydrates

Carbohydrates are chemically simple, but structurally complex

- $(CH_2O)_n$

Like amino acid, simple sugars (monosaccharides) can combine to form polymers.

- **monosaccharides** (monomer)
- **oligosaccharides** (several monomers linked together)
- **polysaccharides** (many monomers linked together

Monosaccharides

Monosaccharides are

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

Classes based on number of carbons

- triose
- tetrose
- pentose
- hexose

Monosaccharides

Trioses

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

Monosaccharides

Trioses

- L and D Glyceraldehyde
  - Contains a chiral carbon
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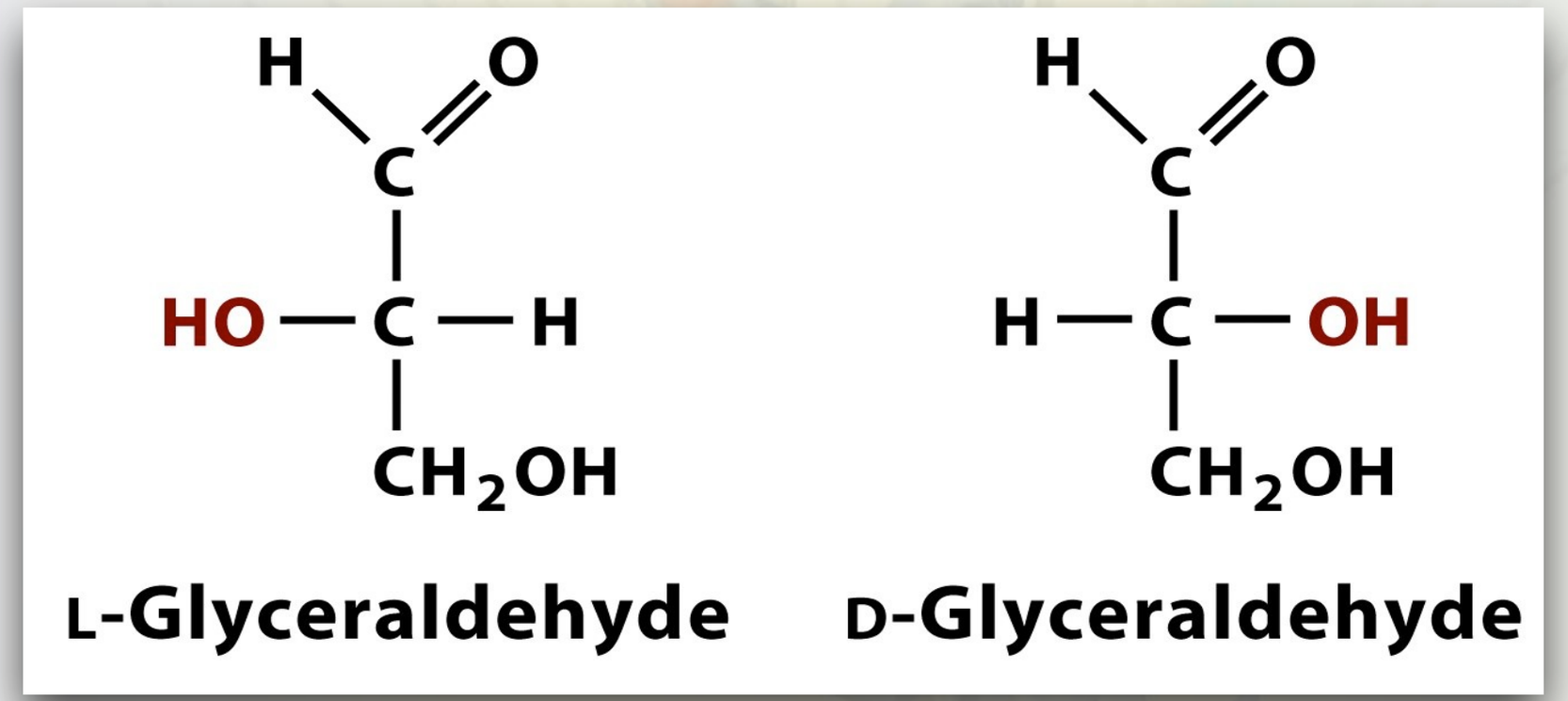

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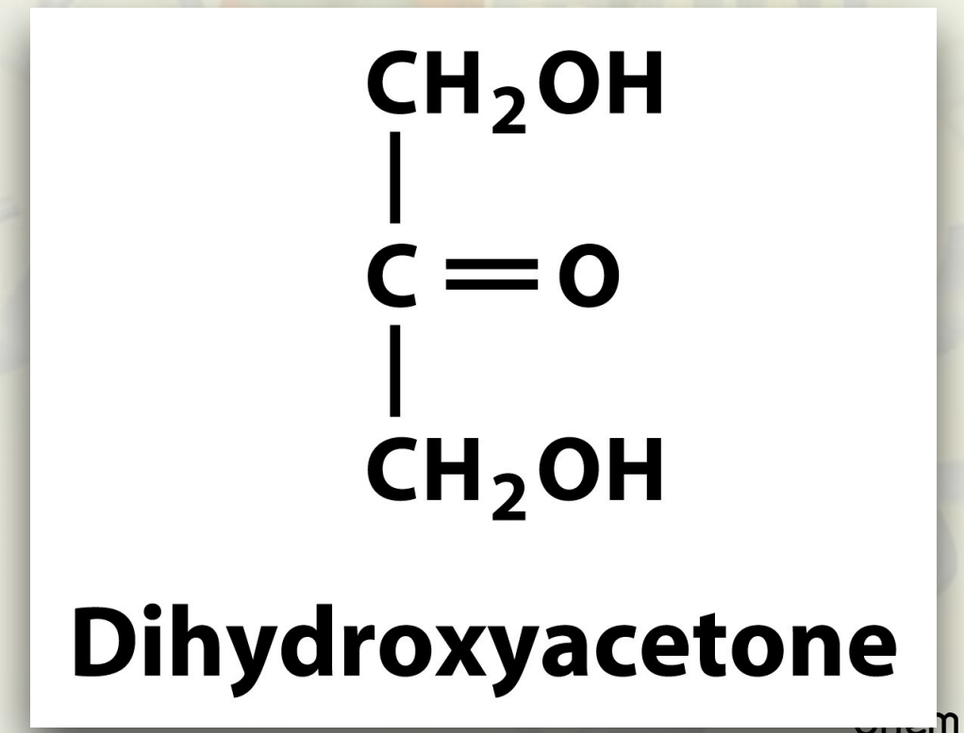

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Monosaccharides

- **Aldoses**
  - Tretroses through hexoses

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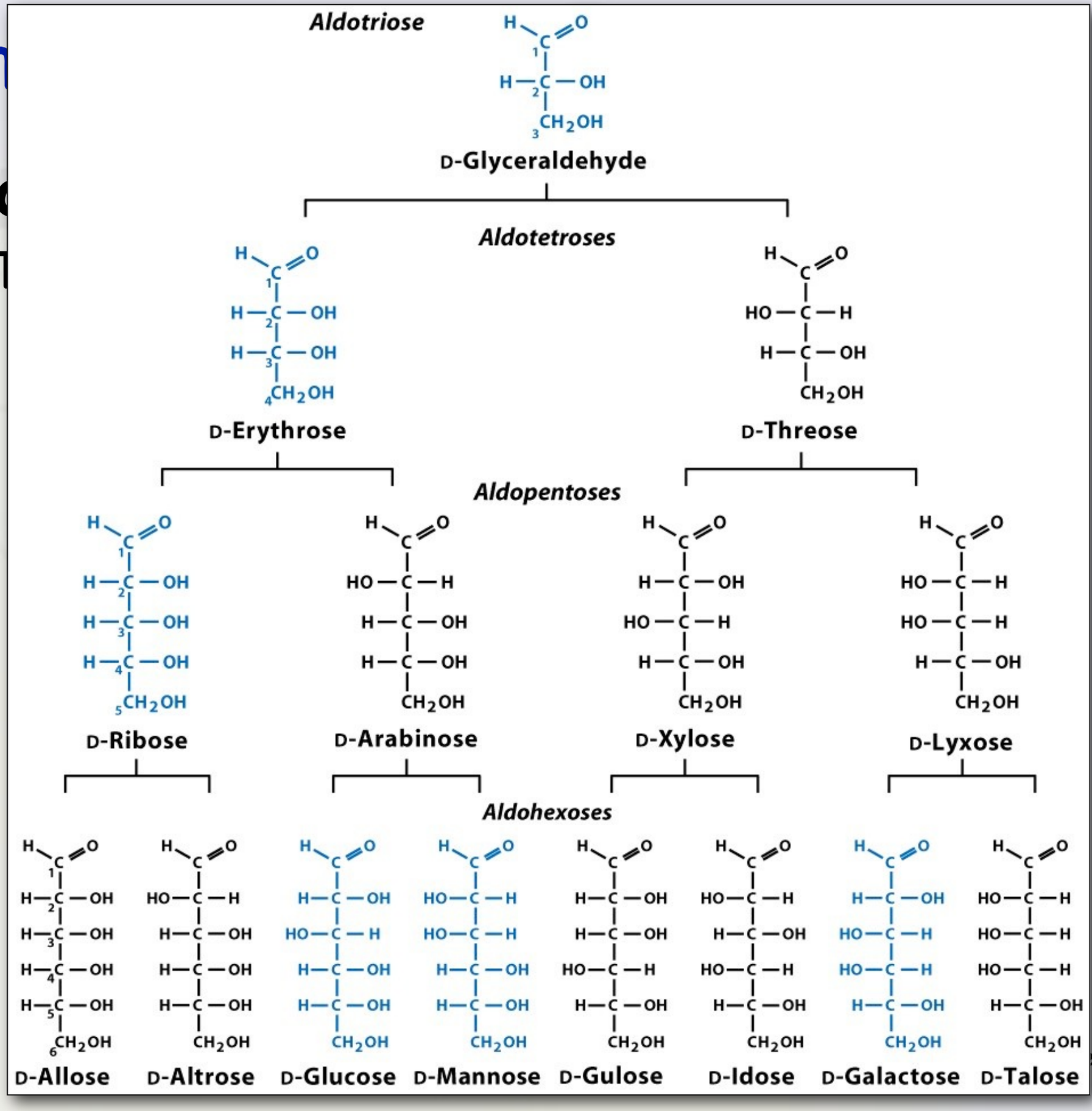
Aldotriose
D-Glyceraldehyde
Aldotetroses
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D-Arabinose
D-Xylose
D-Lyxose
Aldohexoses
D-Allose
D-Altrose
D-Glucose
D-Mannose
D-Gulose
D-Idose
D-Galactose
D-Talose

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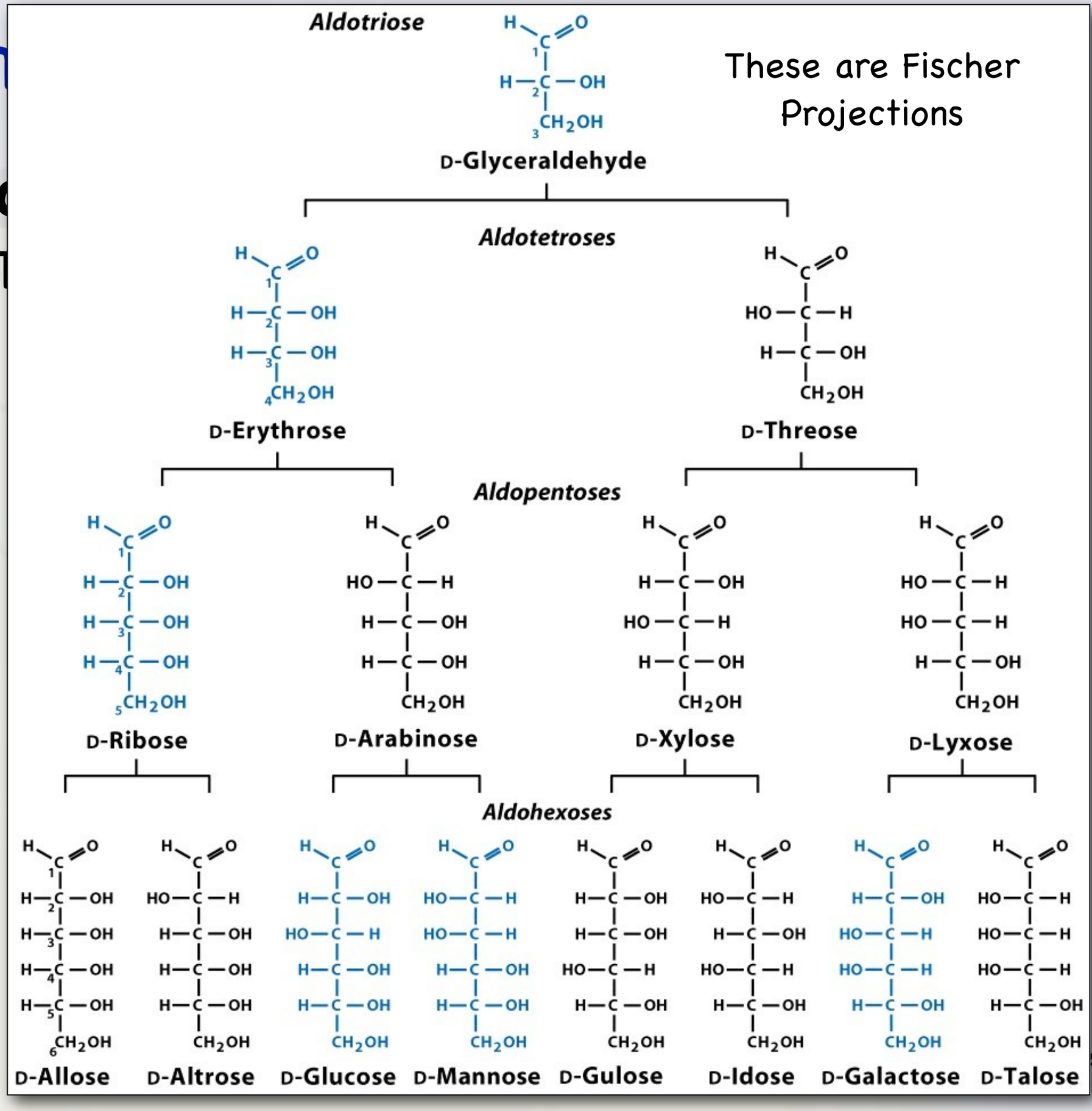
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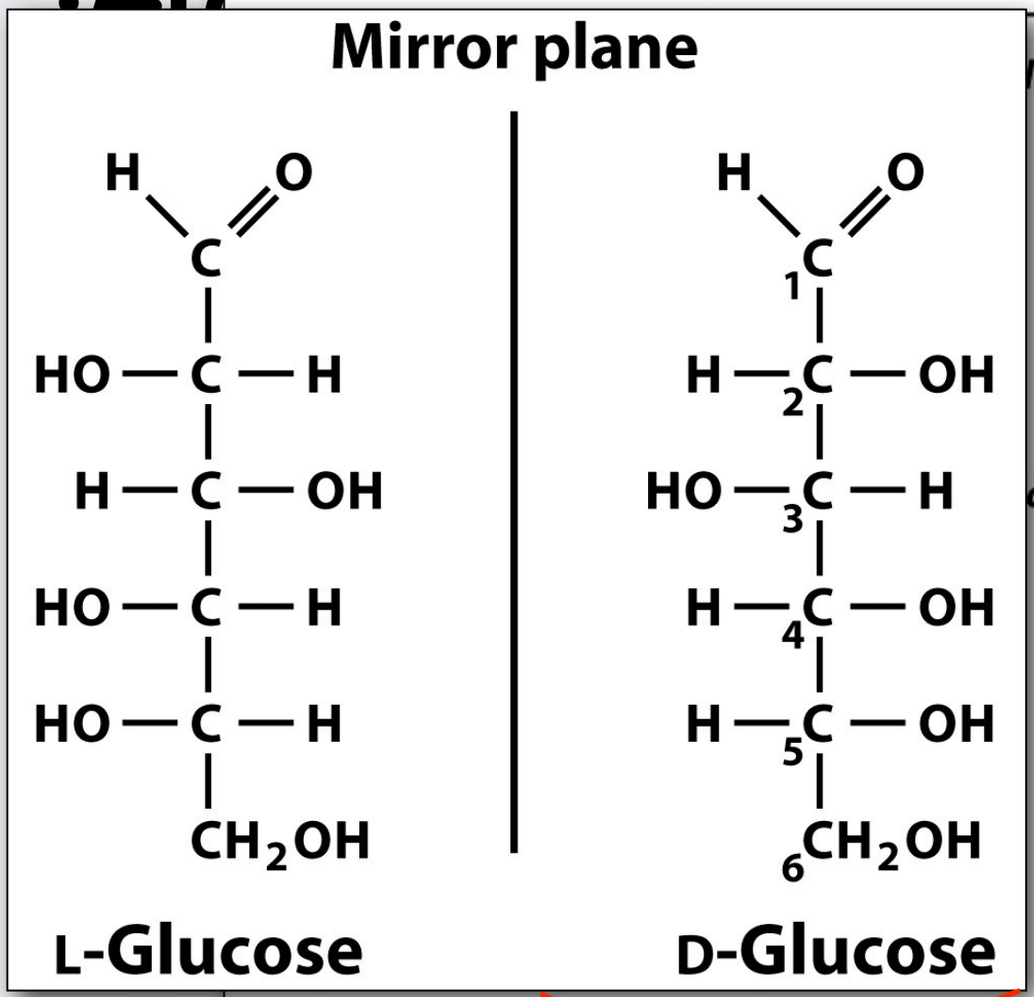
Mirror plane
L-Glucose
D-Glucose

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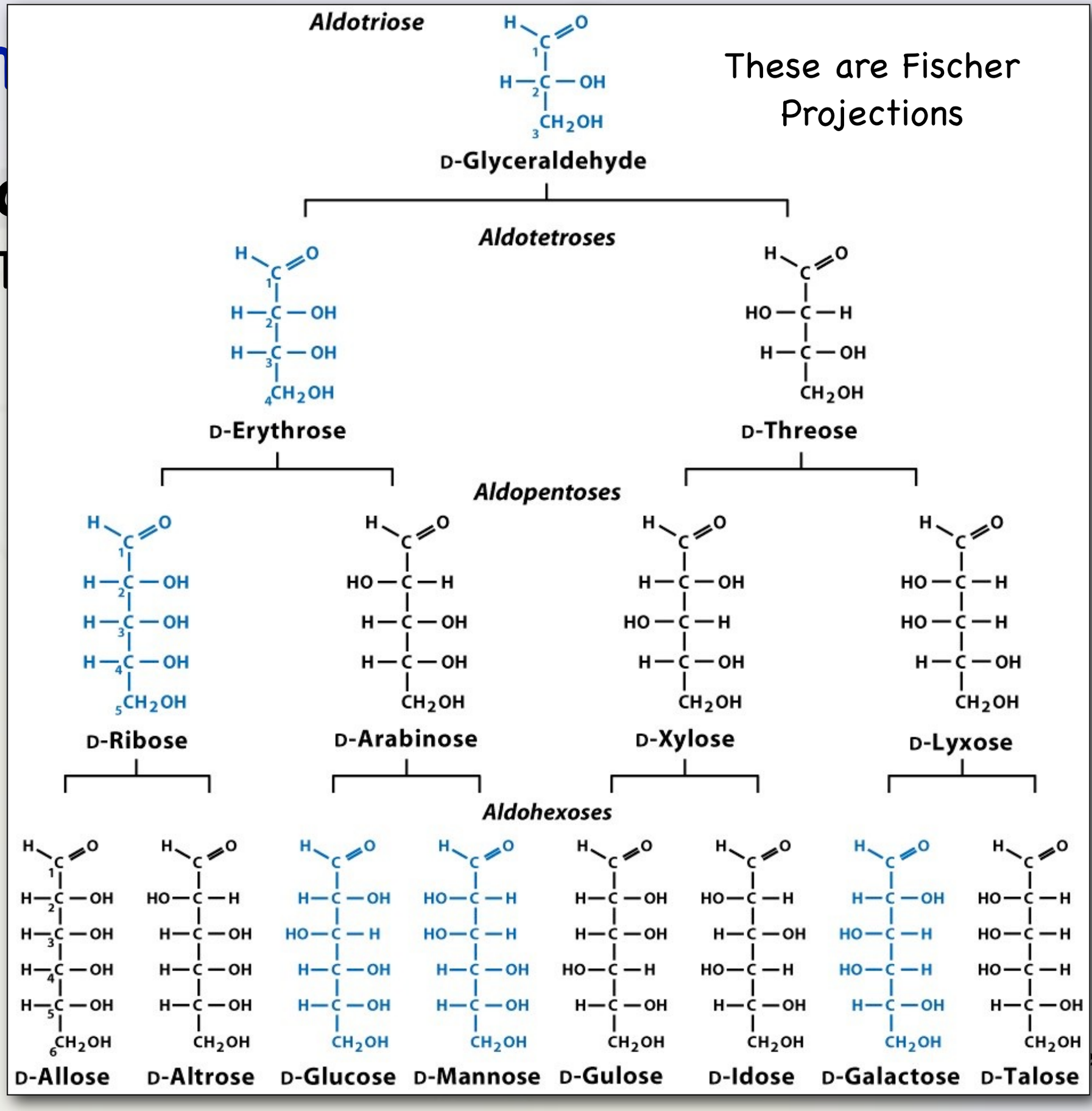
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Monosaccharides

- **Aldoses**
  - Tretroses through hexoses

Monosaccharides

Tretroses through hexoses

- This figure shows only the D-**enantantiomers**
- The L-**enantiomers** are mirror images of the D-**enantiomers**.
- Members of an enantiomeric pair are are distinguished using the chirial carbon that is **furthest** from the carbonyl group.
- Most of the monosaccharides that we will encounter are D-enantiomers.

Monosaccharides

Tretroses through hexoses

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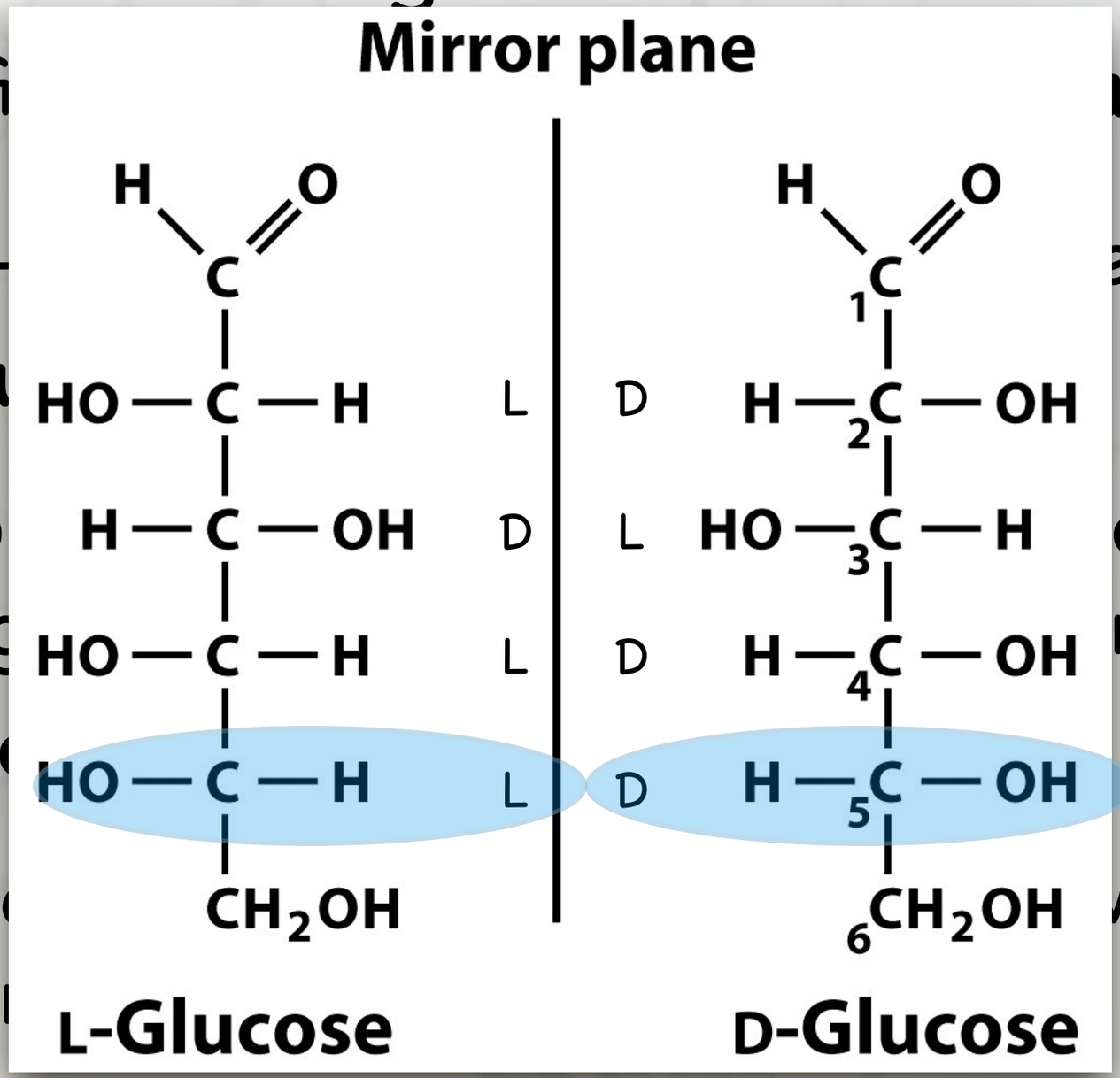

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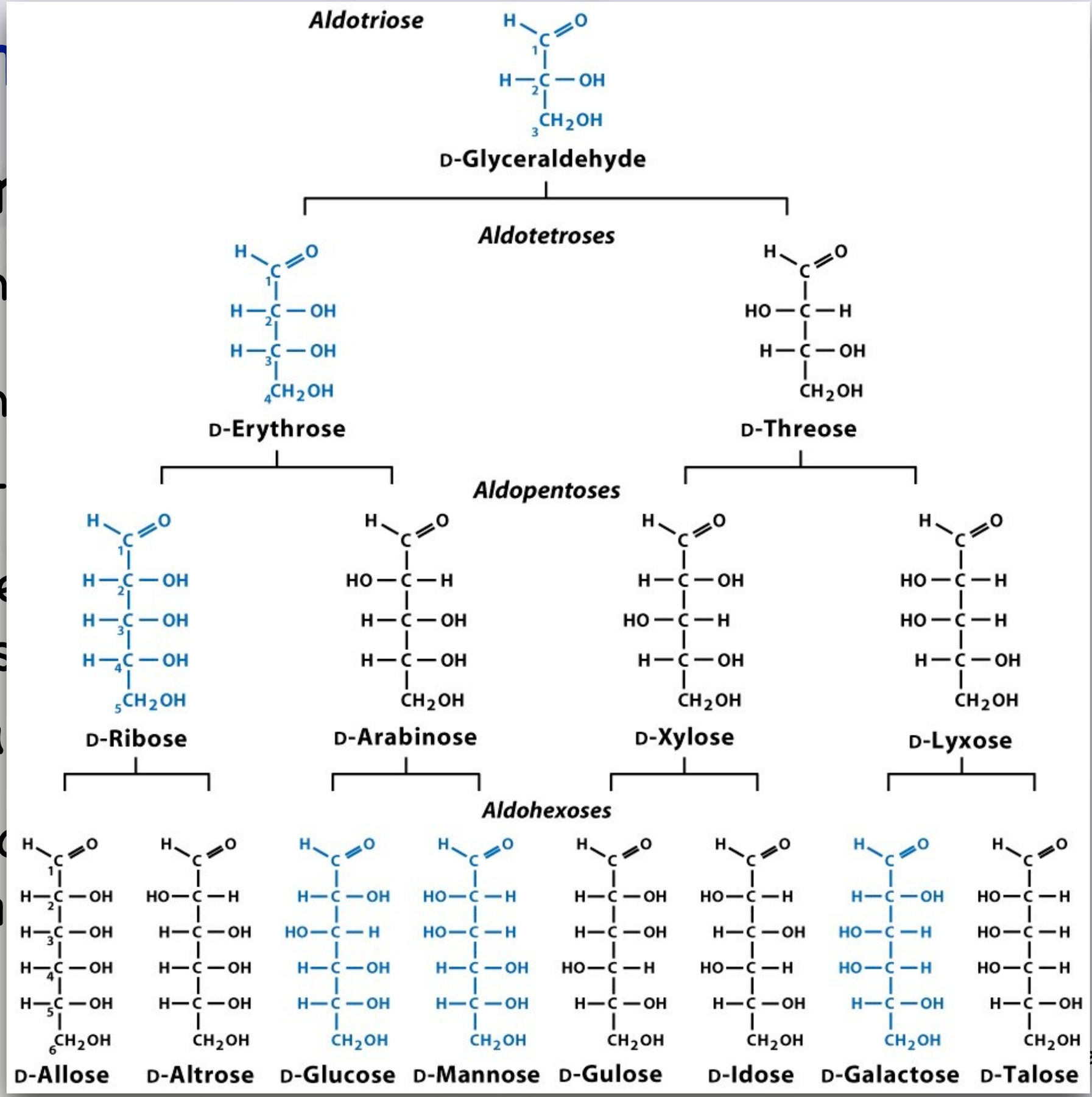

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Monosaccharides

- Types of optical isomers
  - **Enantiomers** are stereoisomers that are mirror images of one another
  - **Epimer** are stereoisomers having more than one chiral carbon that differ from one another at just one chiral carbon.
  - **Diastereomers** are stereoisomers having more than one chiral carbon that differ from one another at multiple chiral carbons.

Monosaccharides

Ketoses

- Tretroses through hexoses

Monos

Ketoses

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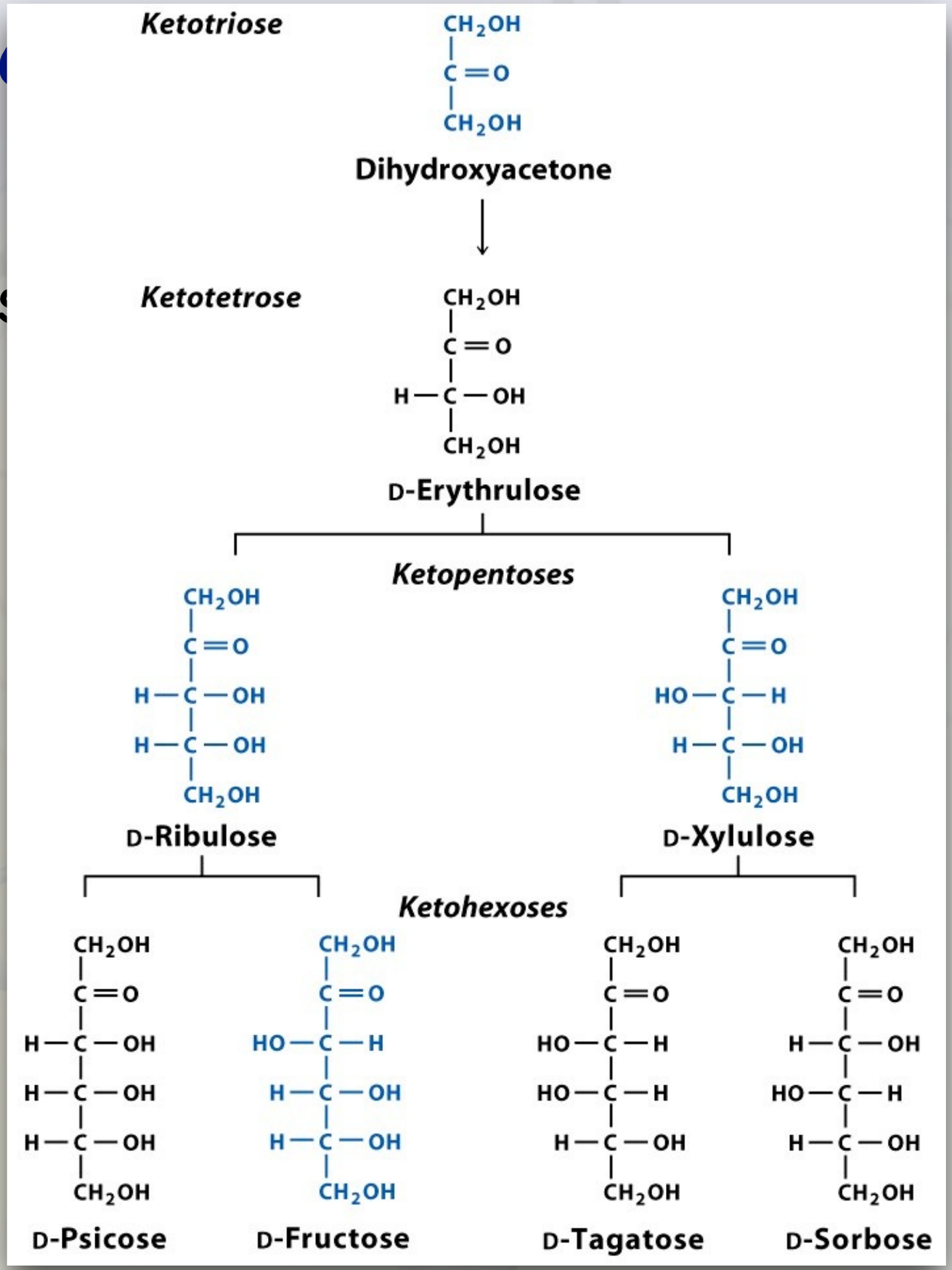

Monosaccharides

Ketoses

- Tretroses through hexoses

Monosaccharides

- The ones to remember
  - Aldoses
    - trisoes
      - D-glyceraldehyde
    - pentoses
      - D-ribose
    - hexoses
      - D-glucose
      - D-mannose
      - D-galactose

