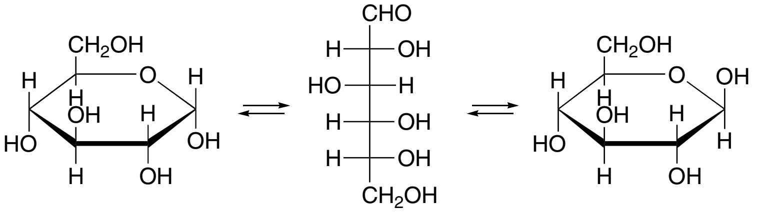
Chapter 27: Carbohydrates

♦ Important terms

Aldose	A monosaccharide containing an aldehyde (27.2)
Ketose	A monosaccharide containing a ketone (27.2)
D-Sugar	A monosaccharide with the O bonded to the stereogenic center farthest from the carbonyl group drawn on the right in the Fischer projection (27.2C)
Epimers	Two diastereomers that differ in configuration around one stereogenic center only (27.3)
Anomers	Monosaccharides that differ in configuration at only the hemiacetal OH group (27.6)
Glycoside	An acetal derived from a monosaccharide hemiacetal (27.7)

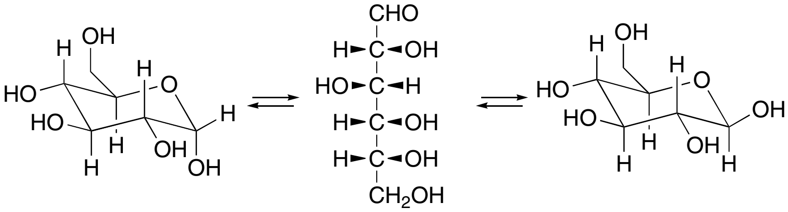
♦ Acyclic, Haworth, and 3-D representations for D-glucose (27.6)

Haworth projection



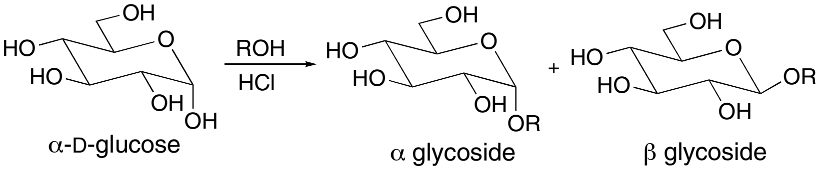
α anomer **acyclic form** **β anomer**

3-D representation



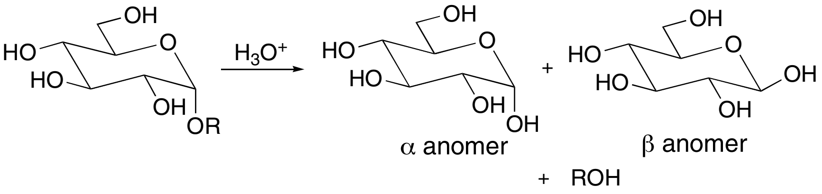
♦ Reactions of monosaccharides involving the hemiacetal

[1] Glycoside formation (27.7A)



- Only the hemiacetal OH reacts.
- A mixture of α and β glycosides forms.

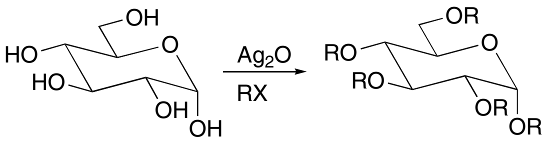
[2] Glycoside hydrolysis (27.7B)



- A mixture of α and β anomers forms.

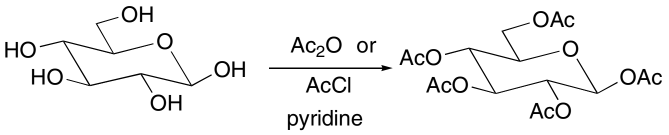
◆ Reactions of monosaccharides at the OH groups

[1] Ether formation (27.8)



- All OH groups react.
- The stereochemistry at all stereogenic centers is retained.

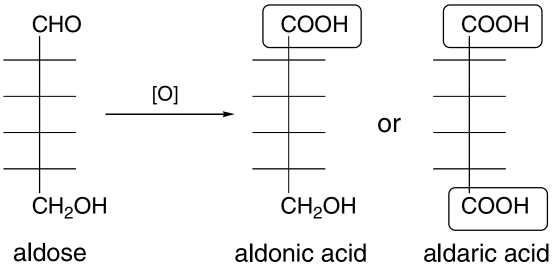
[2] Ester formation (27.8)



- All OH groups react.
- The stereochemistry at all stereogenic centers is retained.

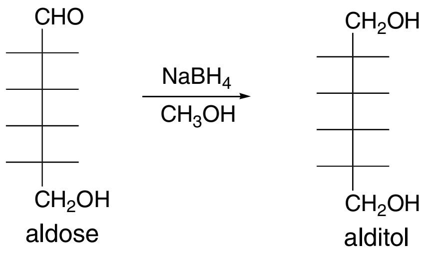
◆ Reactions of monosaccharides at the carbonyl group

[1] Oxidation of aldoses (27.9B)

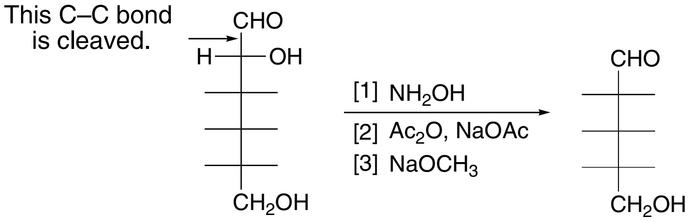


- Aldonic acids are formed using:
  - Ag_2O, NH_4OH
  - Cu^{2+}
  - Br_2, H_2O
- Aldaric acids are formed with HNO_3, H_2O.

[2] Reduction of aldoses to alditols (27.9A)

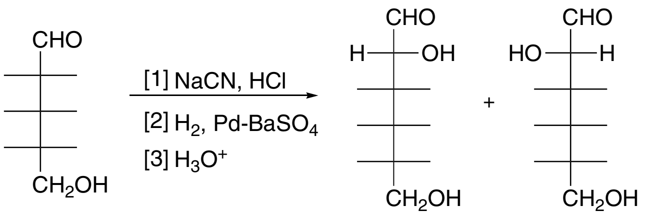


[3] Wohl degradation (27.10A)



- The C1–C2 bond is cleaved to shorten an aldose chain by one carbon.
- The stereochemistry at all other stereogenic centers is retained.
- Two epimers at C2 form the same product.

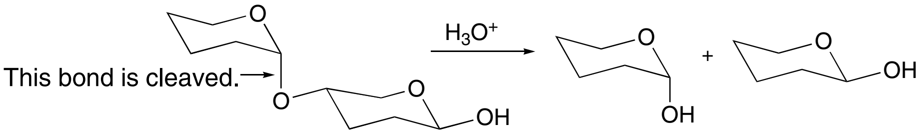
[4] Kiliani–Fischer synthesis (27.10B)



- One carbon is added to the aldehyde end of an aldose.
- Two epimers at C2 are formed.

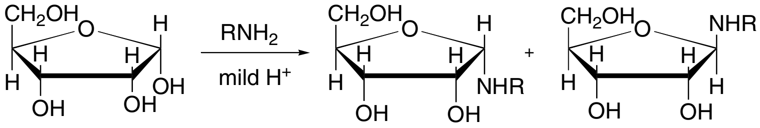
◆ Other reactions

[1] Hydrolysis of disaccharides (27.12)



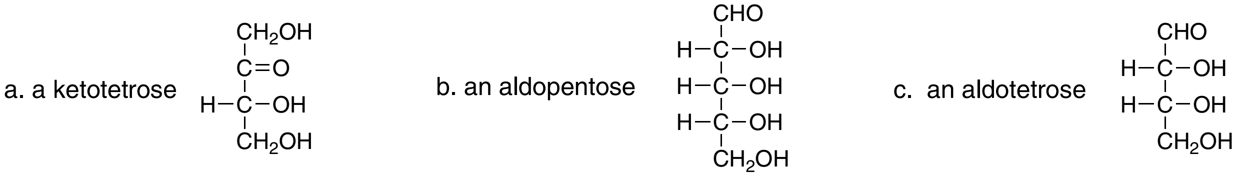
A mixture of anomers is formed.

[2] Formation of *N*-glycosides (27.14B)

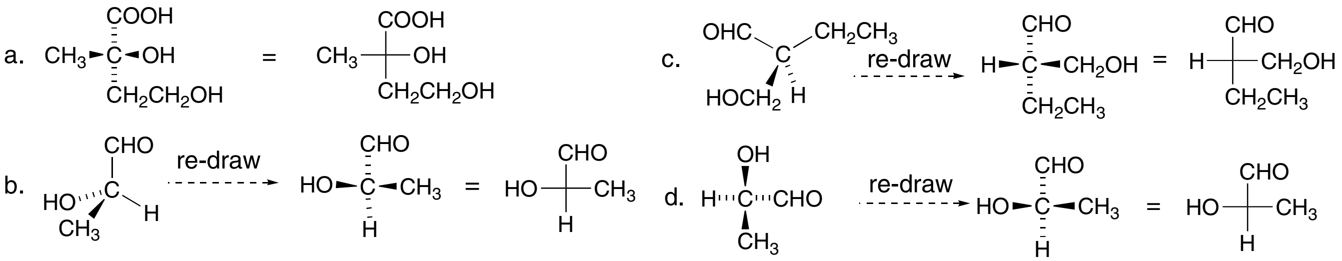


- Two anomers are formed.

27.1 A *ketose* is a monosaccharide containing a ketone. An *aldose* is a monosaccharide containing an aldehyde. A monosaccharide is called: a *triose* if it has three C's; a *tetrose* if it has four C's; a *pentose* if it has five C's; a *hexose* if it has six C's, and so forth.



27.2 Rotate and re-draw each molecule to place the horizontal bonds in front of the plane and the vertical bonds behind the plane. Then use a cross to represent the stereogenic center in a Fischer projection formula.

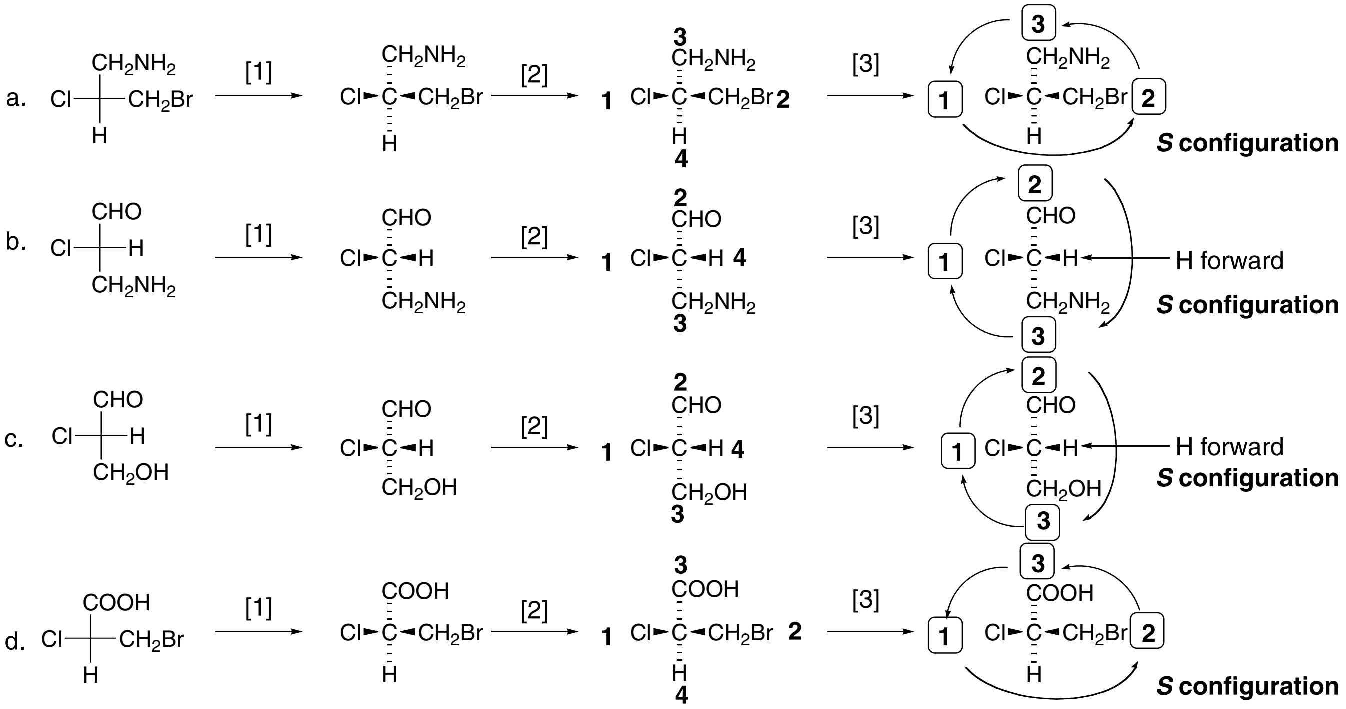


27.3 For each molecule:

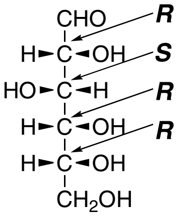
[1] Convert the Fischer projection formula to a representation with wedges and dashes.

[2] Assign priorities (Section 5.6).

[3] Determine *R* or *S* in the usual manner. Reverse the answer if priority group [4] is oriented forward (on a wedge).



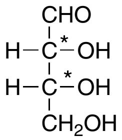
27.4



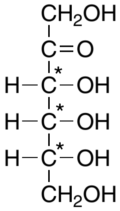
D-glucose

27.5

a. aldotetrose: 2 stereogenic centers



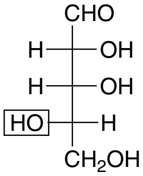
b. a ketohexose: 3 stereogenic centers



[• = stereogenic center]

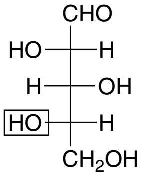
27.6 A D sugar has the OH group on the stereogenic center farthest from the carbonyl on the right. An L sugar has the OH group on the stereogenic center farthest from the carbonyl on the left.

a.



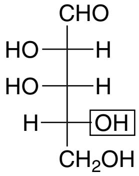
A

OH group on the left: **L sugar**



B

OH group on the left: **L sugar**



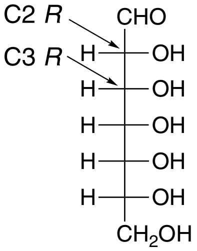
C

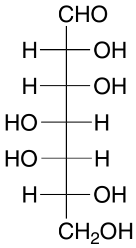
OH group on the right: **D sugar**

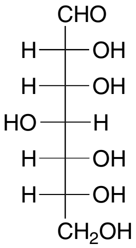
b. **A** and **B** are diastereomers.
A and **C** are enantiomers.
B and **C** are diastereomers.

