

Chem 109 C

Bioorganic Compounds

Armen Zakarian
Office: Chemistry Bldn 2217

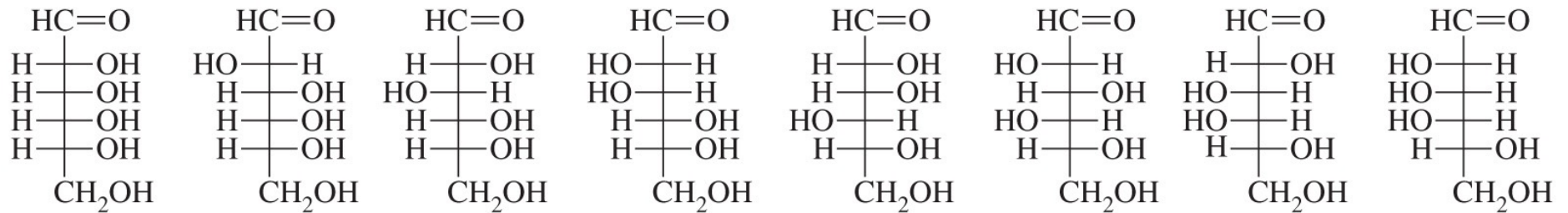
<http://labs.chem.ucsb.edu/~zakariangroup/courses.html>

sections covered: see syllabus

in Chapter 20:

**all except 20.13 - the anomeric effect
20.17, 20.19 (artificial sweeteners)**

Carbohydrates: Stereochemistry of Glucose



1

2

3

4

5

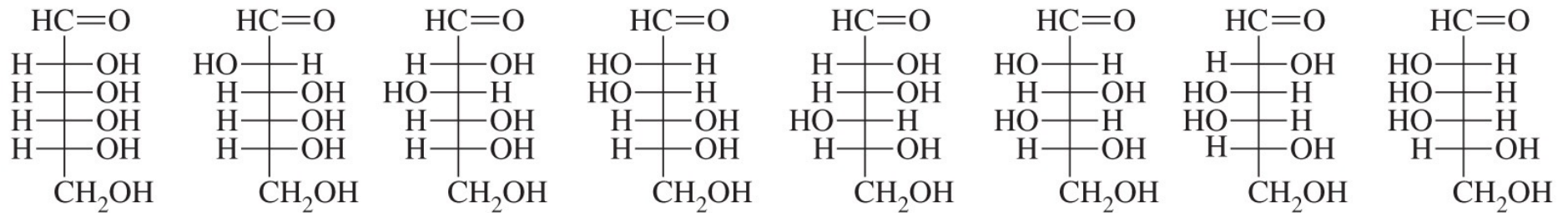
6

7

8

known: an aldohexose

Carbohydrates: Stereochemistry of Glucose



1

2

3

4

5

6

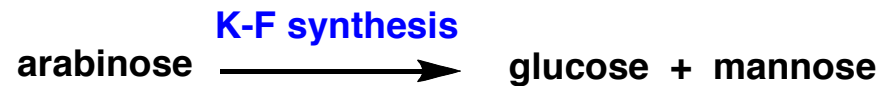
7

8

known: an aldohexose

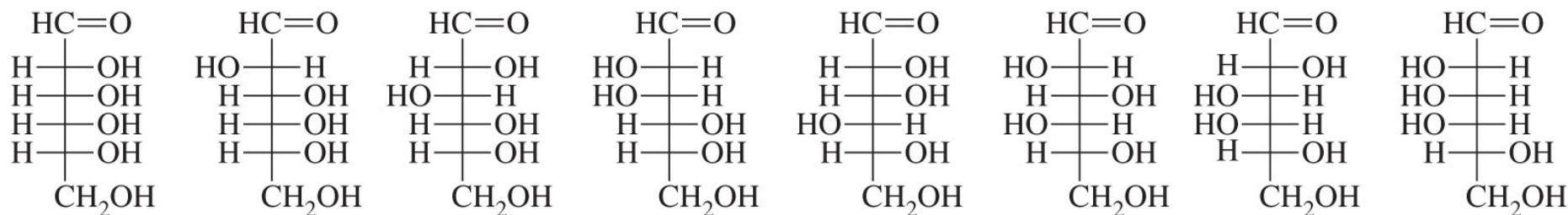
experiment

conclusion



C2 epimers

Carbohydrates: Stereochemistry of Glucose



1 2

3 4

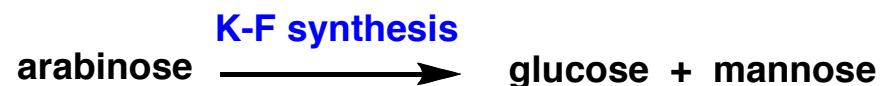
5 6

7 8

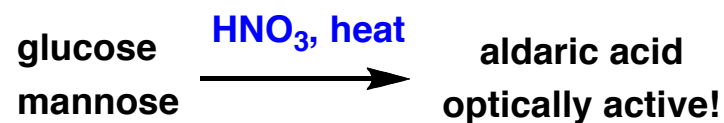
known: an aldohexose

experiment

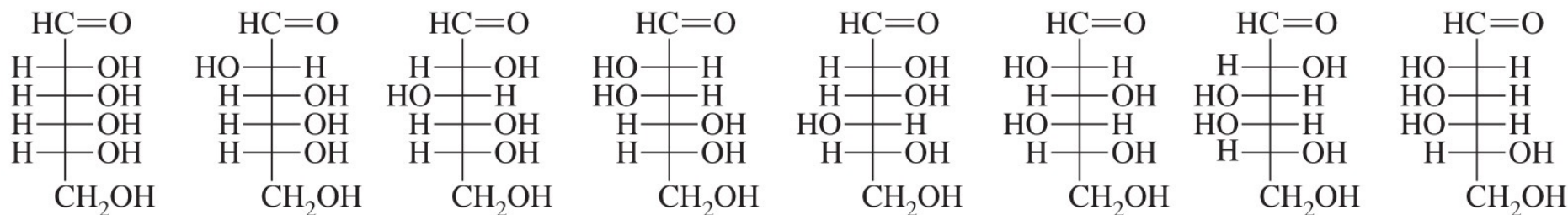
conclusion



C2 epimers



Carbohydrates: Stereochemistry of Glucose



1 2

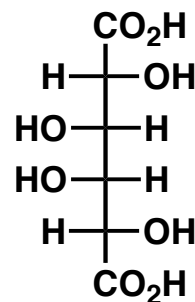
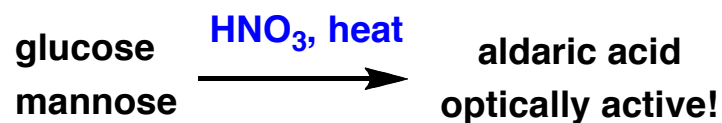
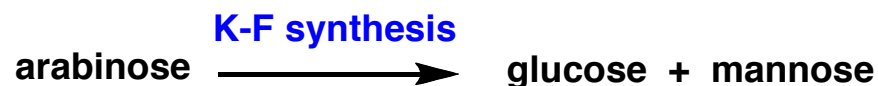
3 4

5 6

7 8

known: an aldohexose

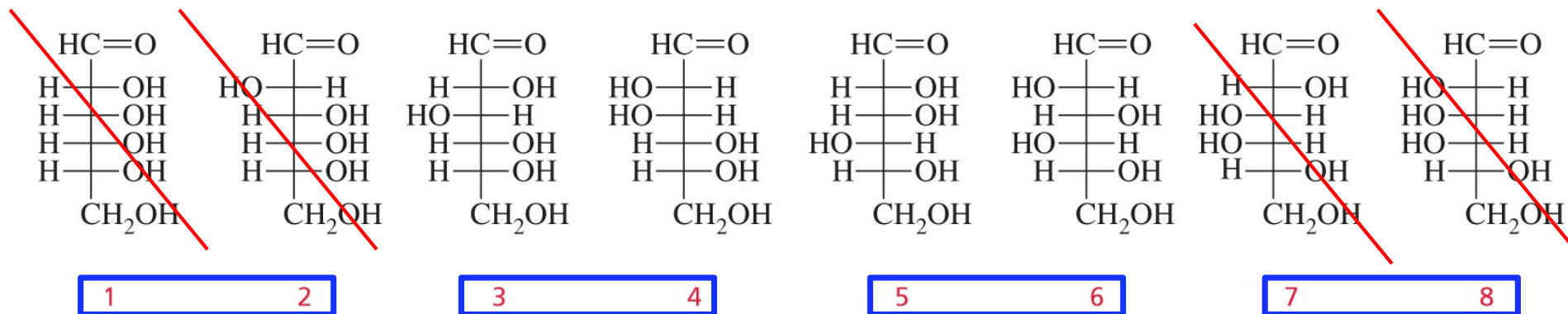
experiment



conclusion

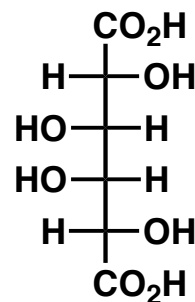
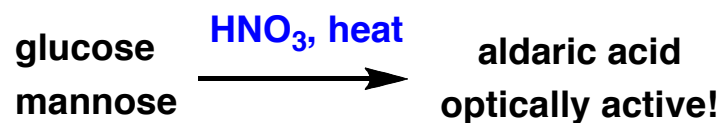
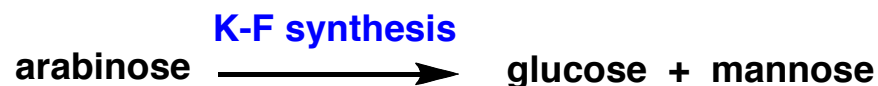
C2 epimers