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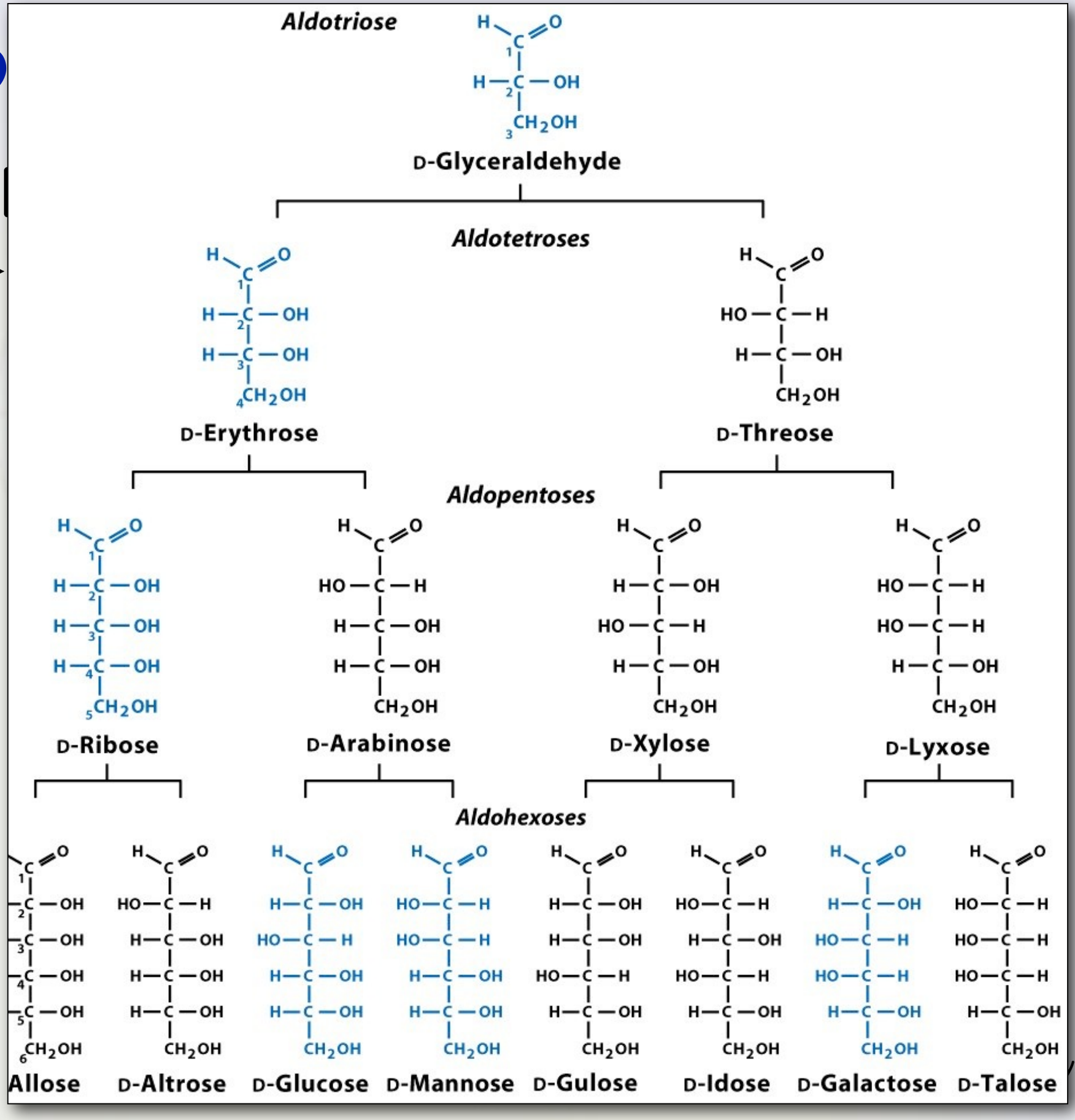
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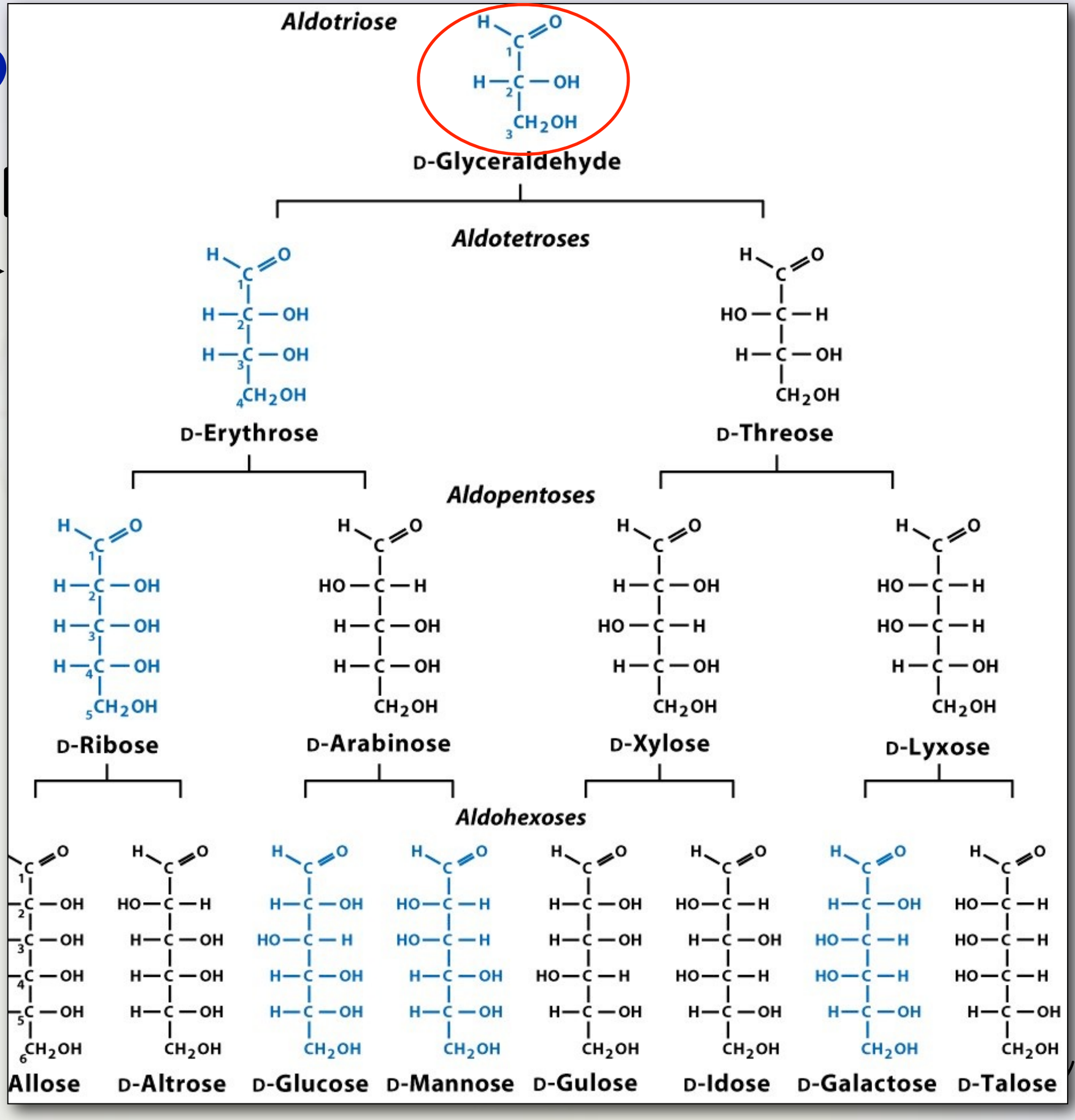
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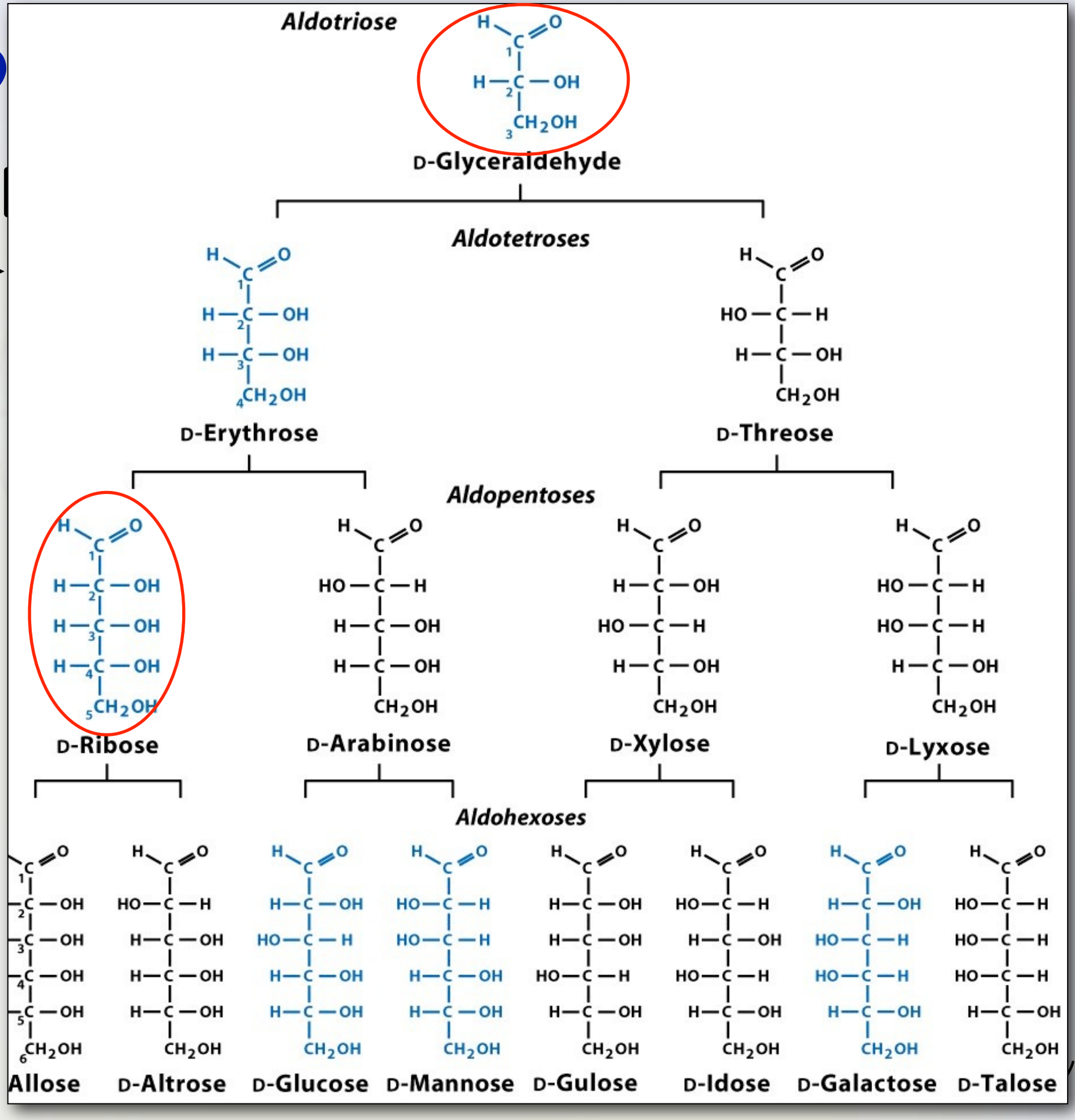
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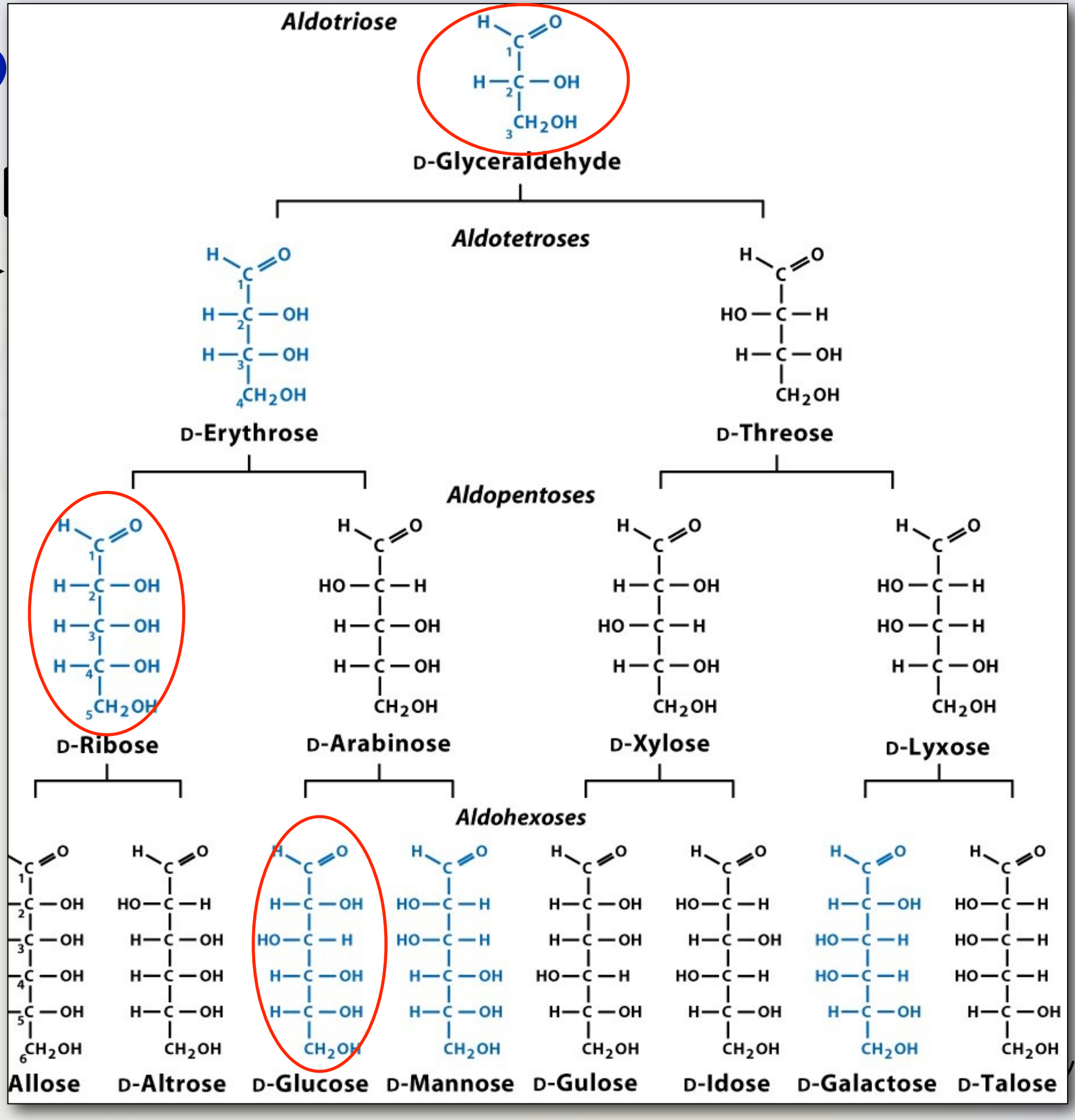
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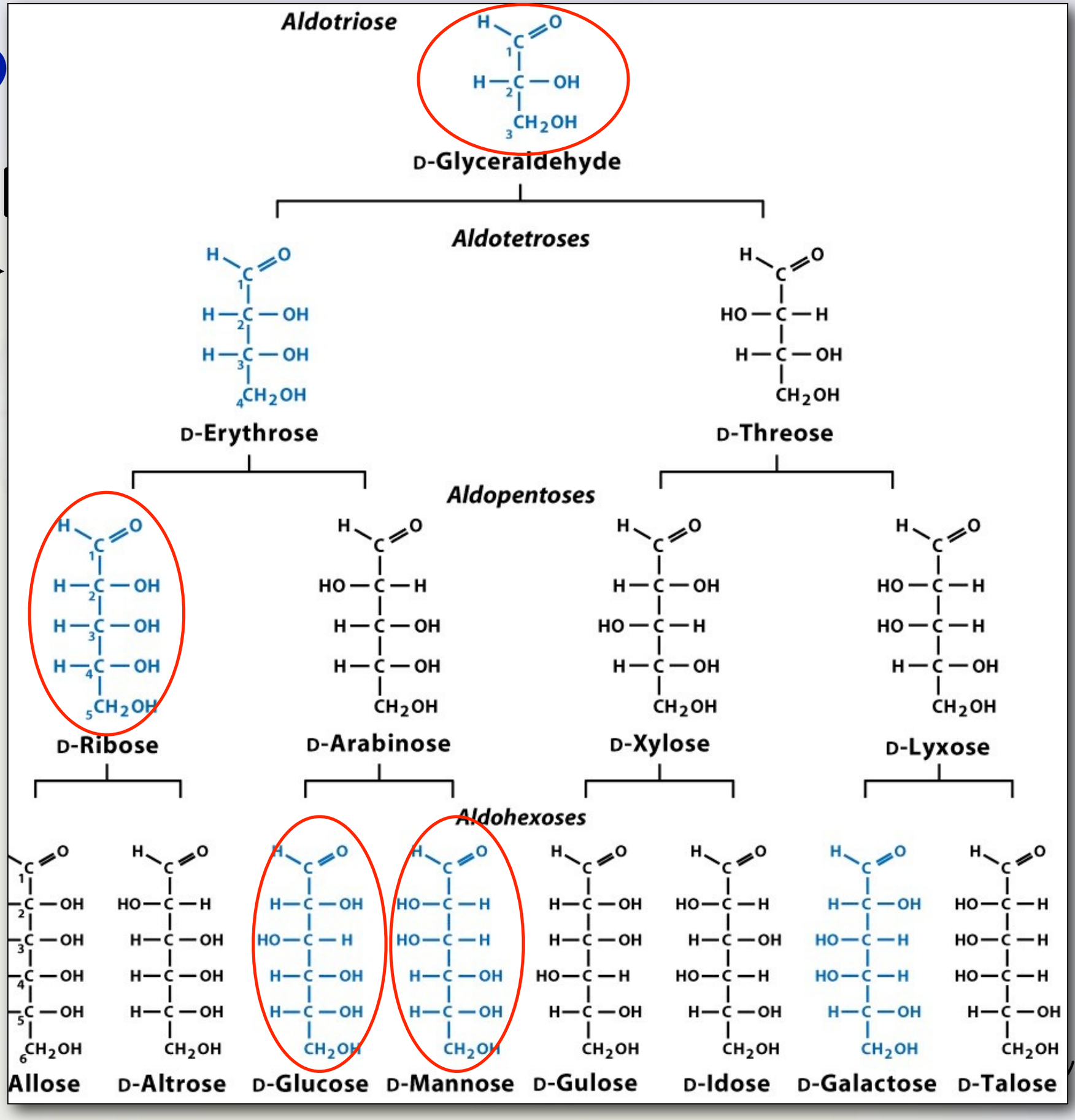
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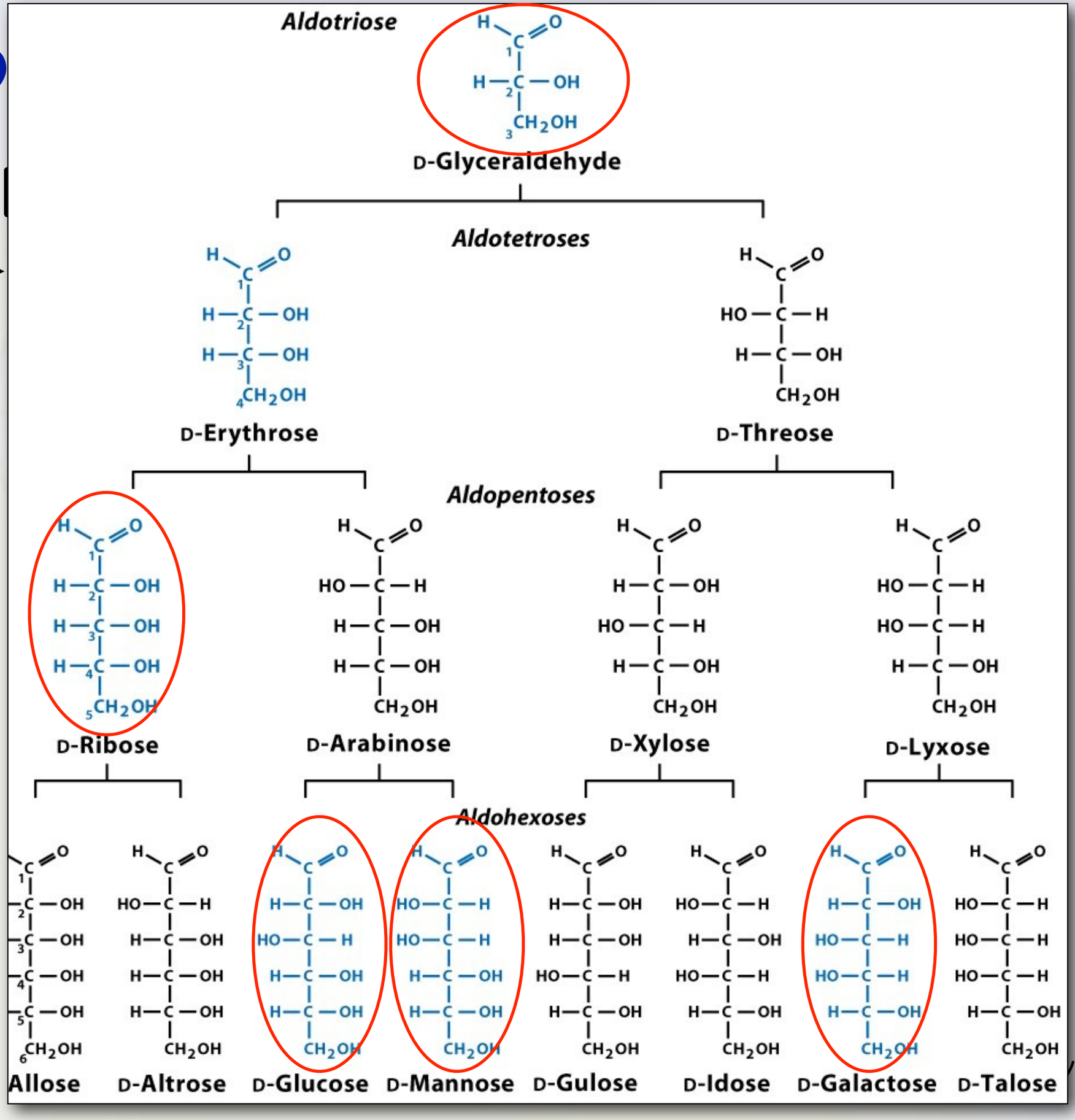
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    - hexoses
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      - D-galactose

Monosaccharides

- The ones to remember
  - Ketoses
    - trisoes
      - dihydroxyacetone
    - pentoses
      - D-ribulose
      - D-xylulose
    - hexoses
      - D-fructose

Monos

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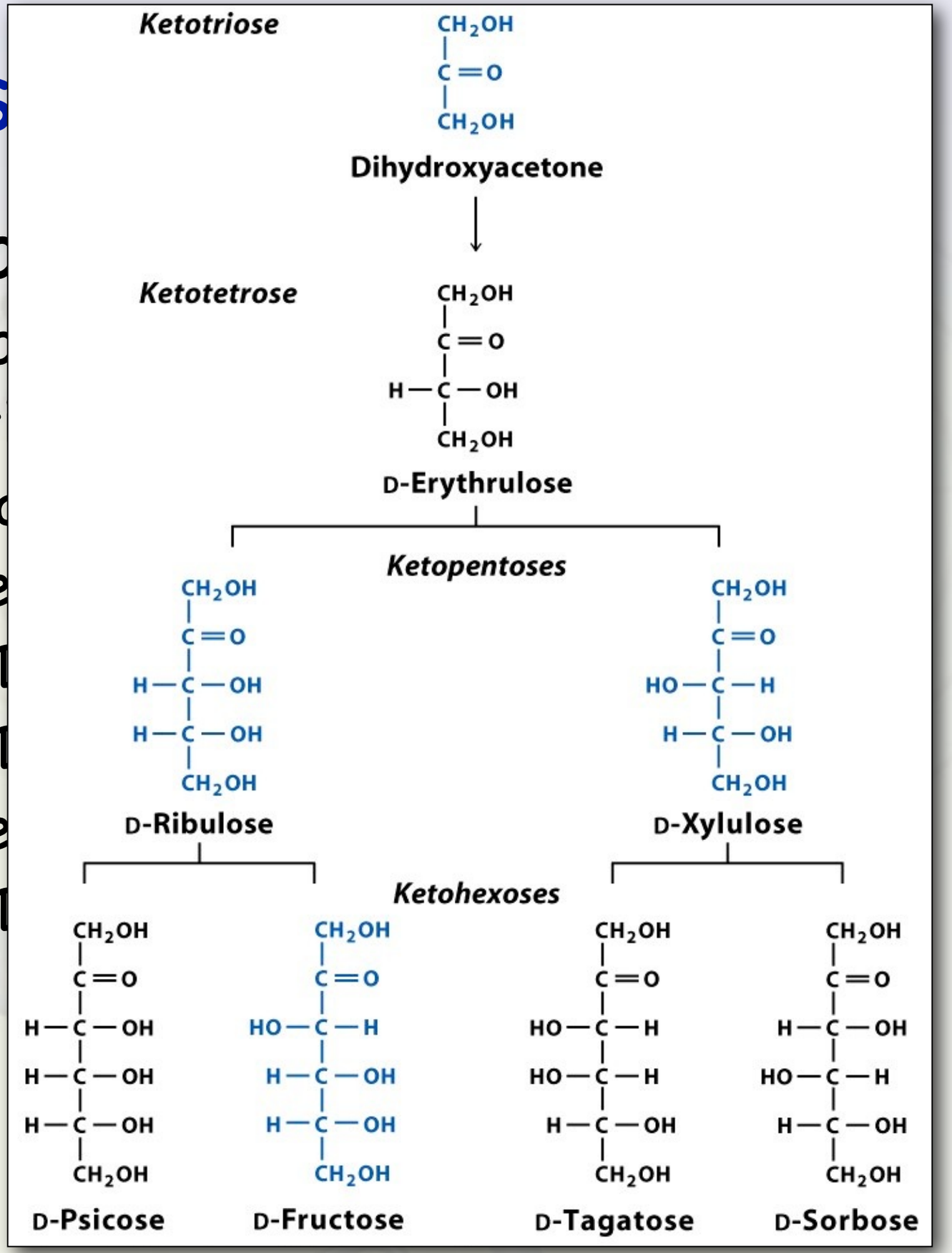

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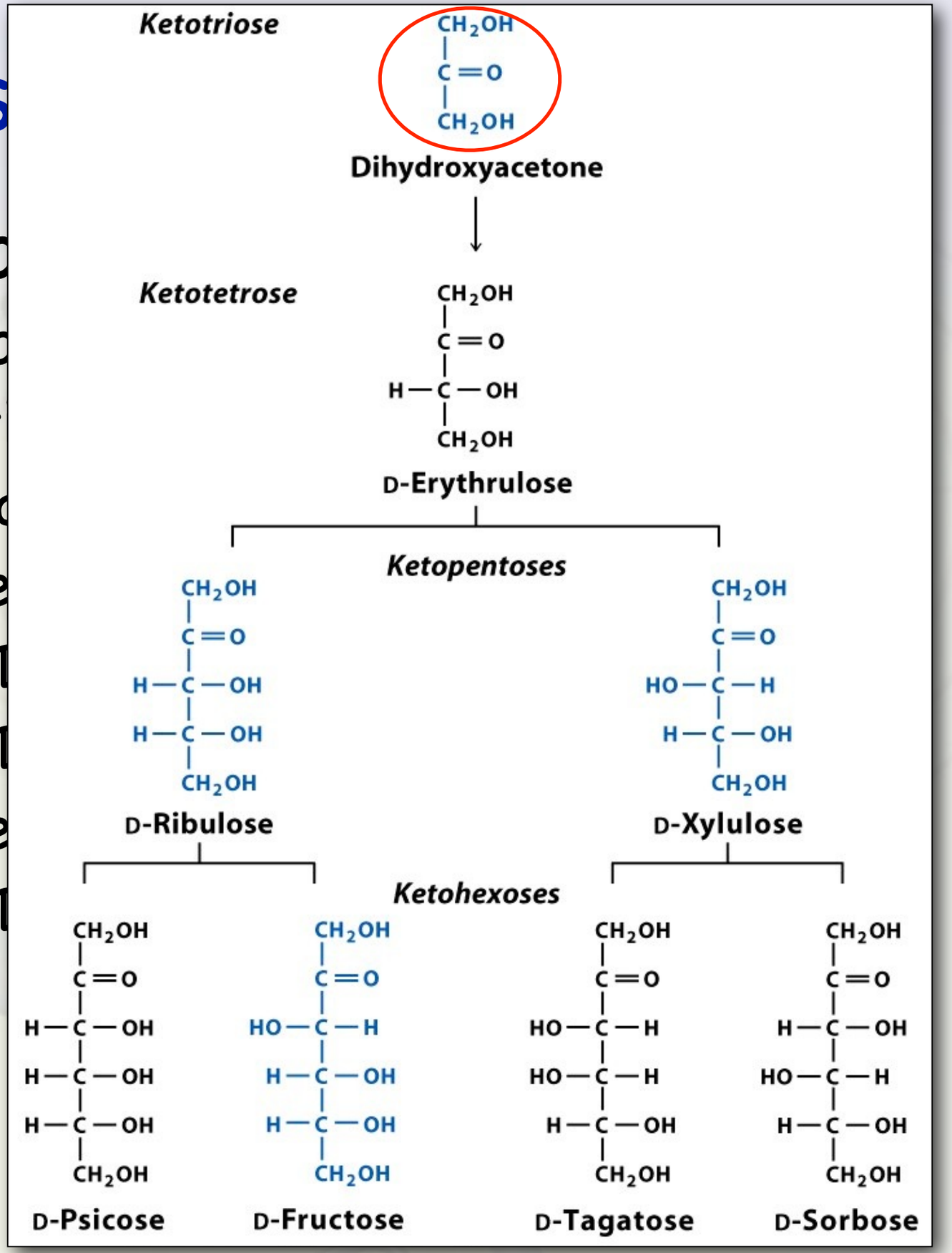

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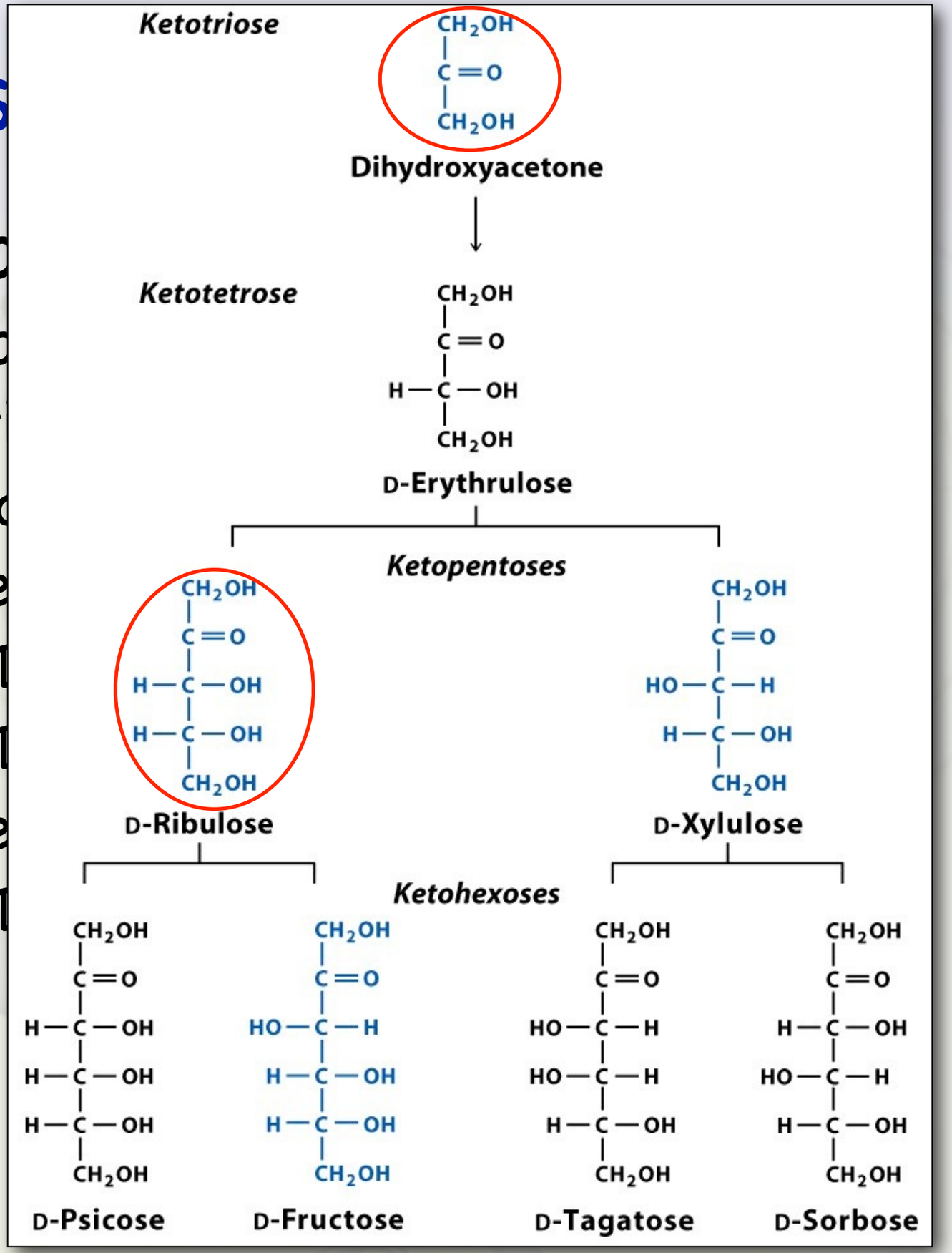

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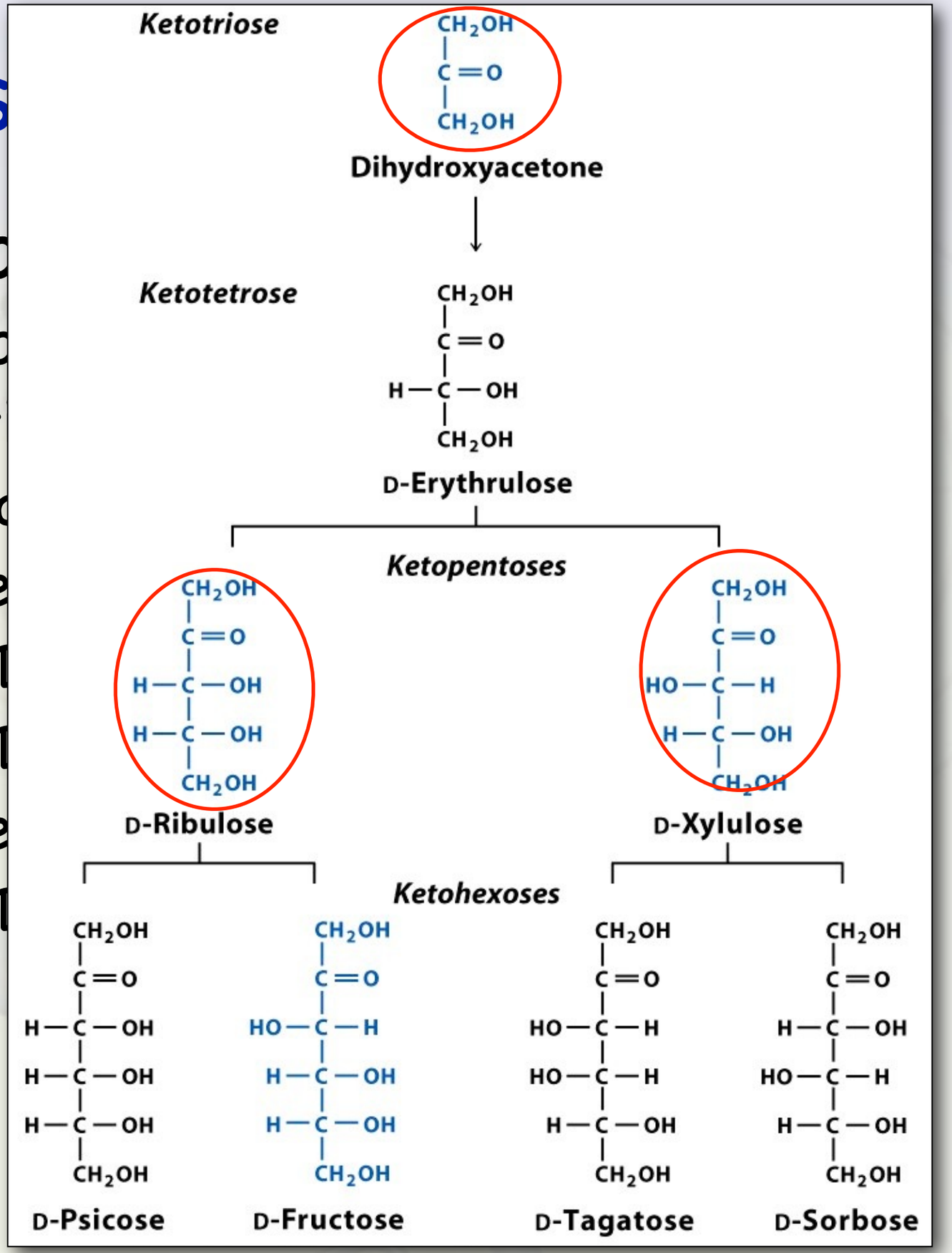

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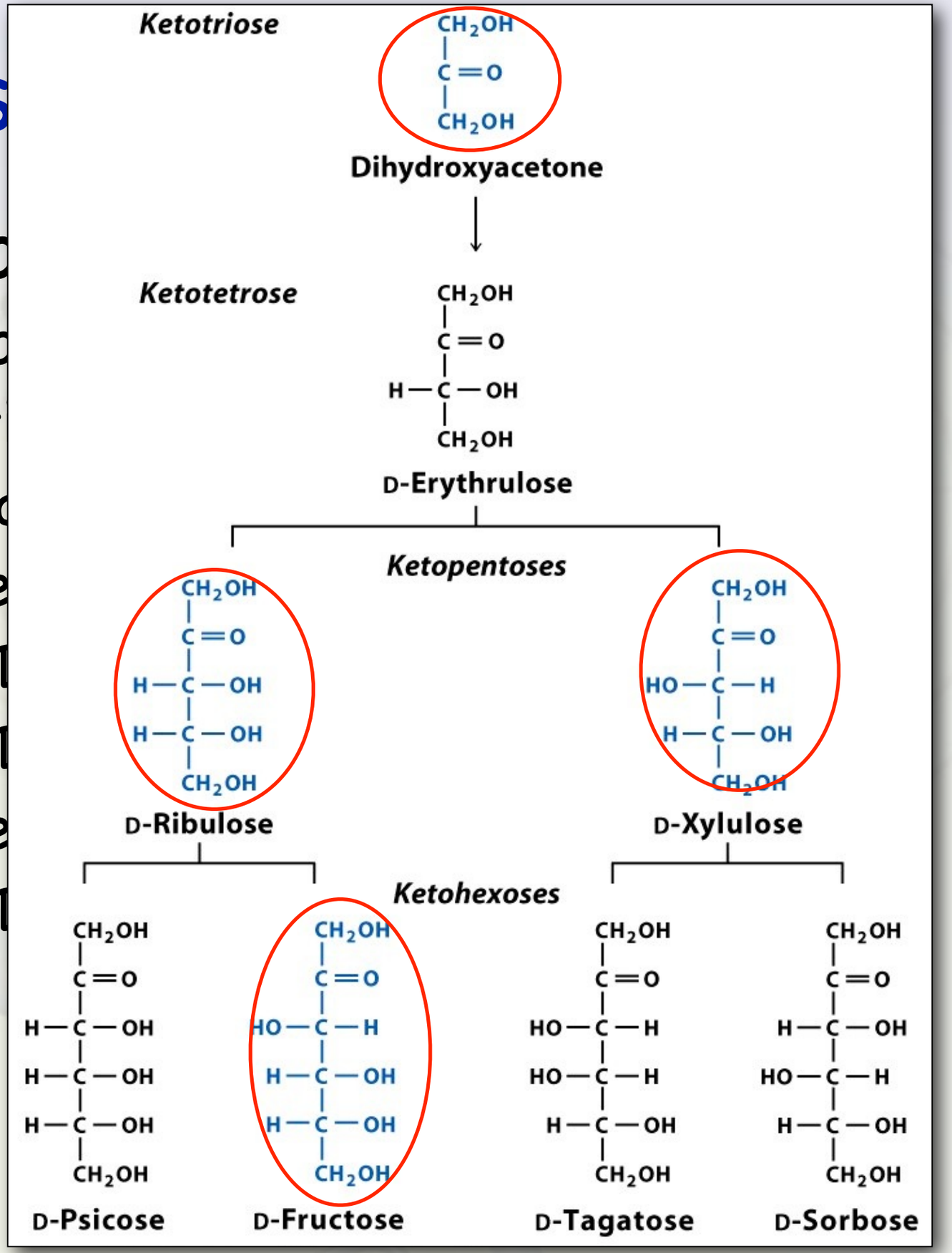