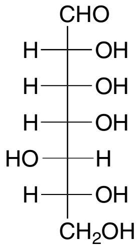
27.7 The D- notation signifies the position of the OH group on the stereogenic carbon farthest from the carbonyl group, and does not correlate with dextrorotatory or levorotatory. The latter terms describe a physical phenomenon, the direction of rotation of plane-polarized light.

27.8 There are 32 aldoheptoses; 16 are D sugars.

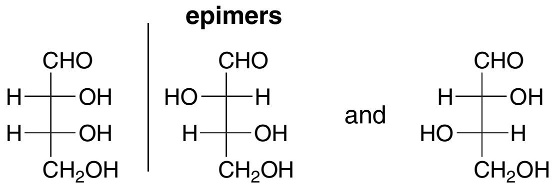








27.9 *Epimers* are two diastereomers that differ in the configuration around only one stereogenic center.

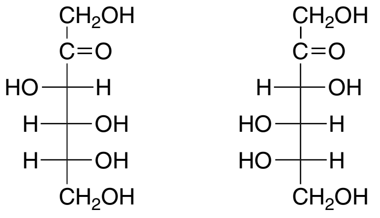


D-erythrose D-threose L-threose

27.10 a. D-allose and L-allose: **enantiomers**
- b. D-altrose and D-gulose: **diastereomers** but not epimers
- c. D-galactose and D-talose: **epimers**
- d. D-mannose and D-fructose: **constitutional isomers**
- e. D-fructose and D-sorbose: **diastereomers** but not epimers
- f. L-sorbose and L-tagatose: **epimers**

27.11

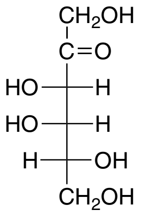
a.



D-fructose L-fructose

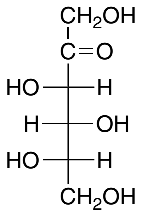
enantiomers

b.



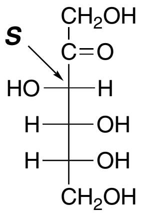
D-tagatose

c.

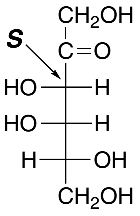


L-sorbose

27.12



D-fructose



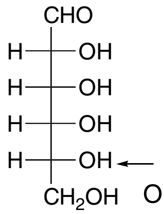
D-tagatose

27.13 Step [1]: Place the O atom in the upper right corner of a hexagon, and add the CH_2OH group on the first carbon counterclockwise from the O atom.

Step [2]: Place the anomeric carbon on the first carbon clockwise from the O atom.

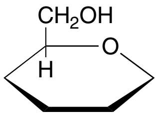
Step [3]: Add the substituents at the three remaining stereogenic centers, clockwise around the ring.

a. Draw the α anomer of:



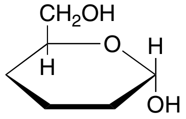
farthest away C, OH on right = D sugar

[1]



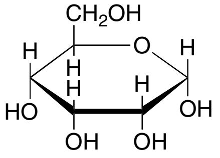
D sugar, CH_2OH is drawn up.

[2]



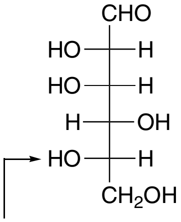
α anomer OH is down for a D sugar.

[3]



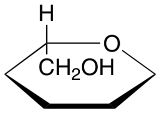
First three substituents are on the right so they are drawn down.

b. Draw the α anomer of:



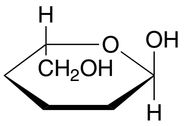
farthest away C, OH on left = L sugar

[1]



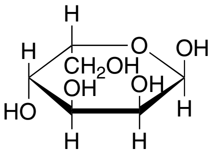
L sugar, CH_2OH is drawn down.

[2]



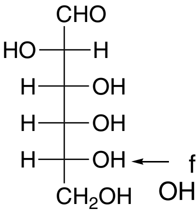
The α anomer has the OH and CH_2OH trans. In an L sugar, the OH must be drawn up.

[3]



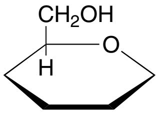
The first two substituents are on the left so they are drawn up. The third is on the right, drawn down.

c. Draw the β anomer of:



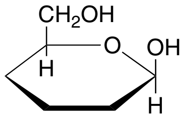
farthest away C, OH on right = D sugar

[1]



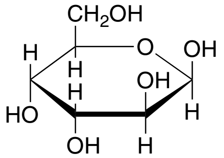
D sugar, CH_2OH is drawn up.

[2]



β anomer OH is up for a D sugar.

[3]



The first substituent is on the left so it is drawn up. The other two are on the right, drawn down.

27.14 To convert each Haworth projection into its acyclic form:

[1] Draw the C skeleton with the CHO on the top and the CH_2OH on the bottom.

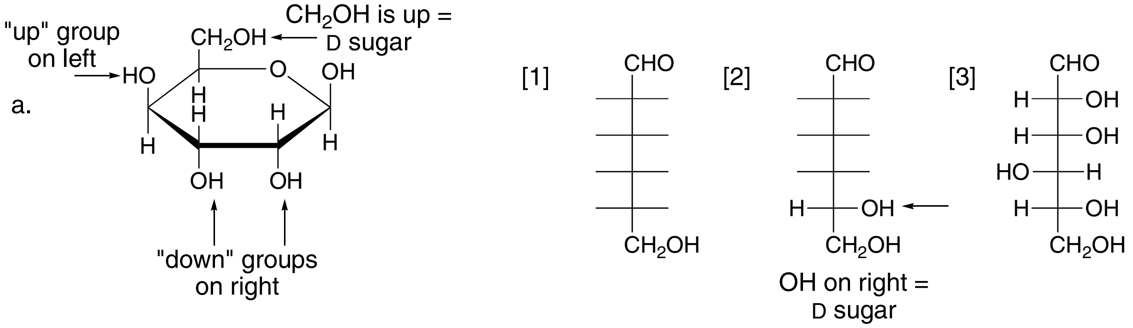
[2] Draw in the OH group farthest from the C=O.

A CH_2OH group drawn up means a D sugar; a CH_2OH group drawn down means an L sugar.

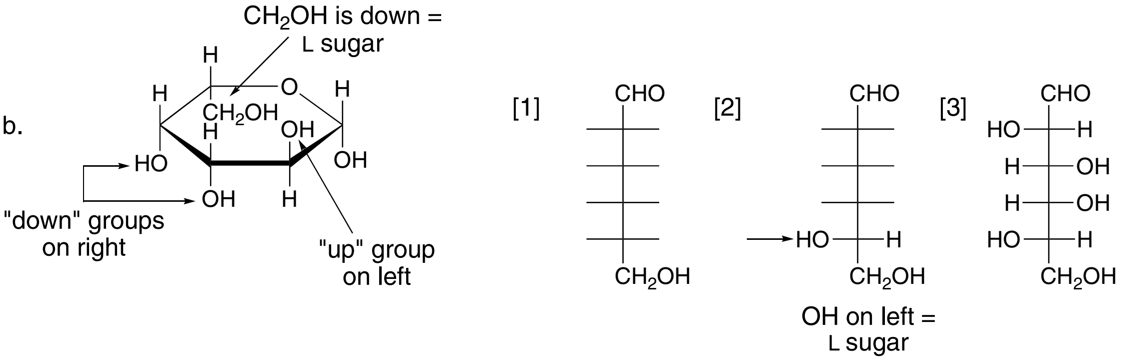
[3] Add the three other stereogenic centers, counterclockwise around the ring.

"Up" groups go on the left, and "down" groups go on the right.

a.



b.

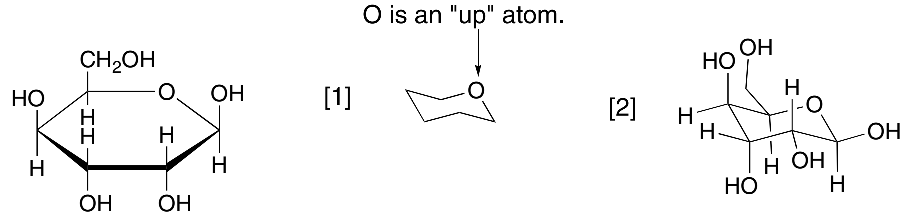


27.15 To convert a Haworth projection into a 3-D representation with a chair cyclohexane:

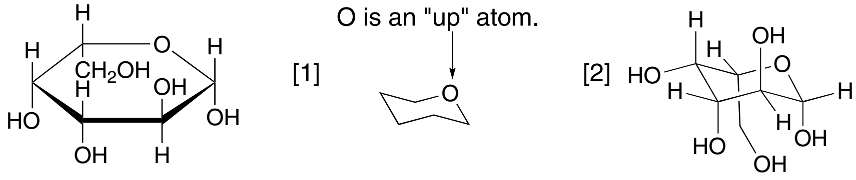
[1] Draw the pyranose ring as a chair with the O as an "up" atom.

[2] Add the substituents around the ring.

a.

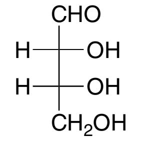


b.



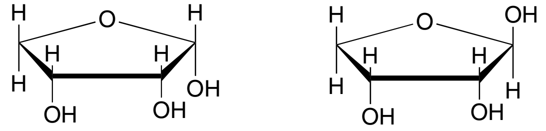
With so many axial groups, this is not the more stable conformation of this sugar.

27.16 Cyclization always forms a new stereogenic center at the anomeric carbon, so two different anomers are possible.



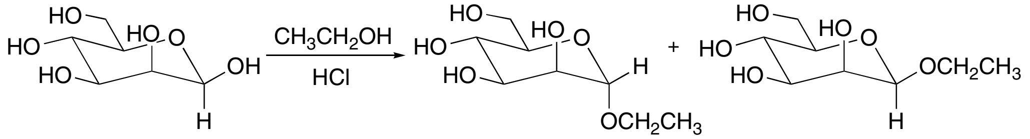
D-erythrose

Two anomers of D-erythrose:



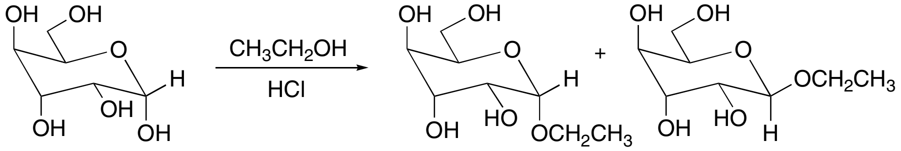
27.17

a.



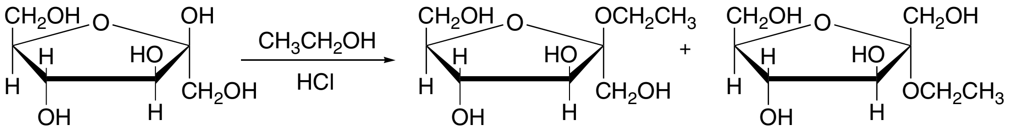
β-D-mannose

b.



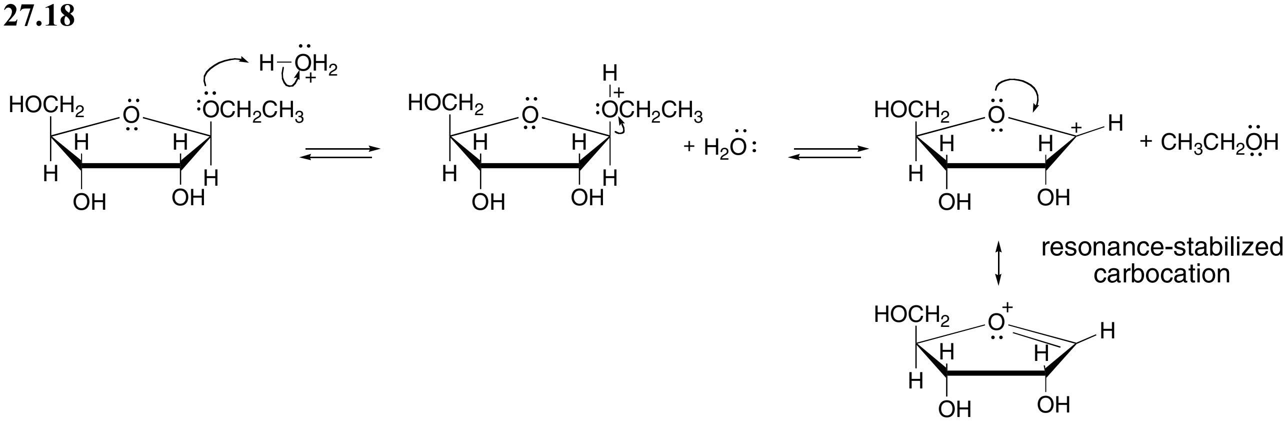
α-D-gulose

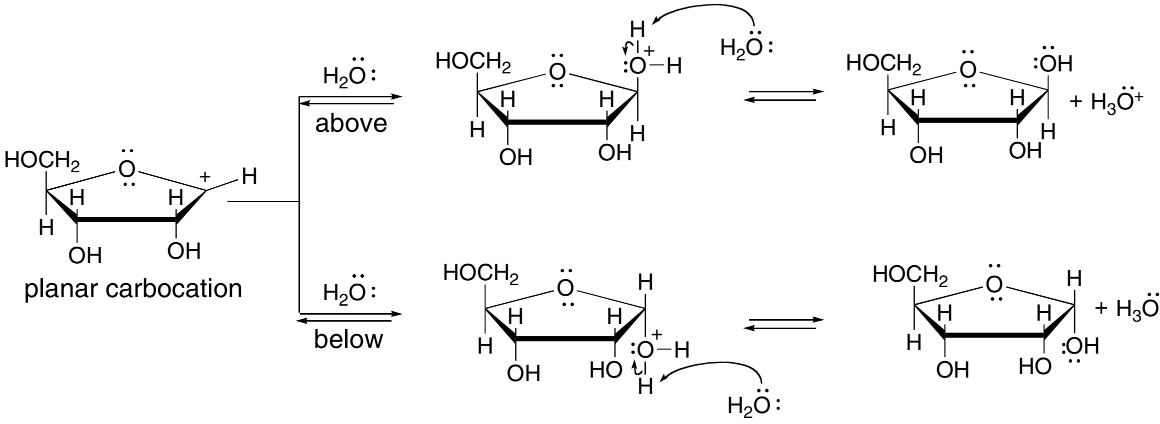
c.