Carbohydrates: Stereochemistry of Glucose



known: an aldohexose

experiment

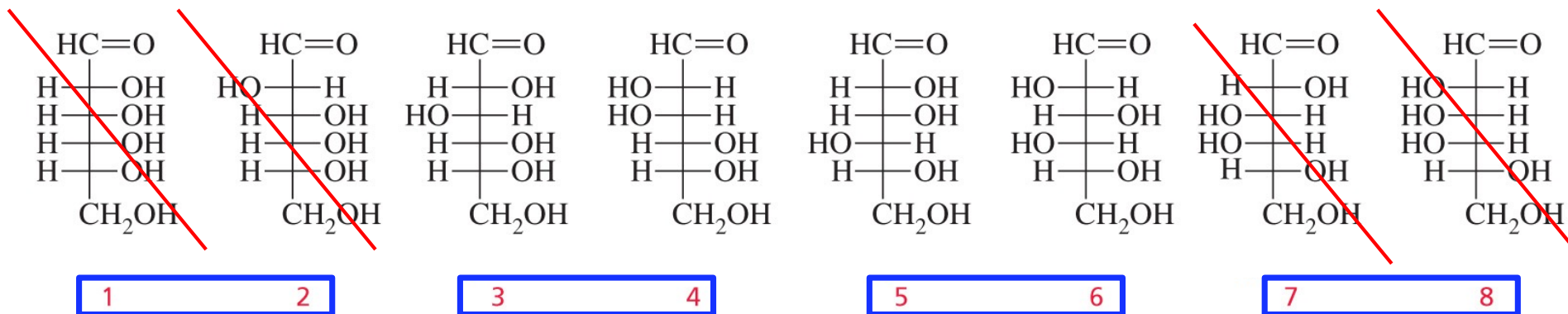


conclusion

C2 epimers

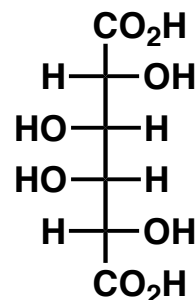
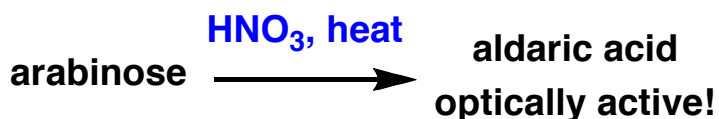
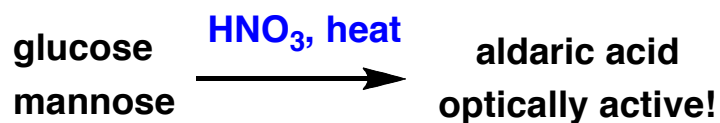
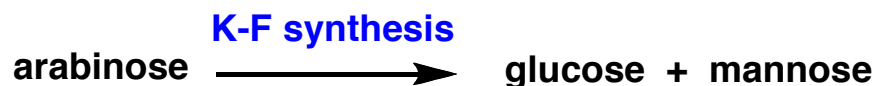
**not structures
1,2,7,8**

Carbohydrates: Stereochemistry of Glucose



known: an aldohexose

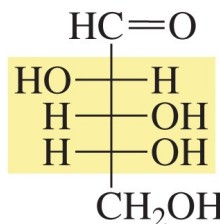
experiment



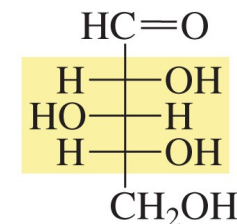
conclusion

C2 epimers

not structures 1,2,7,8

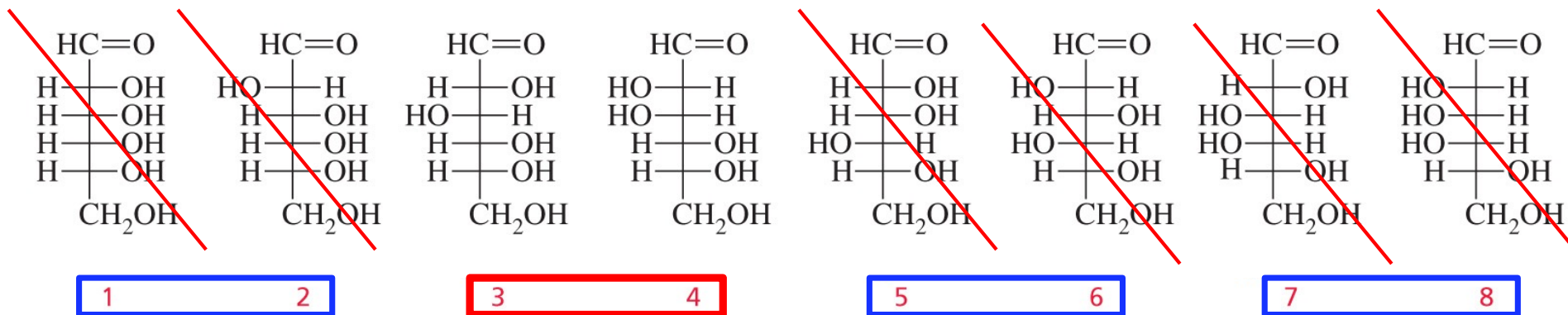


the structure of (-)-arabinose if (+)-glucose and (+)-mannose are sugars 3 and 4



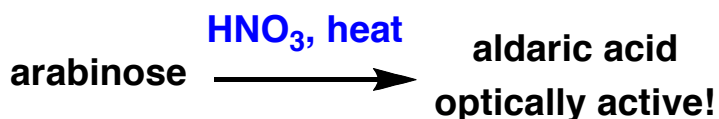
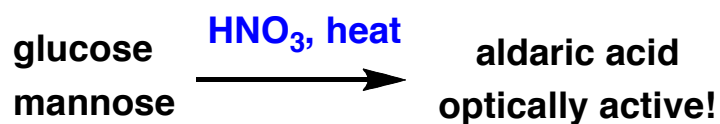
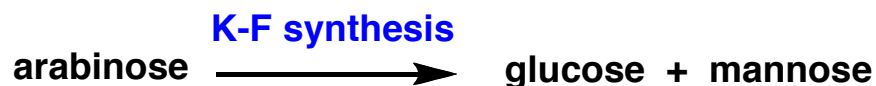
the structure of (-)-arabinose if (+)-glucose and (+)-mannose are sugars 5 and 6

Carbohydrates: Stereochemistry of Glucose



known: an aldohexose

experiment

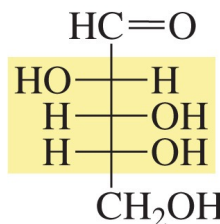
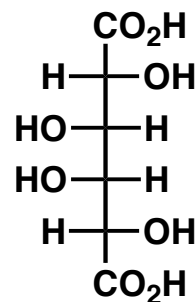