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    - trisoes
      - dihydroxyacetone
    - pentoses
      - D-ribulose
      - D-xylulose
    - hexoses
      - D-fructose

Monosaccharides

- Cyclization of aldoses and ketoses

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

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

  - Both of these reactions leads to the formation of a new chiral carbon

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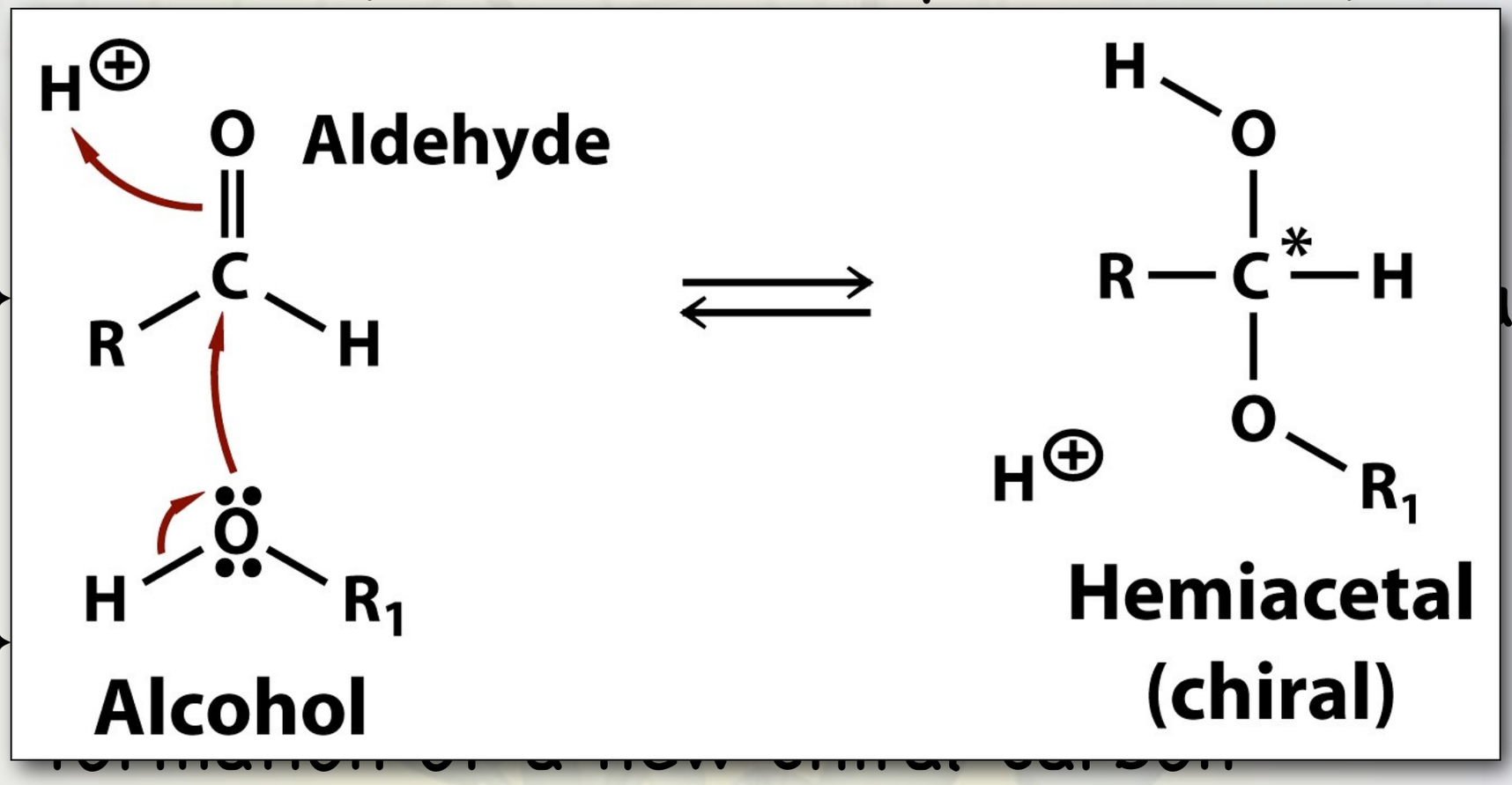

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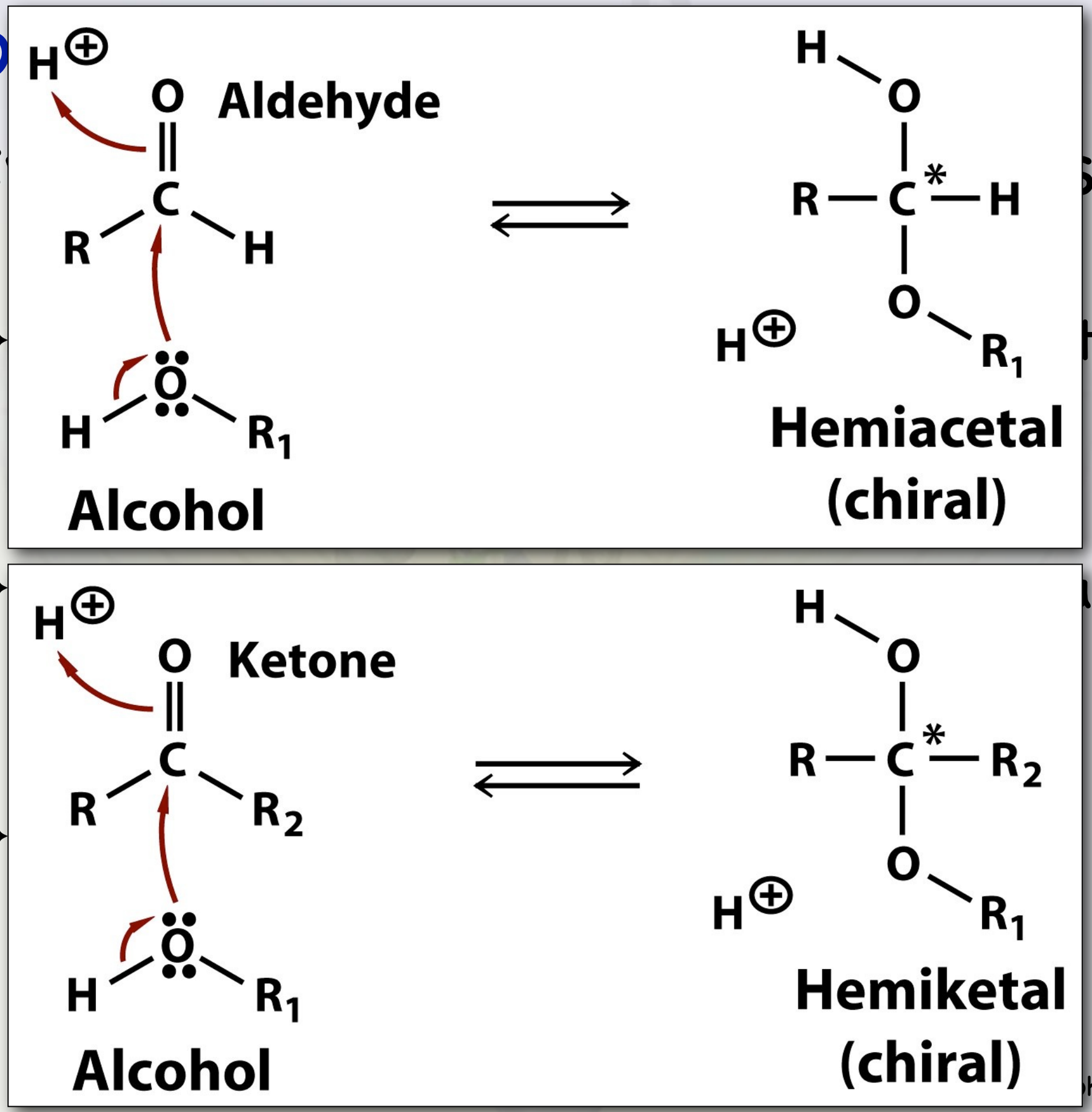

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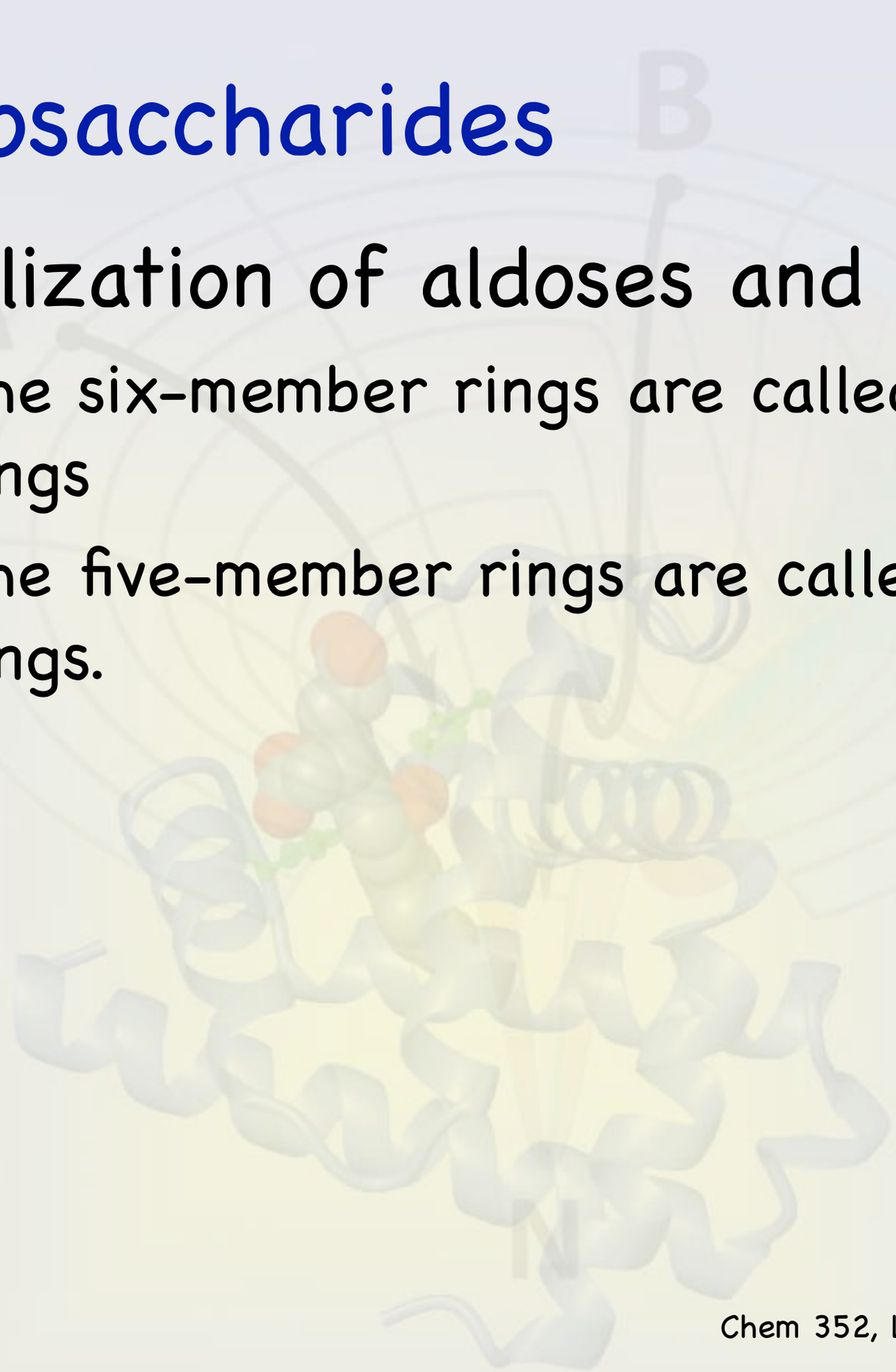
  - The six-member rings are called **pyranose** rings
  - The five-member rings are called **furanose** rings.



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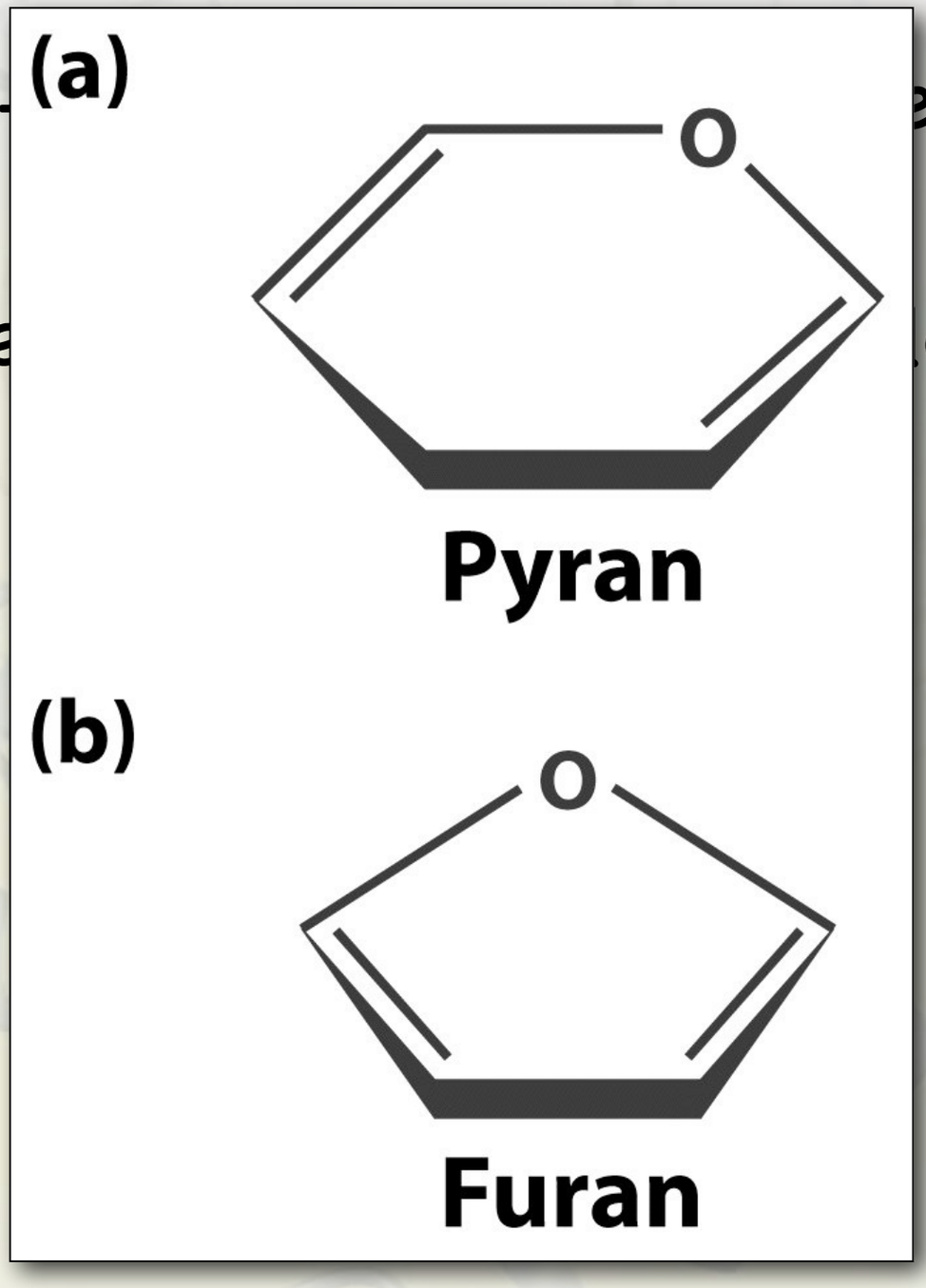

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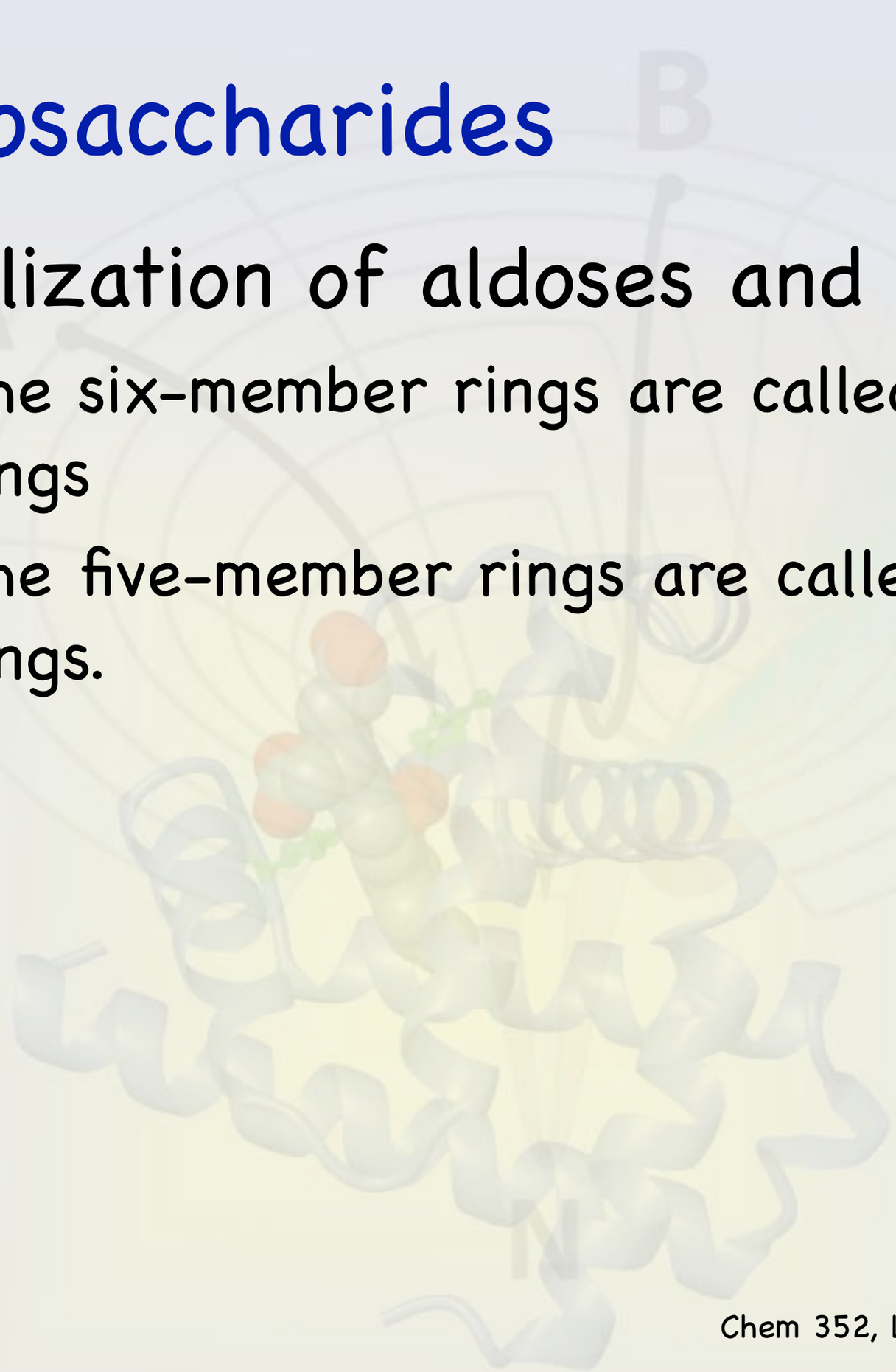

Monosaccharides

- Cyclization of aldoses and ketoses
  - For aldoses and ketoses, this reaction occurs intramolecularly and leads to a cyclic molecule.
  - The chiral hemiacetal or hemiketal carbon is called the **anomeric carbon.**
    - The new stereoisomers are designated α (-OH down) and β **anomers** (-OH up).
- **Haworth projections** are used to represent the cyclic form of monosaccharides.

Monosaccharides

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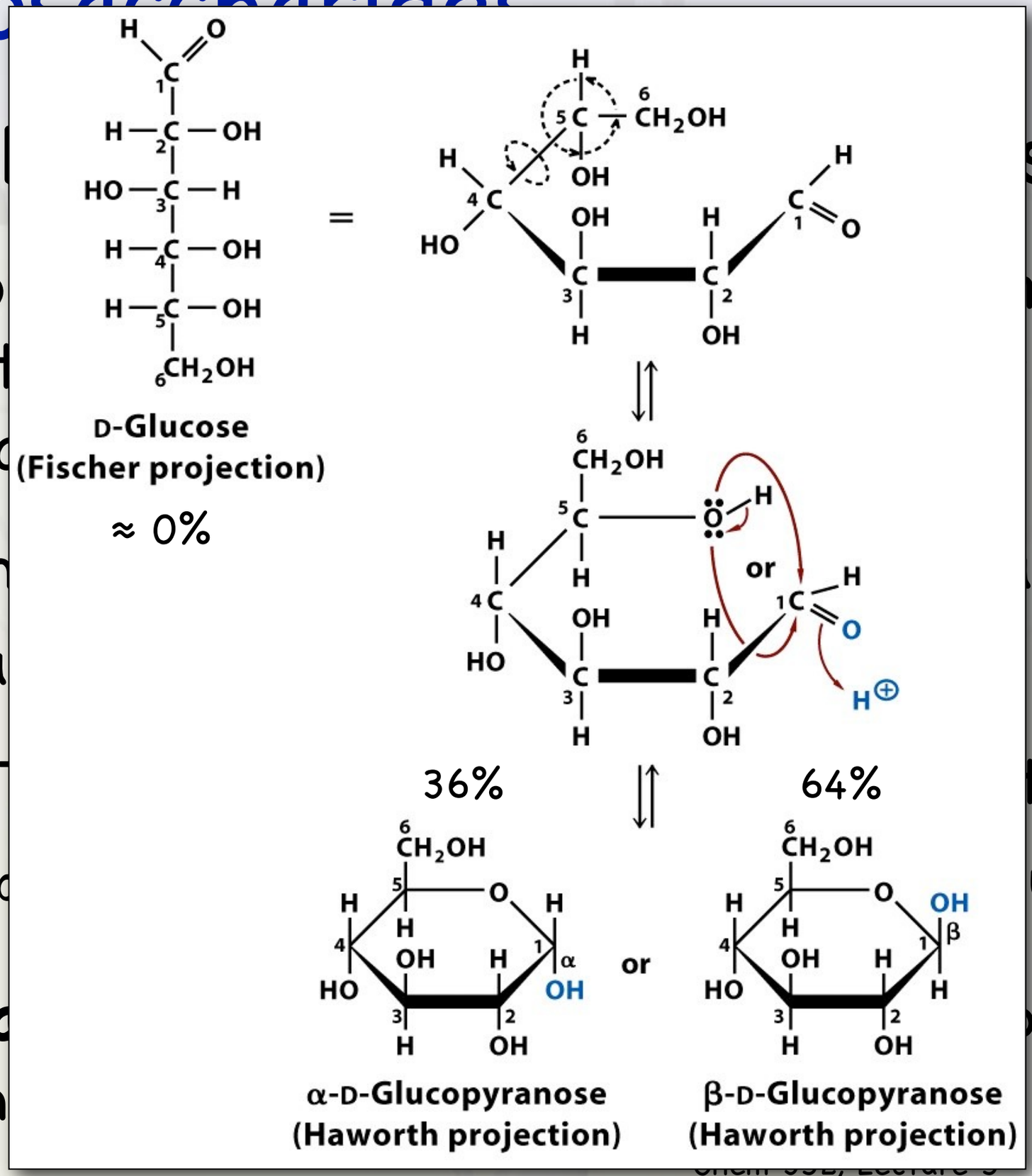

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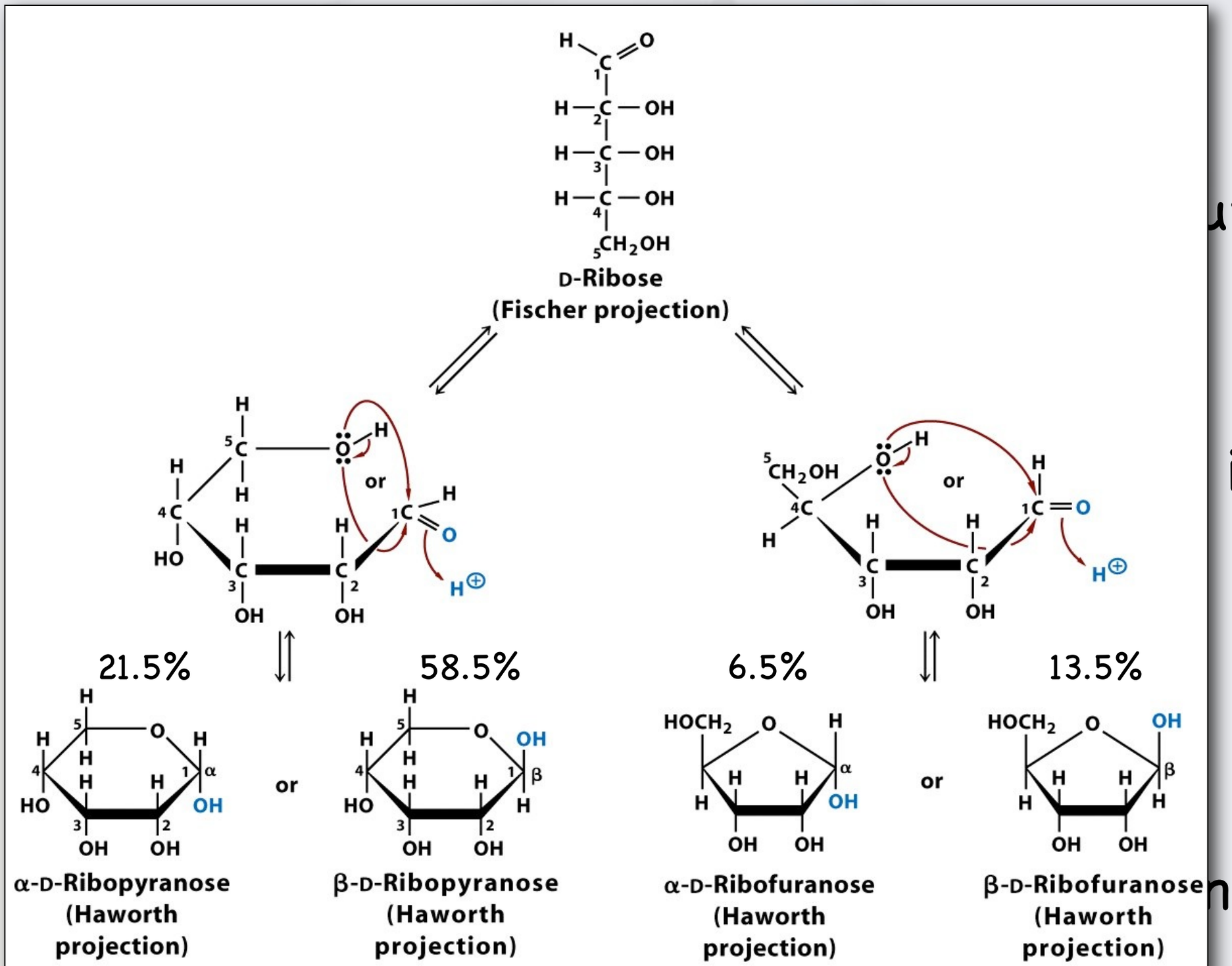

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  - **pyranose** rings
    - D-glucopyranose (aldohexose)
    - D-mannopyranose (aldohexose)
    - D-galactopyranose (aldohexose)
  - **furanose** rings
    - D-fructofuranose (ketohexose)
    - D-ribofuranose (aldopentose)

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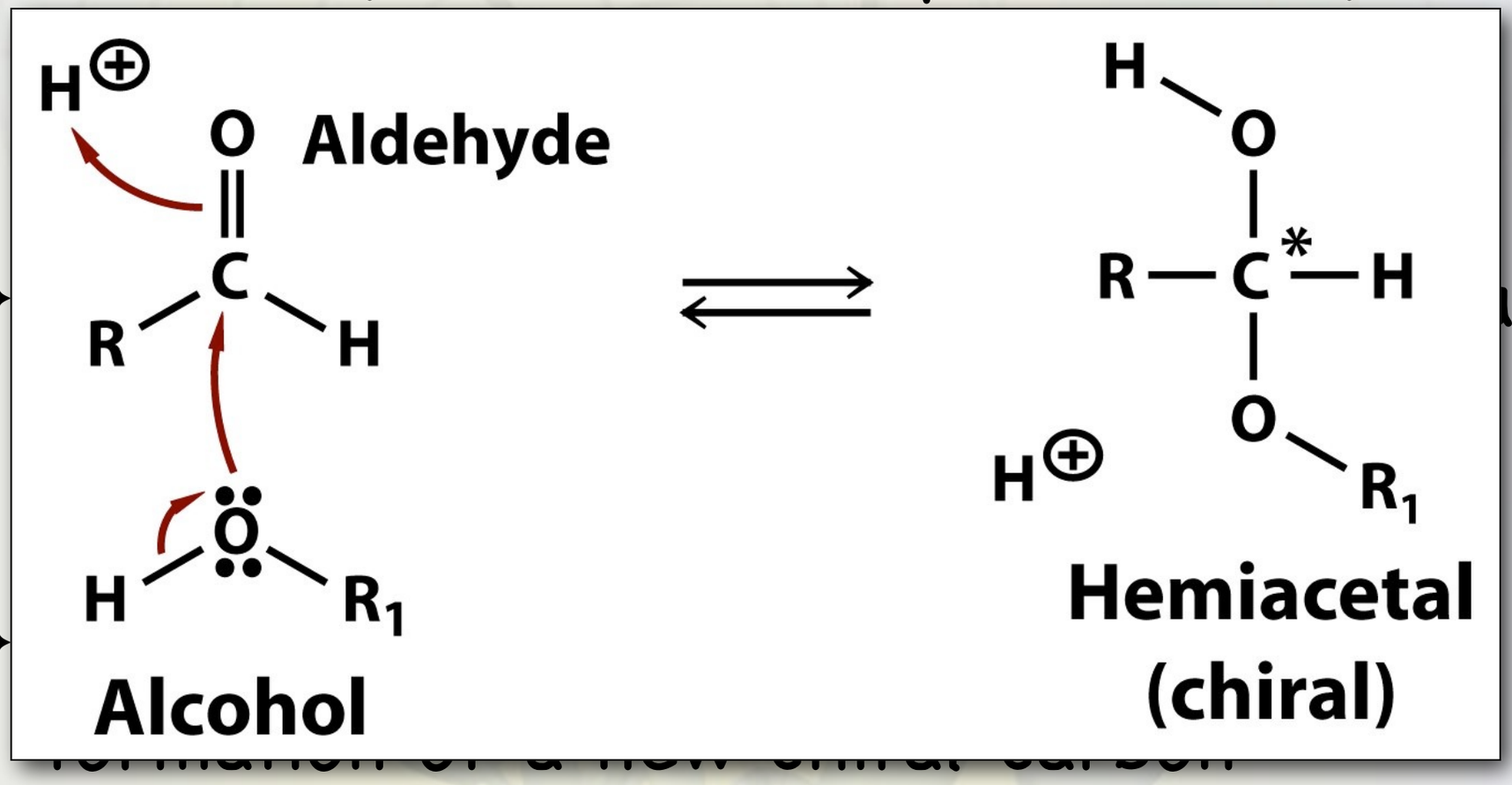

Monosaccharides

- Conformations of Monosaccharides
  - Monosaccharides can have different conformations.

Monosaccharides

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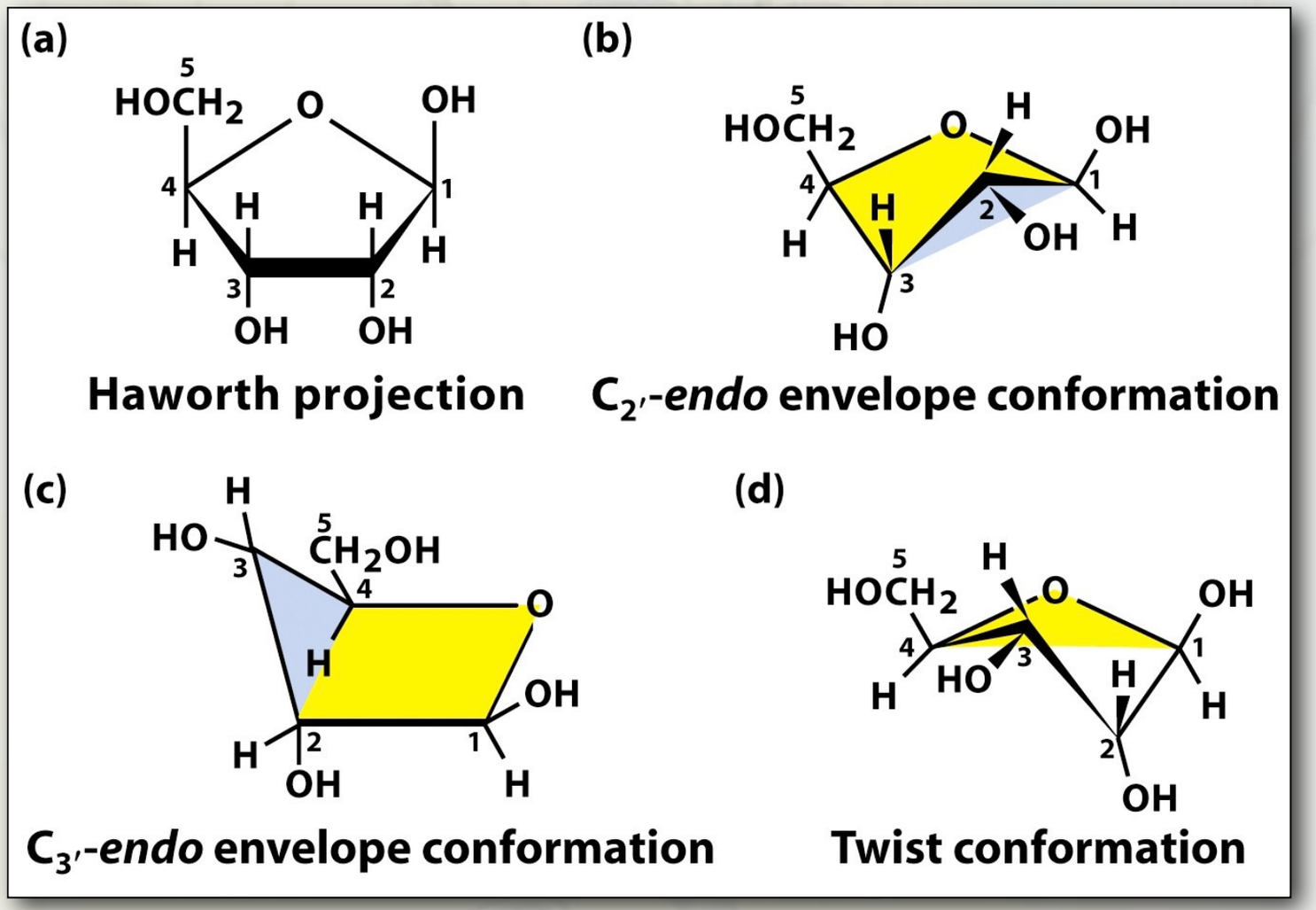
  - Monosaccharides can have different conformations.