β-D-fructose

27.18

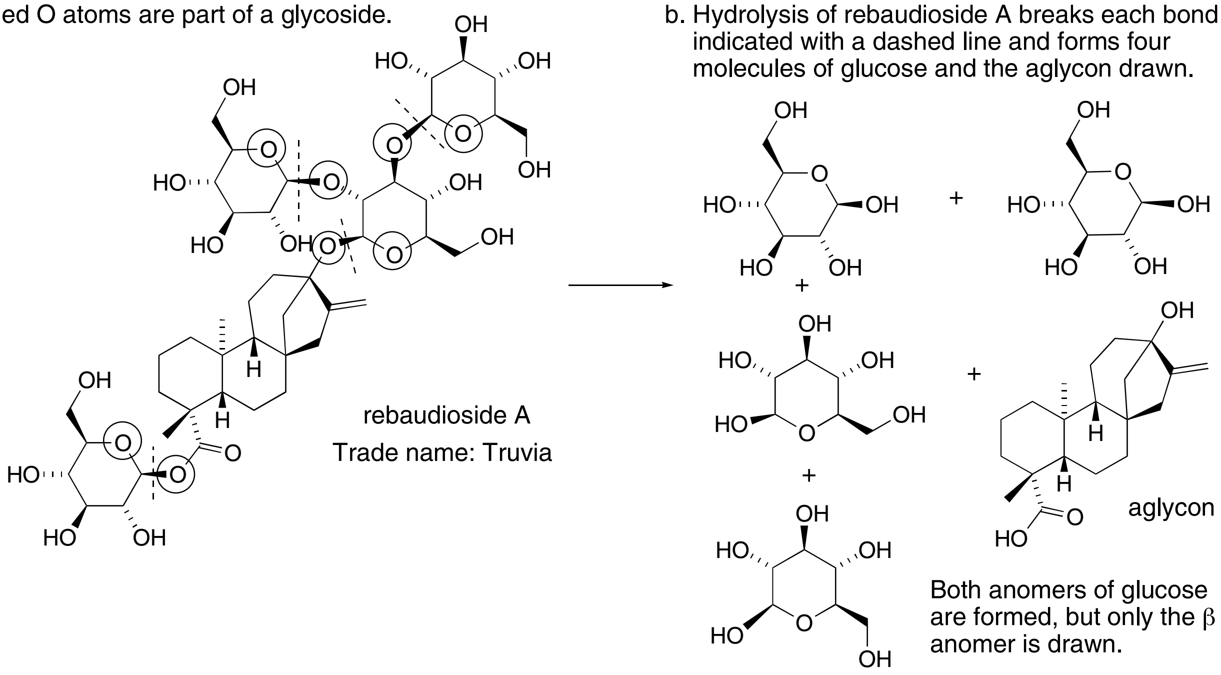




27.19

a. All circled O atoms are part of a glycoside.

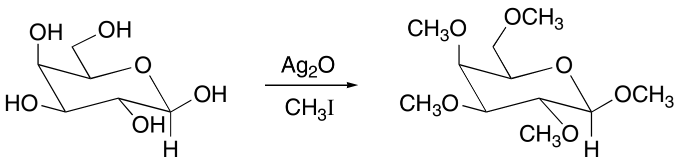
b. Hydrolysis of rebaudioside A breaks each bond indicated with a dashed line and forms four molecules of glucose and the aglycon drawn.



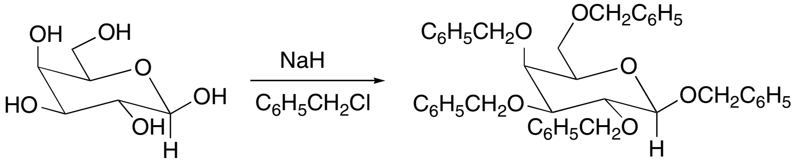
Both anomers of glucose are formed, but only the β anomer is drawn.

27.20

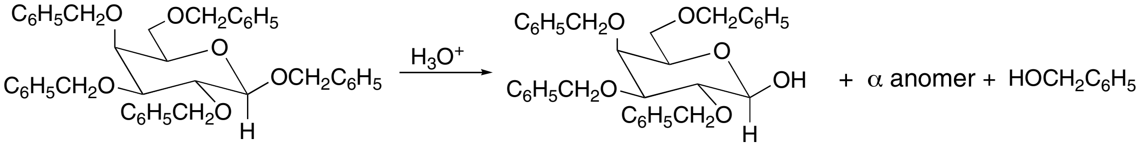
a.

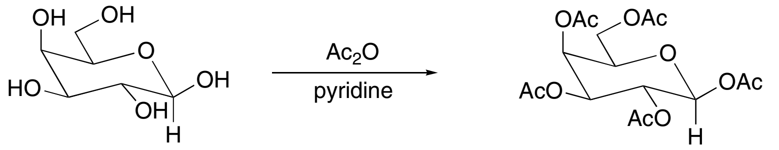


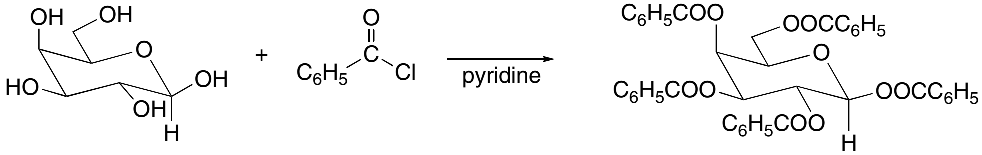
b.

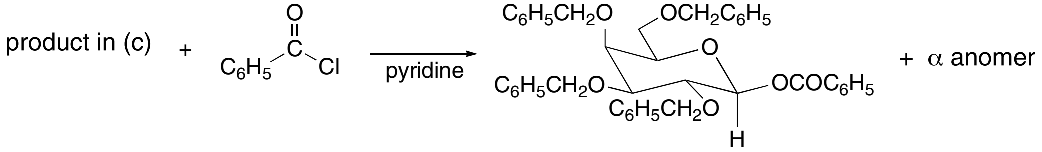


c.

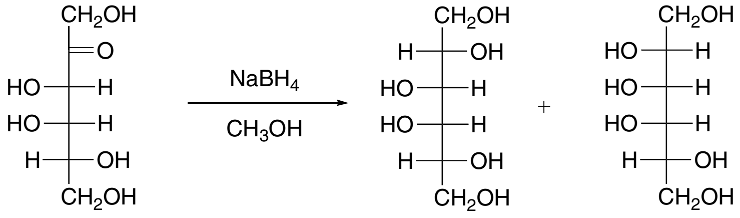


d.


e.


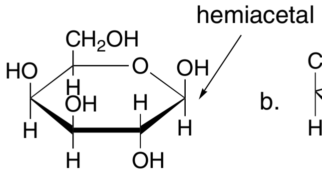
f.


27.21

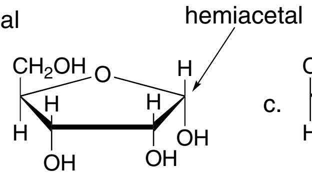


D-tagatose **D-galactitol** **D-talitol**

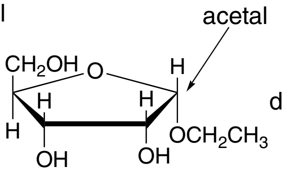
27.22 Carbohydrates containing a hemiacetal are in equilibrium with an acyclic aldehyde, making them reducing sugars. Glycosides are acetals, so they are not in equilibrium with any acyclic aldehyde, making them nonreducing sugars.

a.


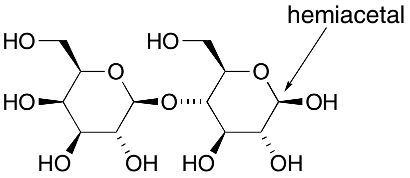
reducing sugar

b.


reducing sugar

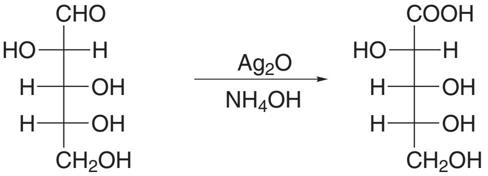
c.


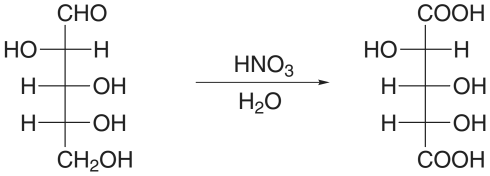
nonreducing sugar

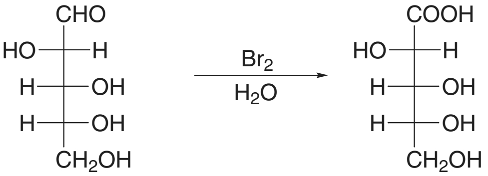
d.


lactose
reducing sugar

27.23

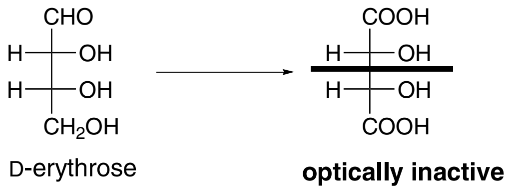
a.


c.


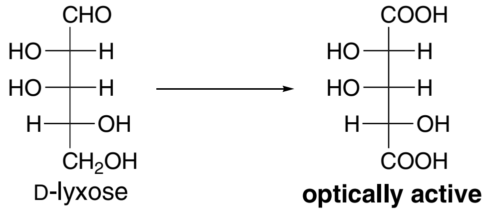
b.


27.24 Molecules with a plane of symmetry are optically inactive.

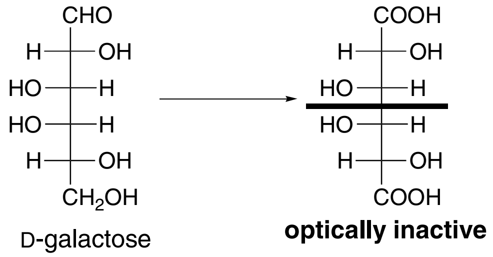
a.



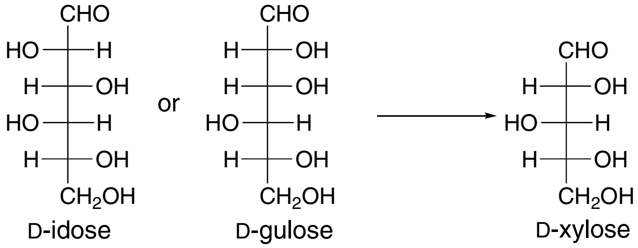
b.



c.

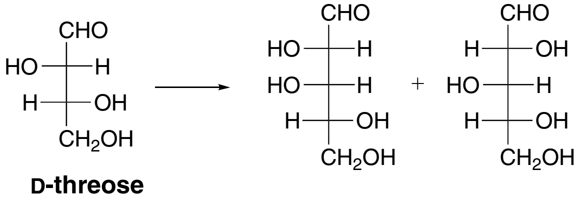


27.25

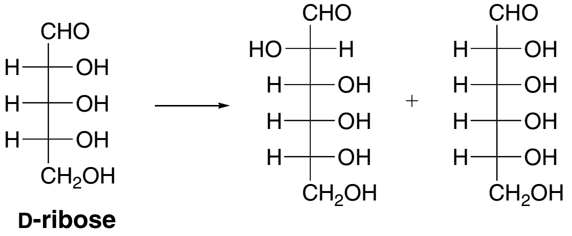


27.26

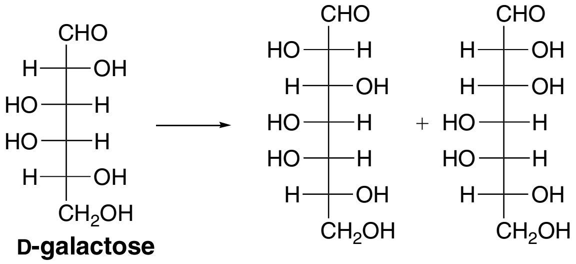
a.



b.

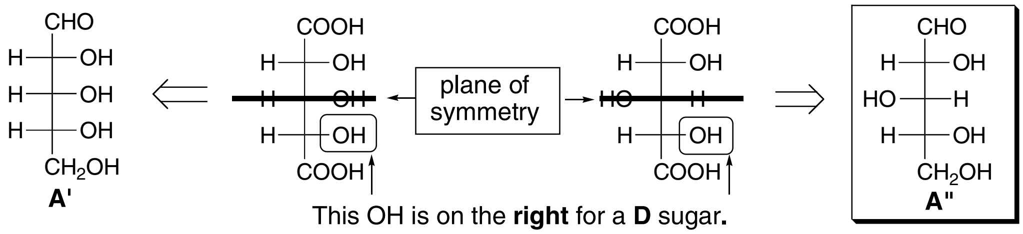


c.



27.27

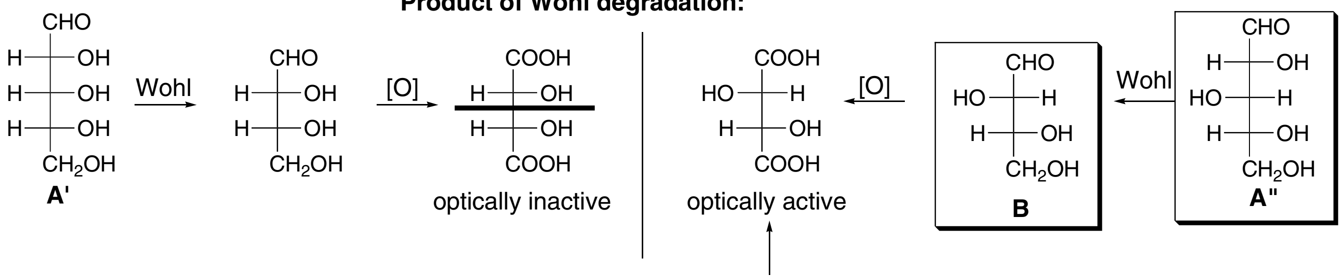
Possible optically inactive D-aldaric acids:



This OH is on the **right** for a **D** sugar.

There are two possible structures for the D-aldopentose (**A'** and **A"**), and the Wohl degradation determines which structure corresponds to **A**.

Product of Wohl degradation:



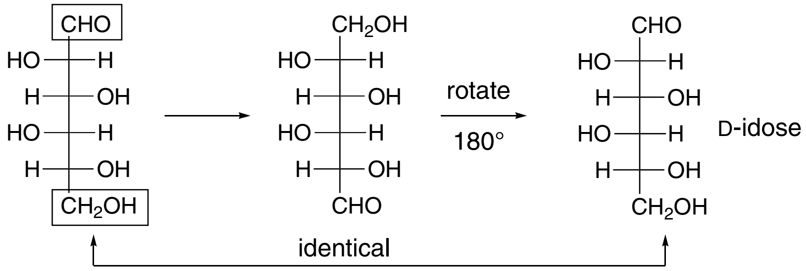
This is **A**.

optically inactive

optically active

Since this compound has no plane of symmetry, its precursor is **B**, and thus **A"** = **A**.