3 or 4

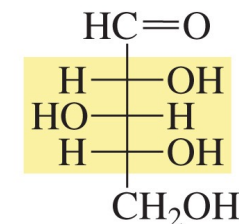
conclusion

C2 epimers

not structures 1,2,7,8

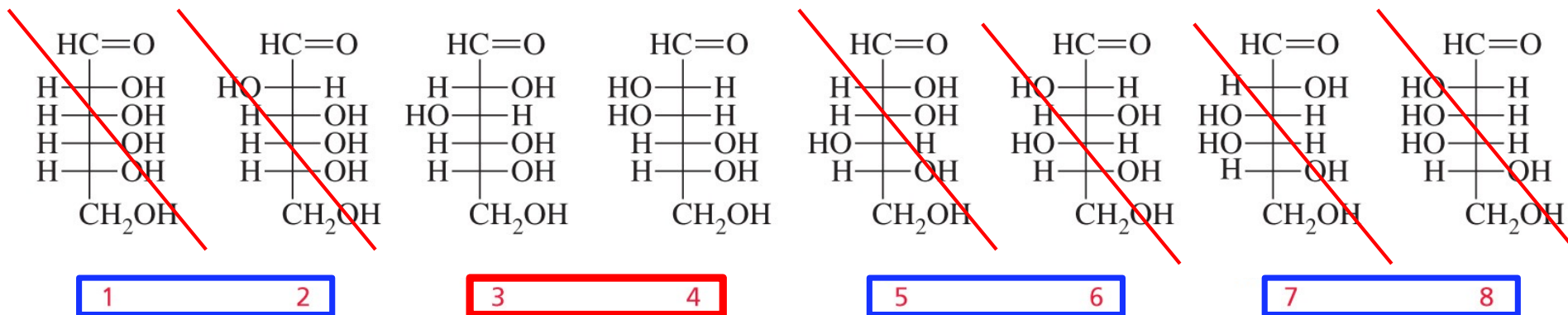


the structure of (-)-arabinose if (+)-glucose and (+)-mannose are sugars 3 and 4



the structure of (-)-arabinose if (+)-glucose and (+)-mannose are sugars 5 and 6

Carbohydrates: Stereochemistry of Glucose

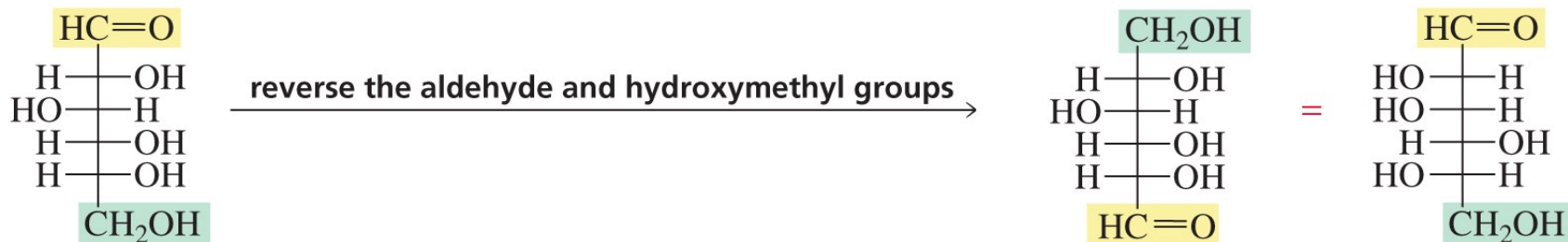


known: an aldohexose

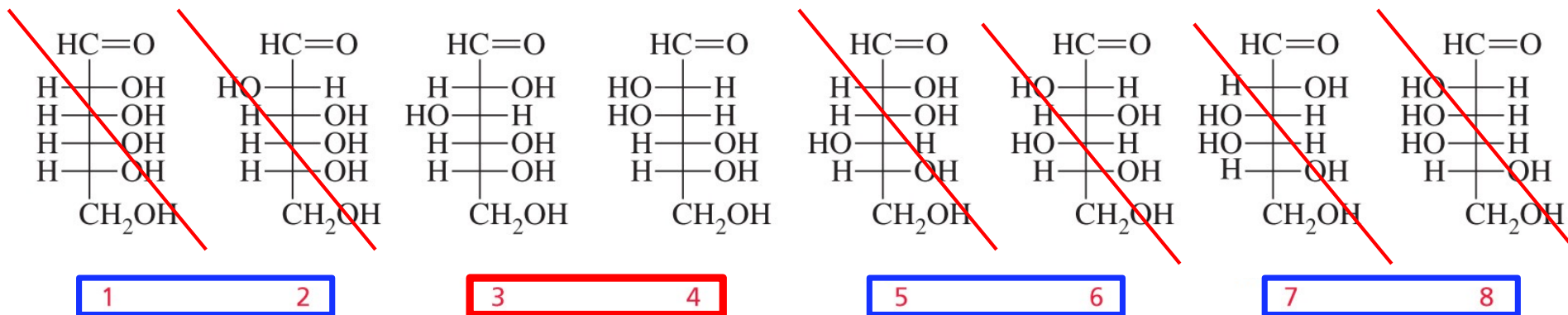
experiment

3 or 4

conclusion



Carbohydrates: Stereochemistry of Glucose

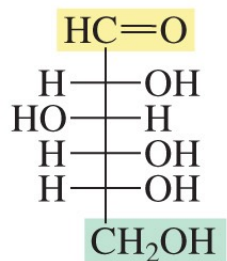


known: an aldohexose

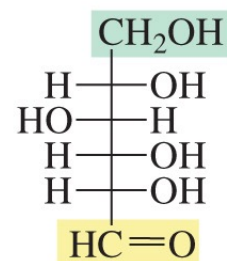
experiment

3 or 4

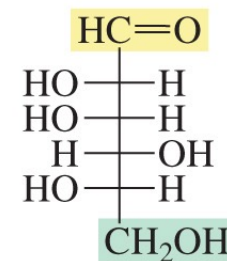
conclusion



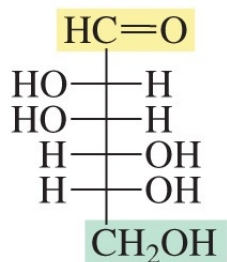
reverse the aldehyde and hydroxymethyl groups →



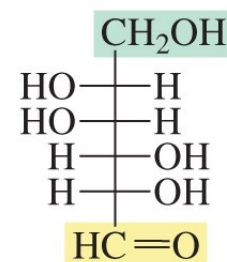
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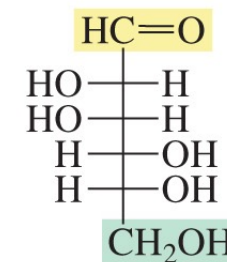
drawn upside down



reverse the aldehyde and hydroxymethyl groups →



=



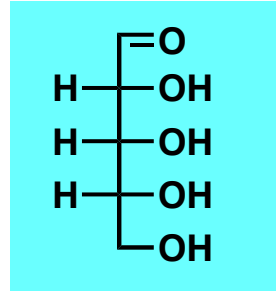
drawn upside down

Carbohydrates: Shortening the Chain

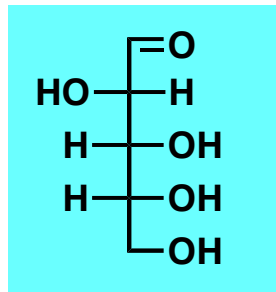
PROBLEM

What two monosaccharides can be degraded to

a. **D-ribose**



b. **D-arabinose**

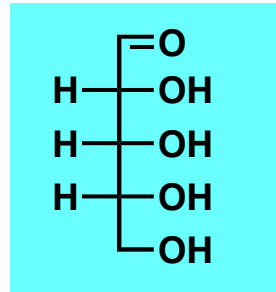


Carbohydrates: Shortening the Chain

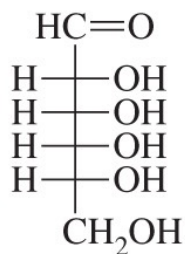
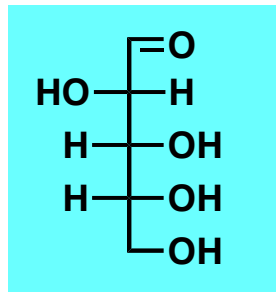
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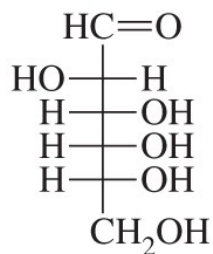


b. **D-arabinose**



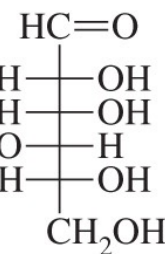
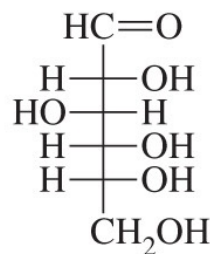
D-allose

1



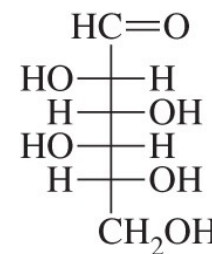
D-altrose

2



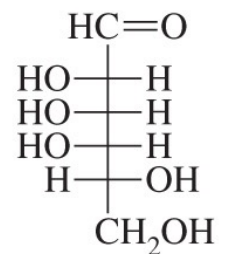
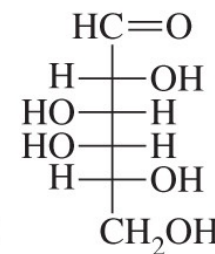
D-gulose