Monosaccharides

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Monosaccharides

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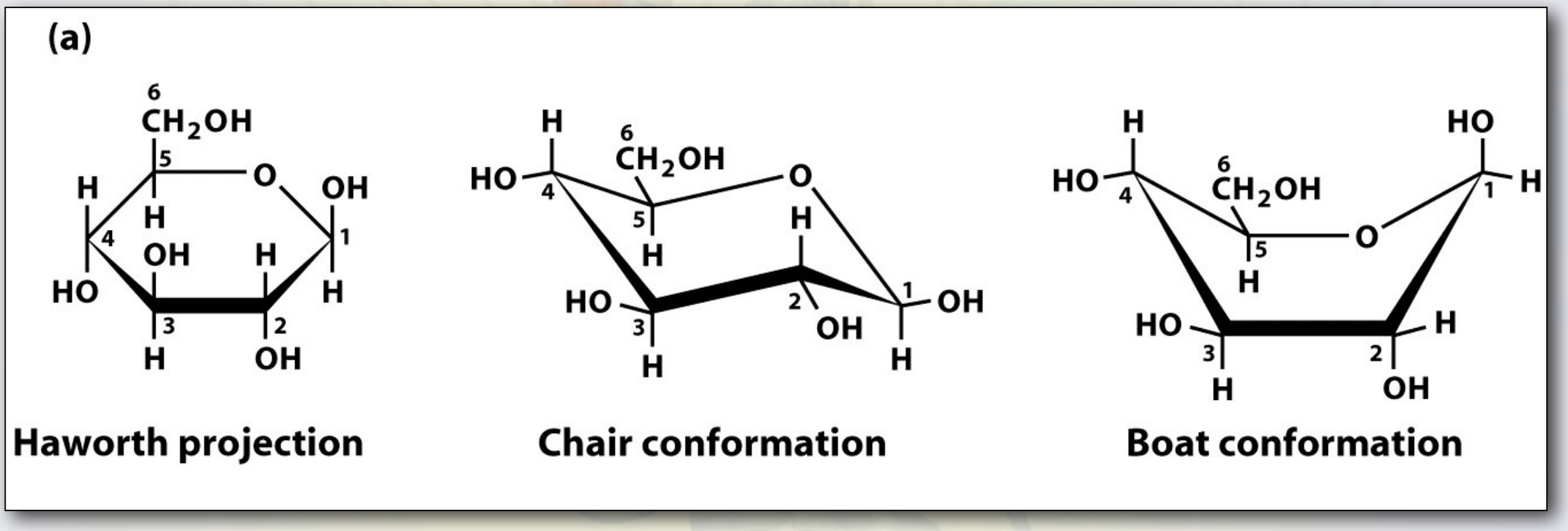

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Monosaccharides

- Derivatives of monosaccharides are produced by chemical modifications.
  - **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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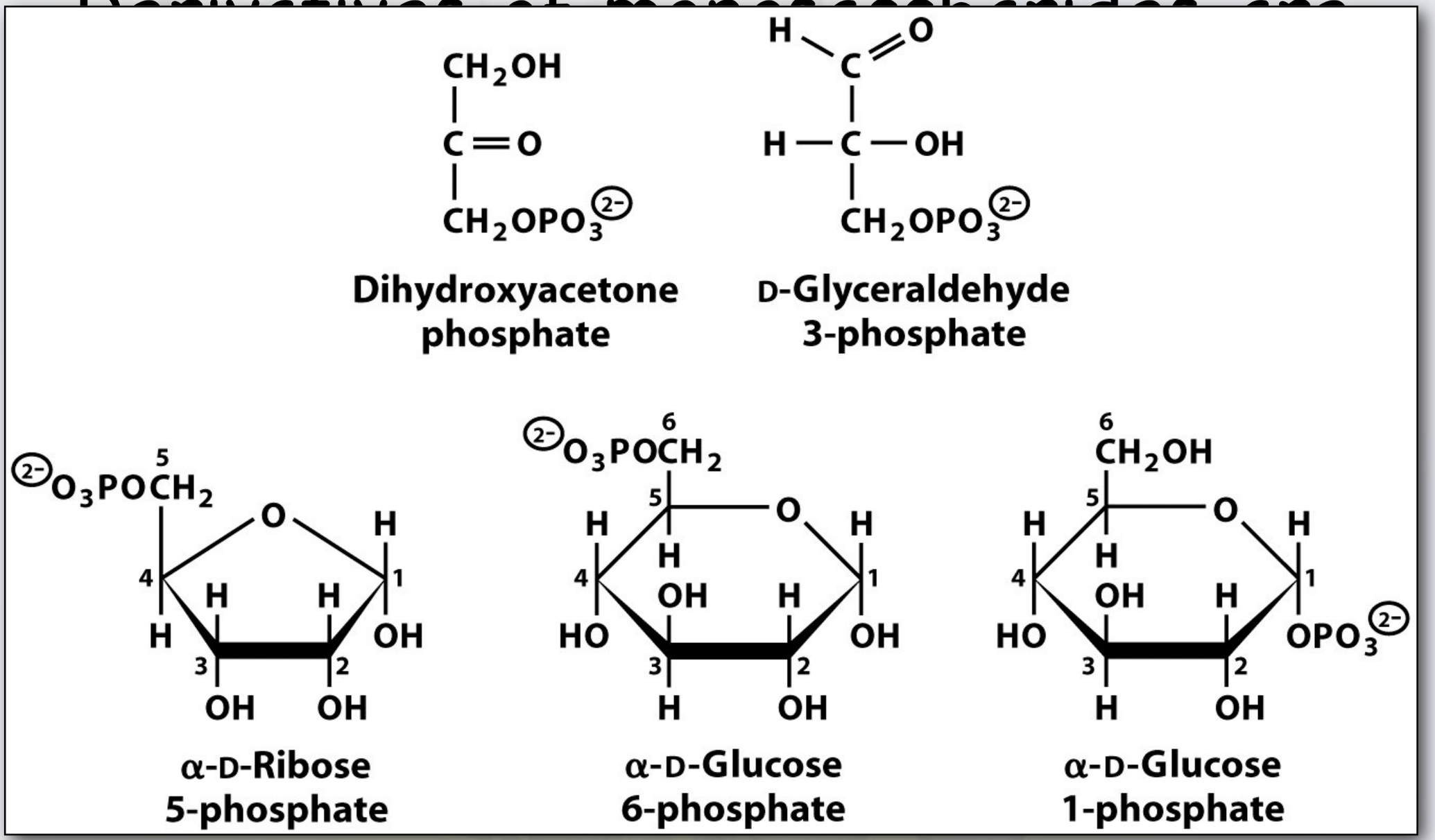

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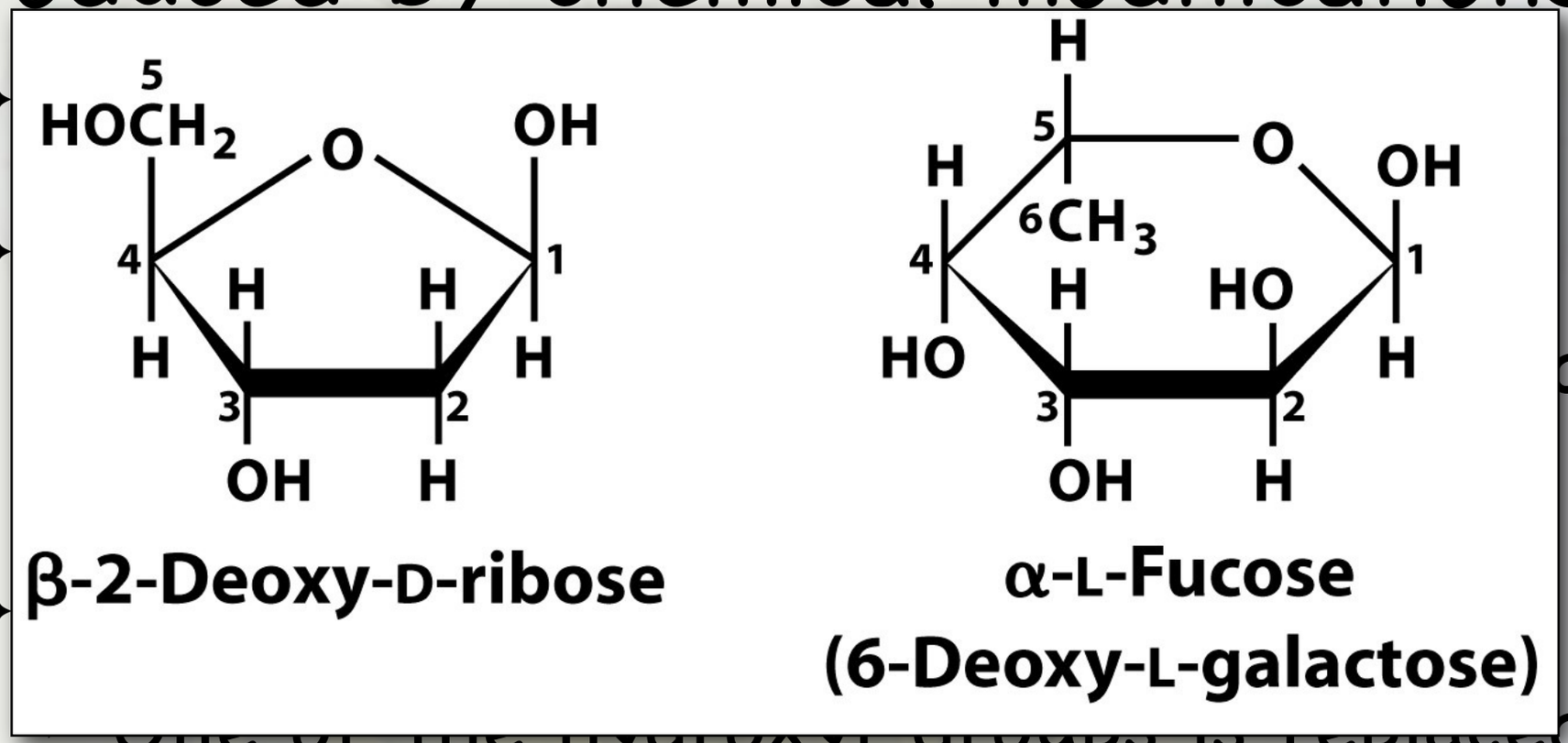

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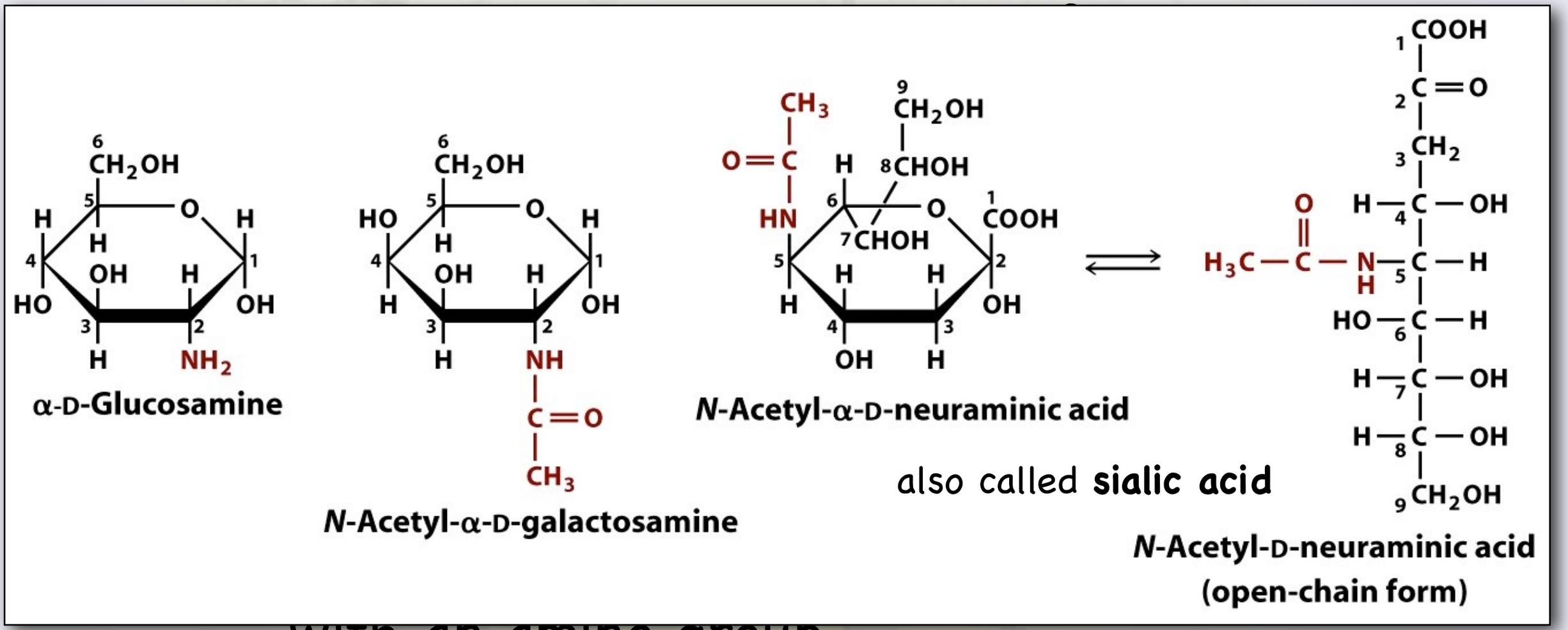

with an amino group.

Monosaccharides

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  - **Phosphate esters**
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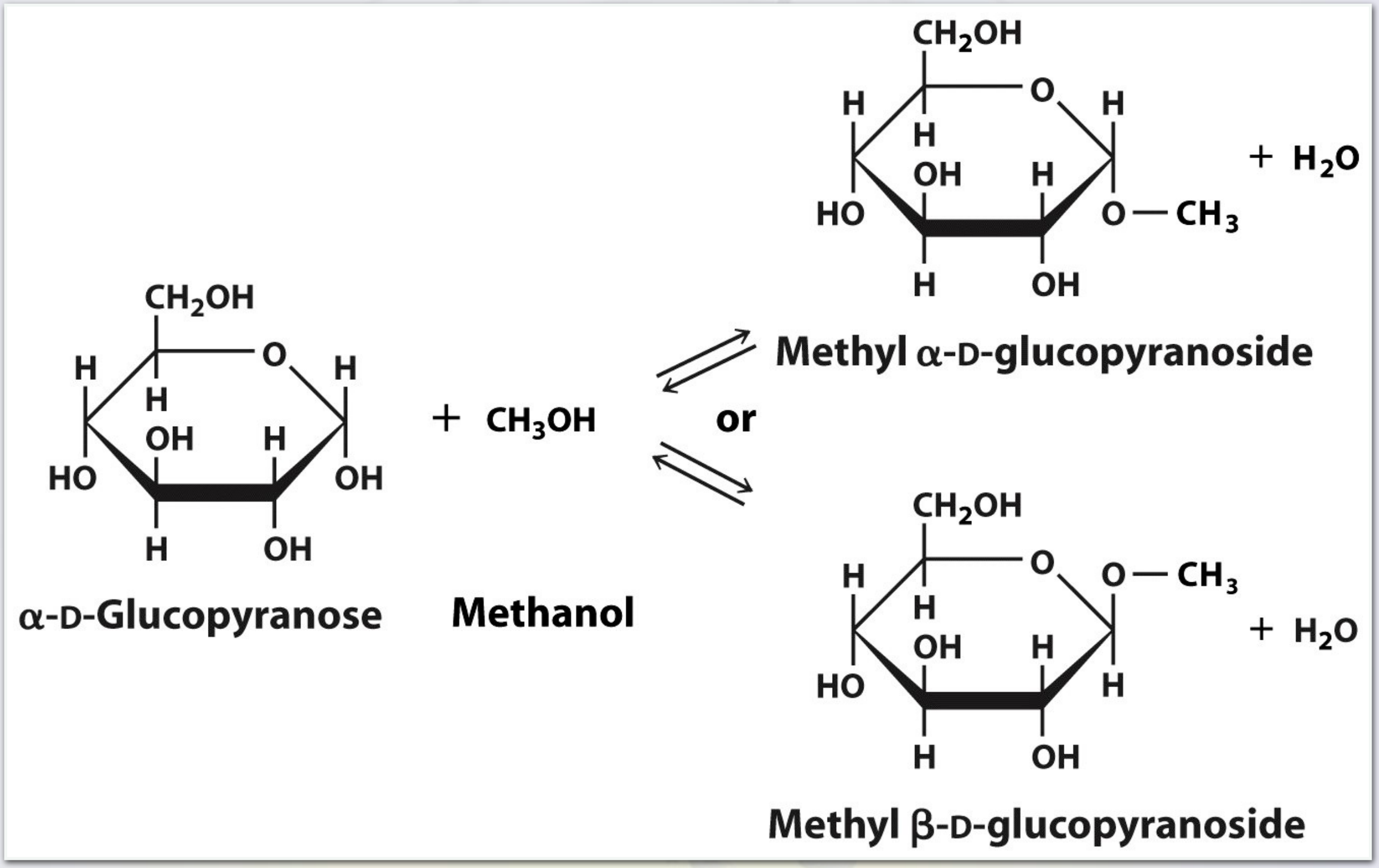
Glycosides

- The **hemiacetal** or **hemiketal** carbon can go on to react with the **hydroxyl group** from another molecule to form an **acetal** or **ketal**.
  - The bond formed is called a **glycosidic bond**.
  - Glycosidic bonds are used to connect one monosaccharide to another.

Glycosides


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

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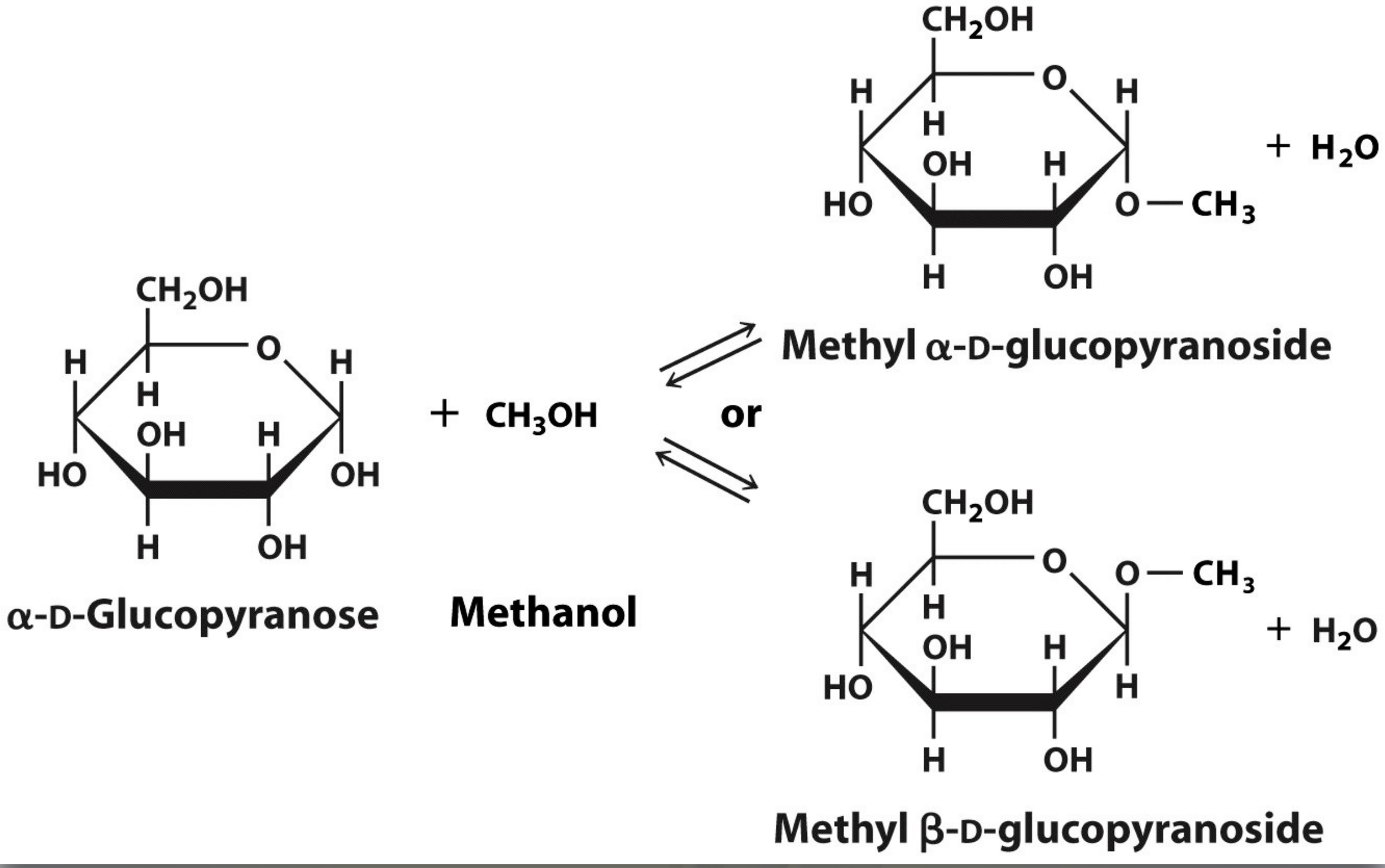
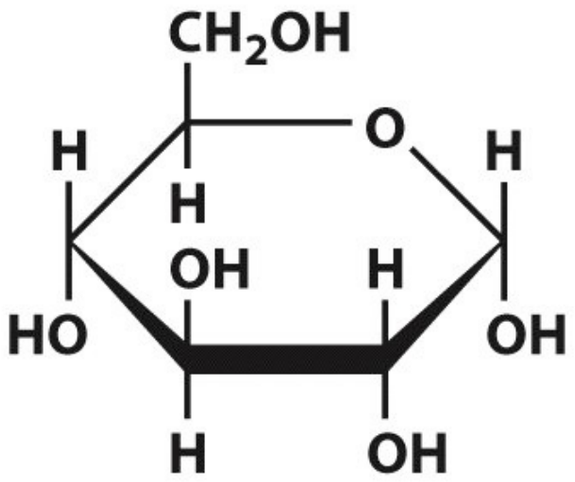
Glycosides

- Unlike hemiacetals and hemiketals, acetals and ketals cannot open and close dynamically,
  - The glycosidic bond blocks a pyranose or furanose ring from reopening again.
- In cells, glycosidic bond formation is enzyme catalyzed and requires a source of free energy.

Glycosides

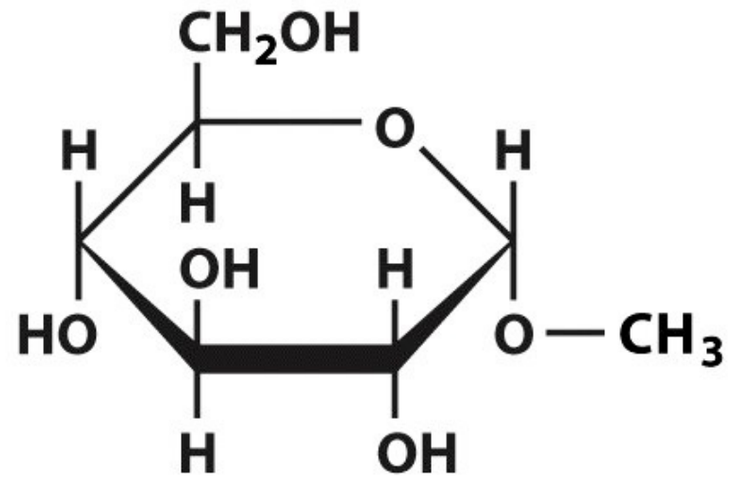

CH2OH
O
H
H
OH
H
HO
OH
H
OH
α-D-Glucopyranose
+ CH3OH
Methanol
or
CH2OH
O
H
H
OH
H
HO
O — CH3
+ H2O
Methyl α-D-glucopyranoside
CH2OH
O
O — CH3
H
H
OH
H
HO
H
H
OH
+ H2O
Methyl β-D-glucopyranoside

Glycosides



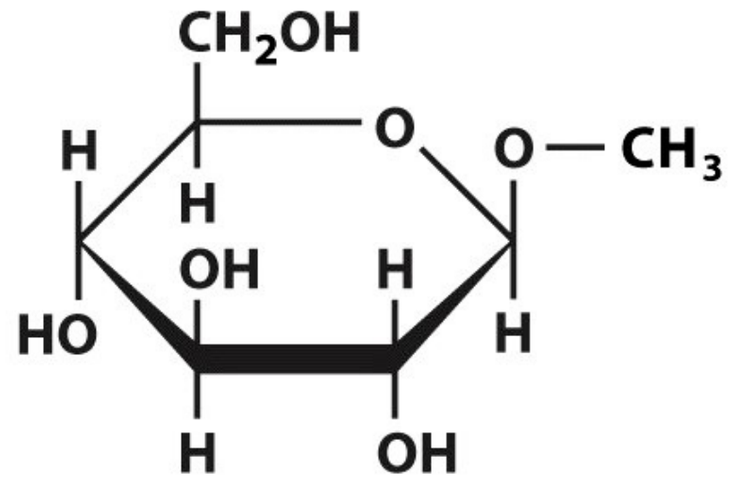
+ CH_3OH

Methanol



+ H_2O

or



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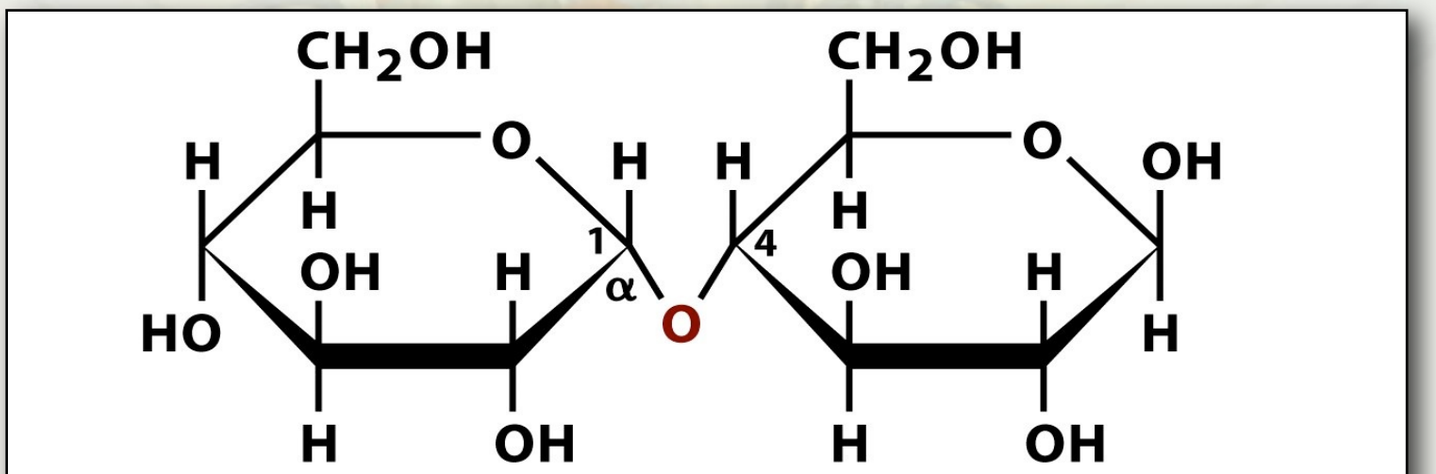
Monosaccharides

Cyclized aldoses and ketoses tend to get locked into the following ring configurations

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

Glycosides

- The glycosidic bond can be used to connect two monosacchrides together to form **disaccharides**.
- Important disaccharides include:
  - **Maltose** (obtained from starch)



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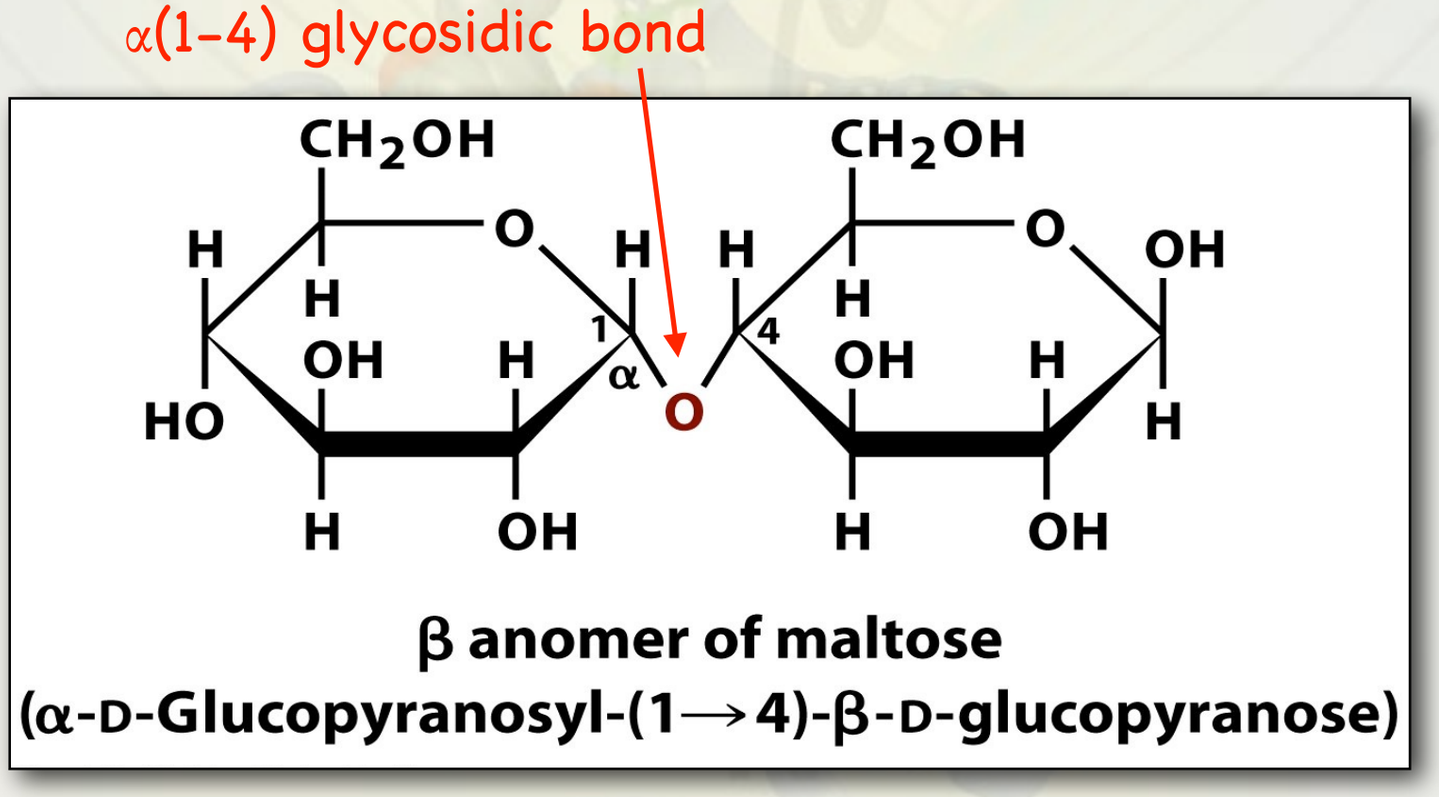

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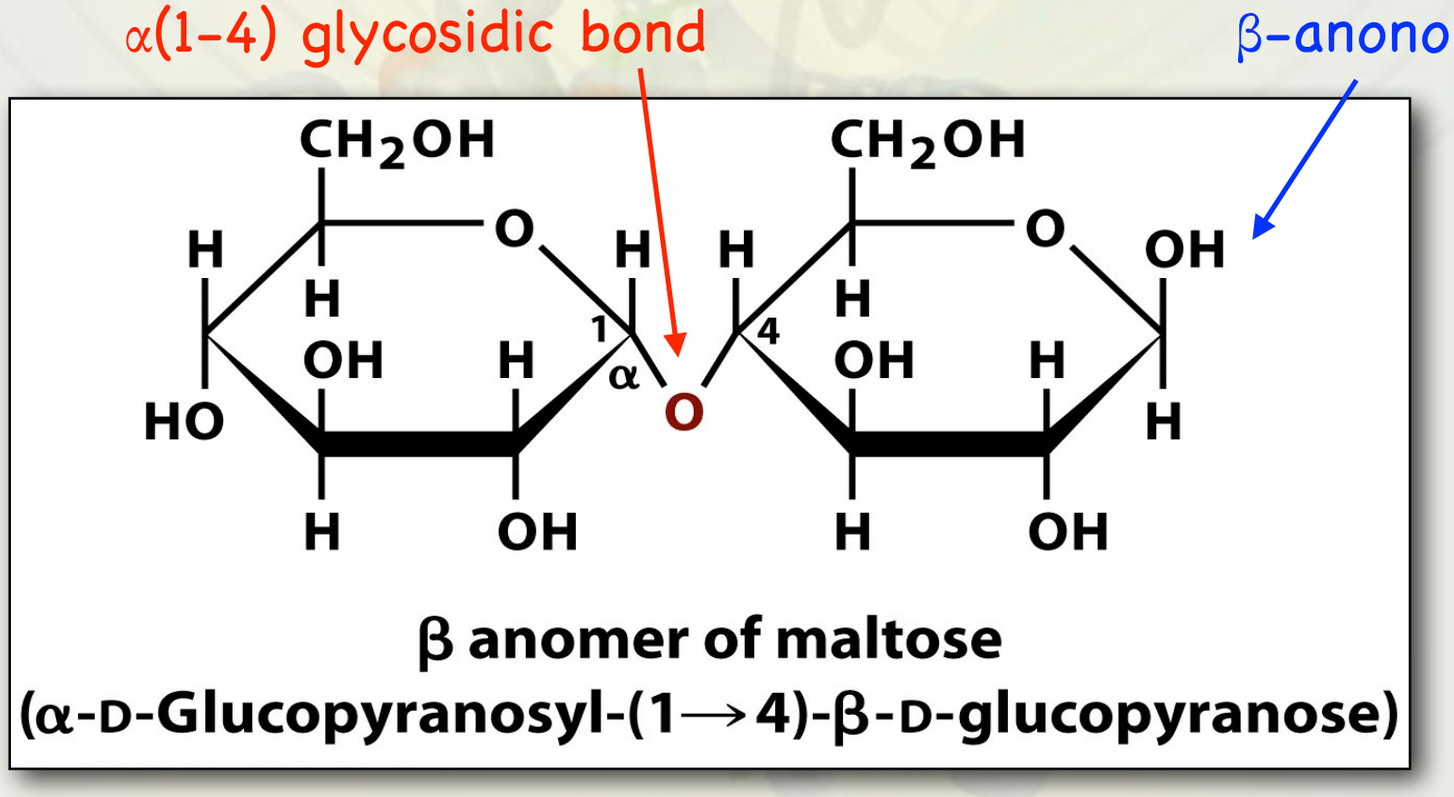

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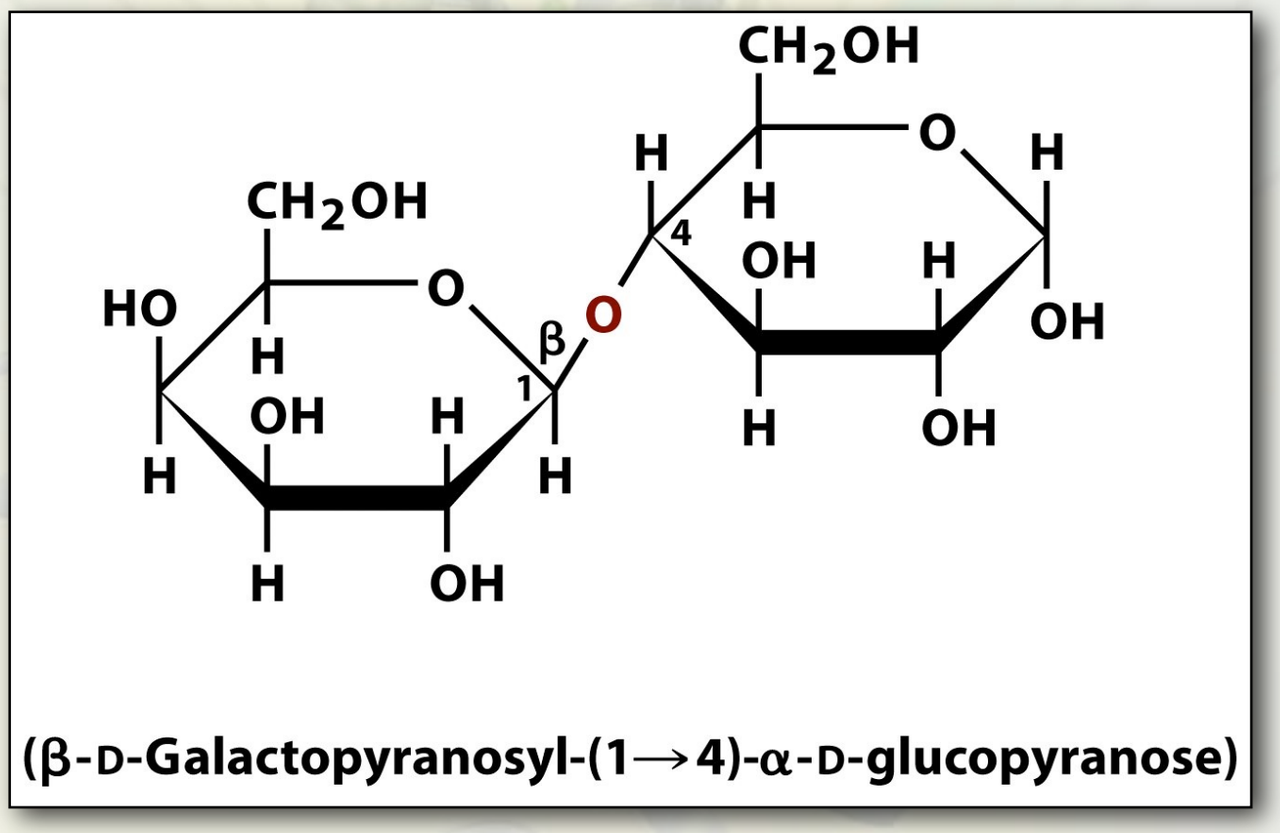
- Important disaccharides include:
  - **Lactose**