27.28

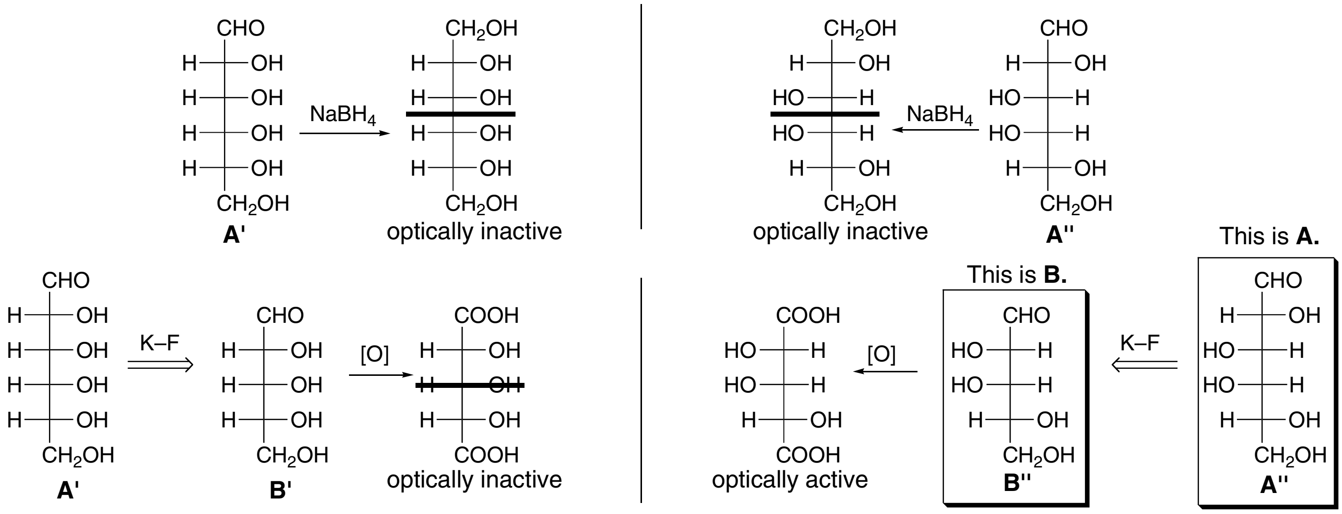


D-idose

identical

27.29

Optically inactive alditols formed from $NaBH_4$ reduction of a D-aldohexose.



optically inactive

optically inactive

This is **A.**

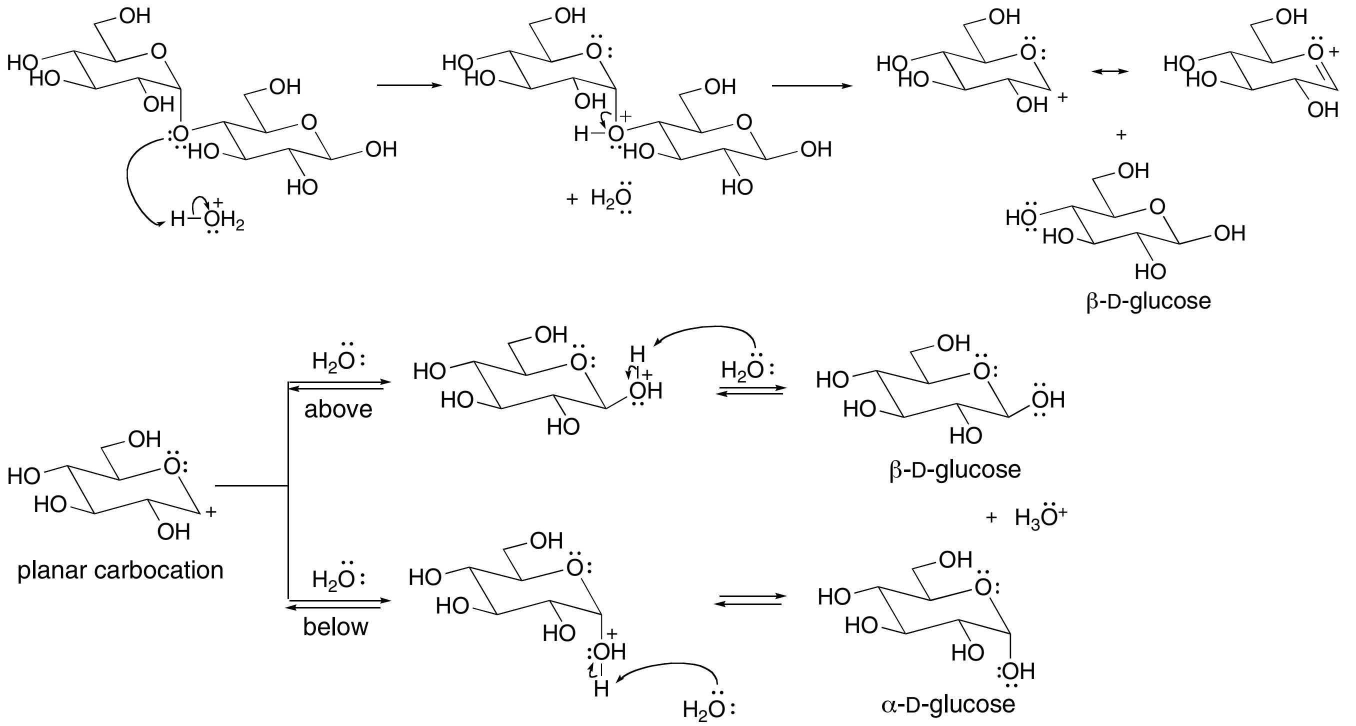
optically inactive

optically active

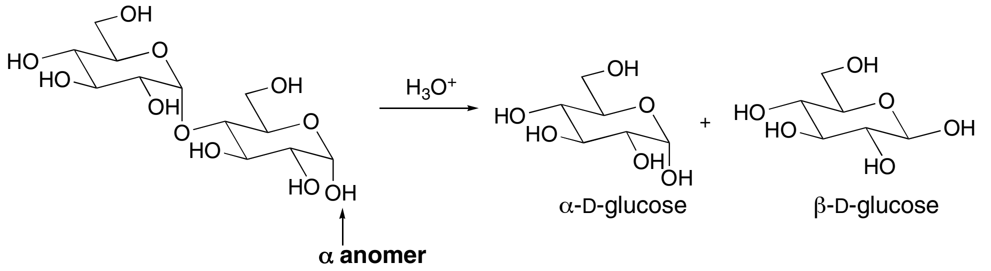
This is **B.**

Two D-aldohexoses (**A'** and **A''**) give optically inactive alditols on reduction. **A''** is formed from **B''** by Kiliani–Fischer synthesis. Since **B''** affords an optically active aldaric acid on oxidation, **B''** is **B** and **A''** is **A**. The alternate possibility (**A'**) is formed from an aldopentose **B'** that gives an optically inactive aldaric acid on oxidation.

27.30

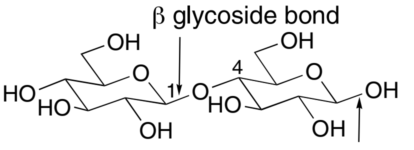


27.31



The same products are formed on hydrolysis of the α and β anomers of maltose.

27.32

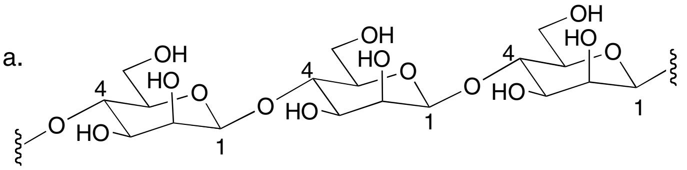


cellobiose

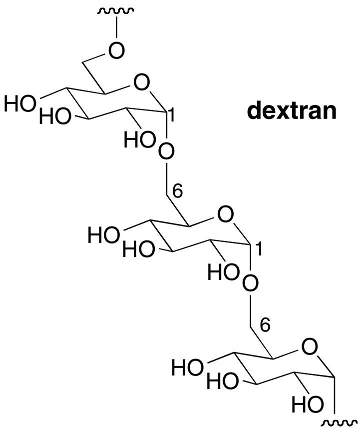
Two possible anomers here. β OH is drawn.

27.33

a.

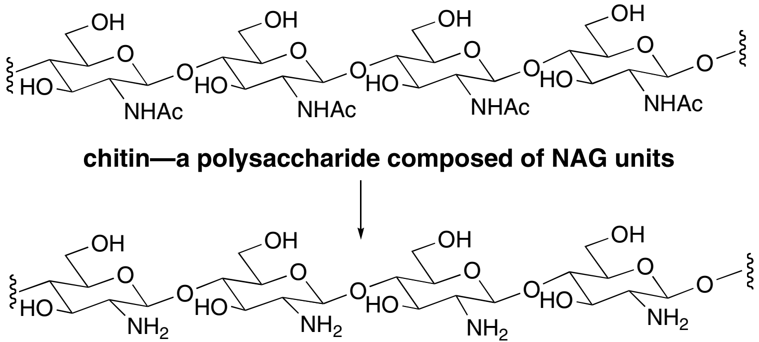


b.



dextran

27.34

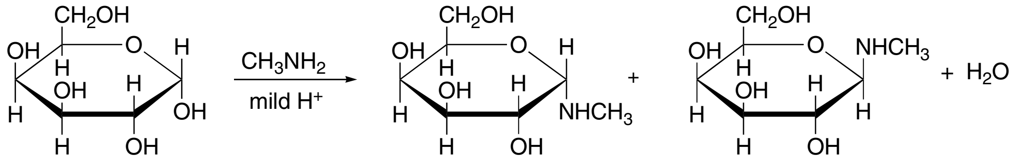


chitin—a polysaccharide composed of NAG units

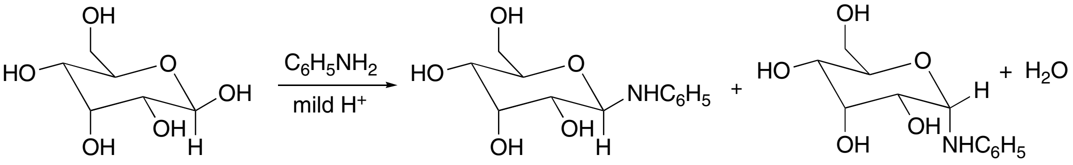
chitosan

27.35

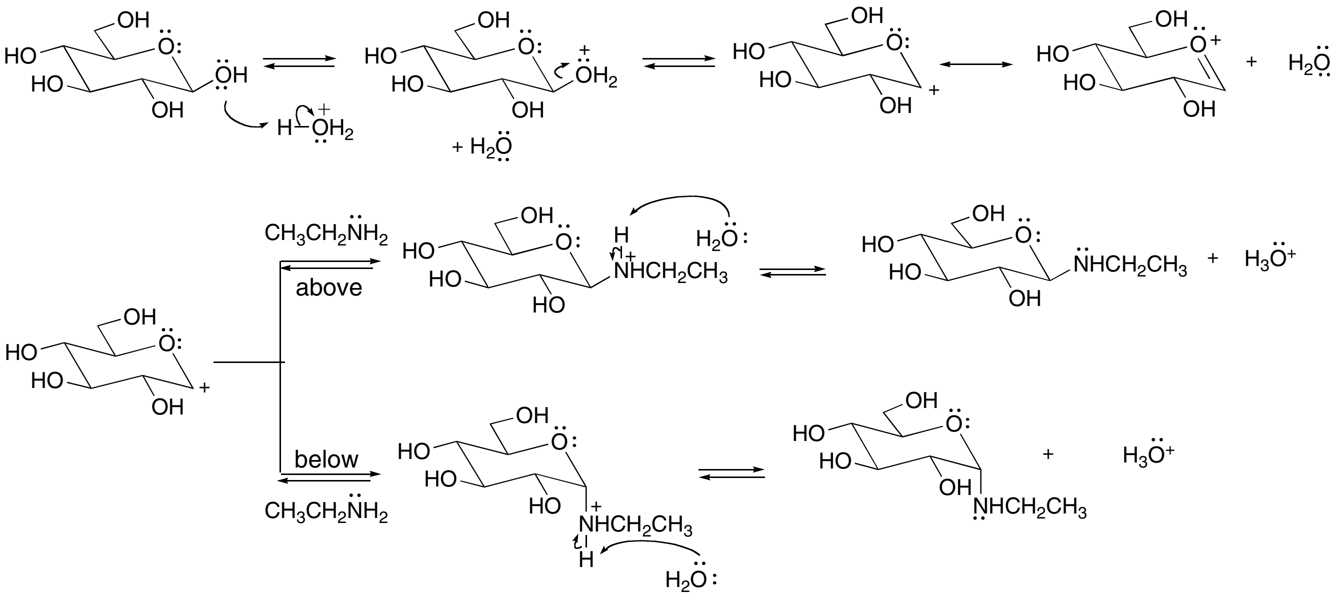
a.



b.

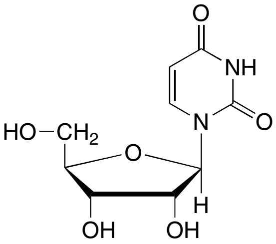


27.36

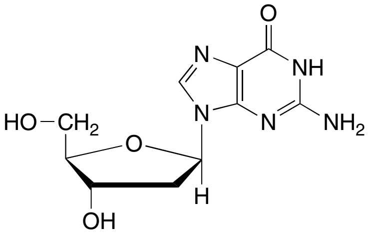


27.37

a.



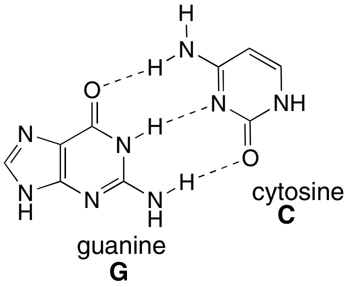
b.

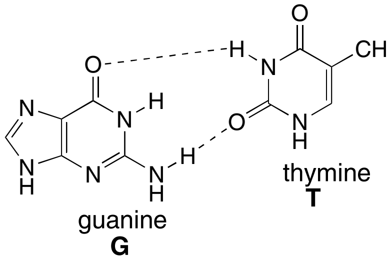


27.38

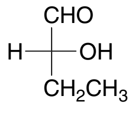
a. Two purine bases (A and G) are both bicyclic bases. Therefore they are too big to hydrogen bond to each other on the inside of the DNA double helix.

b. Hydrogen bonding between guanine and cytosine has three hydrogen bonds, whereas between guanine and thymine there are only two. This makes hydrogen bonding between guanine and cytosine more favorable.