5



D-idose

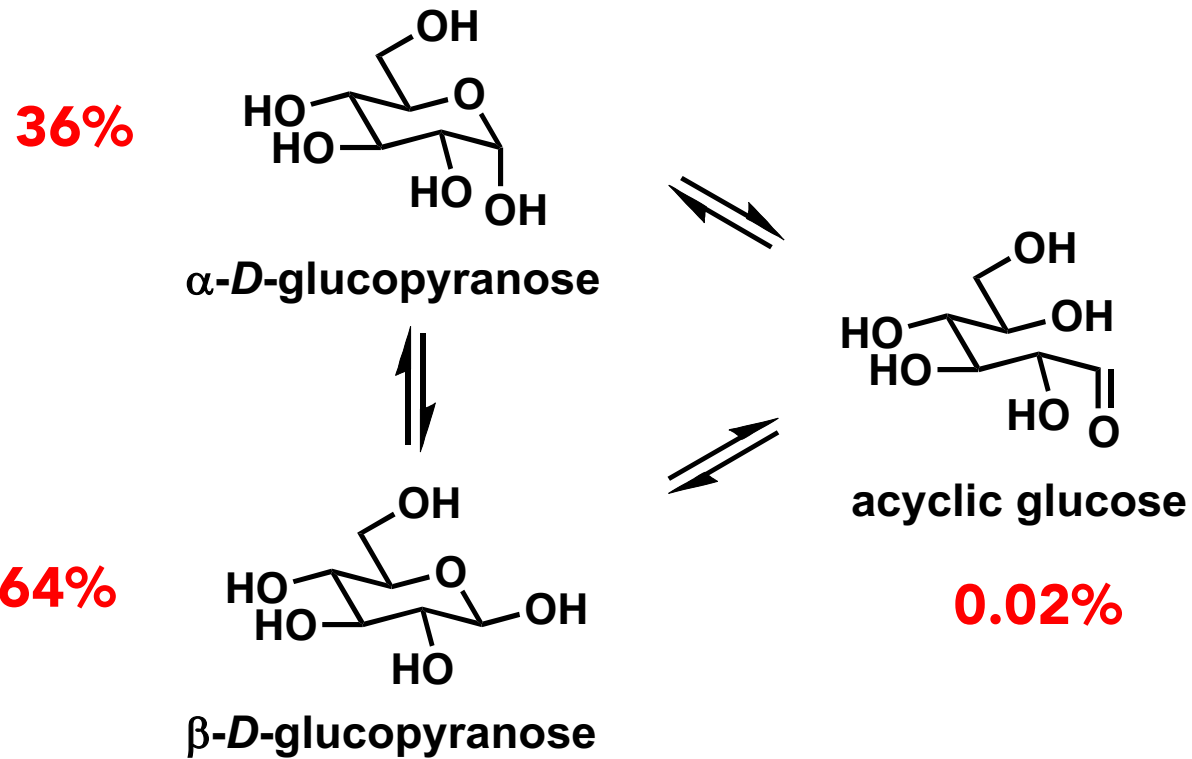
6



D-talose

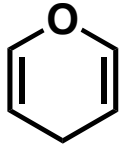
8

Carbohydrates: **Cyclic Hemiacetals**

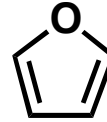


in aqueous solution

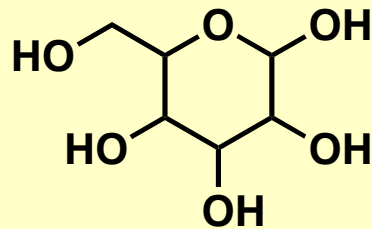
Carbohydrates: **More Classification**



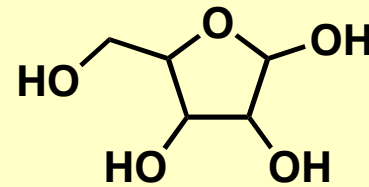
pyran



furan



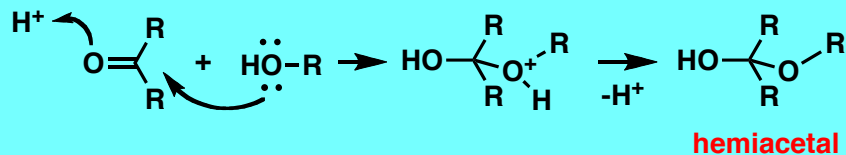
pyranose



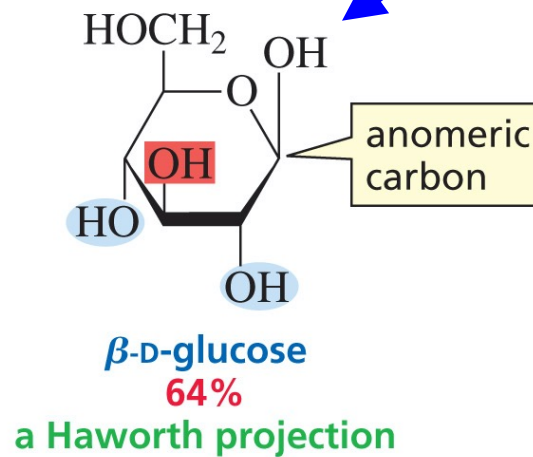
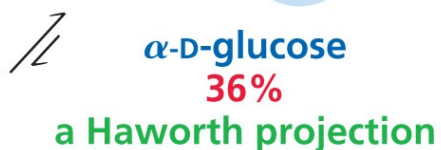
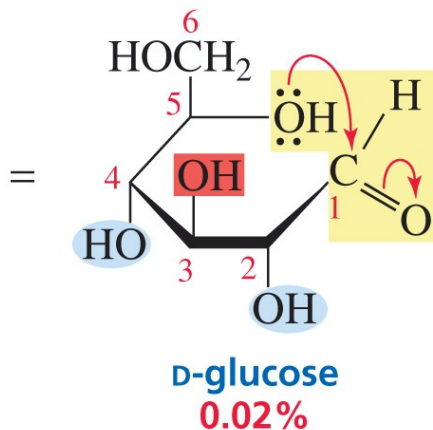
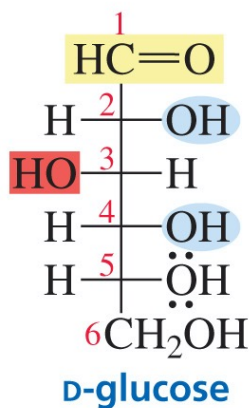
furanose

Carbohydrates: Haworth projections

fundamental reactivity



section 16.9

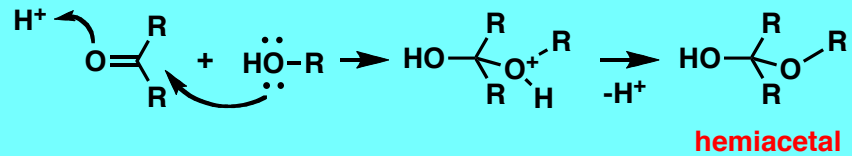


anomeric carbon

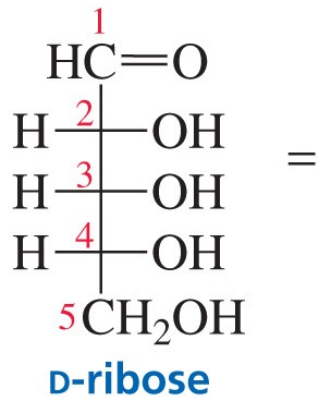
anomeric hydroxyl group

Carbohydrates: Cyclic Hemiacetals

fundamental reactivity



section 16.9



forms a furanose

Carbohydrates: **Cyclic Hemiacetals**

PRACTICE PROBLEM

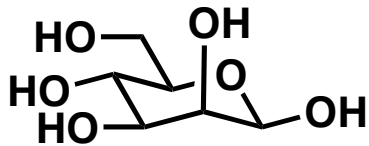
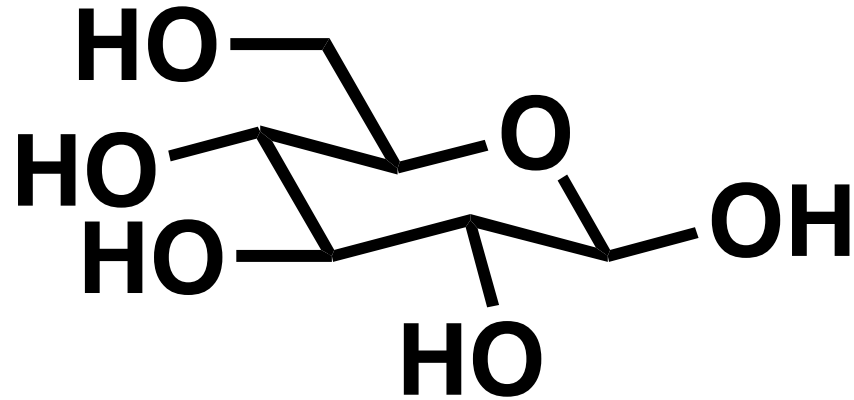
Draw the following sugars using the Haworth projections:

a. β -D-galactopyranose

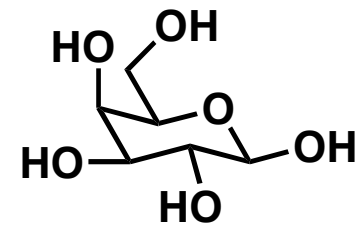
b. α -L-glucopyranose

Carbohydrates: **Cyclic Hemiacetals**

Glucose - most stable aldohexose:



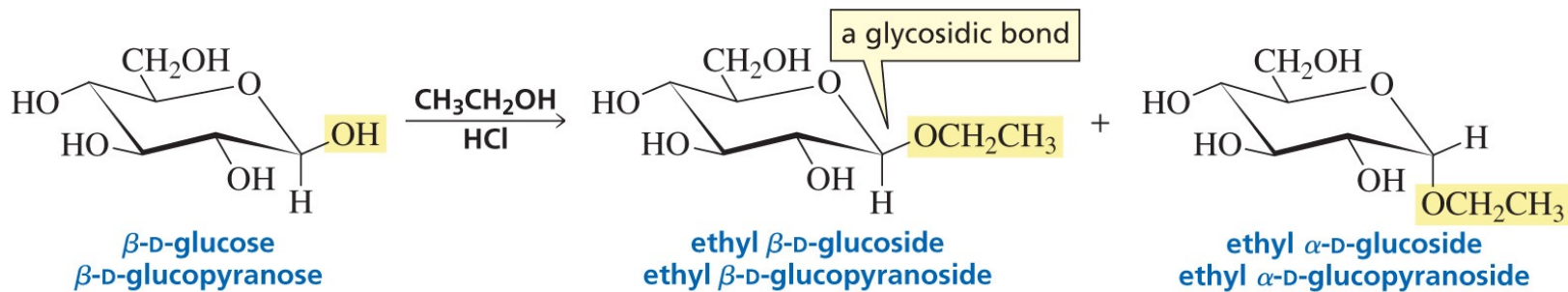
mannose



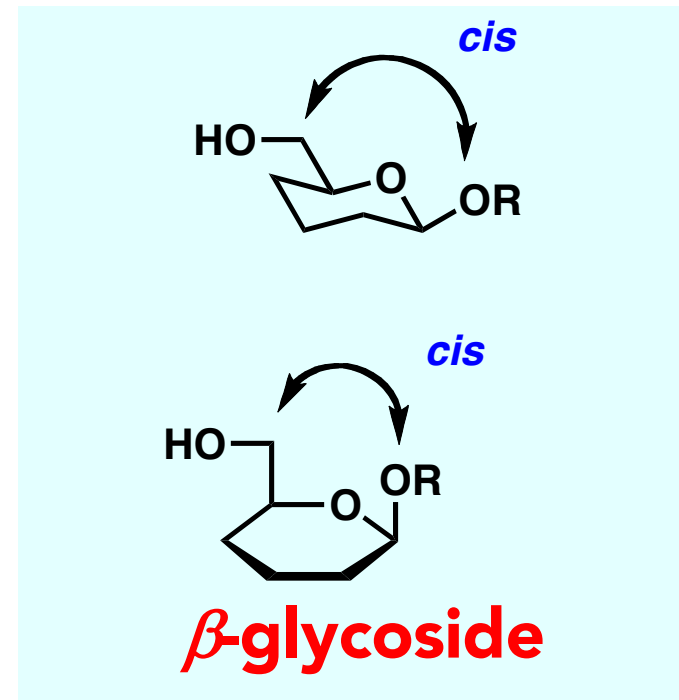
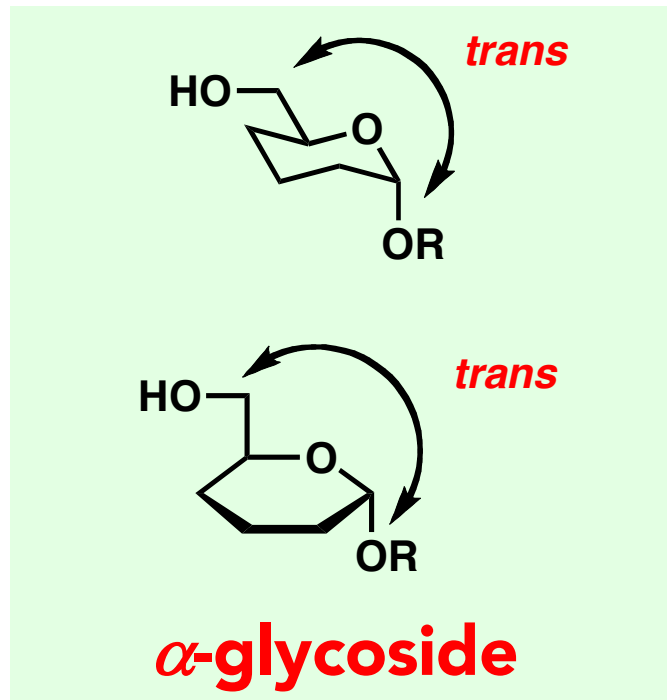
galactose

Carbohydrates: **Glycosides**

Formation of glycosides:

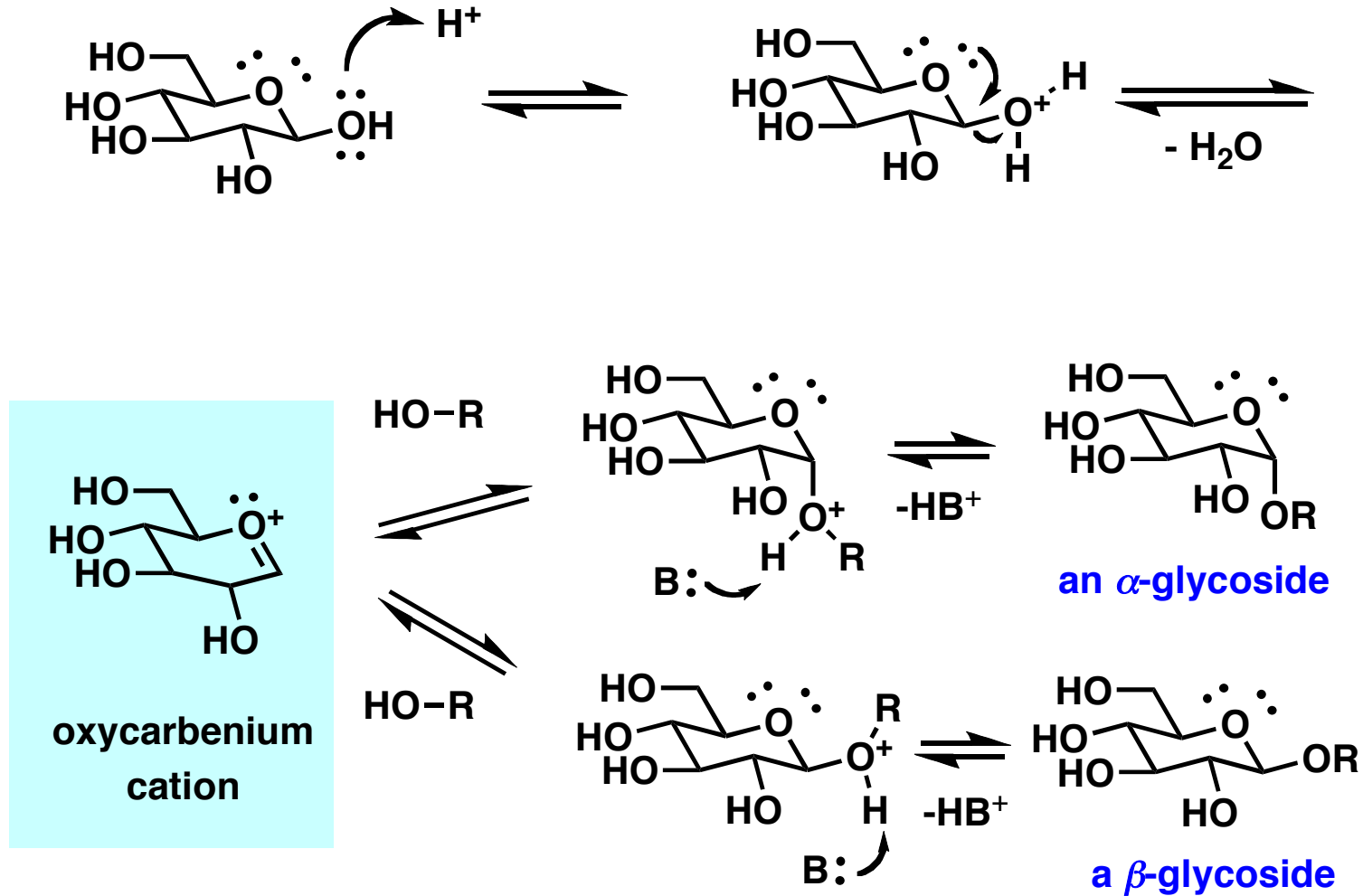


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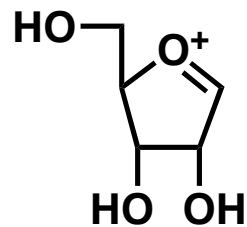
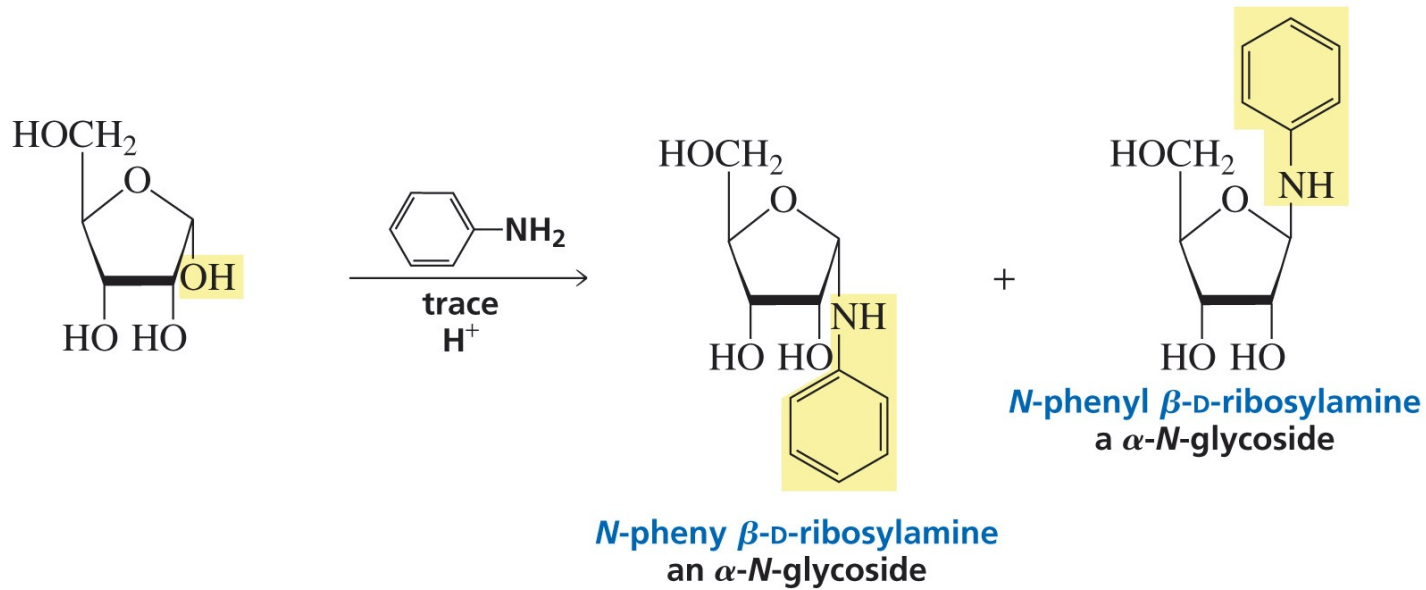
Carbohydrates: Glycosides

mechanism for glycoside formation:



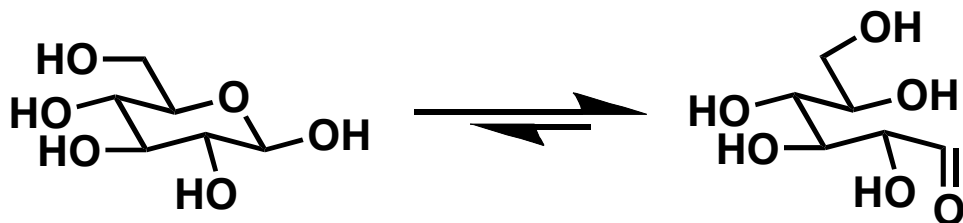
Carbohydrates: Glycosides

N-glycoside formation:

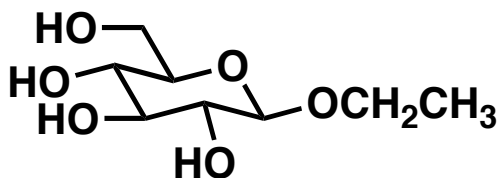


oxycarbenium
cation

Carbohydrates: Reducing and Non-reducing



reducing sugar: aldehyde reactivity is accessible



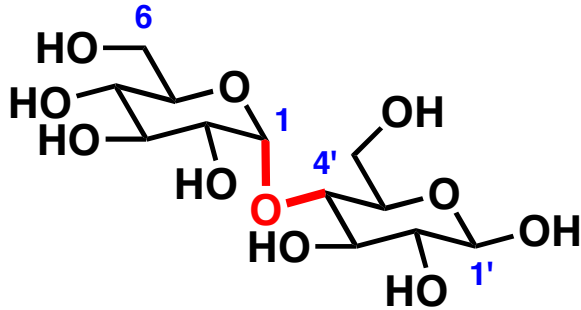
non-reducing sugar: stable acetal

Tollens reagent:

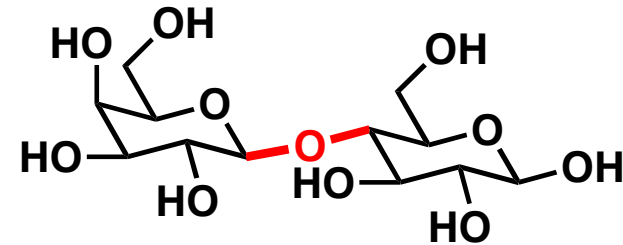
Ag⁺, HO⁻



Carbohydrates: **Disaccharides**

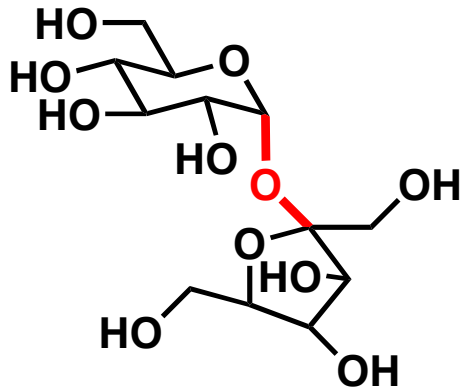


an α -1,4'-glycosidic linkage



an β -1,4'-glycosidic linkage

lactose

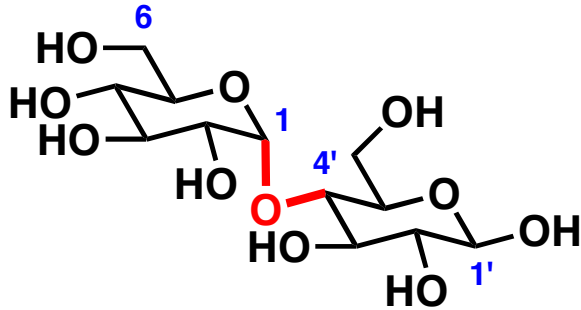


an α -linkage at glucose

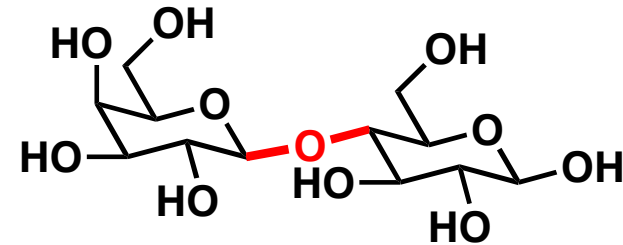
a β -linkage at fructose

sucrose - table sugar

Carbohydrates: **Disaccharides**

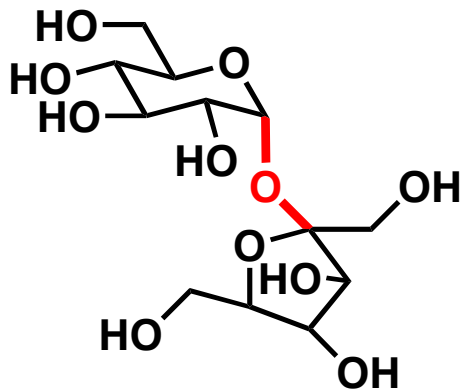


an α -1,4'-glycosidic linkage



an β -1,4'-glycosidic linkage

lactose



an α -linkage at glucose

a β -linkage at fructose

sucrose - table sugar

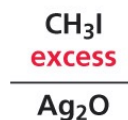
PRACTICE PROBLEM

which ones are reducing sugars ?

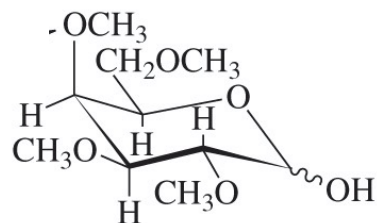
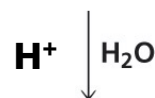
Carbohydrates: **Disaccharides**

Disaccharide identification, similar to PROBLEM 68

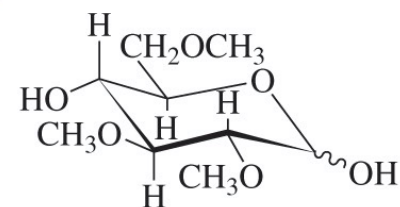
disaccharide X



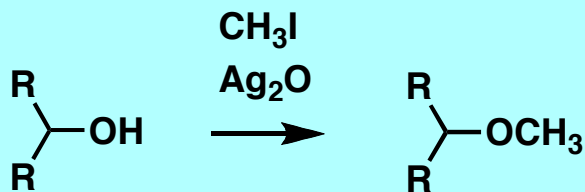
fully
O-methylated
disaccharide X



2,3,4,6-tetra-O-methylgalactose



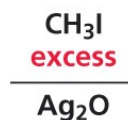
2,3,6-tri-O-methylglucose



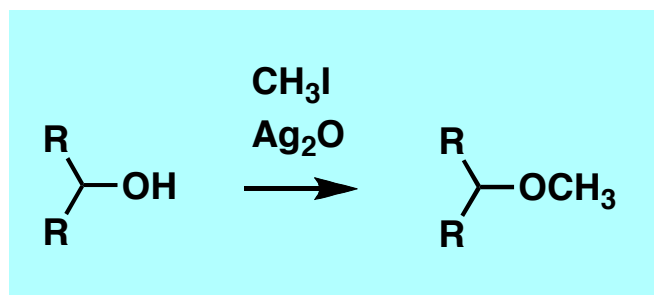
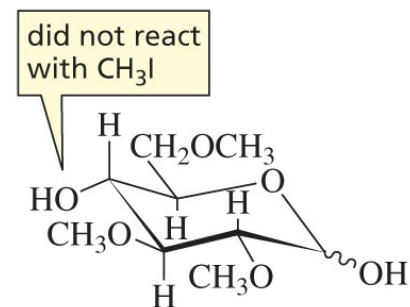
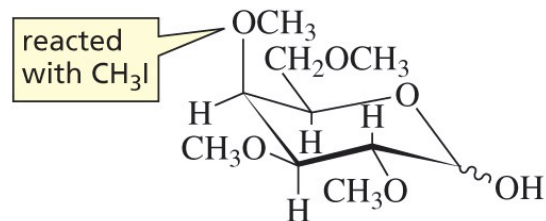
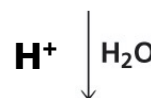
Carbohydrates: Disaccharides