(β-D-Galactopyranosyl-(1→4)-α-D-glucopyranose)

Glycosides

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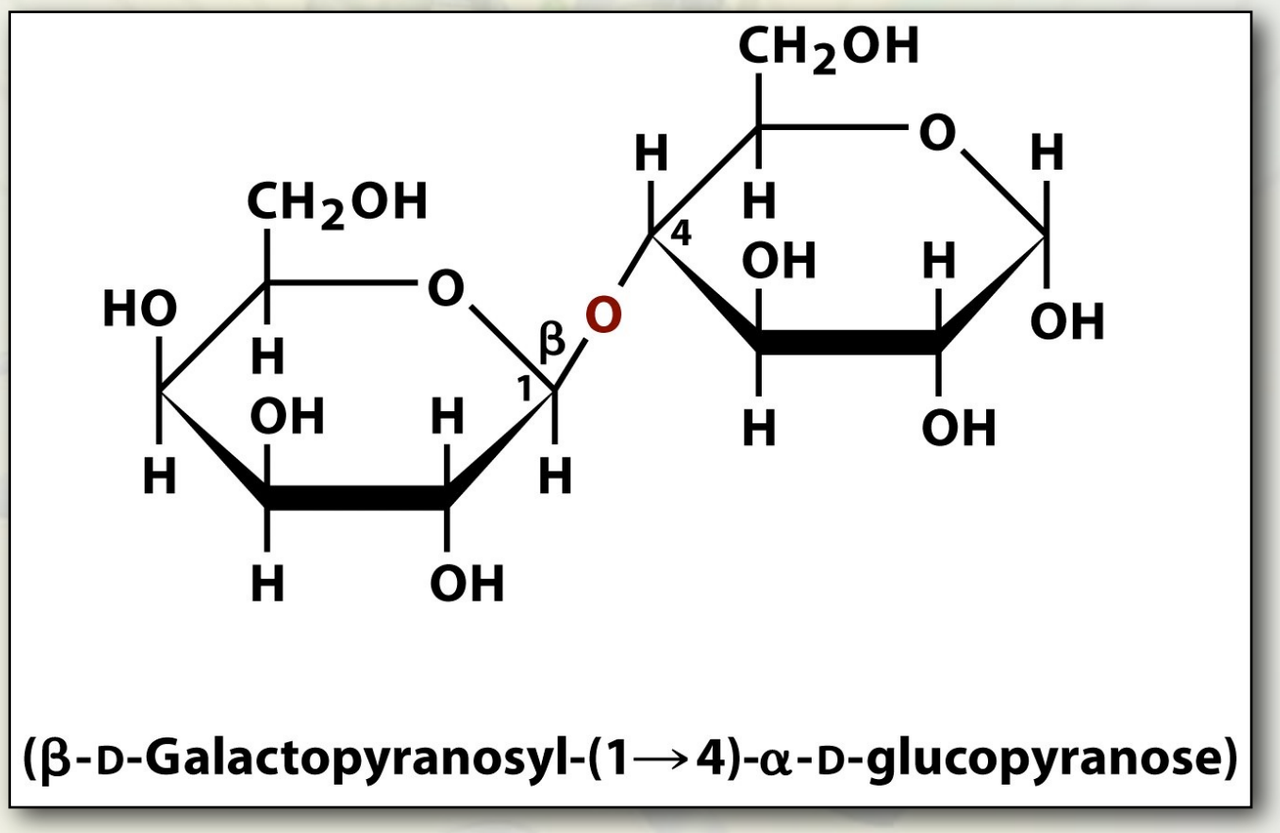
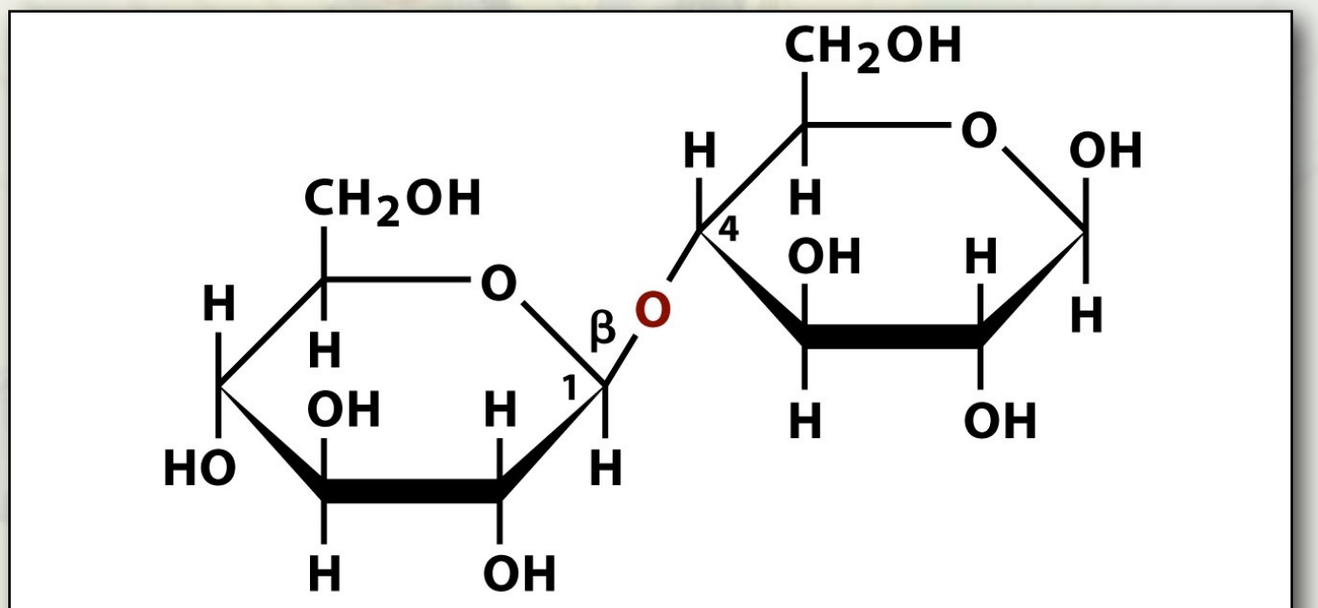
- Important disaccharides include:
  - **Lactose** (milk sugar)



(β-D-Galactopyranosyl-(1→4)-α-D-glucopyranose)

Glycosides

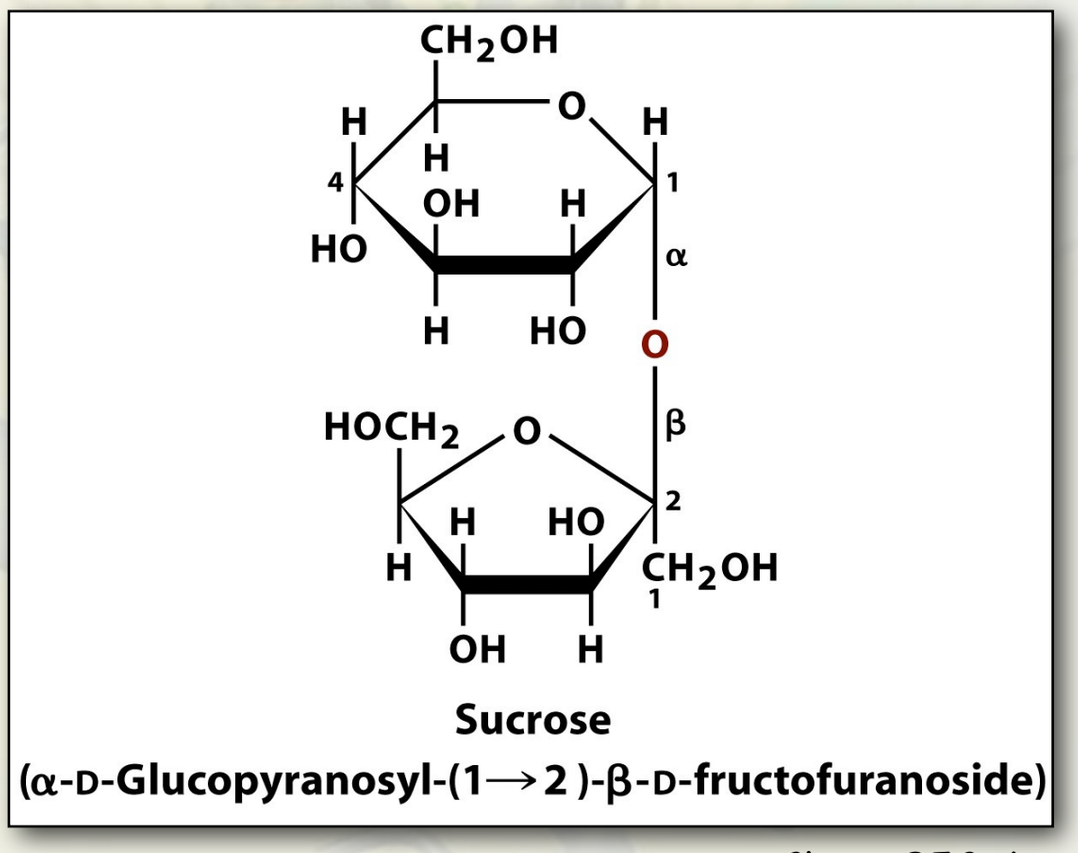
- The glycosidic bond can be used to connect two monosacchrides together to form a **disaccharides**.
- Important disaccharides include:
  - **Cellobiose** (obtained from cellulose)



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

Glycosides

- The glycosidic bond can be used to connect two monosacchrides together to form a **disaccharides**.
- Important disccharides include
  - **Sucrose** (table sugar)



Sucrose

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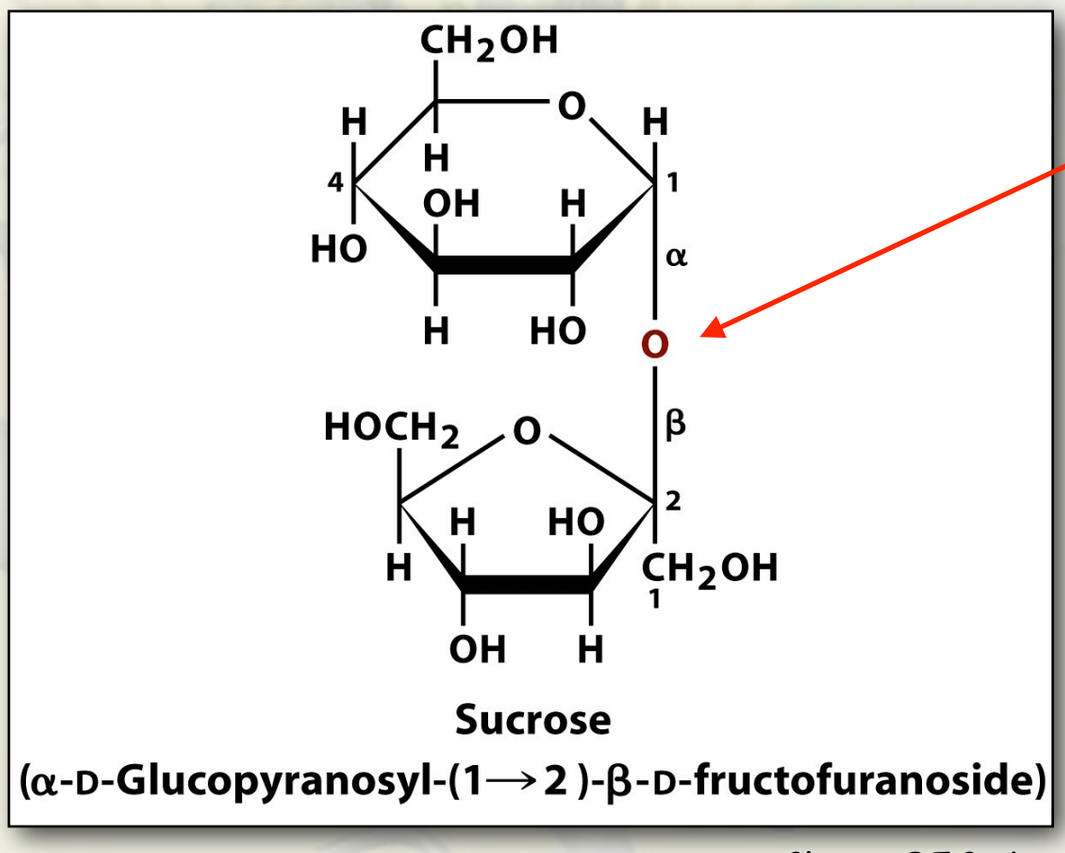


α1–β2 glycosidic bond

Glycosides

- Because a hemiacetal or hemiketal can easily open to expose either an aldehyde or ketone, they can still serve as reducing agents.

$CuSO_4(aq)$
clear blue

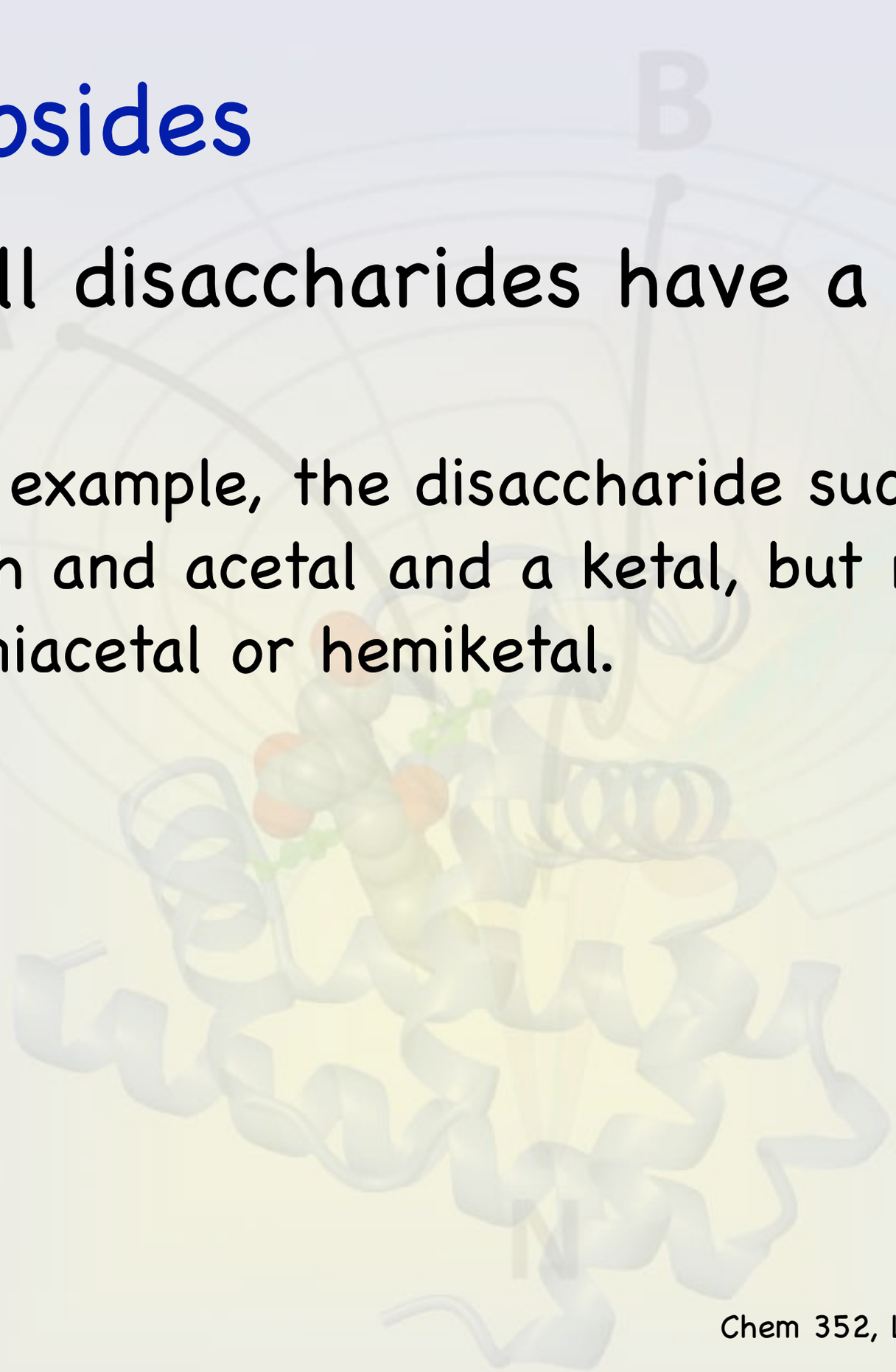
$Cu_2O(s)$
red ppt.

- This is used to distinguish the two monosaccharides in a disaccharide as the **reducina** and the **nonreducina** ends.

Glycosides

Not all disaccharides have a reducing end

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



Glycosides

Not

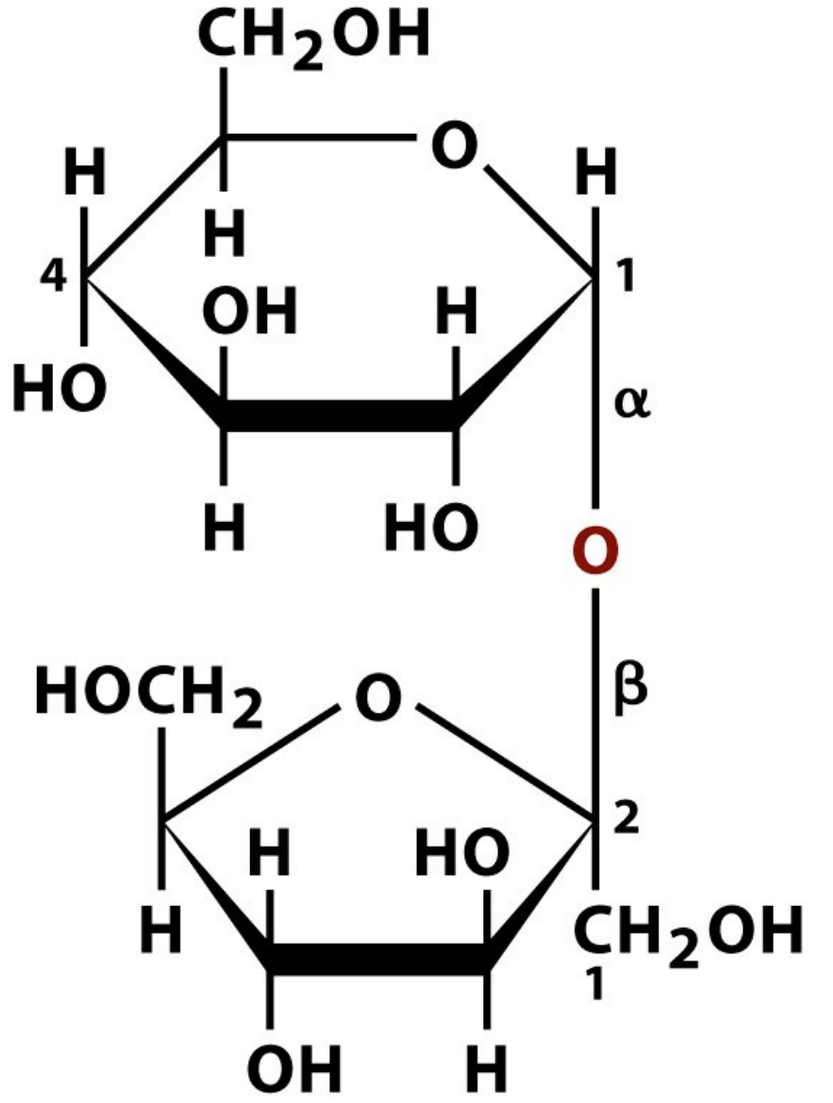
end

- F

b

h

ns



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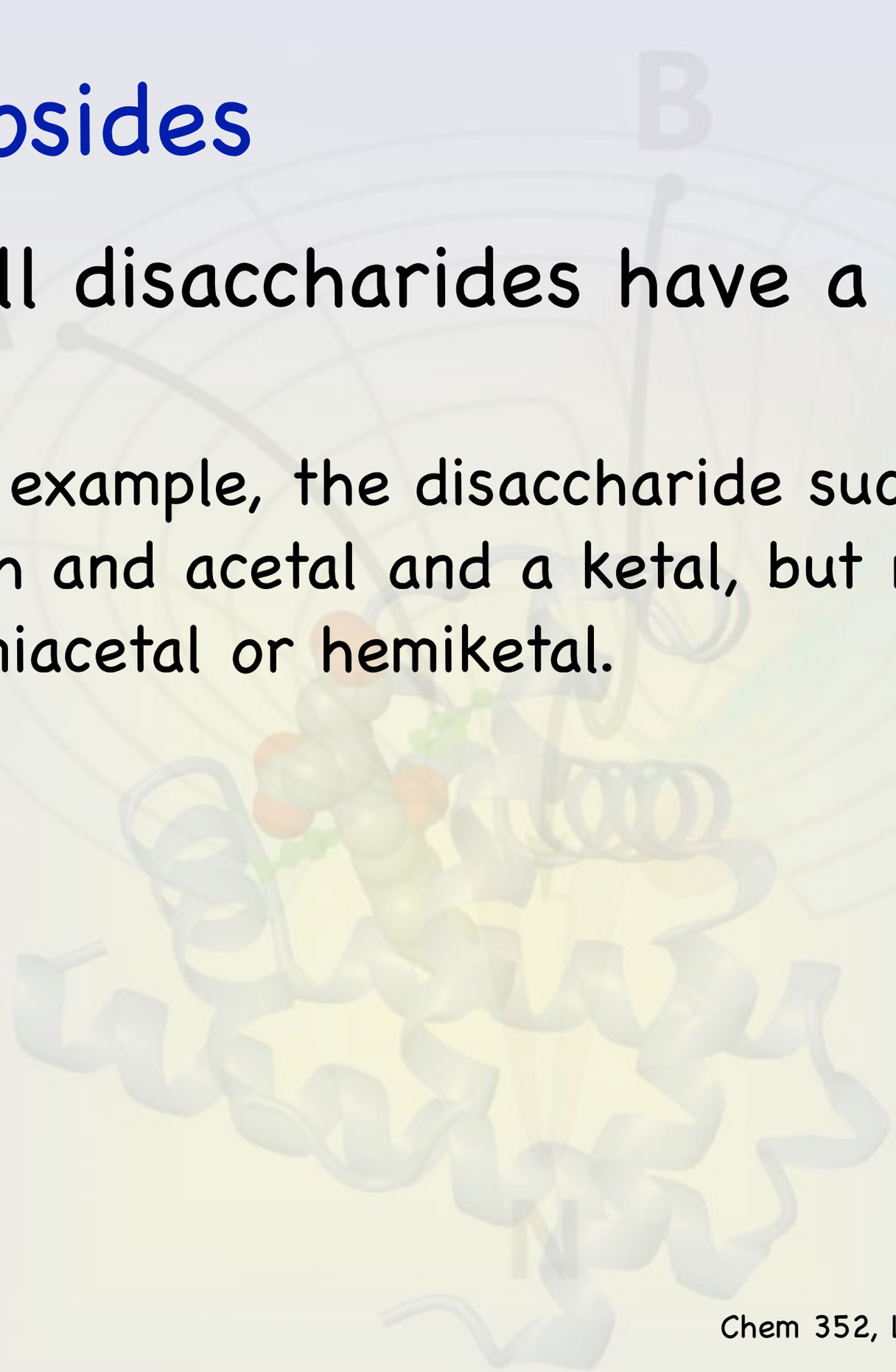


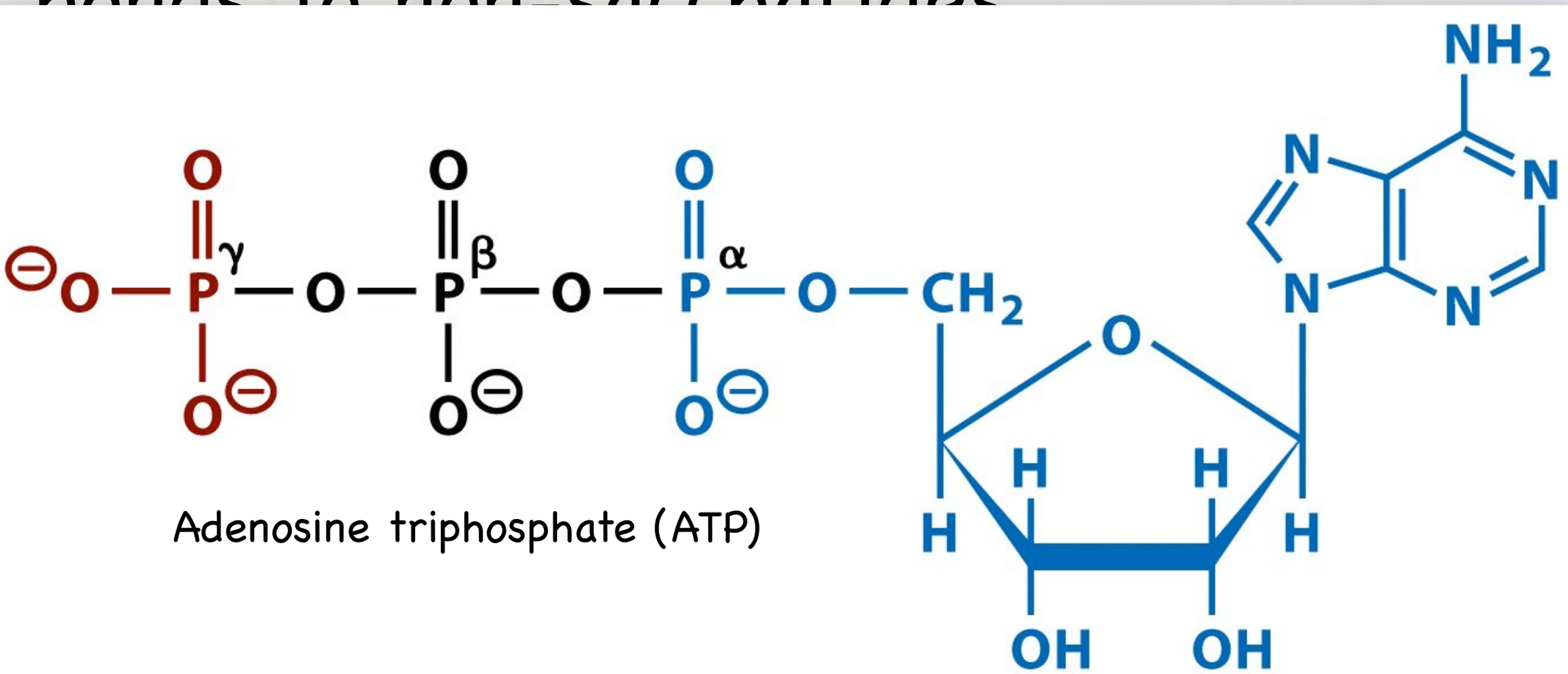
Glycosides

Monosaccharides also from glycosidic bonds to non-saccharides.

- For example, nucleotides.
  - ATP
  - UDP-glucose
  - NAD and NADP
  - FMN and FAD

Glycosides

Monosaccharides also from glycosidic bonds to non-saccharides



Adenosine triphosphate (ATP)

Glycosides

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  - ATP
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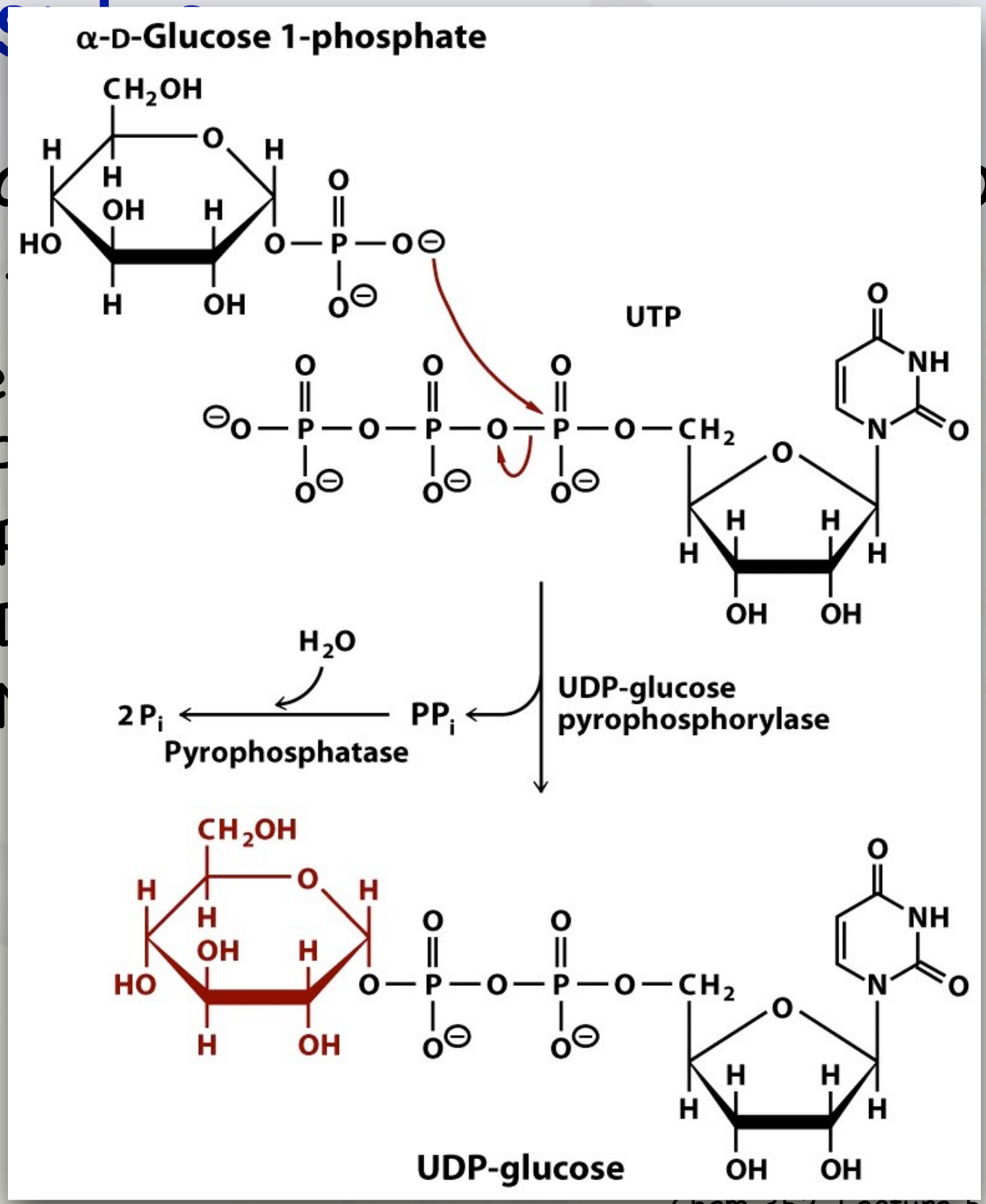
Glycos

Monosc osidic bonds

- For e
  - ATP
  - UDP
  - NAD
  - FMN



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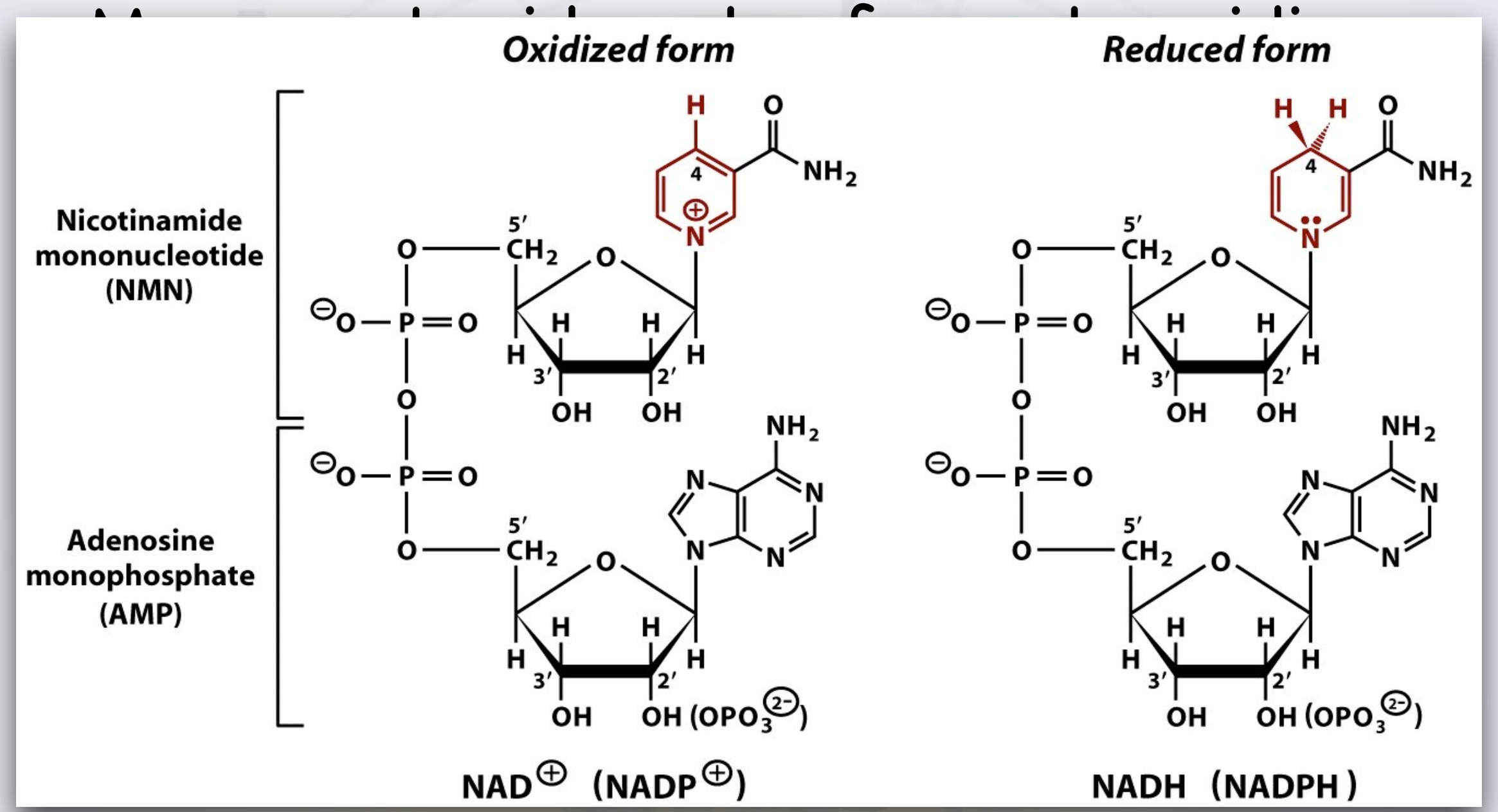
Glycosides


Oxidized form
Reduced form
Nicotinamide mononucleotide (NMN)
Adenosine monophosphate (AMP)
NAD⊕ (NADP⊕)
NADH (NADPH)