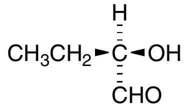




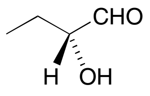
27.39 Label the compounds with *R* or *S* and then classify.



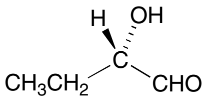
A
R

a.


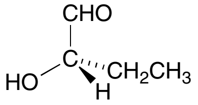
R
identical

b.


R
identical

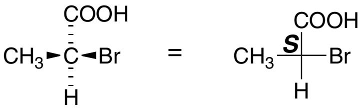
c.


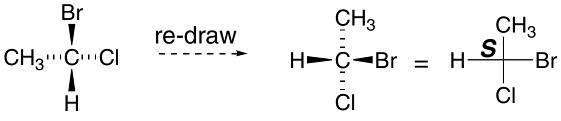
S
enantiomer

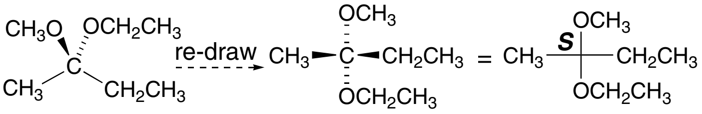
d.


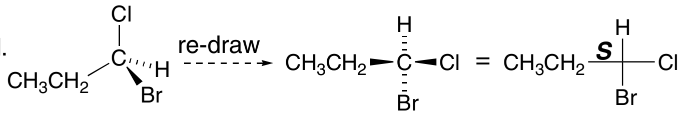
S
enantiomer

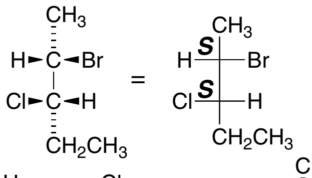
27.40 Use the directions from Answer 27.2 to draw each Fischer projection.

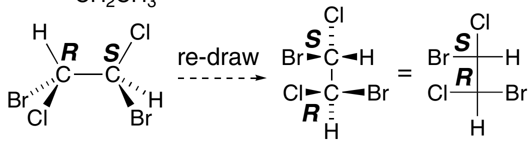
a.


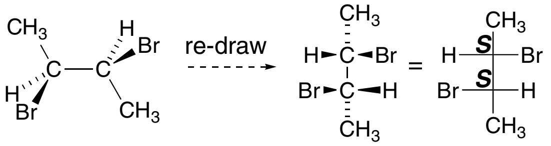
b.


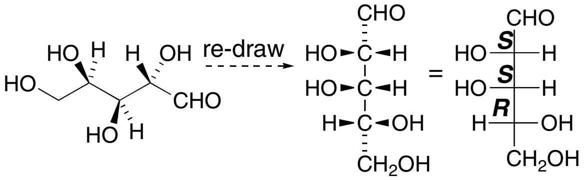
c.


d.


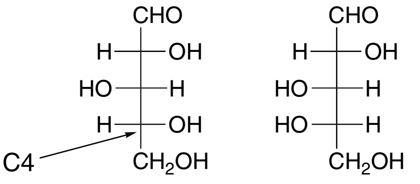
e.


f.


g.


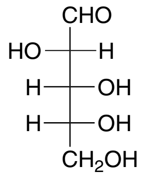
h.


27.41 *Epimers* are two diastereomers that differ in the configuration around only one stereogenic center.

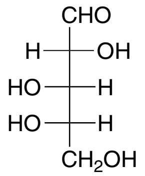


D-xylose **L-arabinose**

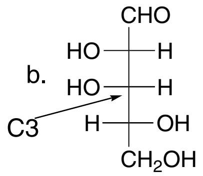
27.42

a.


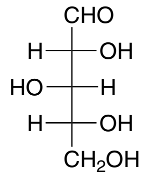
D-arabinose



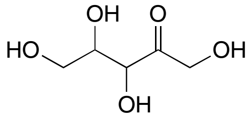
enantiomer

b.


epimer

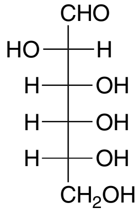
c.


diastereomer
(but not epimer)

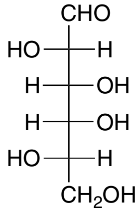
d.


constitutional
isomer

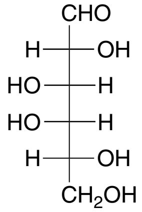
27.43



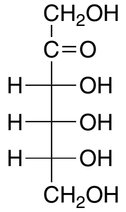
A



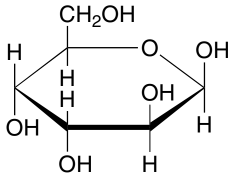
B



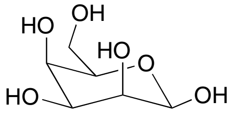
C



D



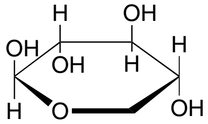
E



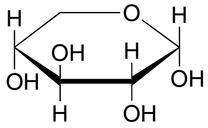
F

a. **A** and **B** **epimers**
b. **A** and **C** **diastereomers**
c. **B** and **C** **enantiomers**
d. **A** and **D** **constitutional isomers**
e. **E** and **F** **diastereomers**

27.44

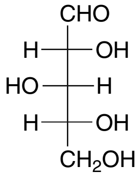


A



B

a. anomers, epimers, diastereomers, reducing sugars
b.

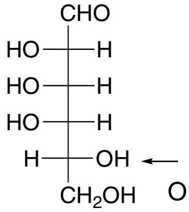


D-xylose

This is the acyclic form of both **A** and **B**.

27.45 Use the directions from Answer 27.13.

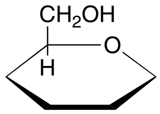
a. β-D-talopyranose



farthest away C, OH on right = D sugar

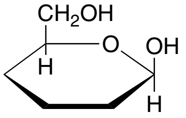
D-talose

[1]



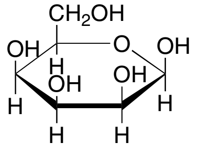
D sugar, CH_2OH is drawn up.

[2]

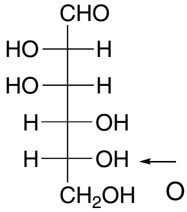


β anomer OH is up for a D sugar.

[3]



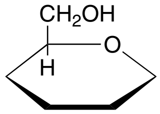
b. β-D-mannopyranose



farthest away C, OH on right = D sugar

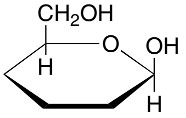
D-mannose

[1]



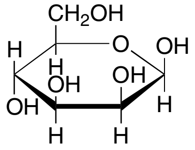
D sugar, CH_2OH is drawn up.

[2]

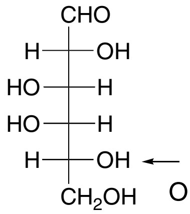


β anomer OH is up for a D sugar.

[3]

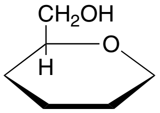


c. α-D-galactopyranose

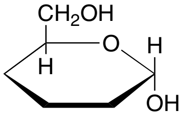


D-galactose

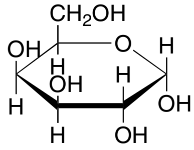
farthest away C, OH on right = D sugar

[1] 

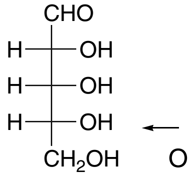
D sugar, CH_2OH is drawn up.

[2] 

α anomer OH is down.

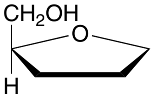
[3] 

d. α-D-ribofuranose

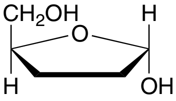


D-ribose

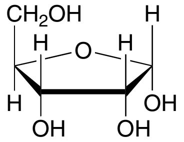
farthest away C, OH on right = D sugar

[1] 

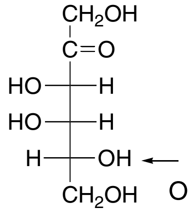
D sugar, CH_2OH is drawn up.

[2] 

α anomer OH is down.

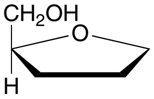
[3] 

e. α-D-tagatofuranose

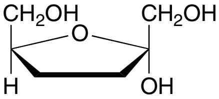


D-tagatose

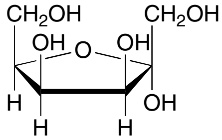
farthest away C, OH on right = D sugar

[1] 

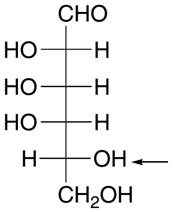
D sugar, CH_2OH is drawn up.

[2] 

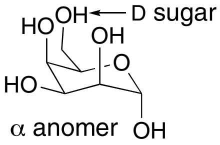
α anomer OH is down.

[3] 

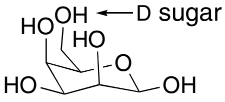
27.46

a. 

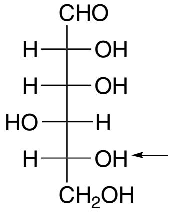
farthest away C, OH on right = D sugar



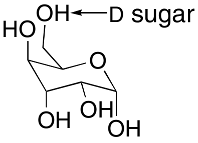
α anomer



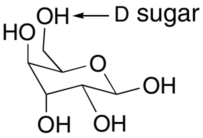
β anomer

b. 

farthest away C, OH on right = D sugar

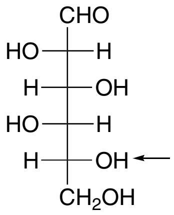


α anomer

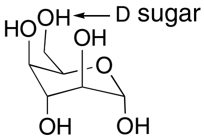


β anomer

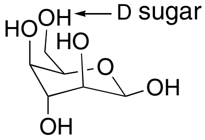
c.



farthest away C,
OH on right = D sugar



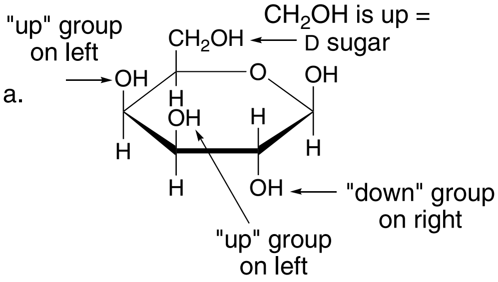
α anomer

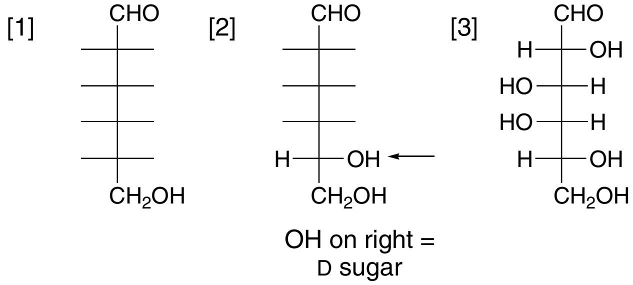


β anomer

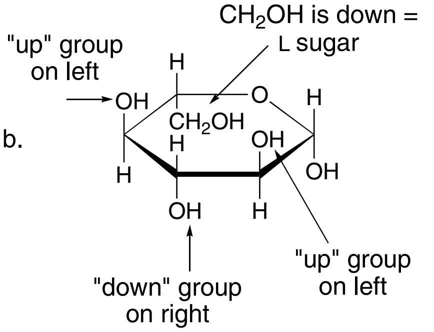
27.47 Use the directions from Answer 27.14.

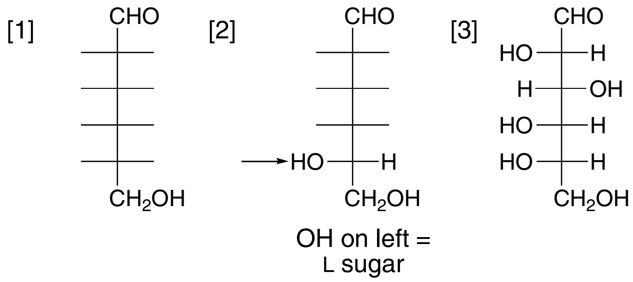
a.



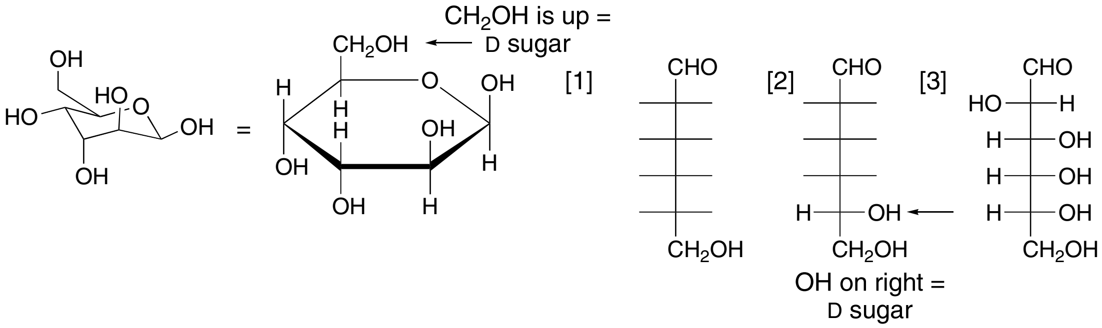


b.

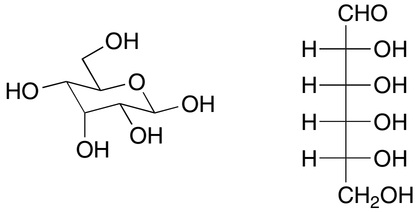




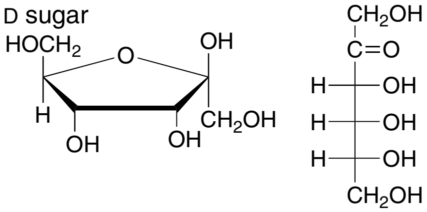
c.



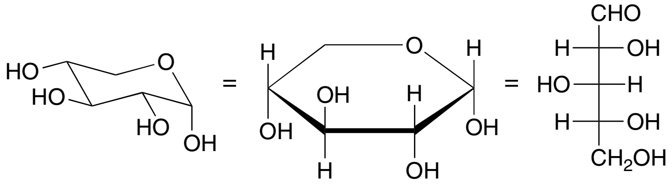
d.



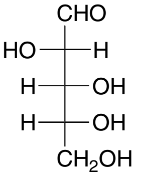
e.



f.