Disaccharide identification, similar to **PROBLEM 68**

disaccharide X



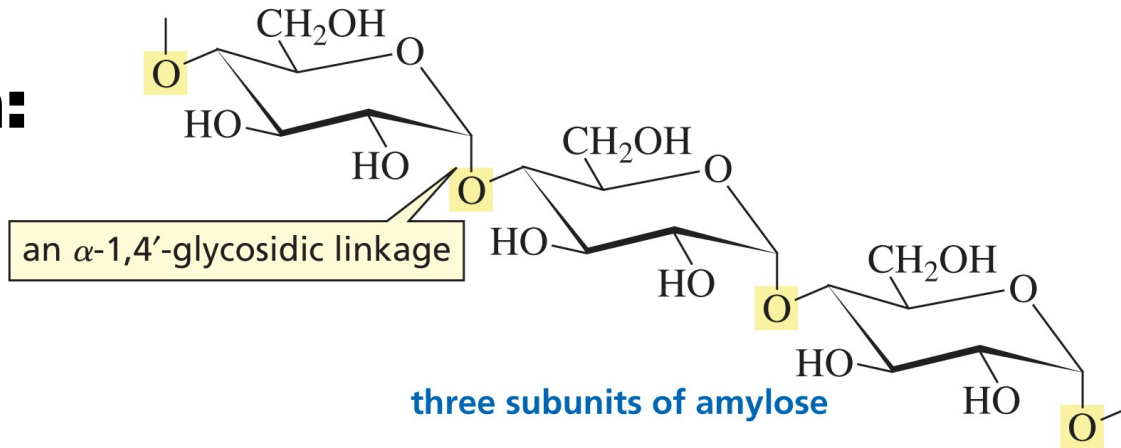
fully
O-methylated
disaccharide X



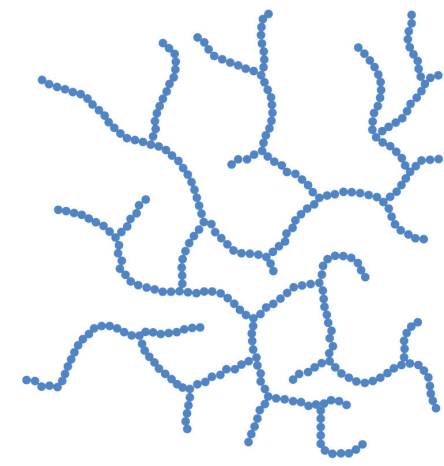
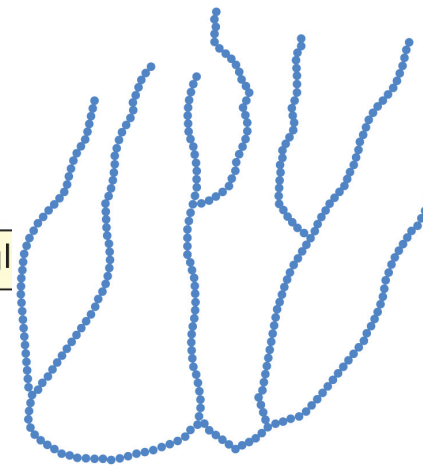
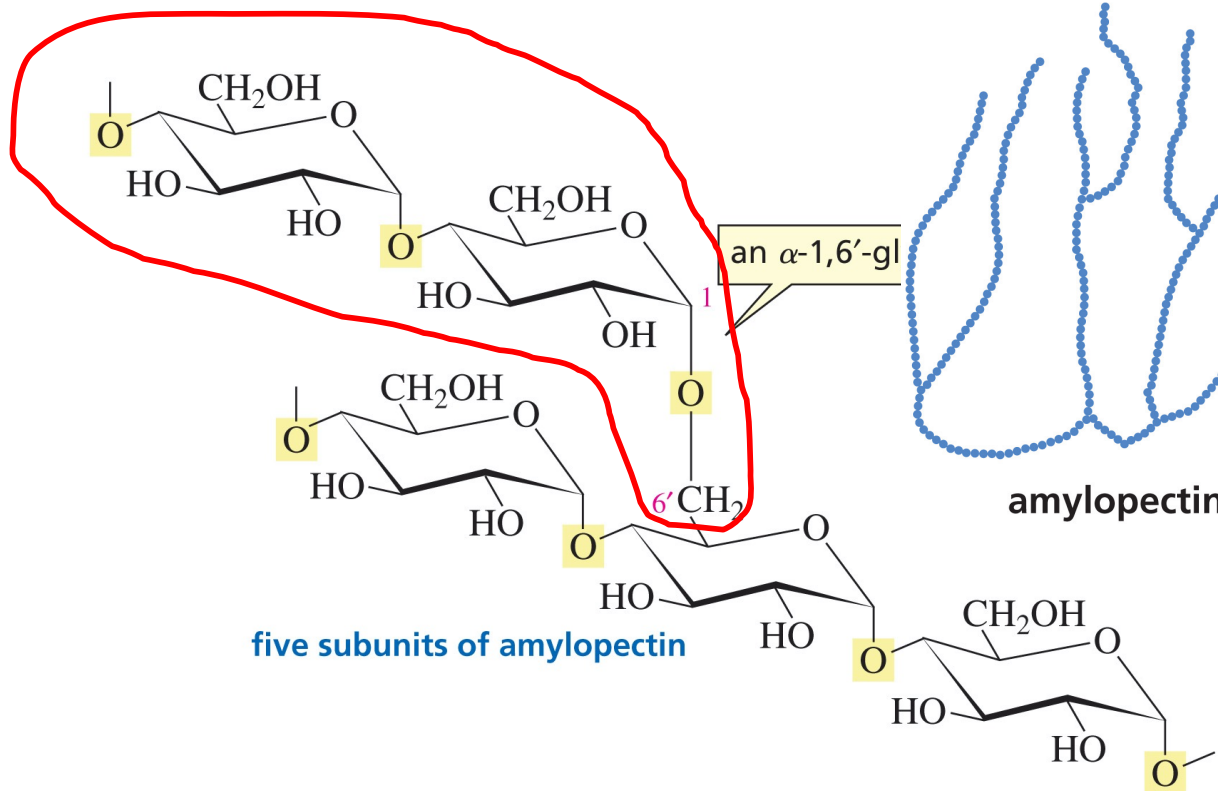
Carbohydrates: Common Polysaccharides

starch:

20%

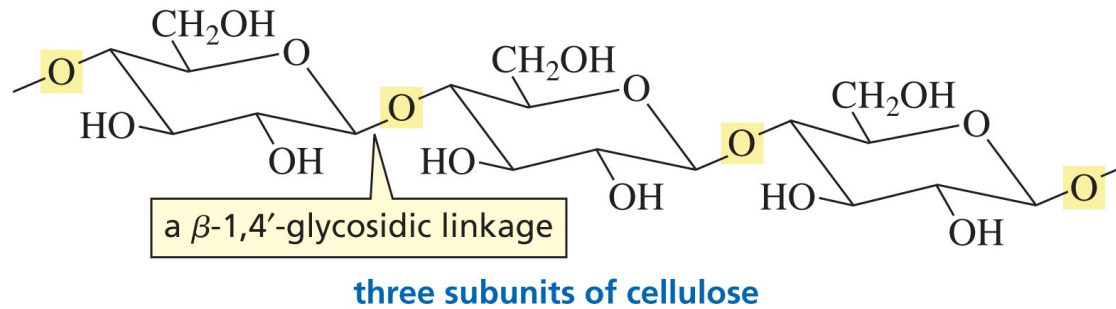


80%



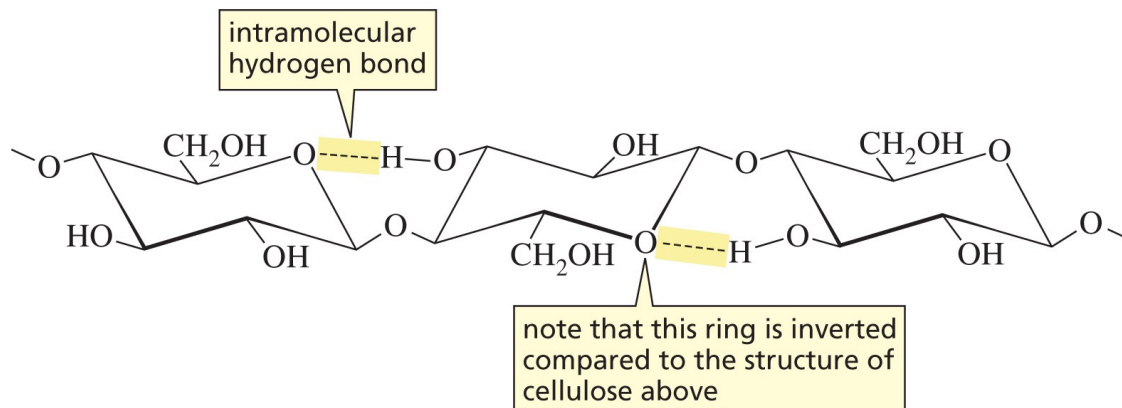
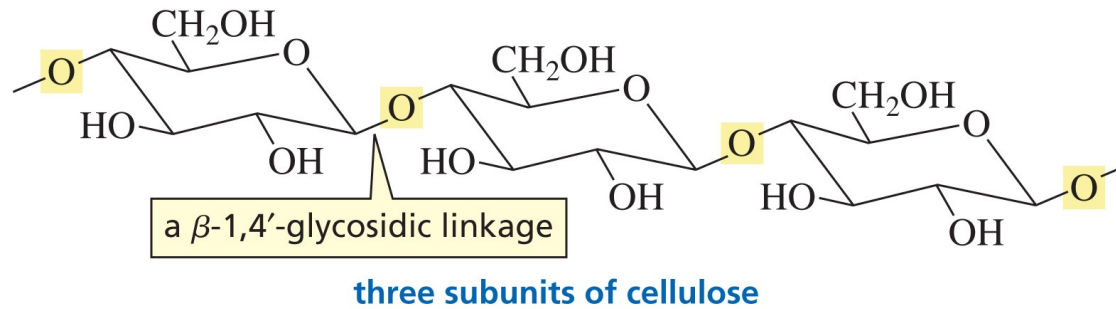
Carbohydrates: Common Polysaccharides