Glycosides

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  - ATP
  - UDP-glucose
  - NAD and NADP
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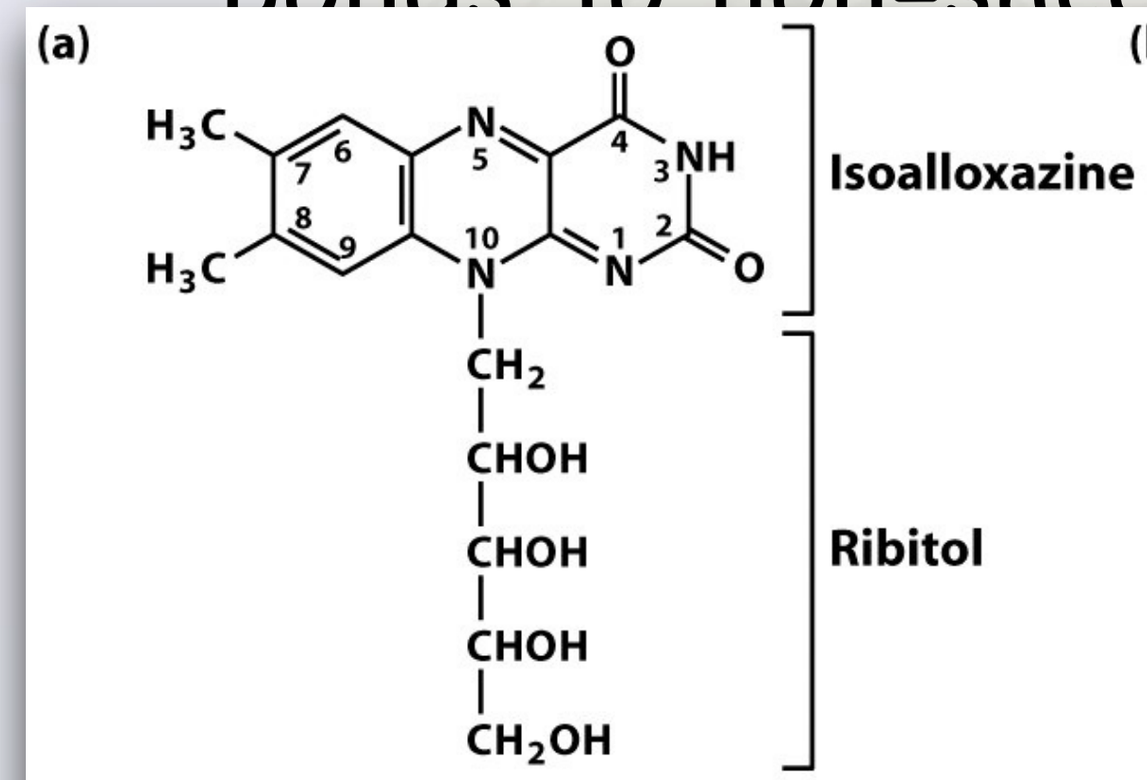
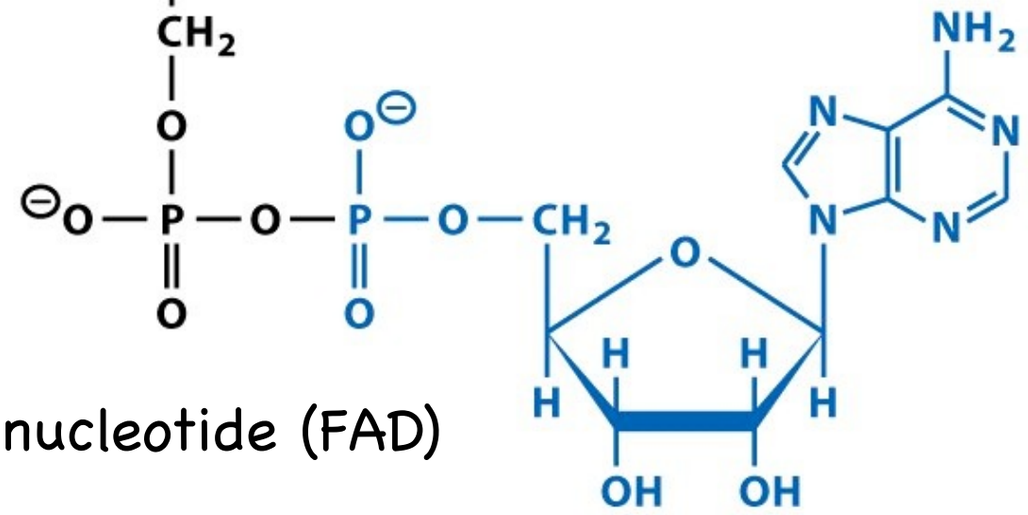
Glycosides

Monosaccharides also from glycosidic bonds to non-saccharides



Flavin mononucleotide (FMN)



Flavin adenine dinucleotide (FAD)

Glycosides

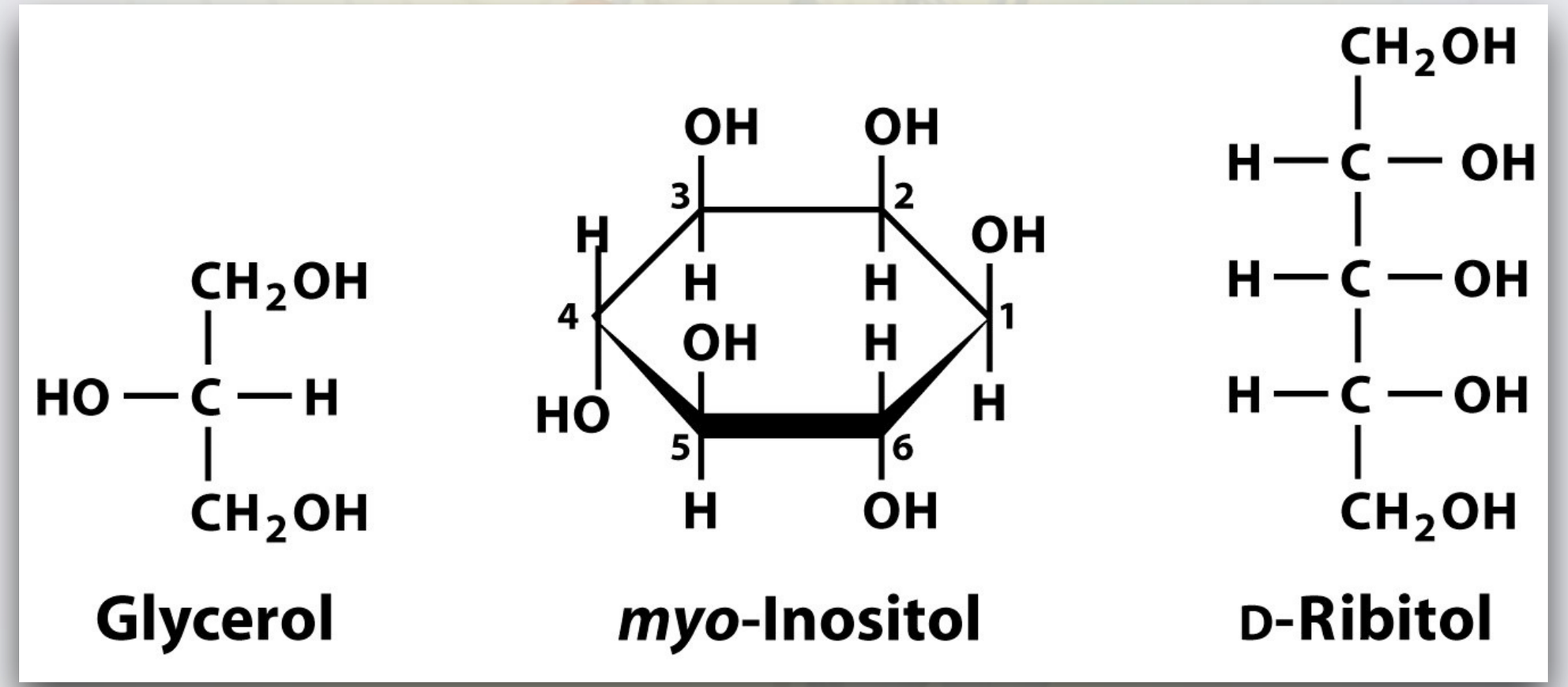
Monosaccharides also from glycosidic bonds to non-saccharides.

- For example, nucleotides.
  - ATP
  - UDP-glucose
  - NAD and NADP
  - FMN and FAD

Glycosides

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

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



Polysaccharides

Expanding the formation of glycosidic bonds can be extended to form polymers of monosaccharides called **glycans**.

- **Homoglycans** contain repeating units of the same monosaccharide.
- **Heteroglycans** contain multiple units of different monosaccharides

Polysaccharides

TABLE 8.2 Structures of some common polysaccharides

Polysaccharide[a]	Component(s)[b]	Linkage(s)
Storage homoglycans		
Starch		
Amylose	Glc	α-(1 → 4)
Amylopectin	Glc	α-(1 → 4), α-(1 → 6) (branches)
Glycogen	Glc	α-(1 → 4), α-(1 → 6) (branches)
Structural homoglycans		
Cellulose	Glc	β(1 → 4)
Chitin	GlcNAc	β(1 → 4)
Heteroglycans		
Glycosaminoglycans	Disaccharides (amino sugars, sugar acids)	Various
Hyaluronic acid	GlcUA and GlcNAc	β(1 → 3), β(1 → 4)

[a]Polysaccharides are unbranched unless otherwise indicated.
[b]Glc, Glucose; GlcNAc, *N*-acetylglucosamine; GlcUA, D-glucuronate.

Polysaccharides

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Polysaccharides

Storage forms of glucose

- Starch (plants)
  - Amylose
  - Amylopectin
- Glycogen (animals)

Structural polysaccharides

- Cellulose (plant)
- Chitin (animals)

Polysaccharides

St

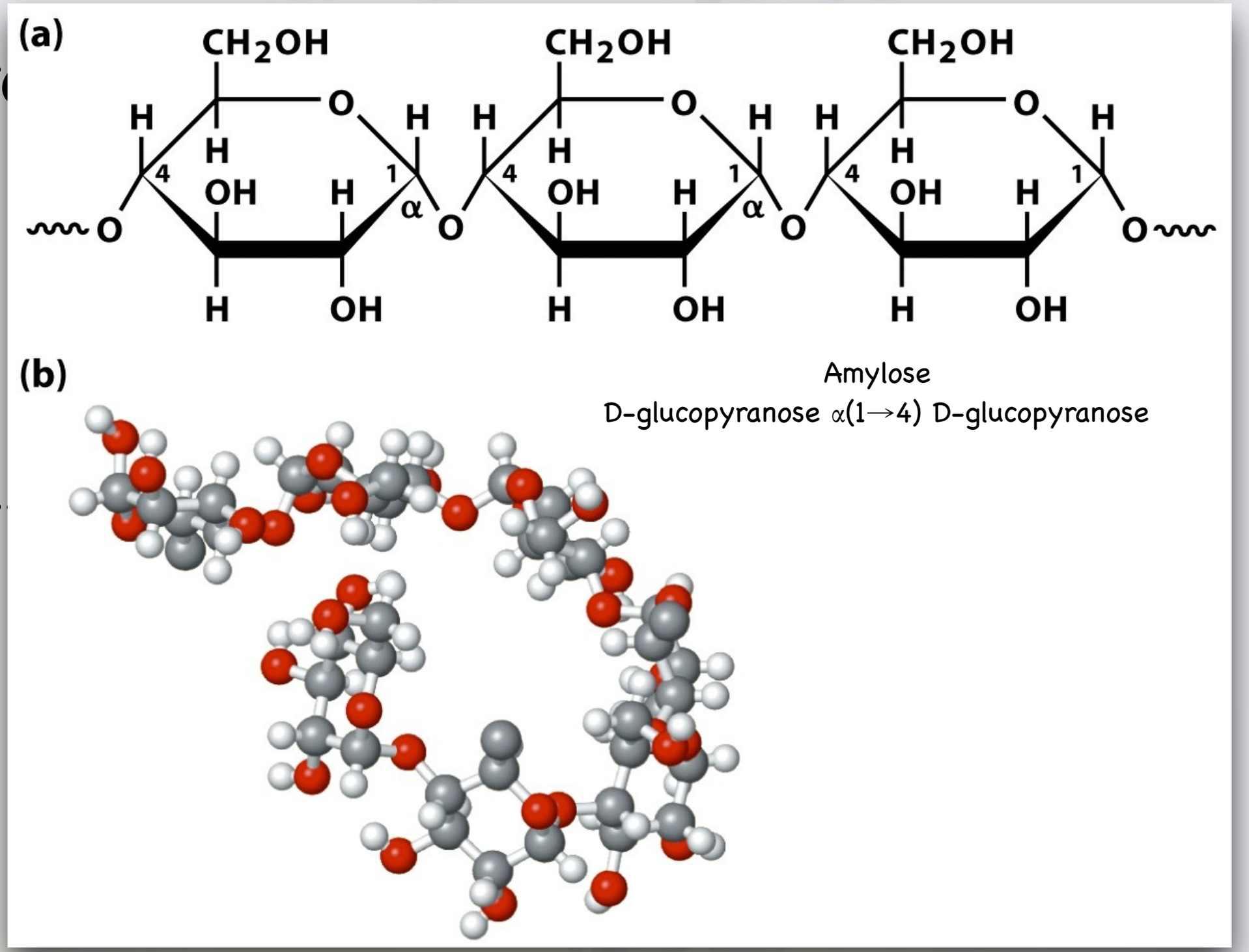
-

-

St

-

-



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Polysaccharides

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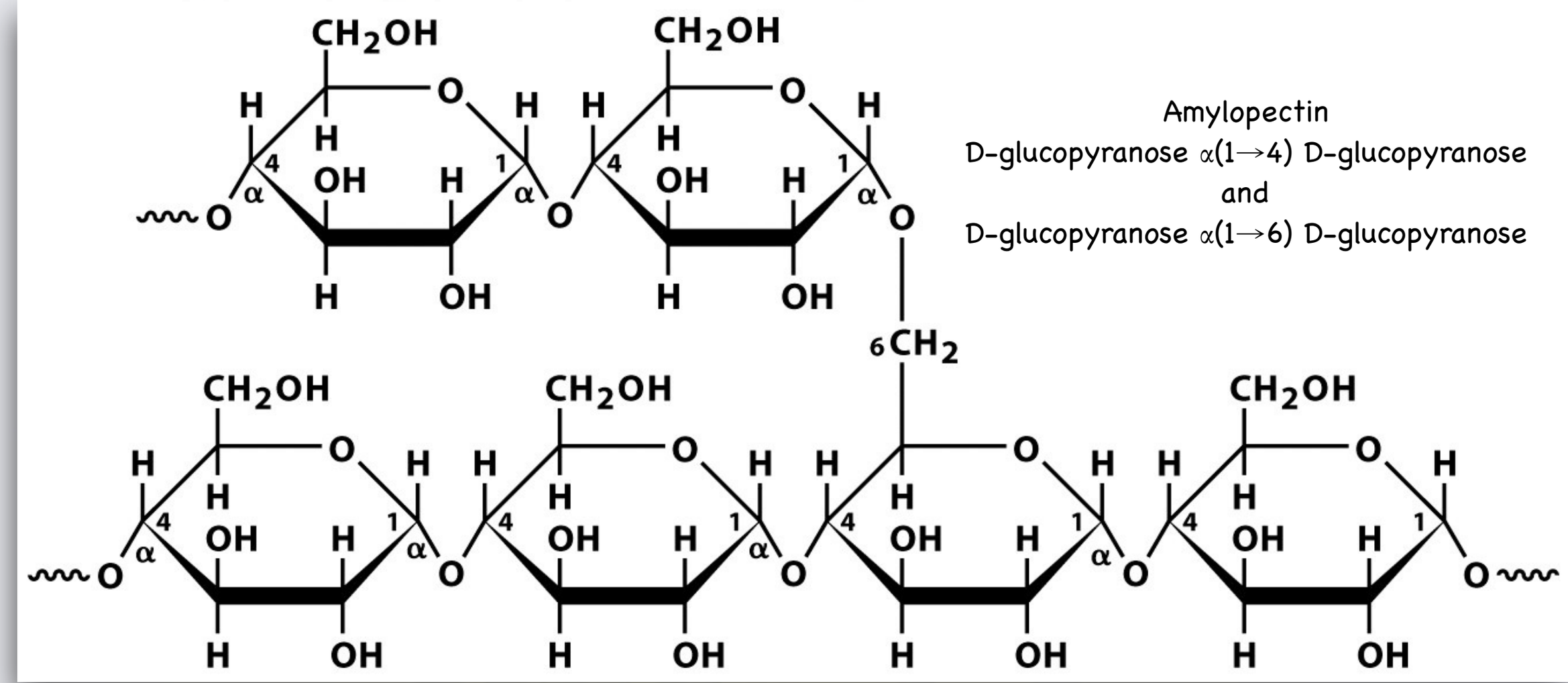


Amylopectin
D-glucopyranose α(1→4) D-glucopyranose
and
D-glucopyranose α(1→6) D-glucopyranose

Polysaccharides

Storage forms of glucose

- Starch (plants)
  - Amylose
  - Amylopectin
- Glycogen (animals)

Structural polysaccharides

- Cellulose (plant)
- Chitin (animals)

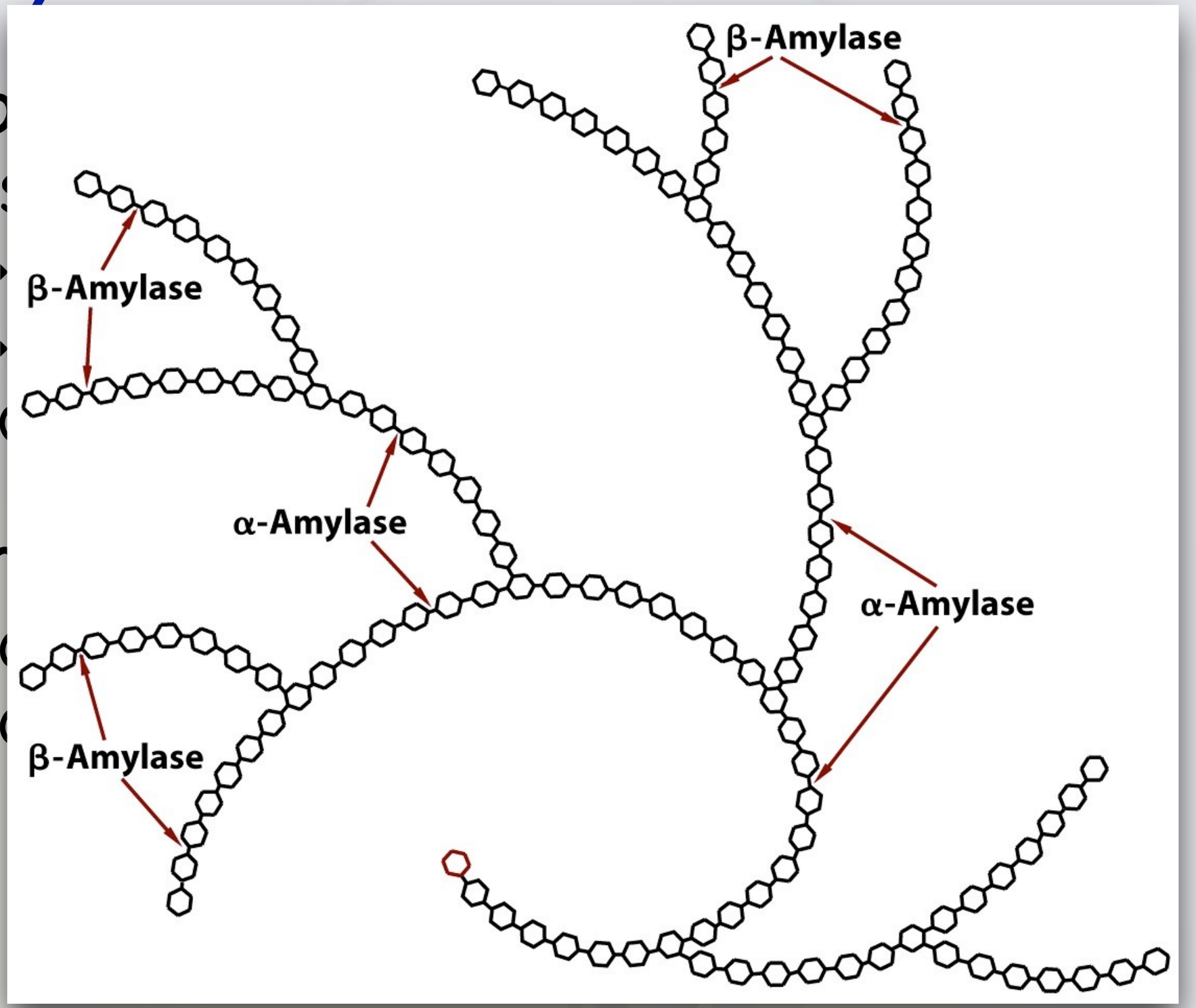
Polysaccharides

Sto

- S
  -
  -
- C

Str

- C
- C



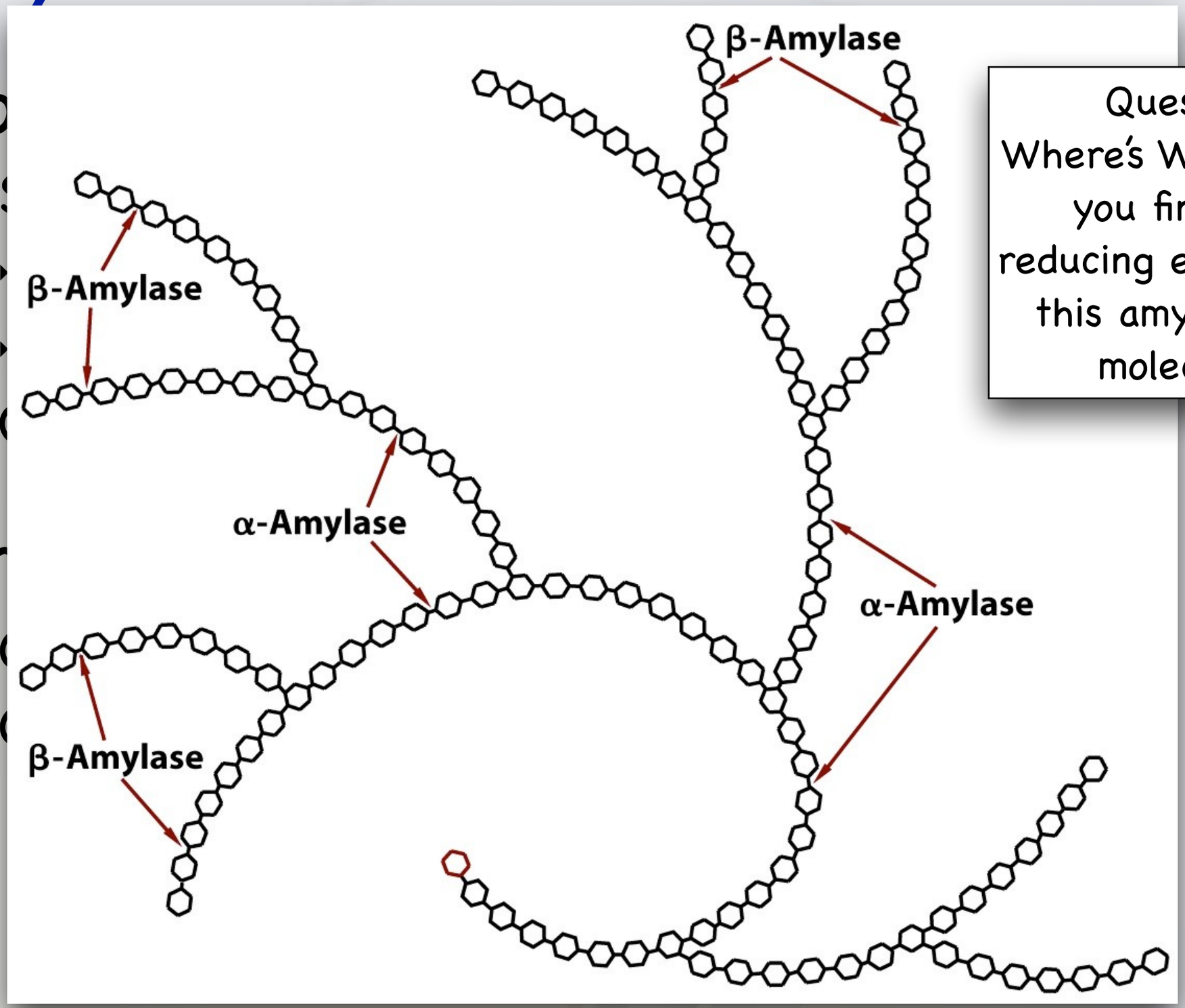
Polysaccharides

Sto

- S
- C

Str

- C
- C



Question
Where's Waldo? Can you find the reducing end of this this amylopectin molecule?

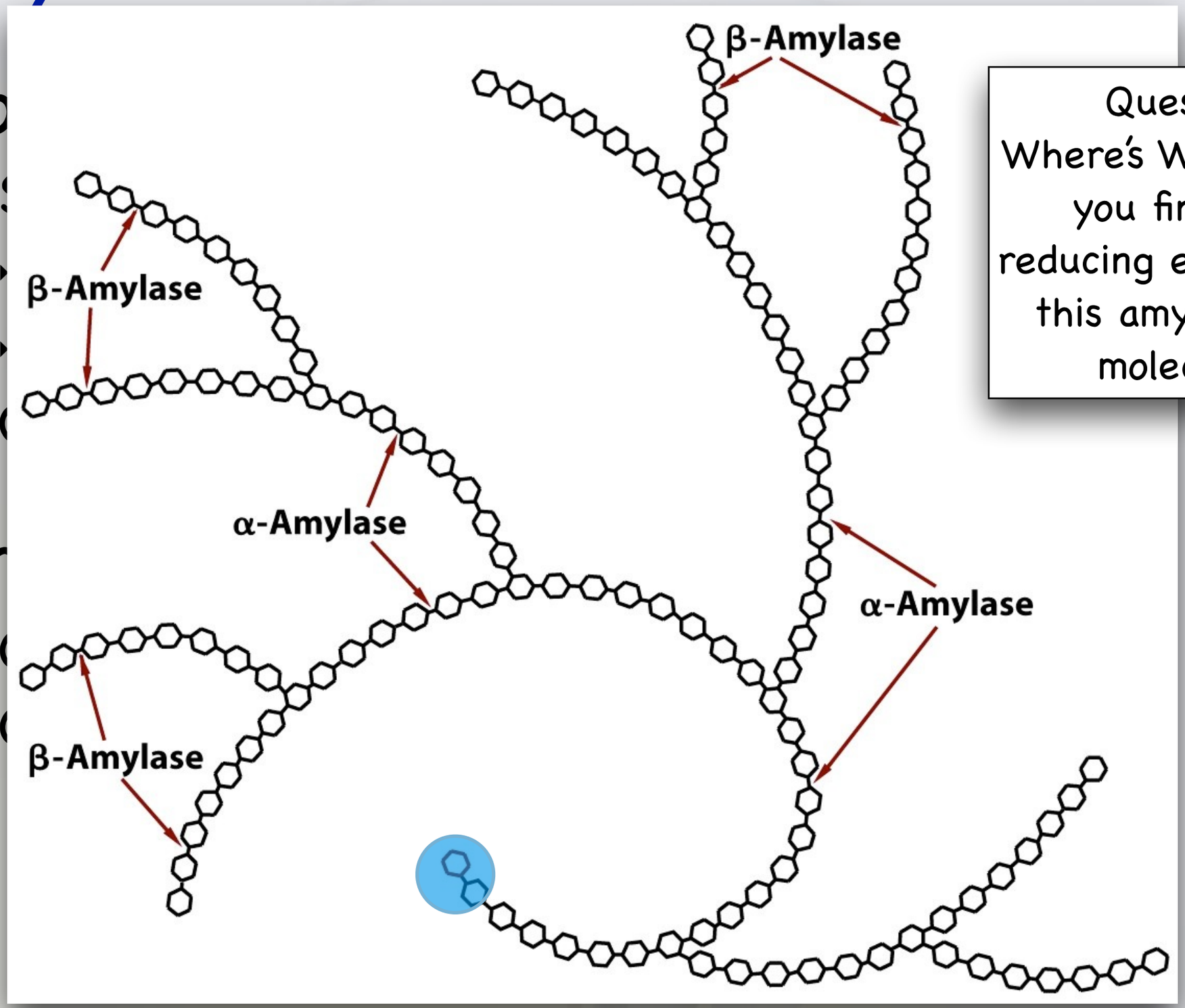
Polysaccharides

Sto

- S
- C

Str

- C
- C



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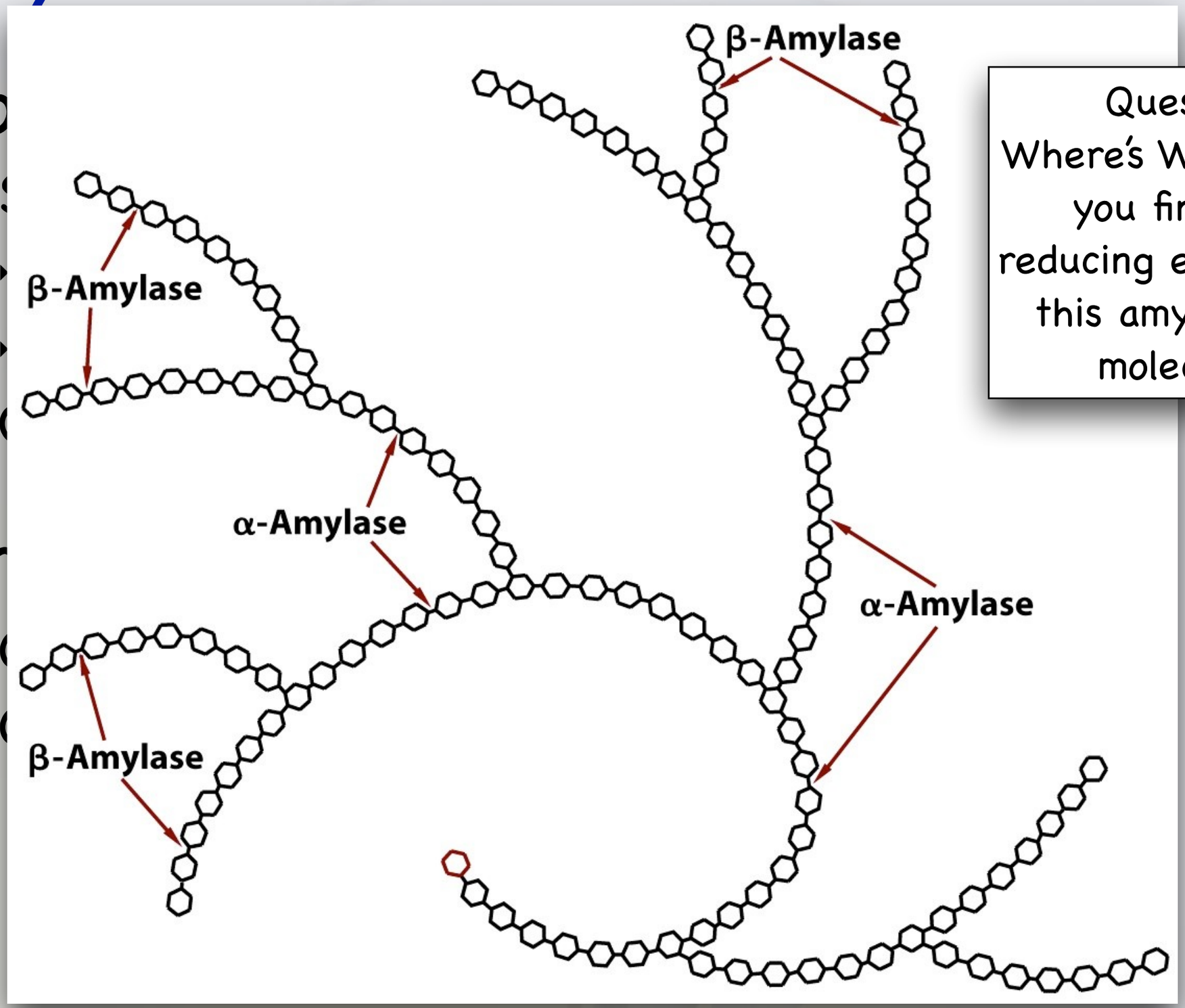

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  -
  -
- C

Str

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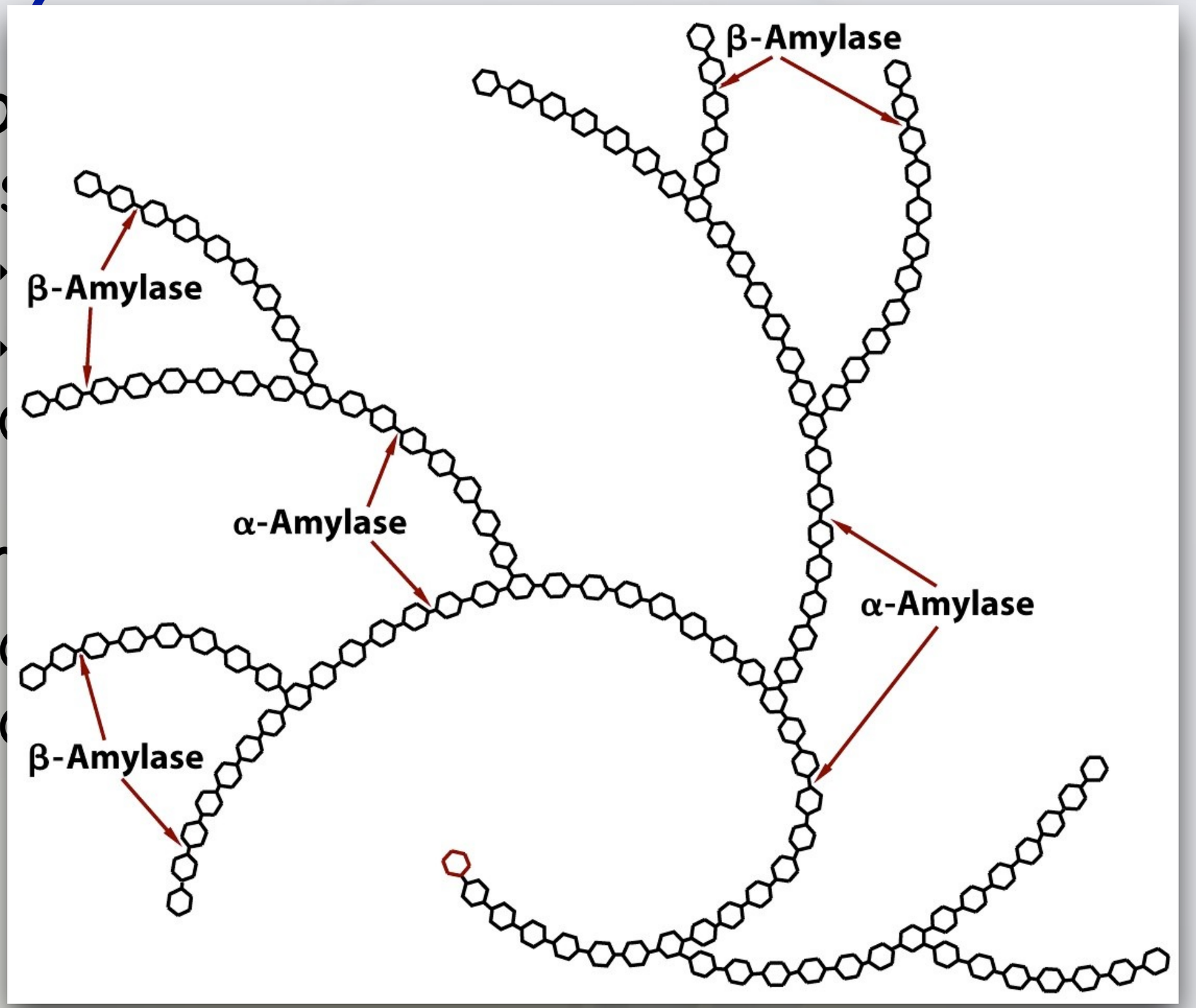

Polysaccharides

Storage forms of glucose

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  - Amylopectin
- Glycogen (animals)

Structural polysaccharides

- Cellulose (plant)
- Chitin (animals)

Polysaccharides

Storage forms of glucose

-

-

St

-

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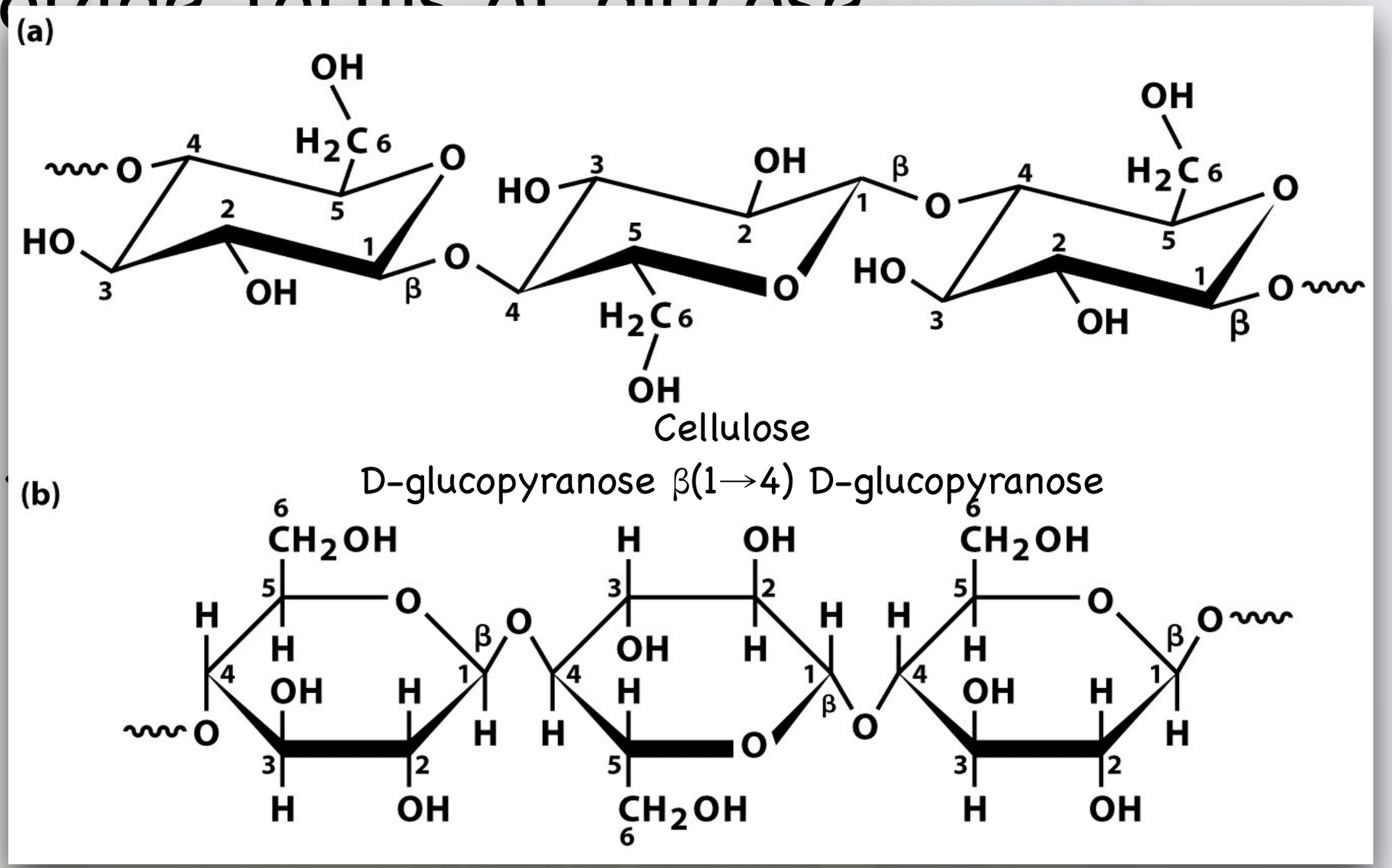