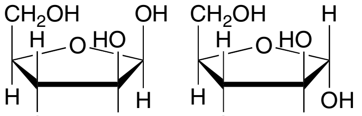


27.48



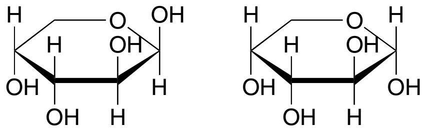
D-arabinose

a.



β anomer α anomer

b.

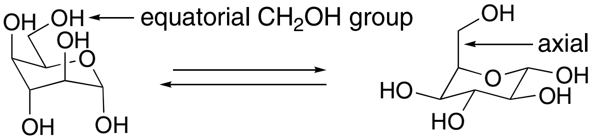


two anomers in the pyranose form

27.49

Two anomers of D-idose, as well as two conformations of each anomer:

α anomer

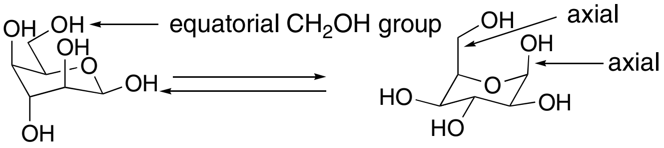


4 axial substituents

4 equatorial OH groups

More stable conformation for the α anomer—the CH_2OH is axial, but all other groups are equatorial.

β anomer

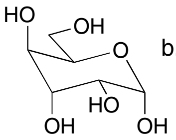


3 axial substituents

3 equatorial OH groups

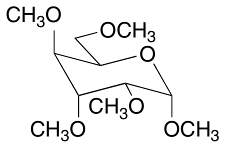
The more stable conformation for the β anomer—the CH_2OH is axial, as is the anomeric OH, but three other OH groups are equatorial.

27.50

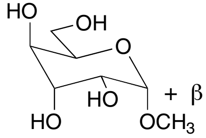


D-gulose

a. CH_3I, Ag_2O

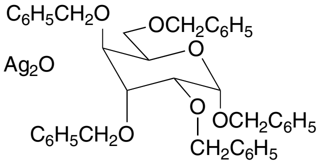


b. CH_3OH, HCl

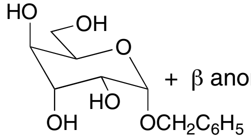


+ β anomer

c. $C_6H_5CH_2Cl$, Ag_2O

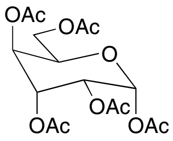


d. $C_6H_5CH_2OH$, HCl

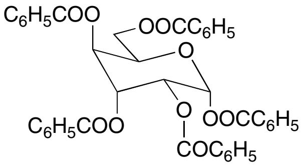


+ β anomer

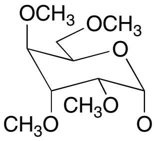
e. Ac_2O, pyridine



f. C_6H_5COCl, pyridine

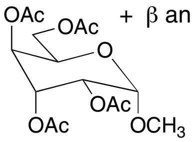


g. The product in (a), then H_3O^+



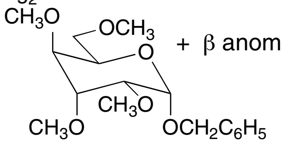
+ β anomer

h. The product in (b), then Ac_2O, pyridine



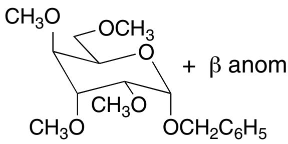
+ β anomer

i. The product in (g), then $C_6H_5CH_2Cl$, Ag_2O



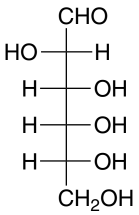
+ β anomer

j. The product in (d), then CH_3I, Ag_2O



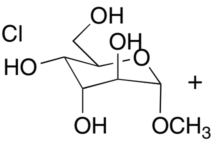
+ β anomer

27.51



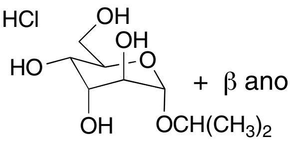
D-altrose

a. CH_3OH, HCl



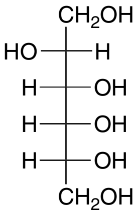
+ β anomer

b. $(CH_3)_2CHOH$, HCl

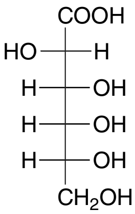


+ β anomer

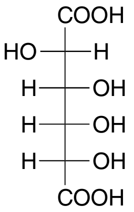
c. $NaBH_4$, CH_3OH



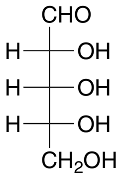
d. Br_2, H_2O



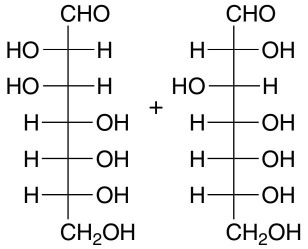
e. HNO_3, H_2O



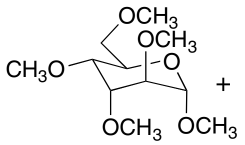
f. [1] NH_2OH
[2] $(CH_3CO)_2O$, $NaOCOCH_3$
[3] $NaOCH_3$



g. [1] NaCN, HCl
[2] H_2, Pd-$BaSO_4$
[3] H_3O^+

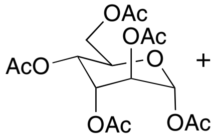


h. CH_3I, Ag_2O



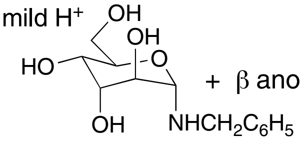
+ β anomer

i. Ac_2O, pyridine



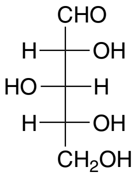
+ β anomer

j. $C_6H_5CH_2NH_2$, mild H^+



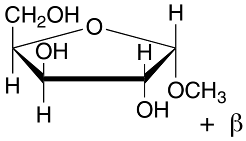
+ β anomer

27.52



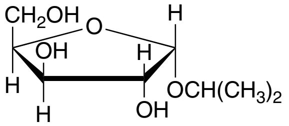
D-xylose

a. CH_3OH, HCl



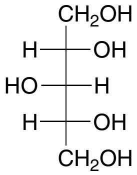
+ β anomer

b. $(CH_3)_2CHOH$, HCl

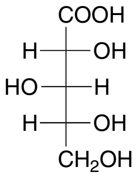


+ β anomer

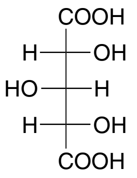
c. $NaBH_4$, CH_3OH



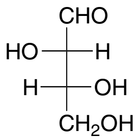
d. Br_2, H_2O



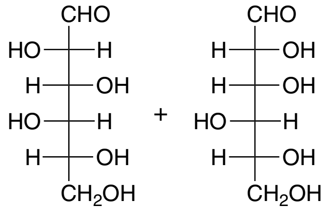
e. HNO_3, H_2O



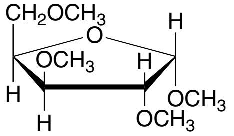
f. [1] NH_2OH
[2] $(CH_3CO)_2O$, $NaOCOCH_3$
[3] $NaOCH_3$



g. [1] NaCN, HCl
[2] H_2, Pd-$BaSO_4$
[3] H_3O^+

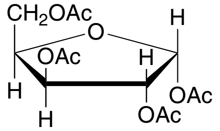


h. CH_3I, Ag_2O



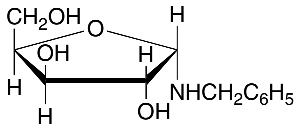
+ β anomer

i. Ac_2O, pyridine



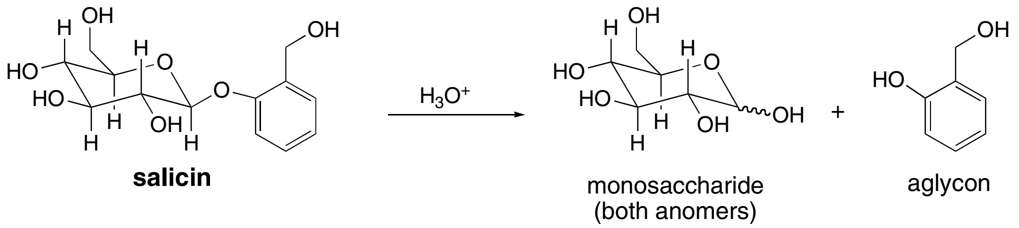
+ β anomer

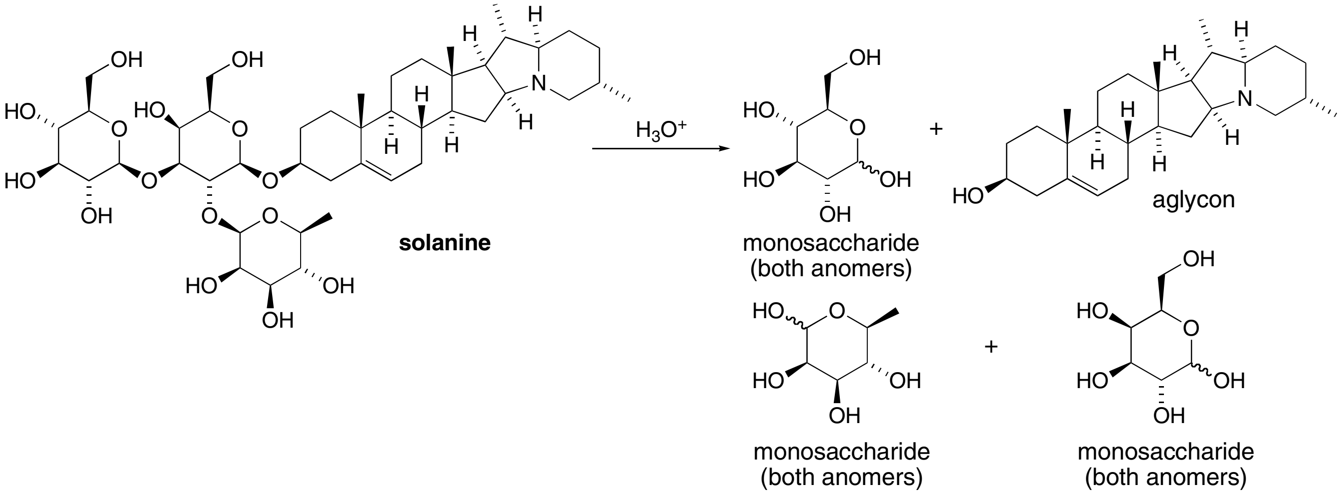
j. $C_6H_5CH_2NH_2$, mild H^+



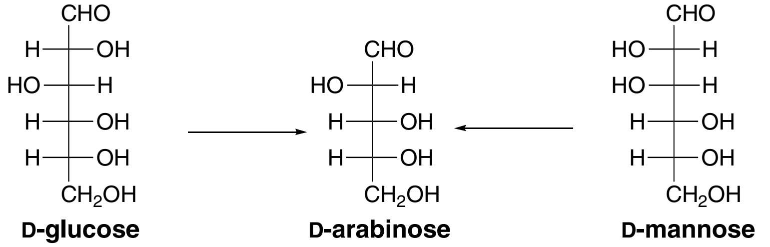
+ β anomer

27.53



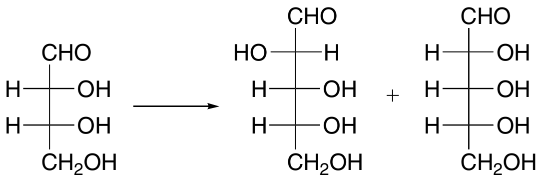


27.54

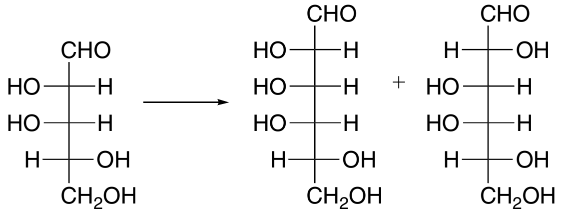


27.55

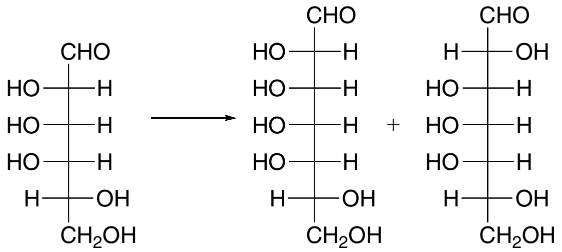
a.



b.

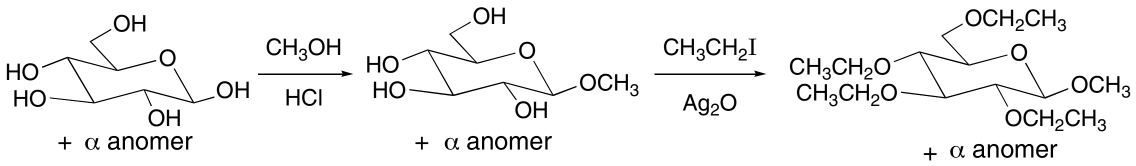


c.

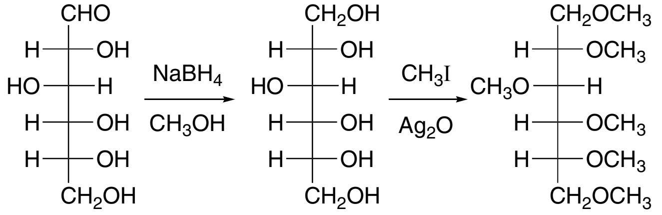


27.56

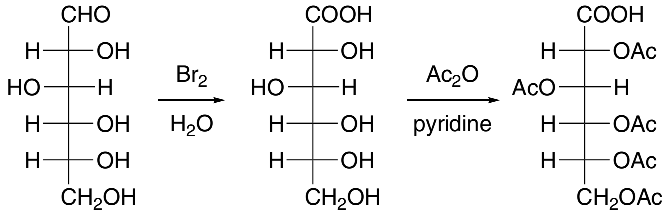
a.



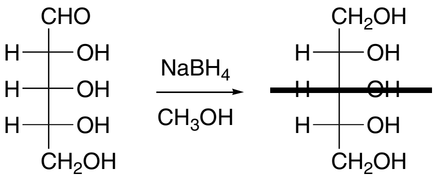
b.



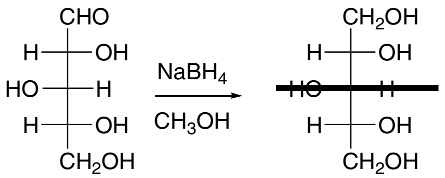
c.