cellulose: 90% of cotton, 50% of wood



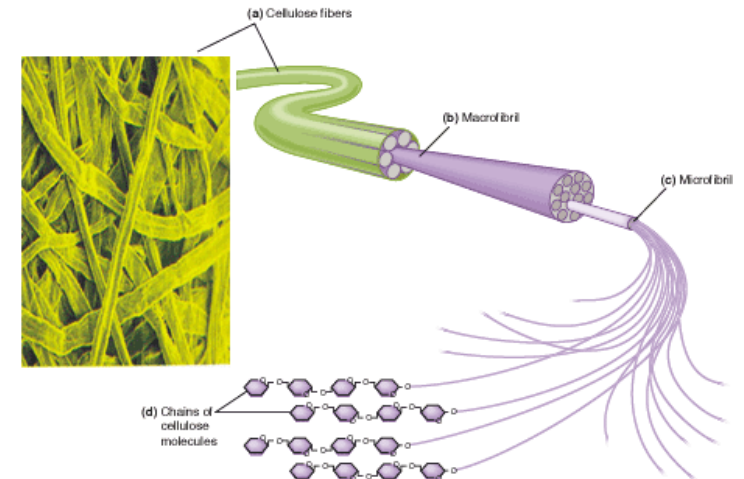
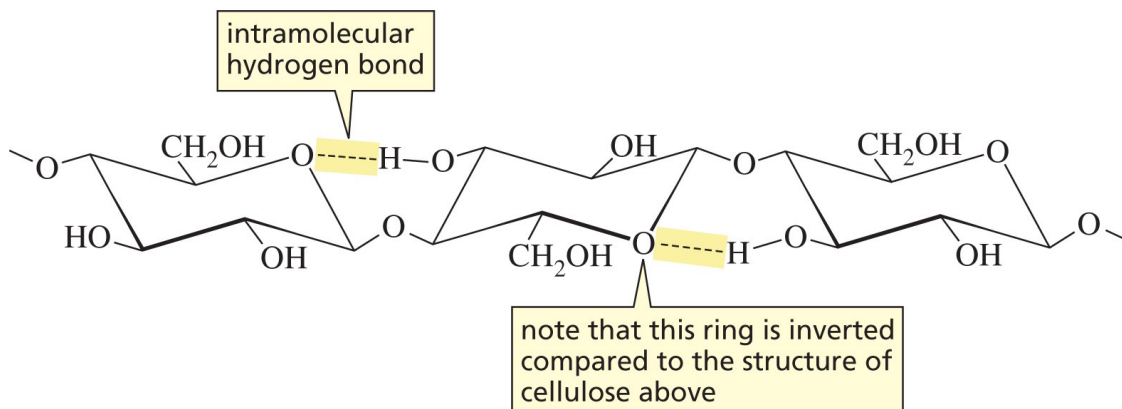
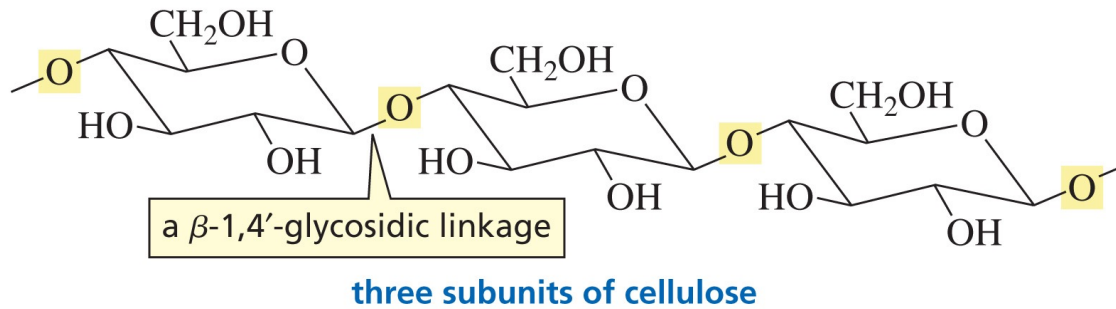
Carbohydrates: Common Polysaccharides

cellulose: 90% of cotton, 50% of wood

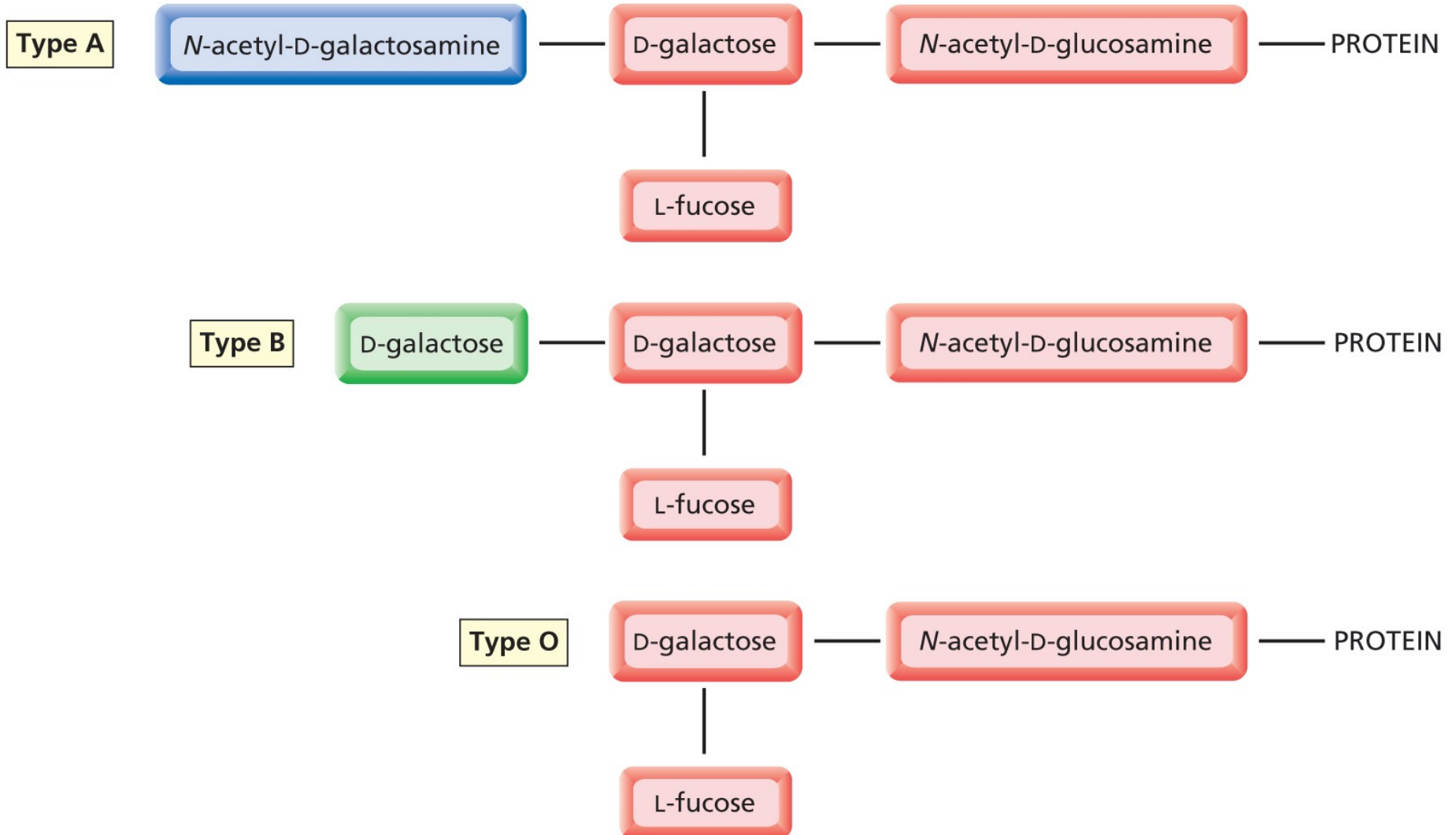


Carbohydrates: Common Polysaccharides

cellulose: 90% of cotton, 50% of wood



Carbohydrates: Common Polysaccharides



Carbohydrates: **Common Polysaccharides**

PRACTICE PROBLEM 53

A D-aldopentose is oxidized by nitric acid to an optically active aldaric acid. A Wohl degradation of the aldopentose leads to a monosaccharide that is oxidized by nitric acid to an optically inactive aldaric acid. Identify the aldopentose

Carbohydrates: **Common Polysaccharides**

PRACTICE PROBLEM 51

Monosaccharide **A** is a diastereomer of D-lyxose. Treatment of **A** with nitric acid forms an optically inactive aldaric acid. **A** undergoes a Kiliani-Fischer synthesis to form **B** and **C**. **B** is oxidized by nitric acid to an optically active aldaric acid, and **C** is oxidized to an optically inactive aldaric acid. Wohl degradation of **A** forms **D**, which is oxidized by nitric acid to an optically inactive aldaric acid. Wohl degradation of **D** forms a D-aldotriose. Identify **A**, **B**, **C**, and **D**.