Polysaccharides

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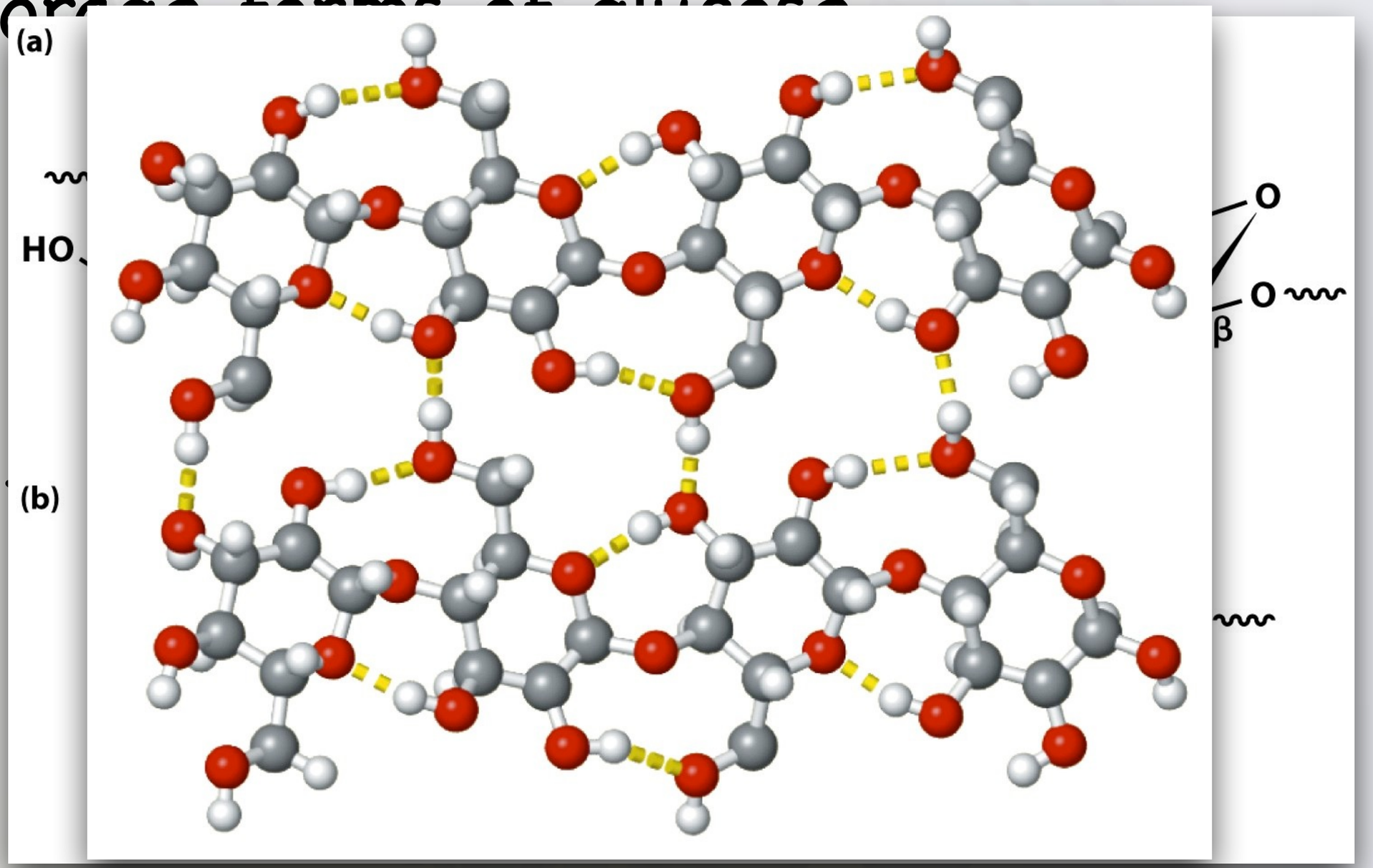

Polysaccharides

Storage forms of glucose

-

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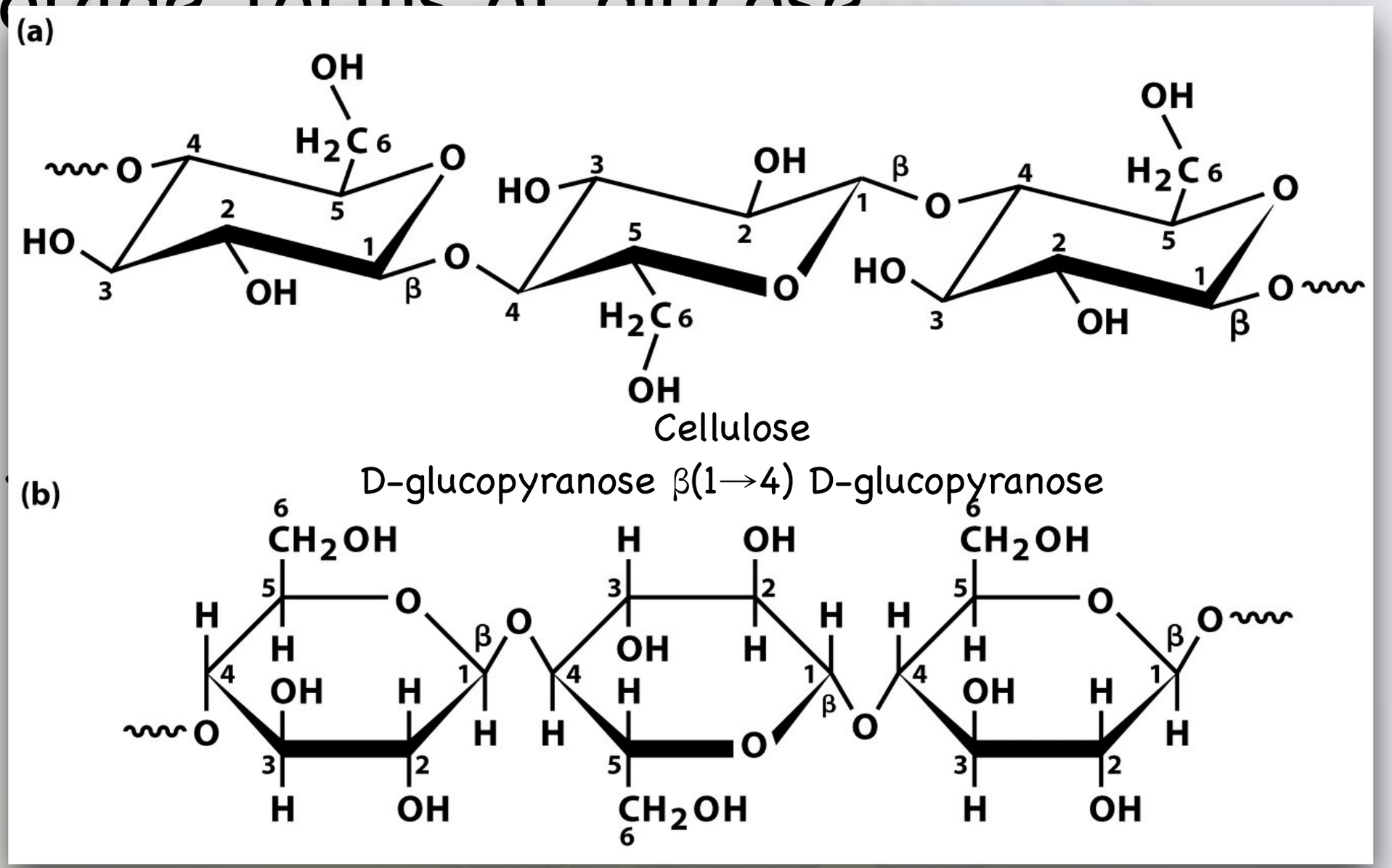


Polysaccharides

Storage forms of glucose

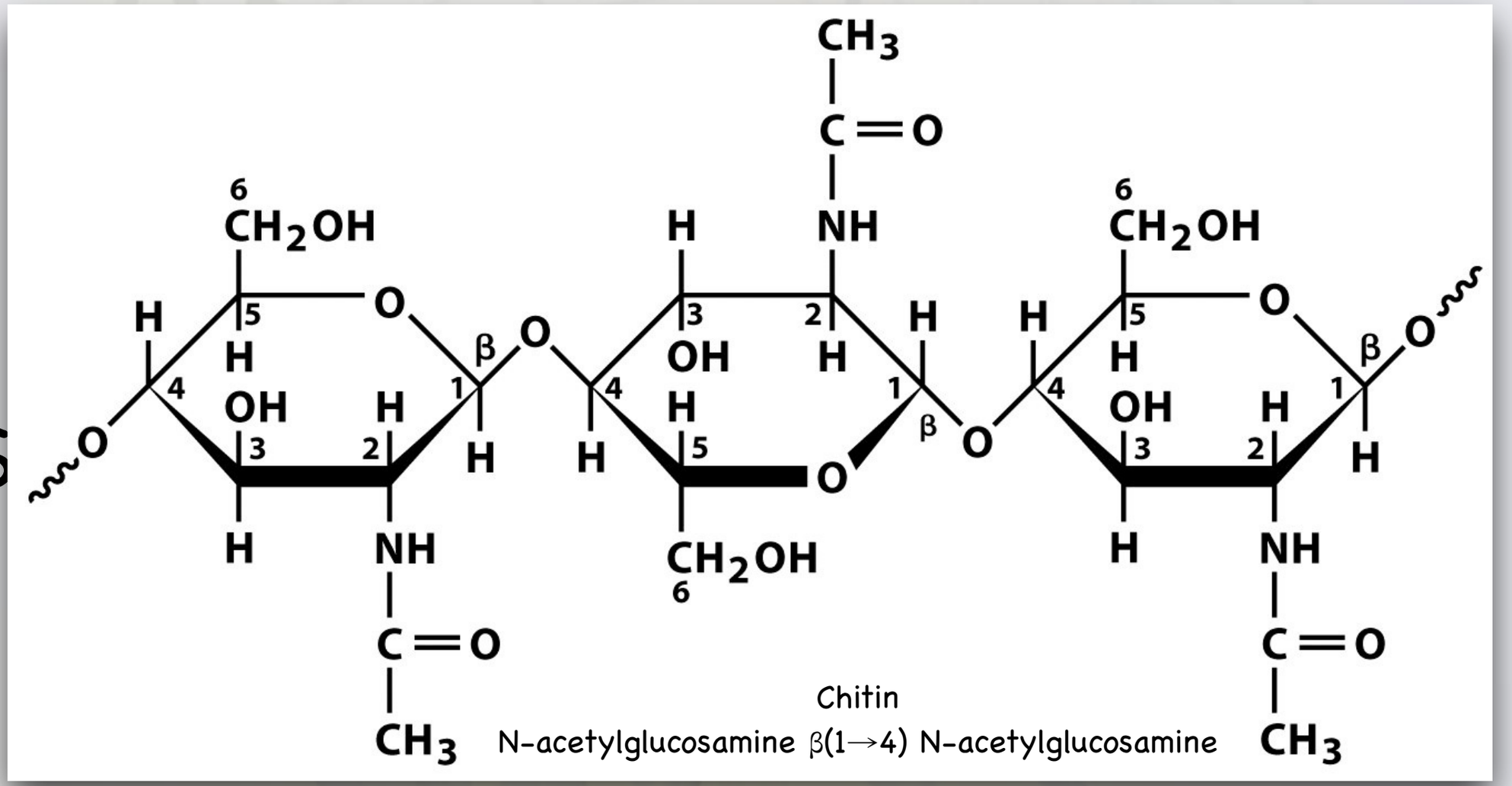
- Starch (plants)
  - Amylose
  - Amylopectin
- Glycogen (animals)

Structural polysaccharides

- Cellulose (plant)
- Chitin (animals)

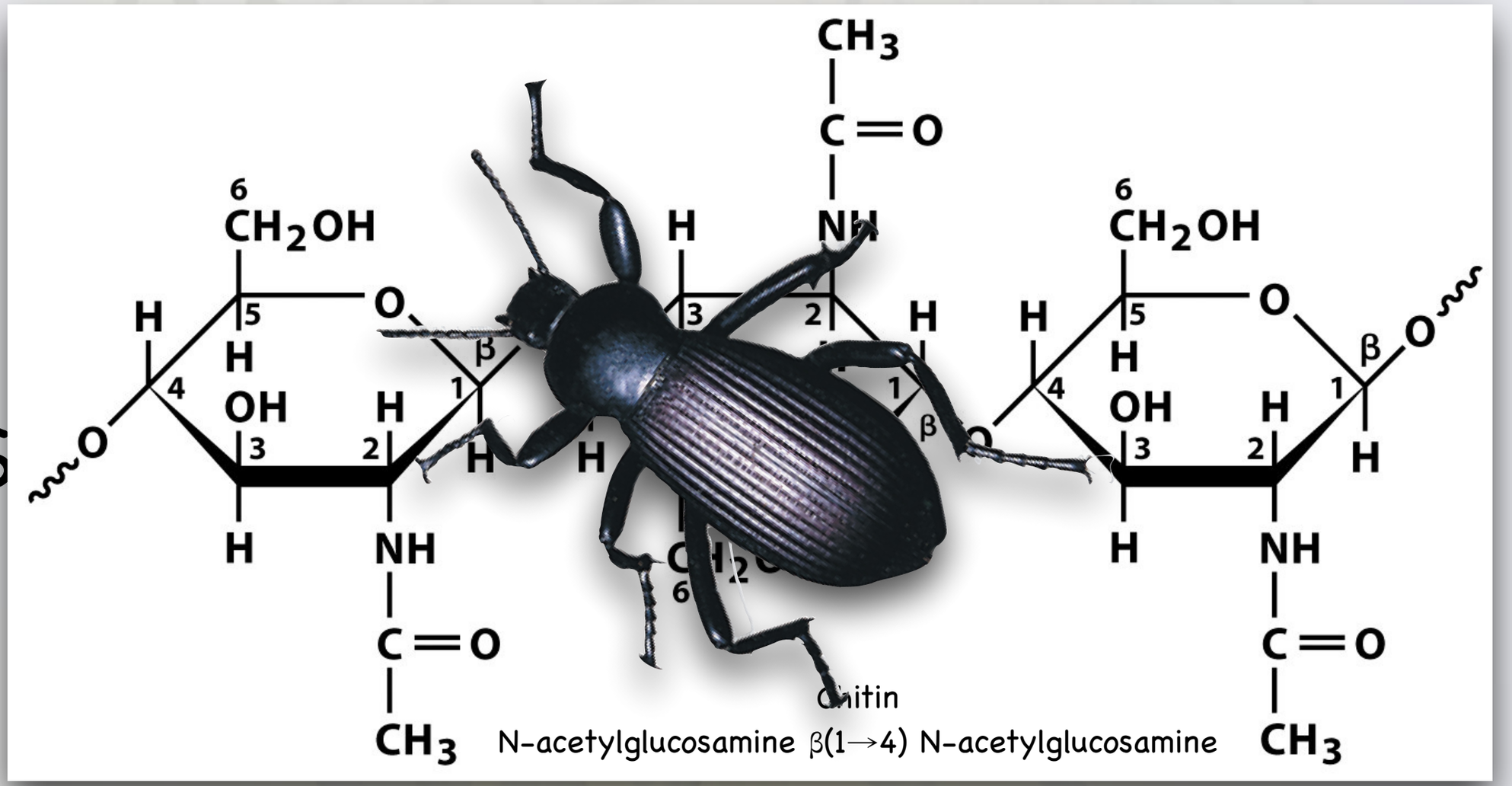
Polysaccharides

Storage forms of glucose



Polysaccharides

Storage forms of glucose



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Glycoconjugates

- Oligo saccharides are often attached to biological molecules
  - To proteins and peptides
    - **Proteoglycans (connective tissue)**
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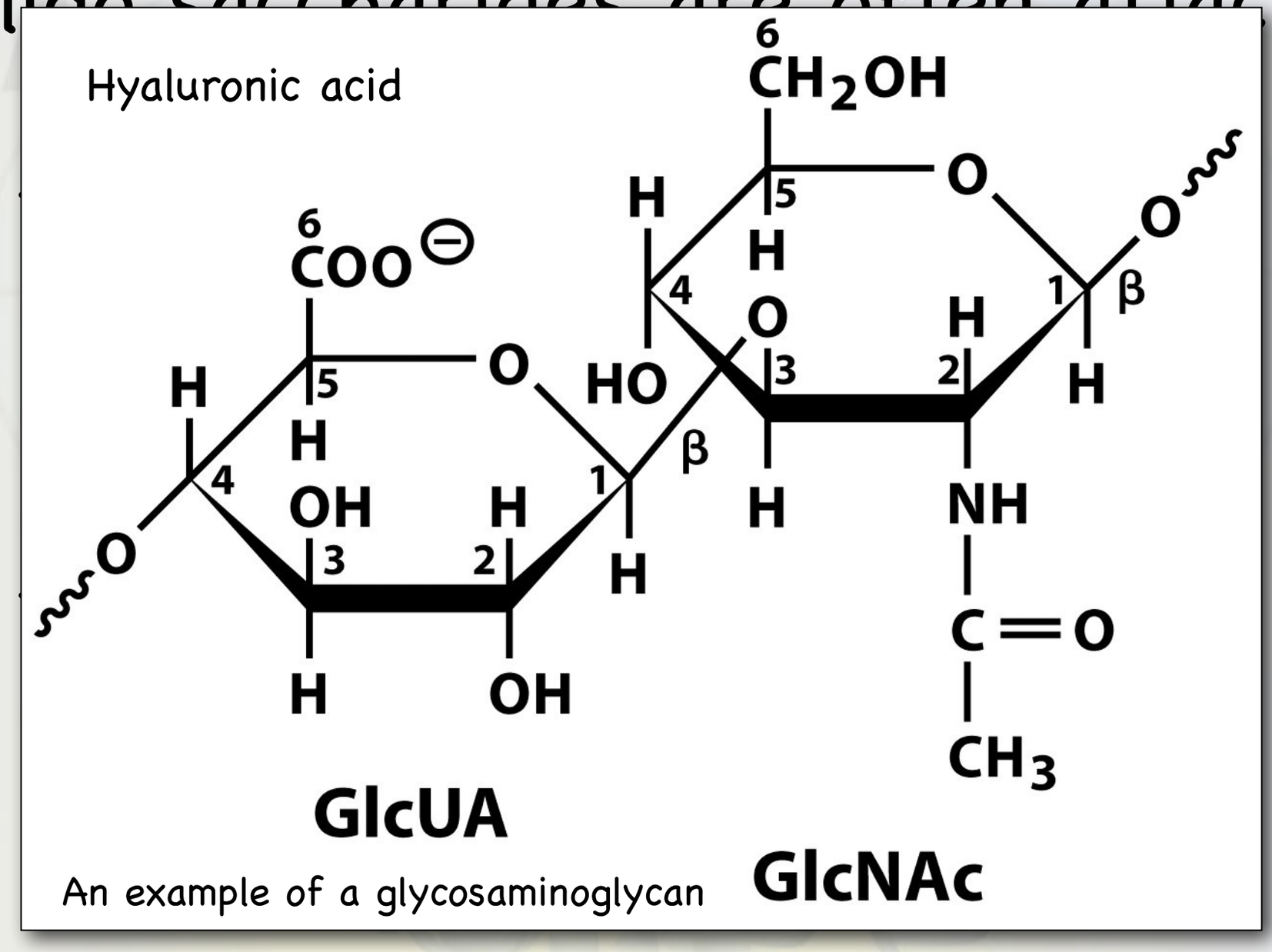

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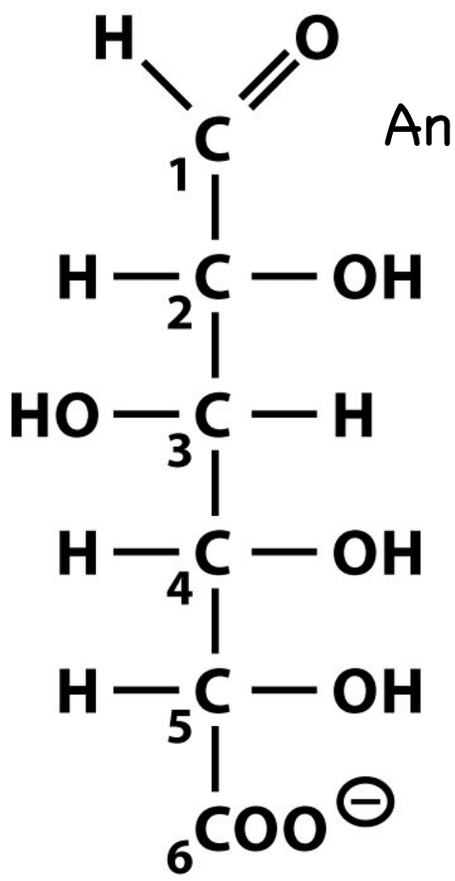
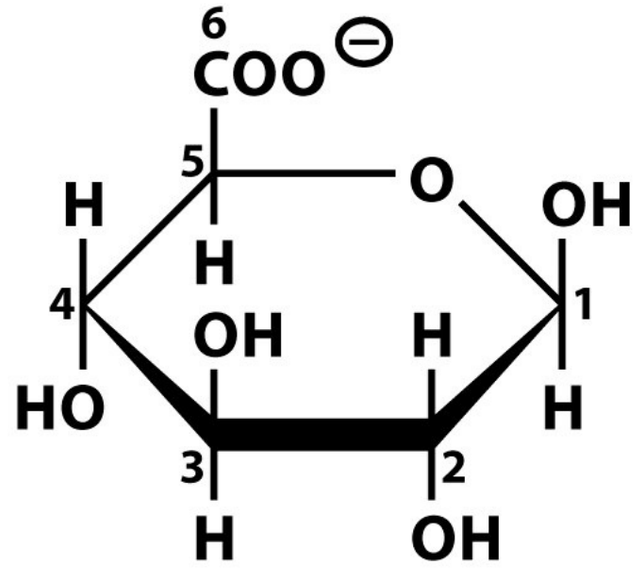
An example of a **sugar acid** (-uronic acid)



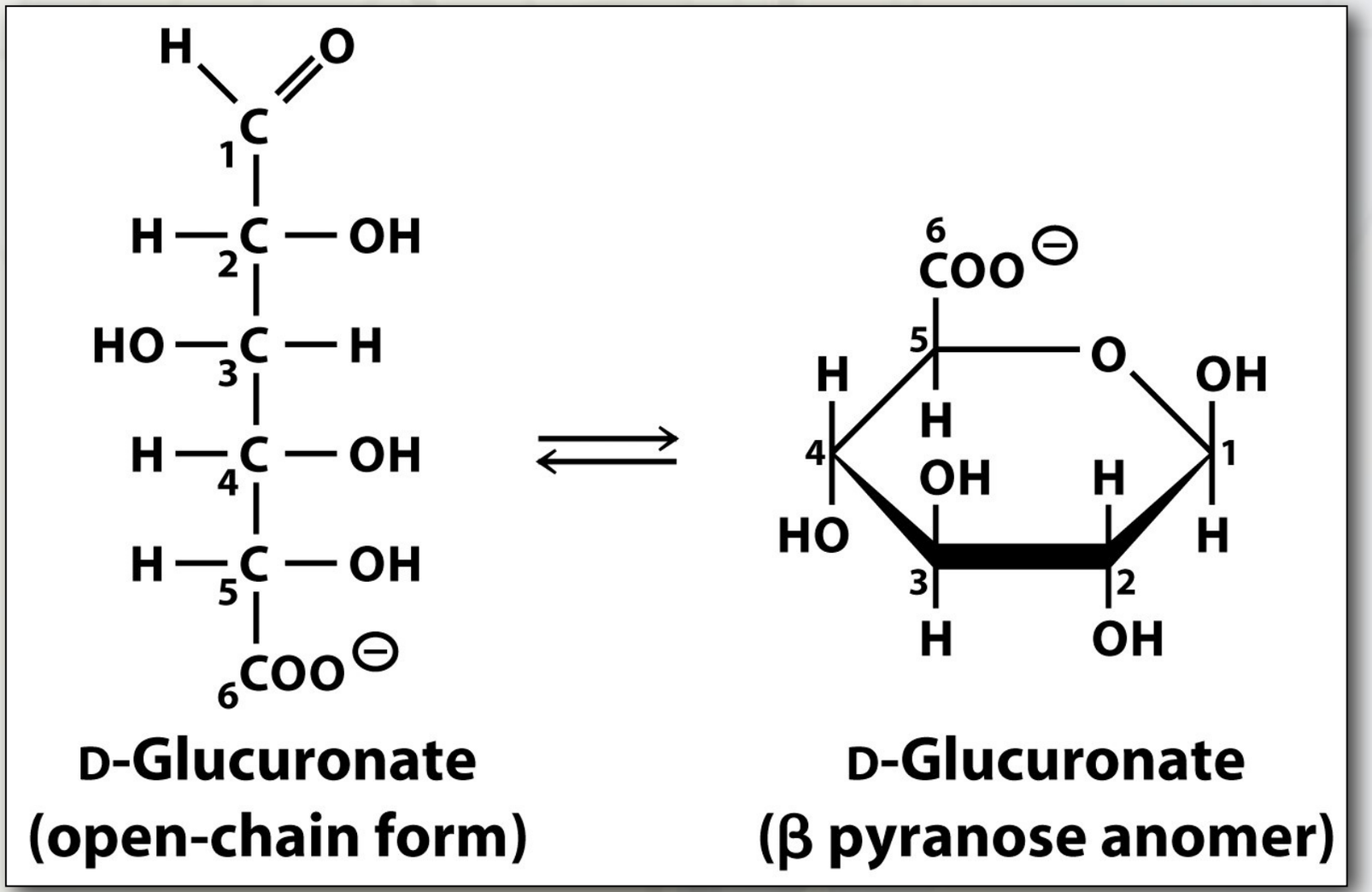
D-Glucuronate (open-chain form)



D-Glucuronate (β pyranose anomer)

Monosaccarides

- **Sugar acids** are sugars in which either the aldehyde or primary alcohol is oxidized to a carboxylic acid.



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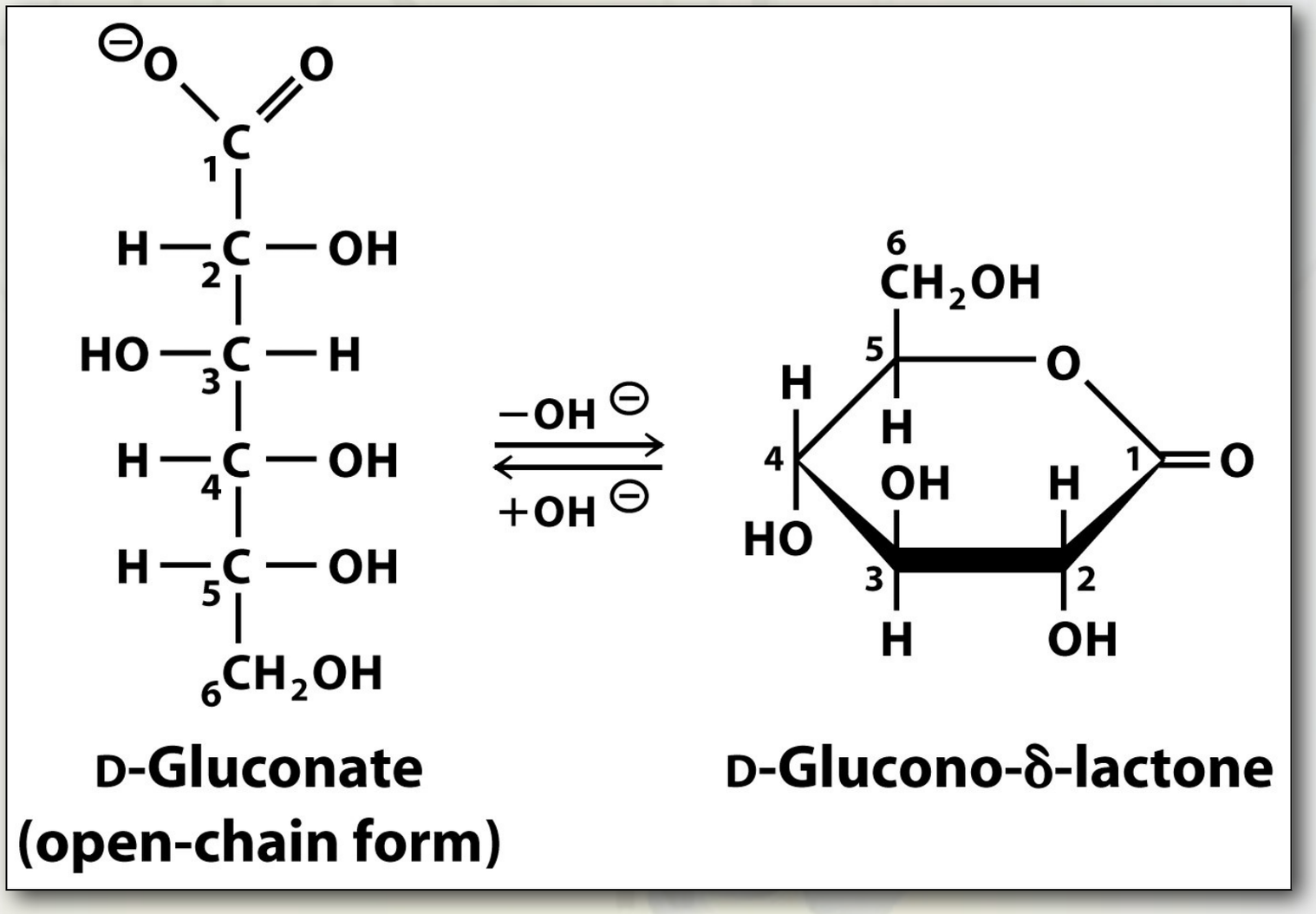