27.57 Molecules with a plane of symmetry are optically inactive.



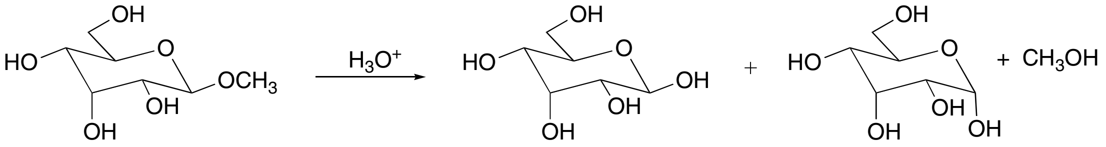
D-ribose



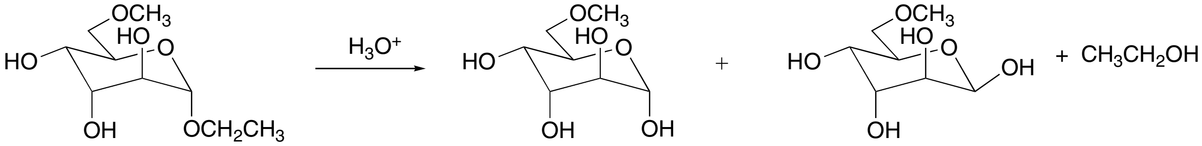
D-xylose

27.58

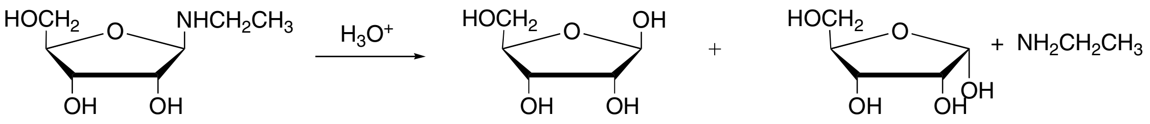
a.



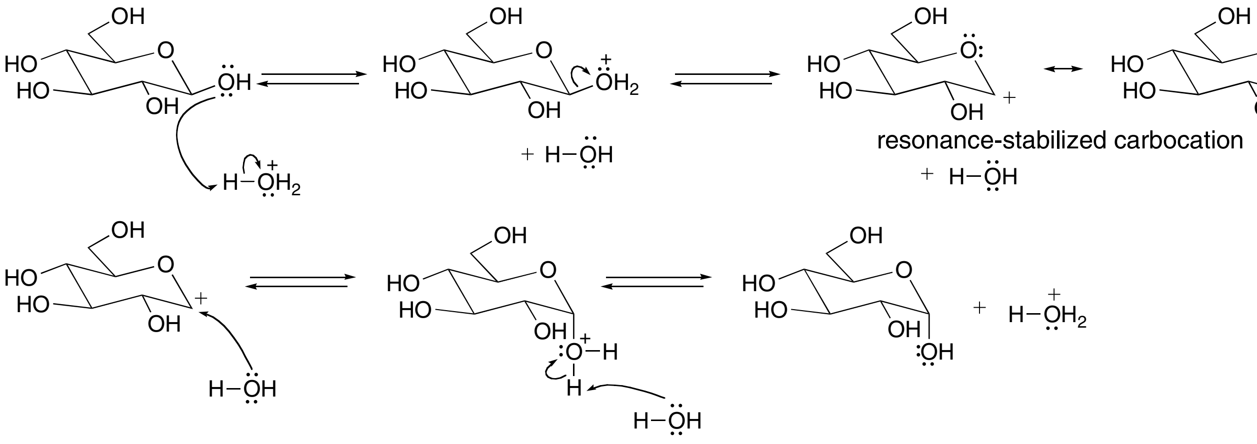
b.



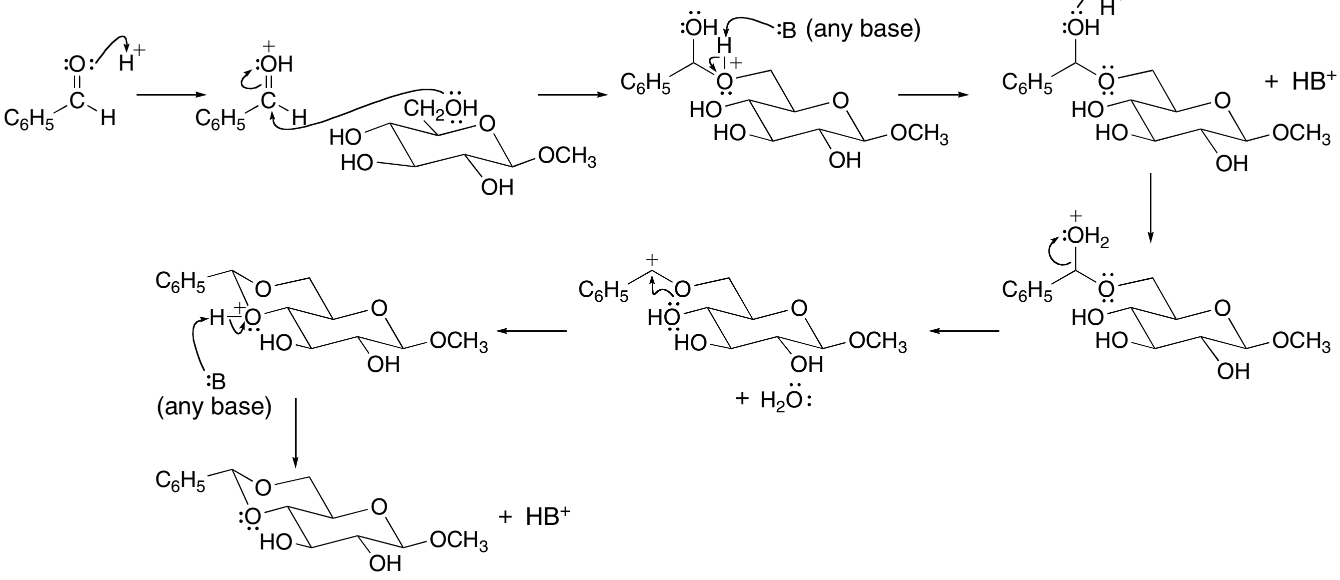
c.



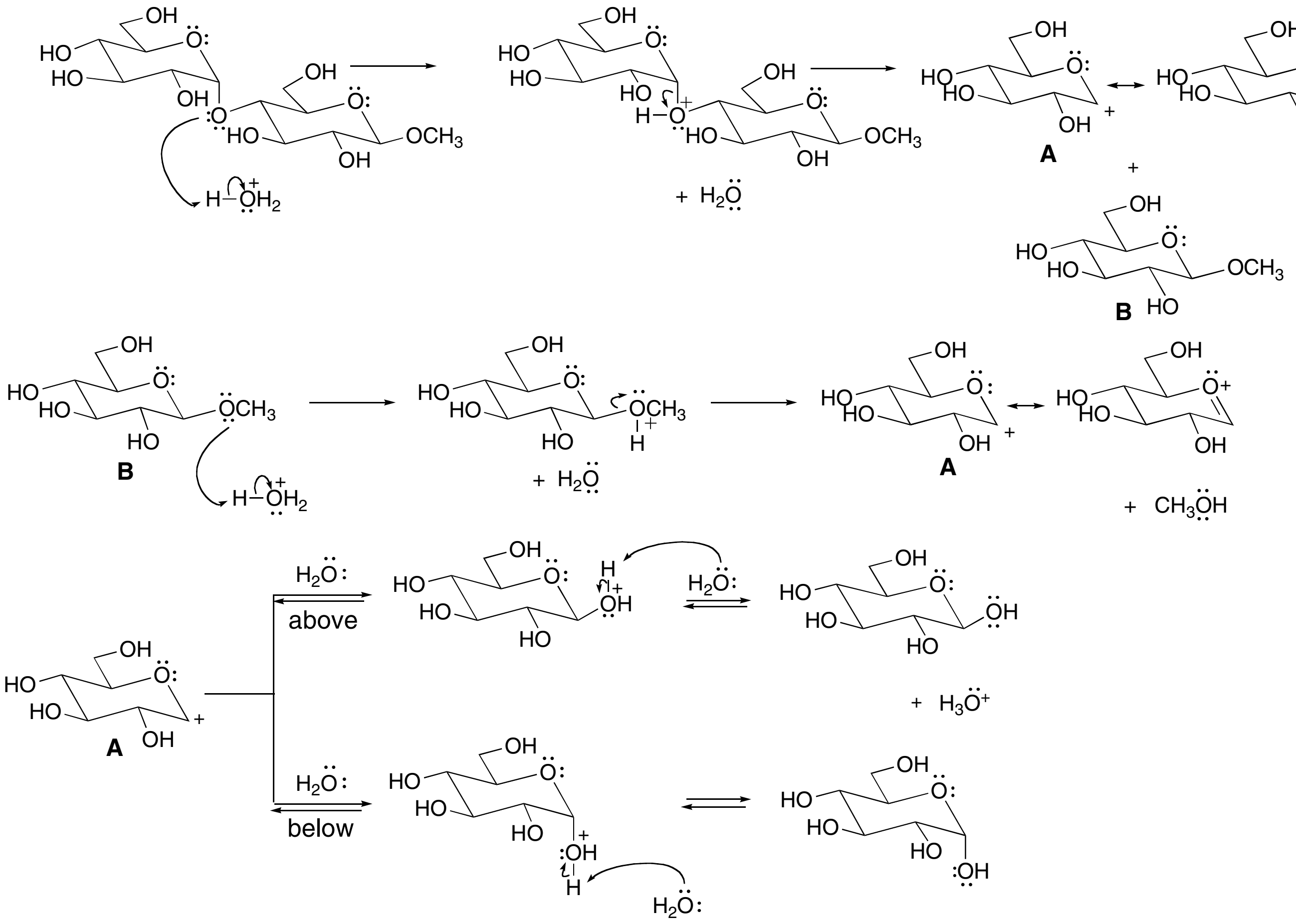
27.59


resonance-stabilized carbocation
+ H–OH
+ H–OH
+ H–OH2

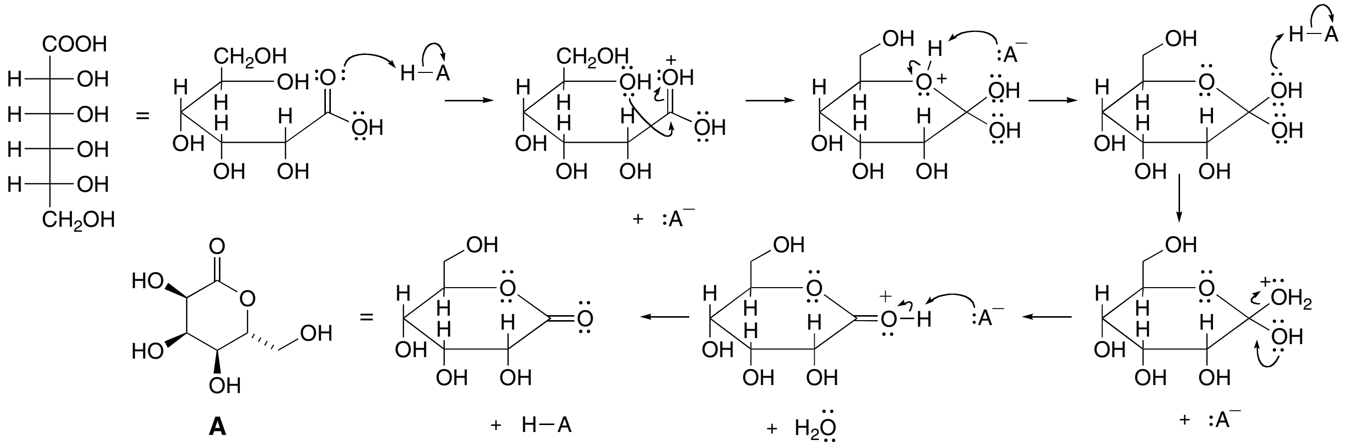
27.60


C6H5
:B (any base)
+ HB+
+ H2O:
:B
(any base)
+ HB+
OCH3

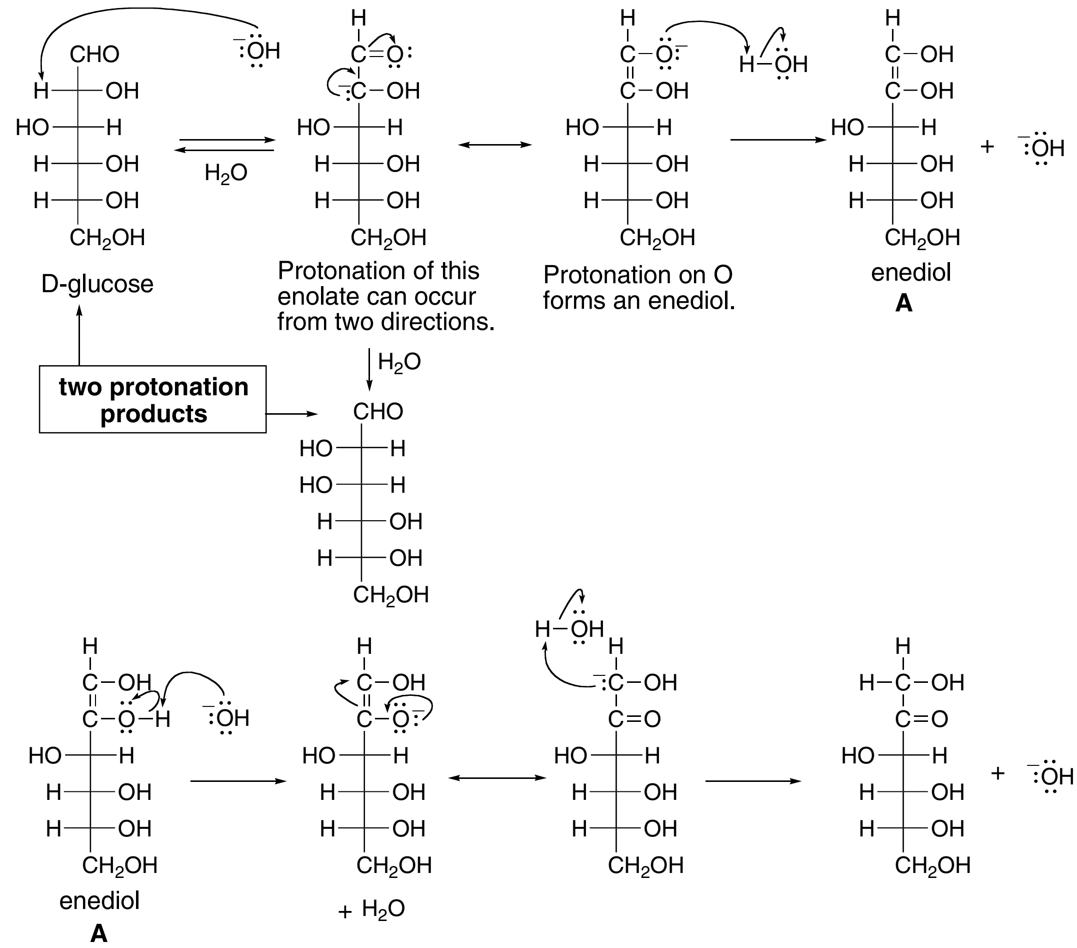
27.61



27.62



27.63



Deprotonation of the OH at C2 of the enediol forms a new enolate that goes on to form the ketohexose.