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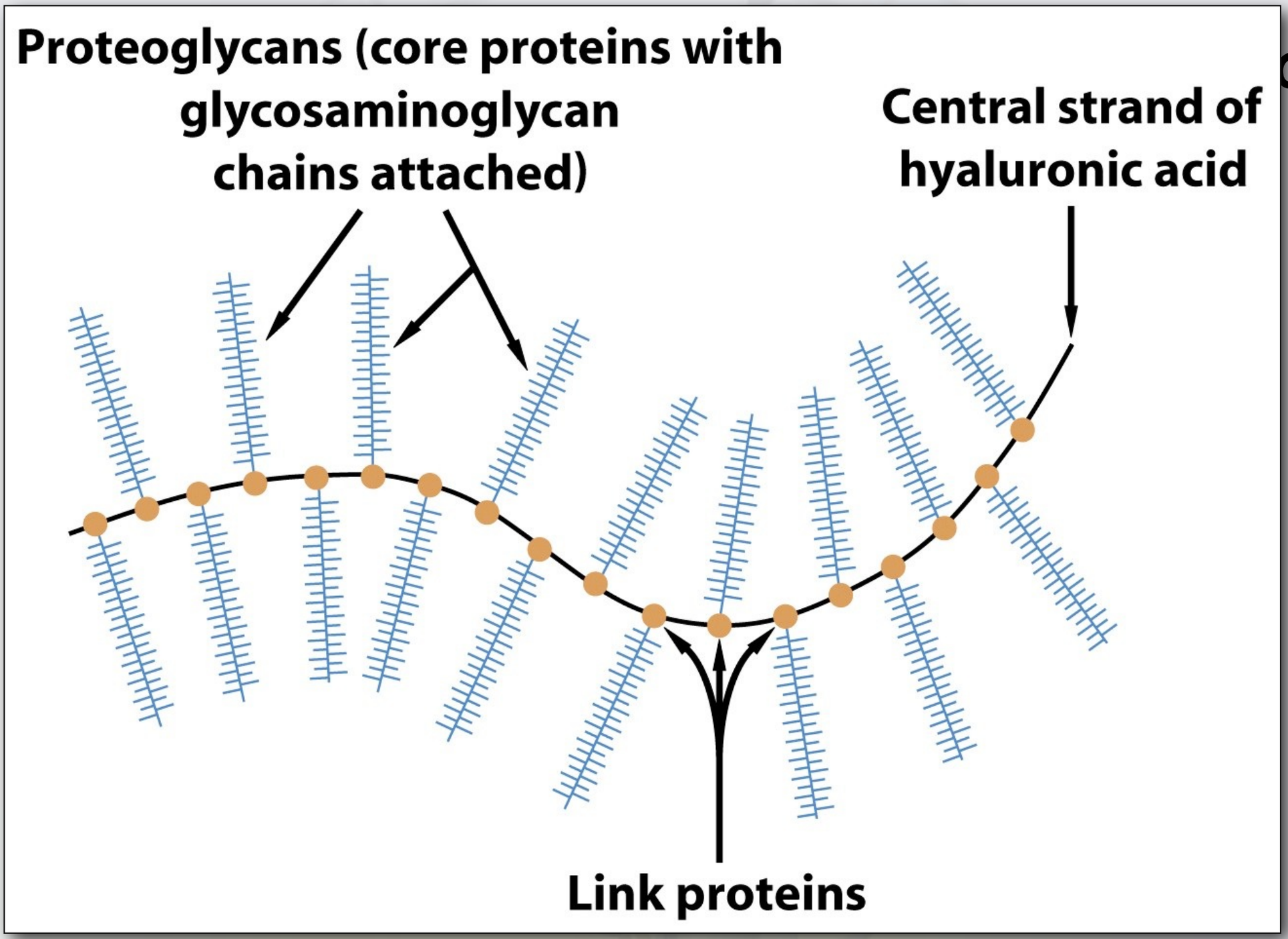
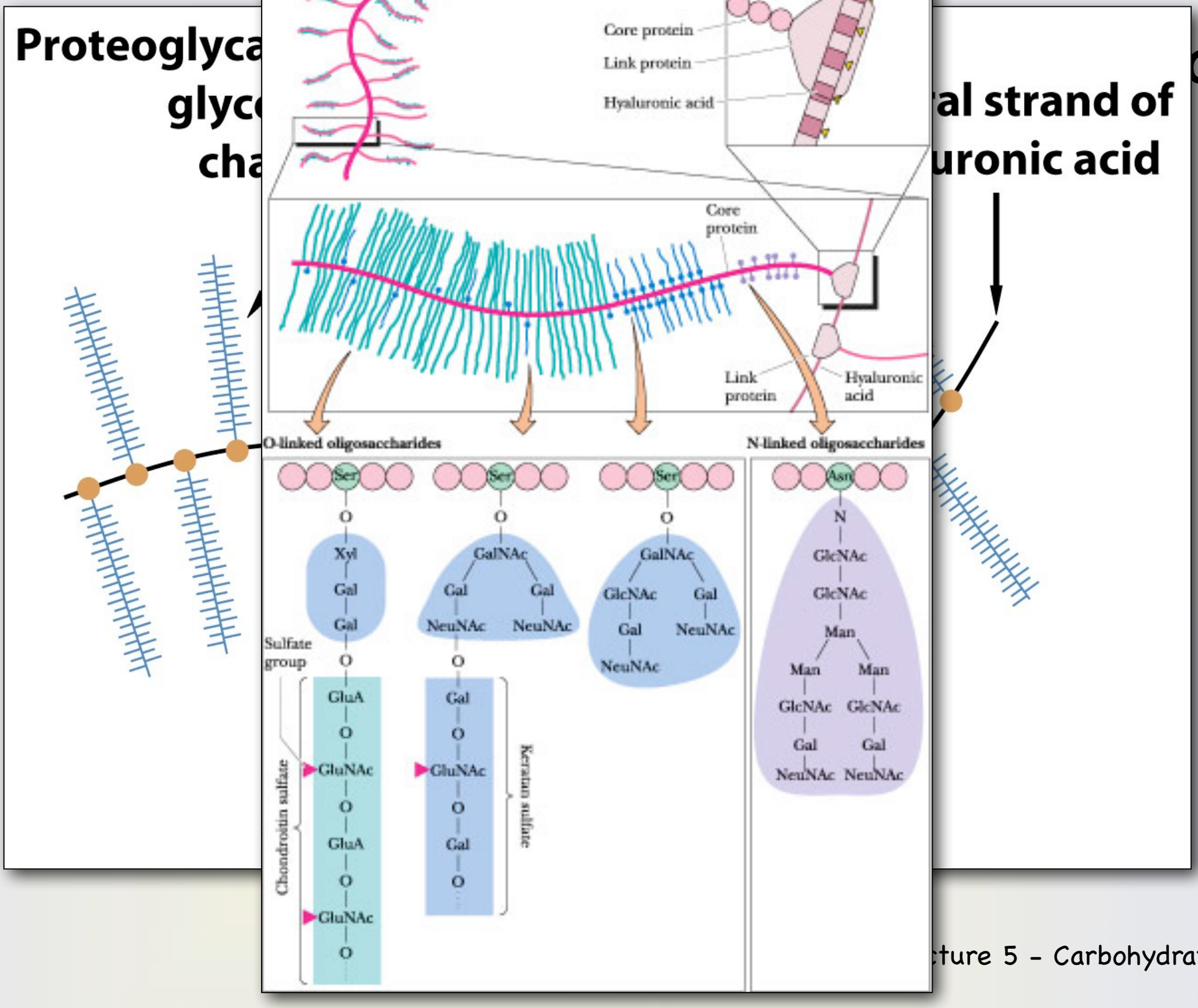
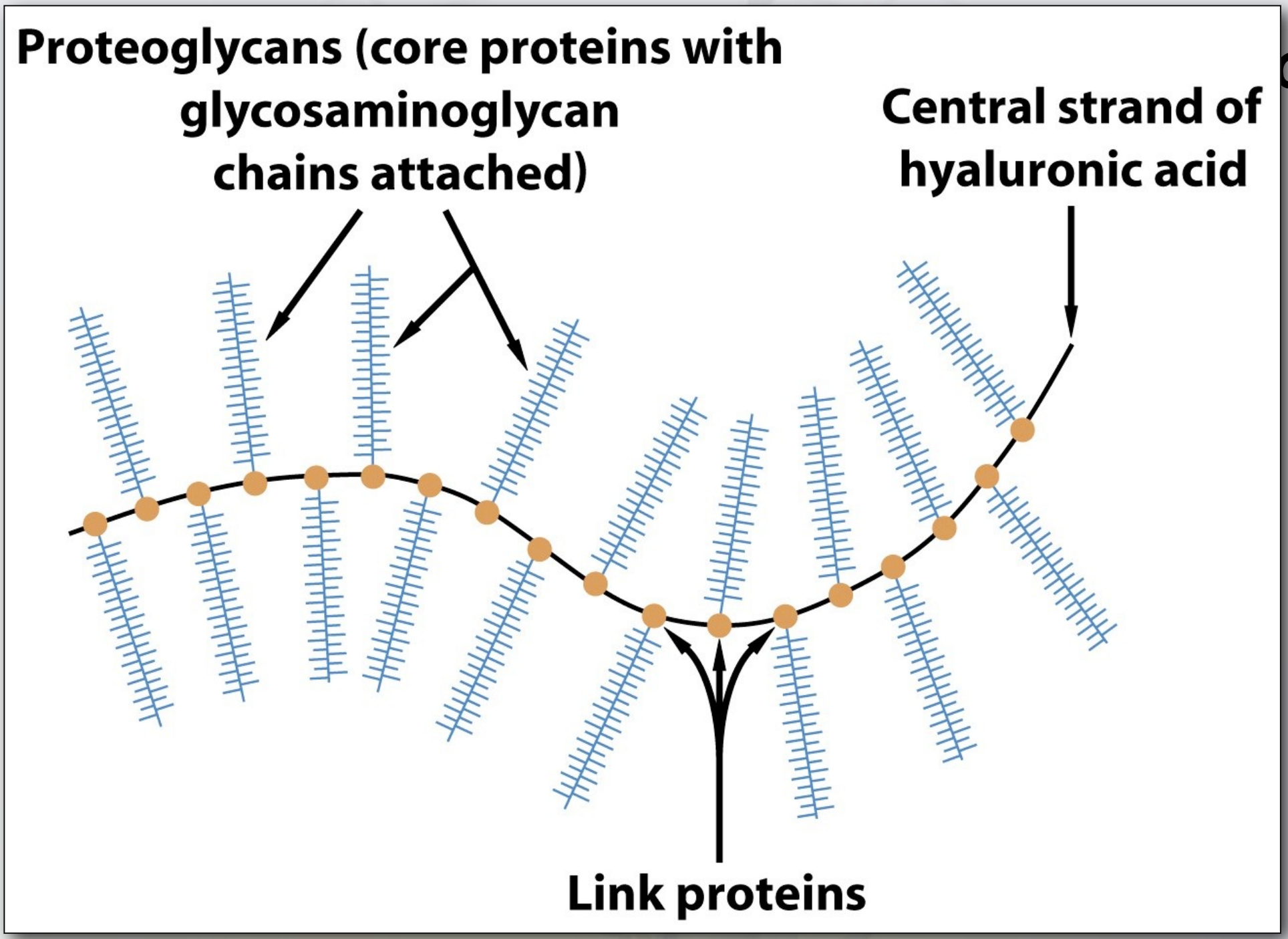


Glycocon


Proteoglyca
glyc
cha
al strand of
uronic acid
Proteoglycan
Carboxylate group
Core protein
Link protein
Hyaluronic acid
Core protein
Link protein
Hyaluronic acid
O-linked oligosaccharides
N-linked oligosaccharides
Ser
Ser
Ser
Asn
O
Xyl
Gal
Gal
GalNAc
Gal
Gal
NeuNAc
NeuNAc
GalNAc
GlcNAc
Gal
Gal
NeuNAc
NeuNAc
N
GlcNAc
GlcNAc
Man
Man
Man
GlcNAc
GlcNAc
Gal
Gal
NeuNAc
NeuNAc
Sulfate group
GluA
GluNAc
GluA
GluNAc
Gal
GluNAc
Gal
Chondroitin sulfate
Keratan sulfate

Glycoconjugates



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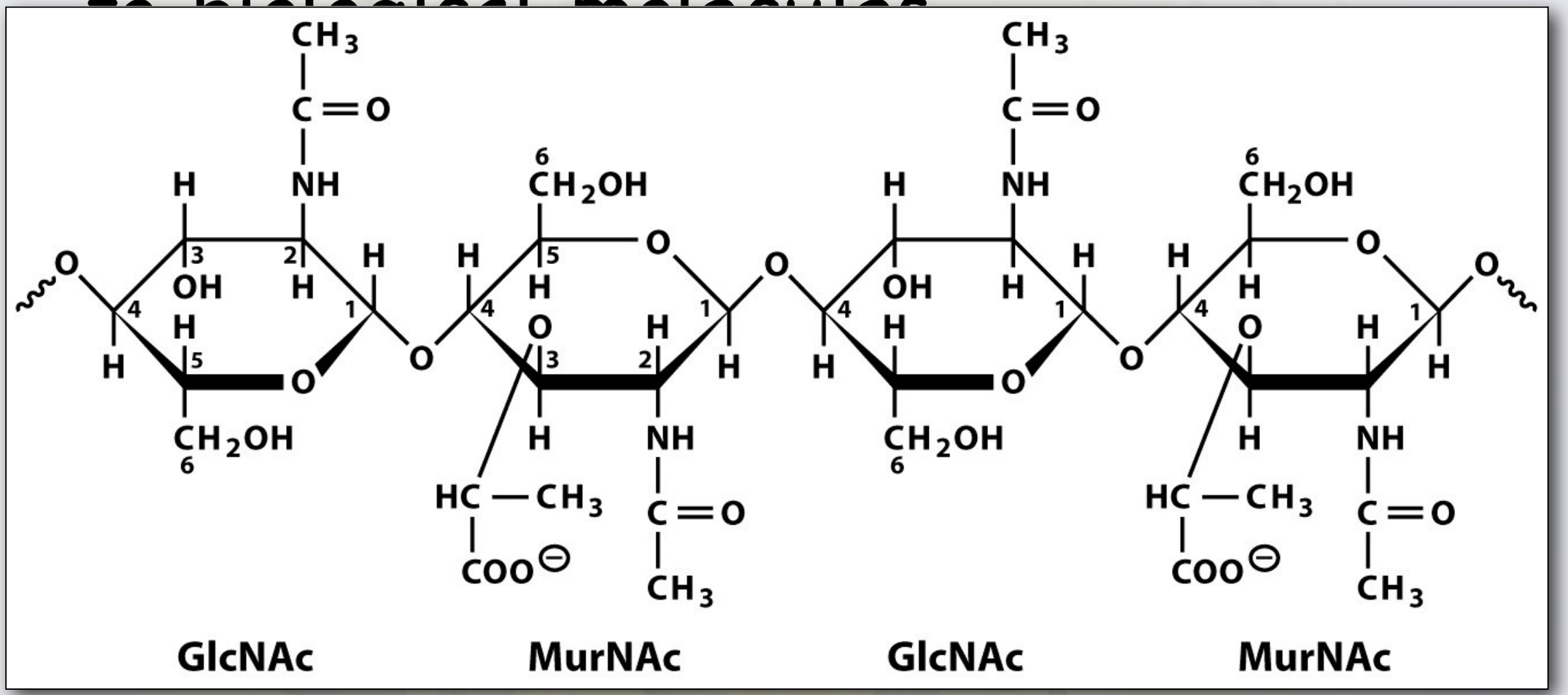

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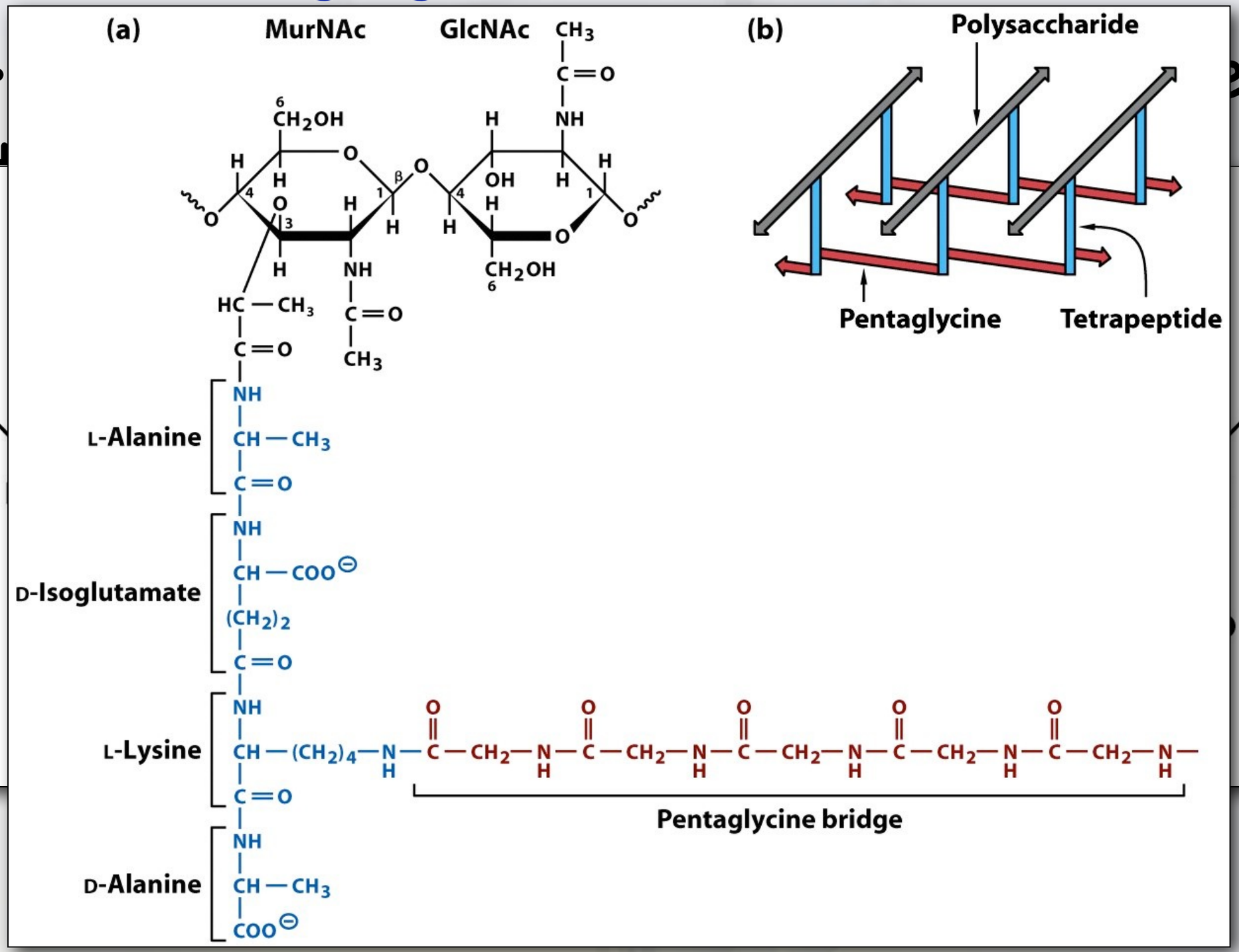

Glycoconjugates

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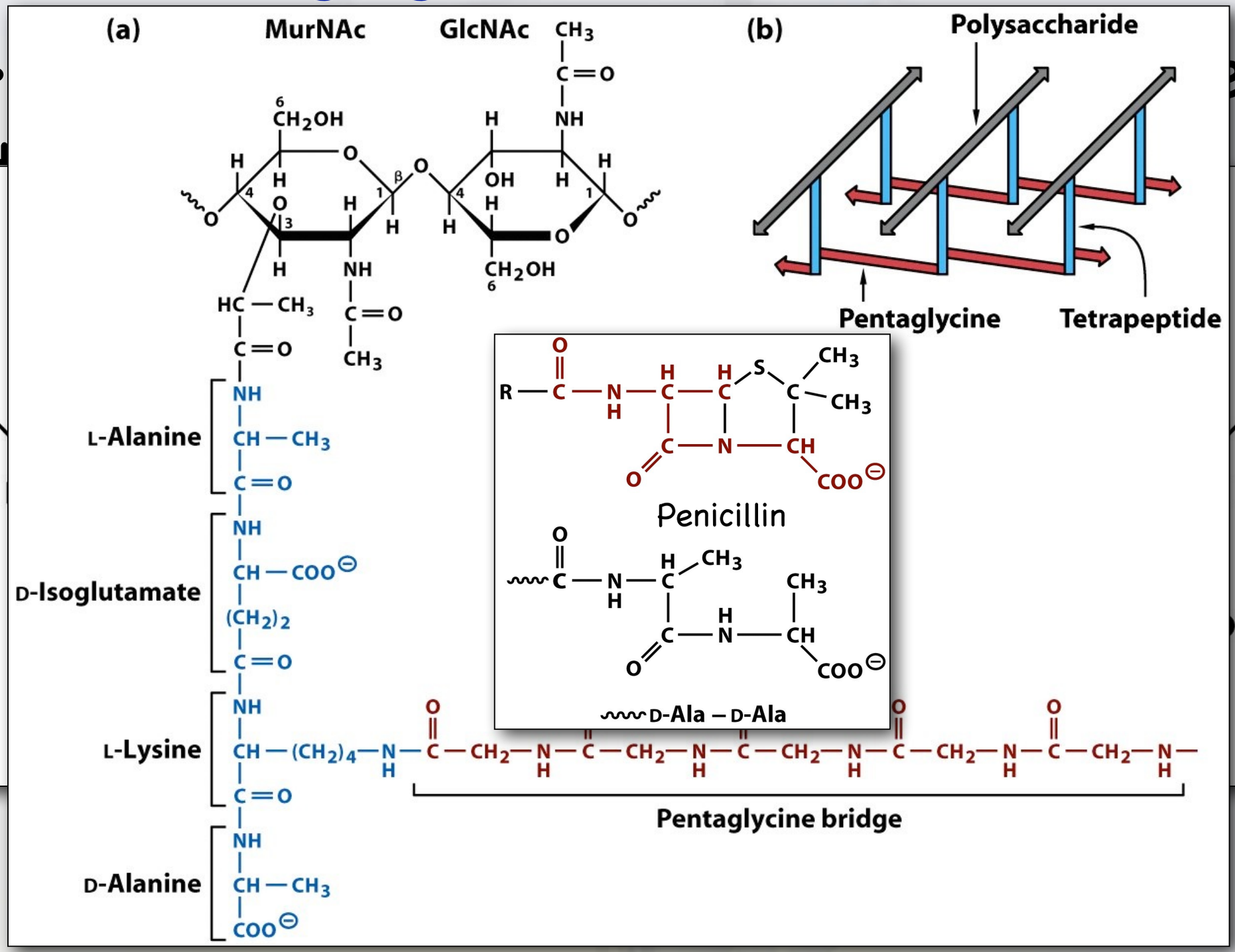

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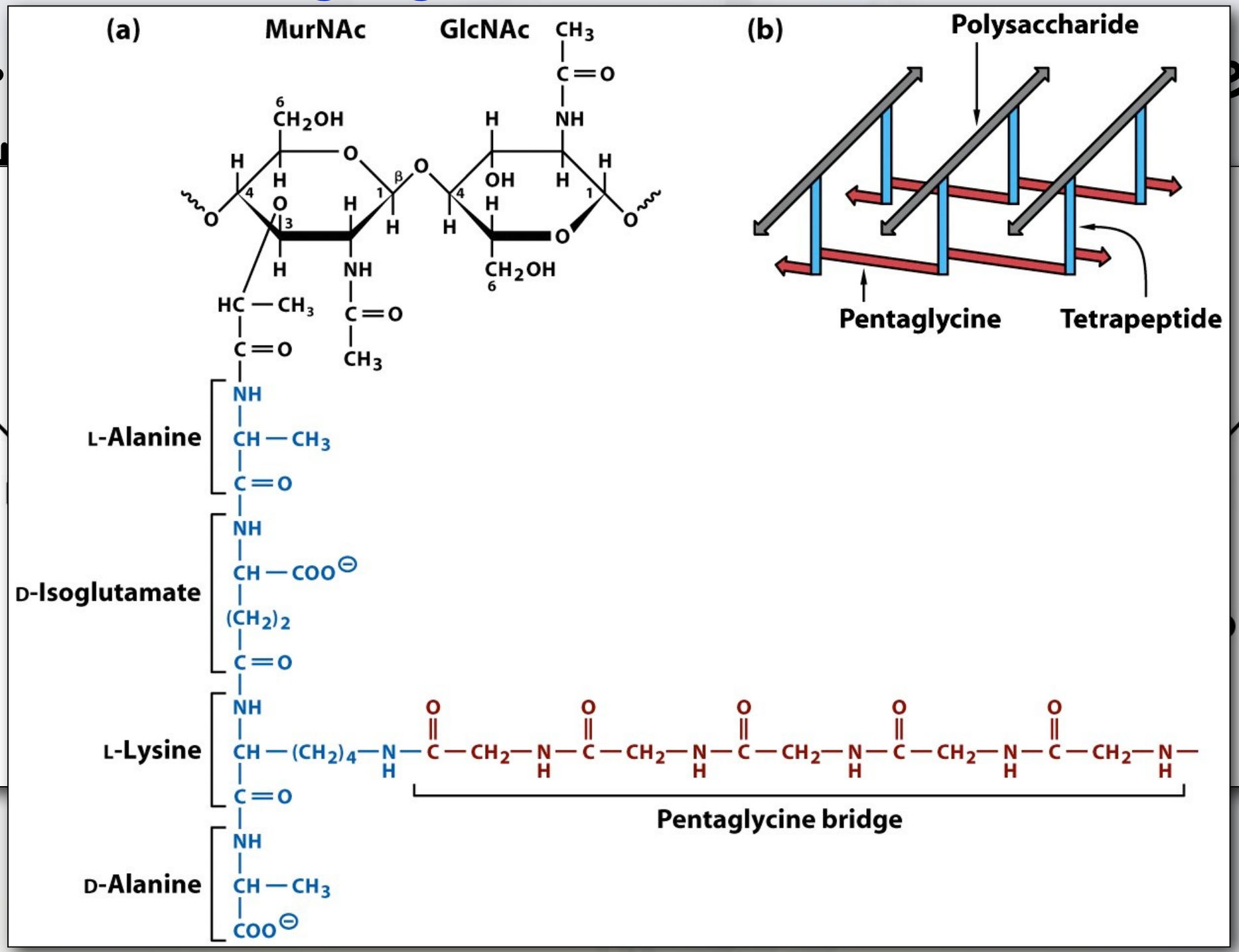

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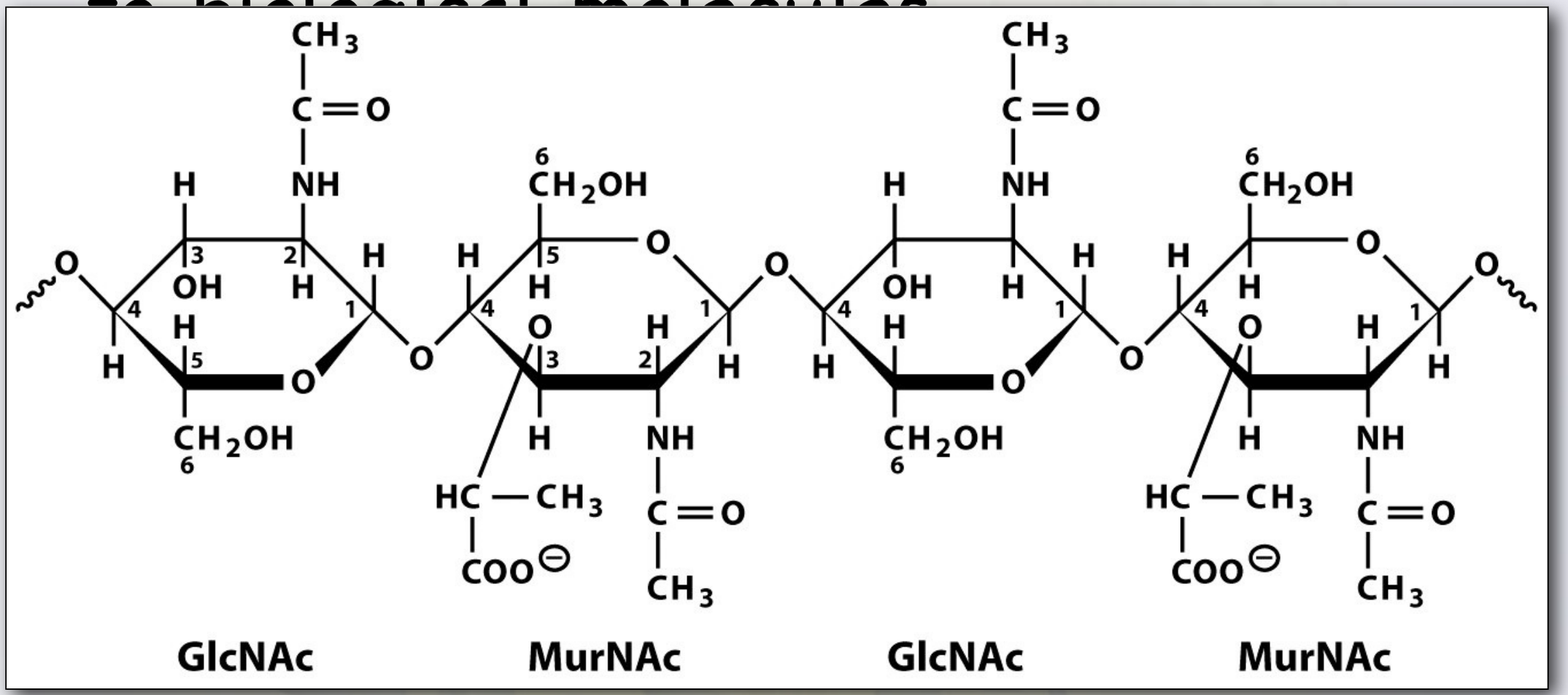

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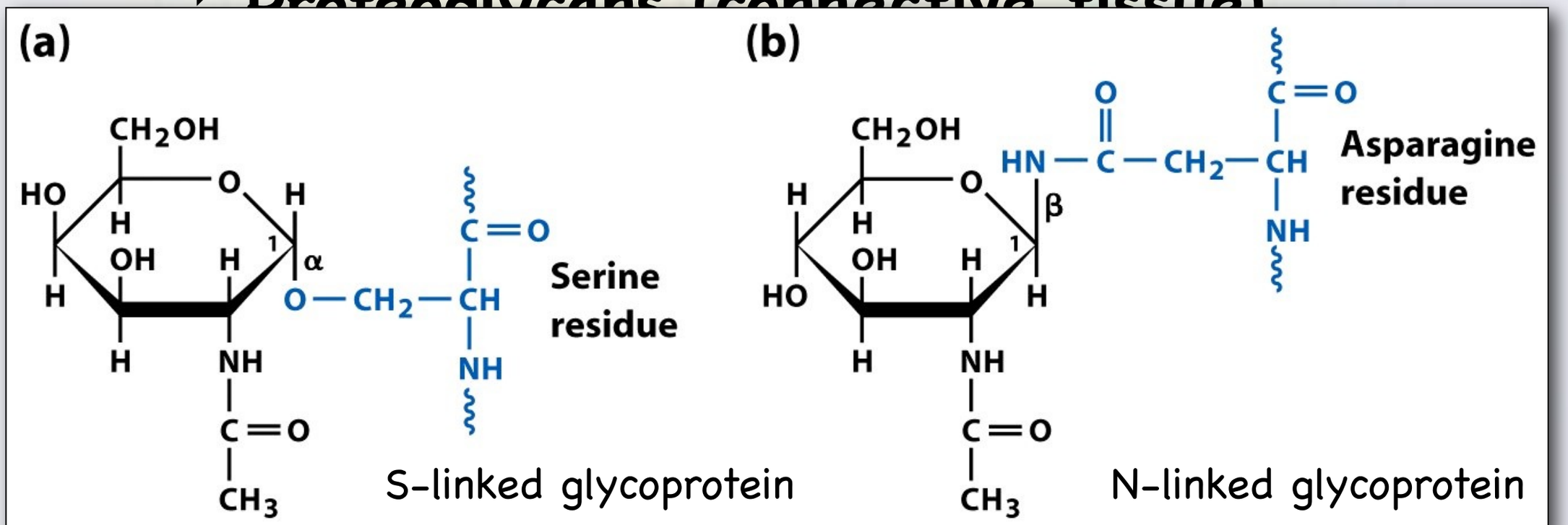

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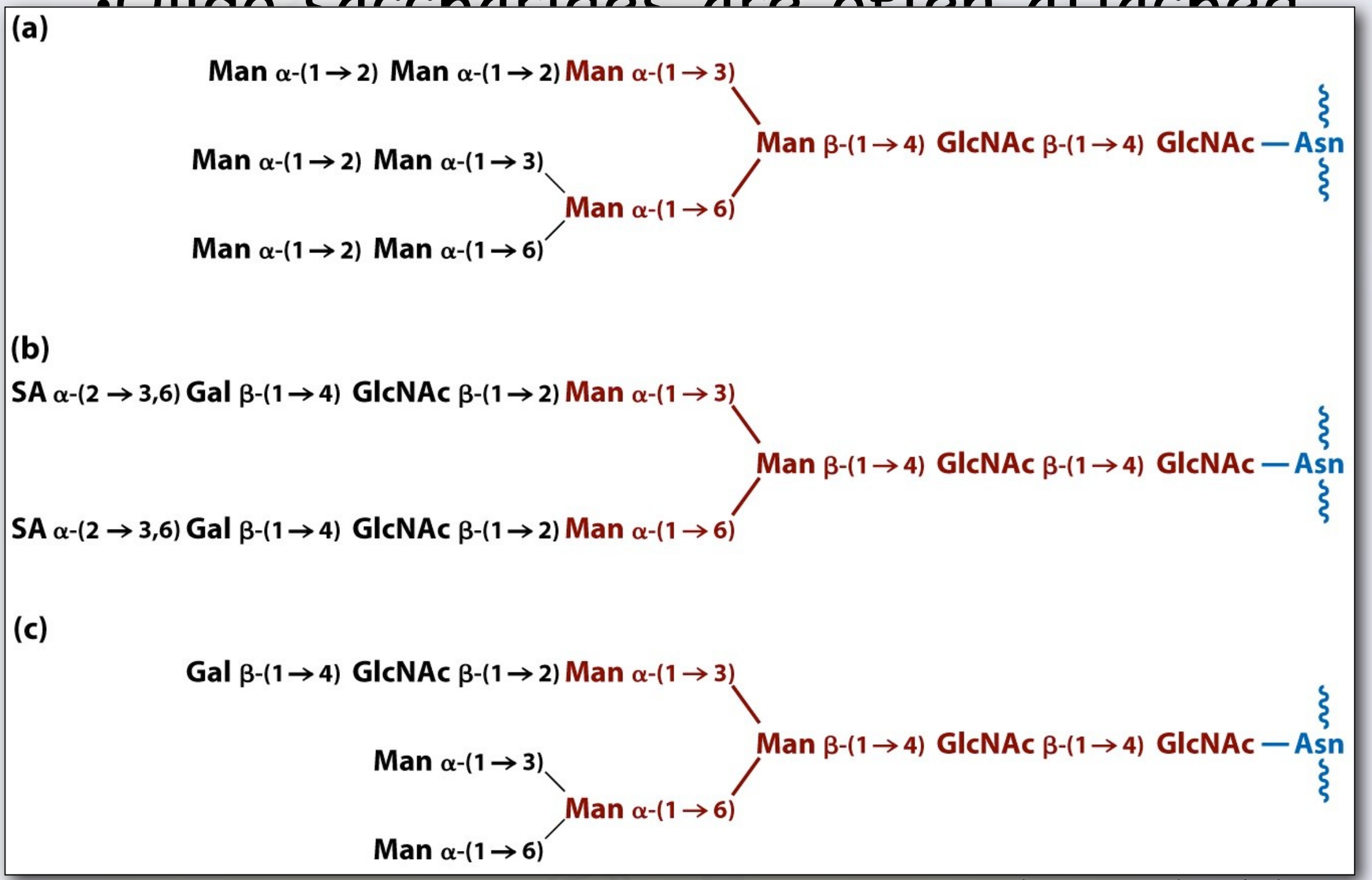

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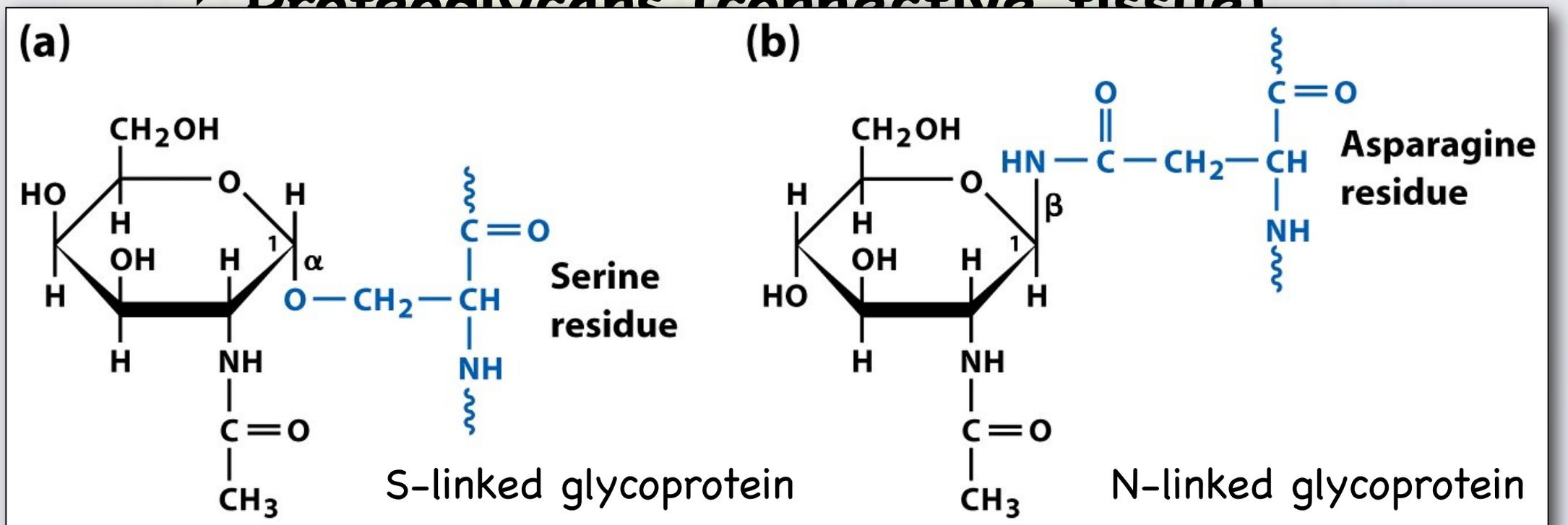

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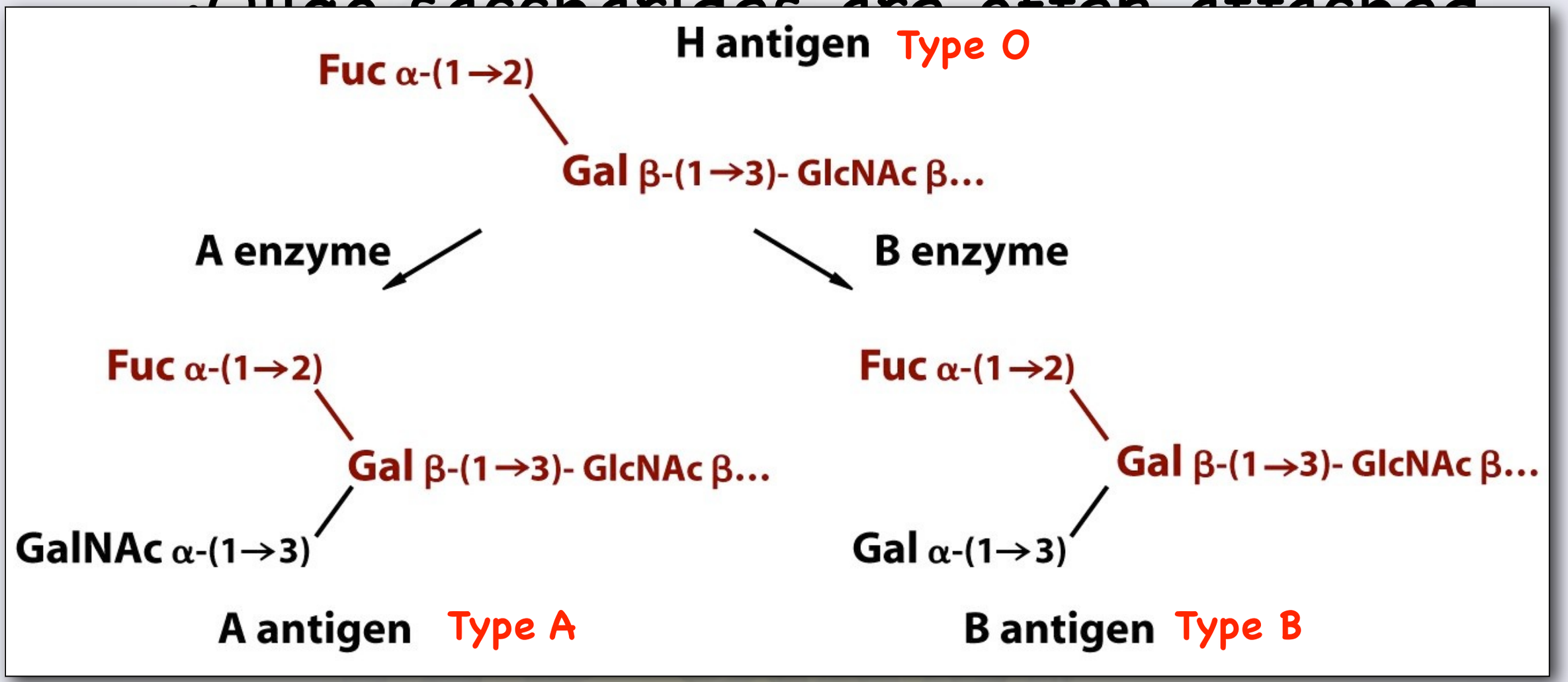

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Which Structures Do I Need to Know?

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

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

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

Next Up

- Lecture 6 - Lipids and Membranes (Chapter 9)