27.64

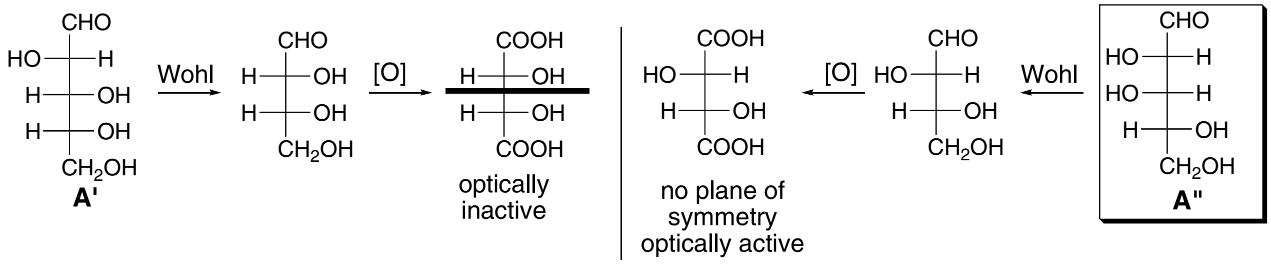
Two D-aldopentoses (**A**' and **A**") yield optically active aldaric acids when oxidized.

Optically active D-aldaric acids:

A'

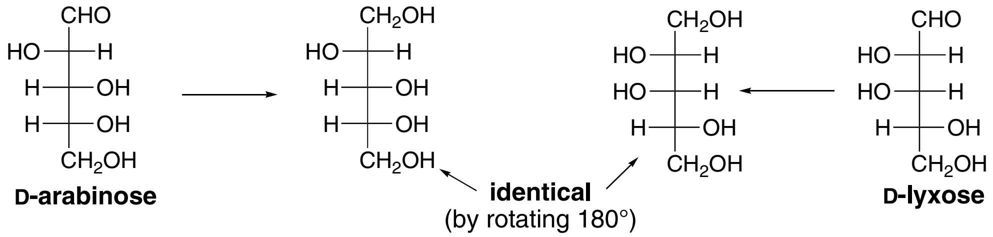
A"

D-lyxose



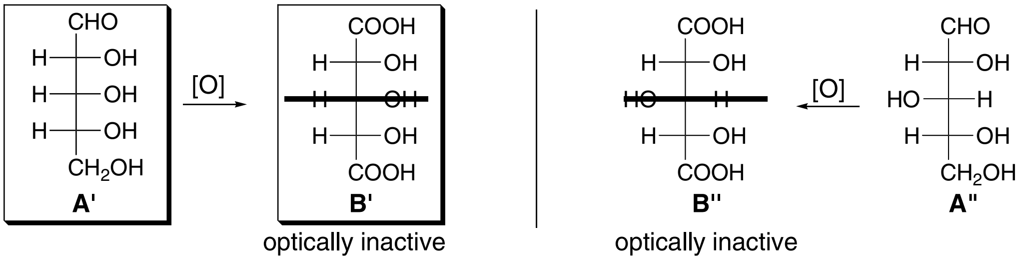
Only **A"** undergoes Wohl degradation to an aldotetrose that is oxidized to an optically active aldaric acid, so **A"** is the structure of the D-aldopentose in question.

27.65

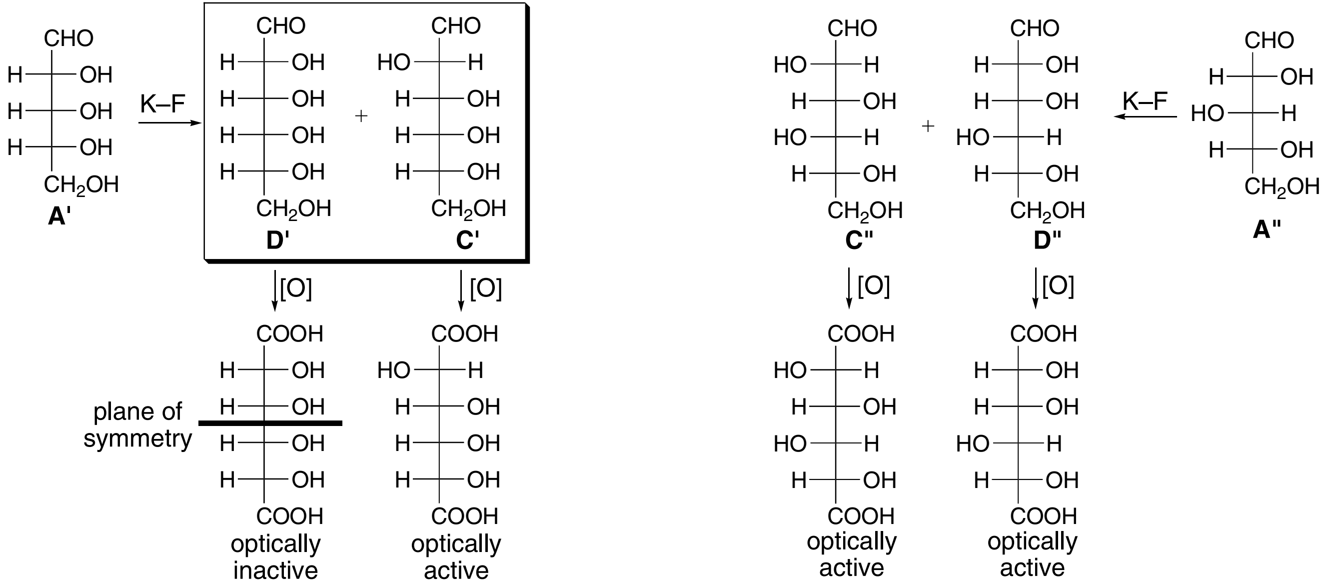


27.66

Only two D-aldopentoses (**A'** and **A"**) yield optically inactive aldaric acids (**B'** and **B"**).



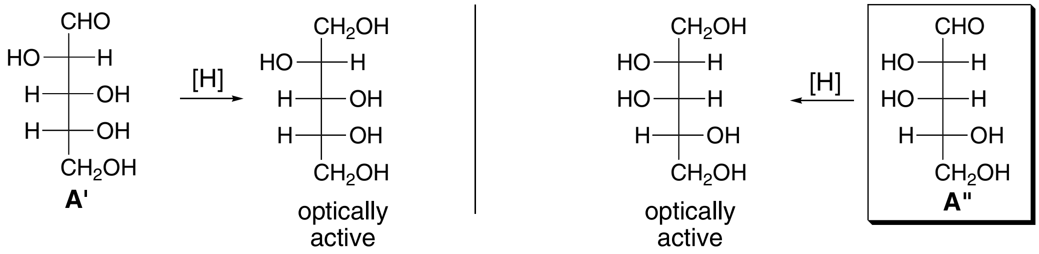
Product of Kiliani–Fischer synthesis:



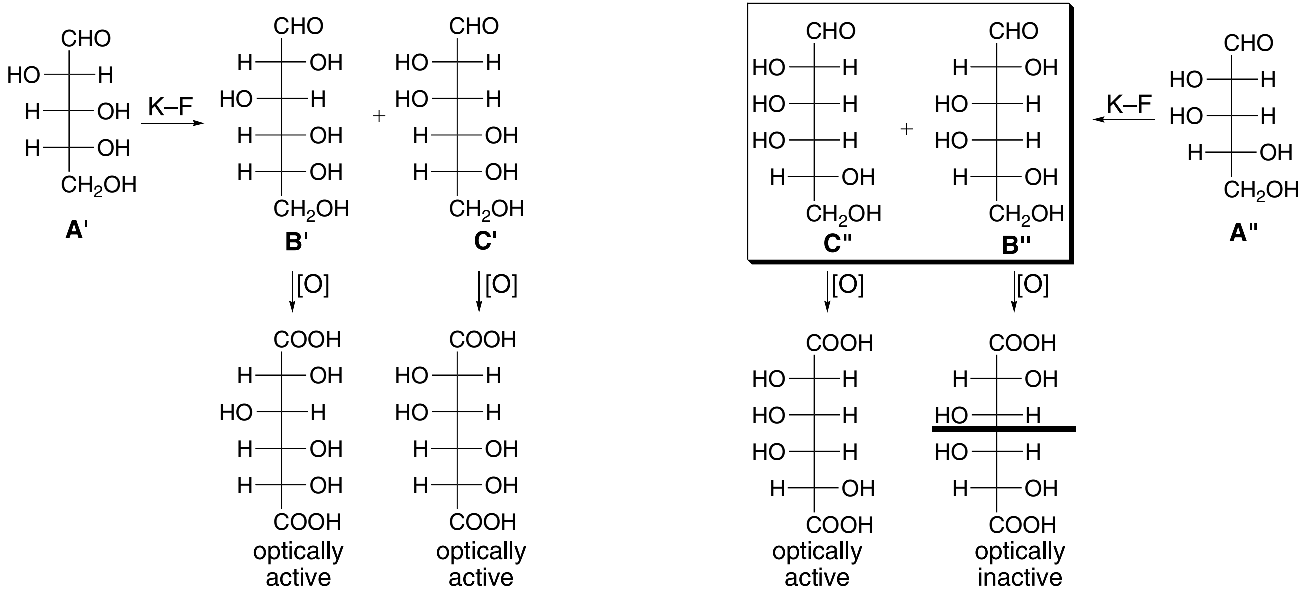
Only **A'** fits the criteria. Kiliani–Fischer synthesis of **A'** forms **C'** and **D'** which are oxidized to one optically active and one optically inactive aldaric acid. A similar procedure with **A''** forms two optically active aldaric acids. Thus, the structures of **A–D** correspond to the structures of **A'–D'**.

27.67

Only two D-aldopentoses (**A'** and **A''**) are reduced to optically active alditols.



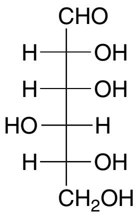
Product of Kiliani–Fischer synthesis:



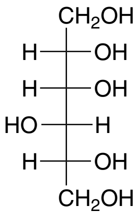
Only **A''** fits the criteria. Kiliani–Fischer synthesis of **A''** forms **B''** and **C''**, which are oxidized to one optically inactive and one optically active diacid. A similar procedure with **A'** forms two optically active diacids. Thus, the structures of **A–C** correspond to **A''–C''**.

27.68

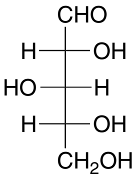
D-gulose



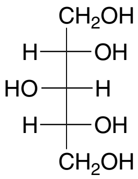
A



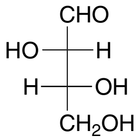
B



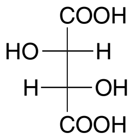
C



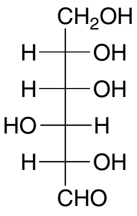
D



E

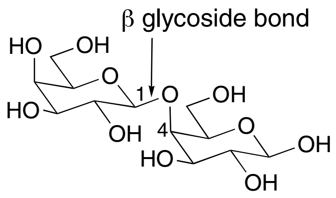


F

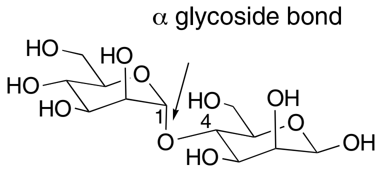


G

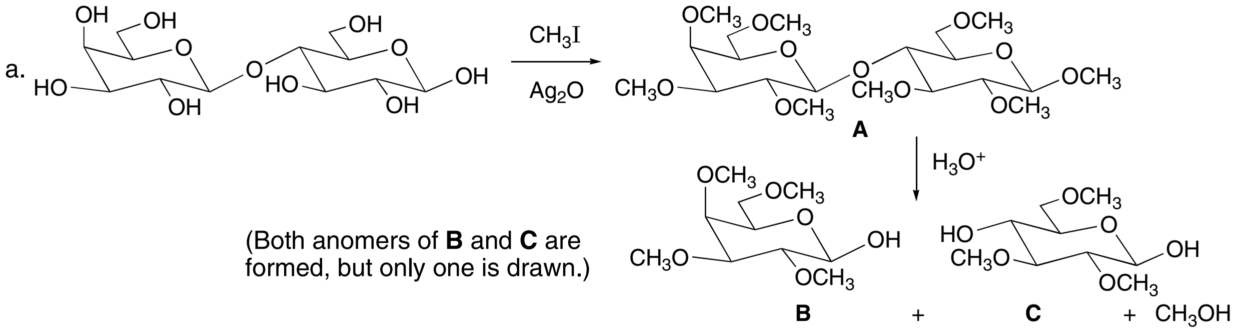
27.69 A disaccharide formed from two galactose units in a 1→4-β-glycosidic linkage:



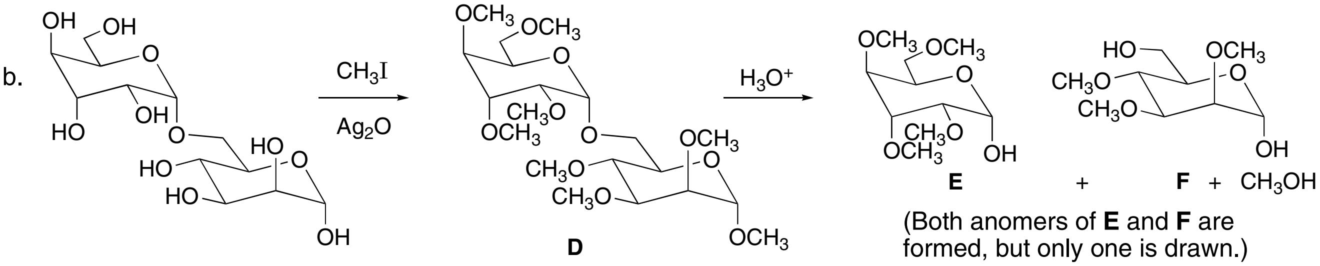
27.70 A disaccharide formed from two mannose units in a 1→4-α-glycosidic linkage:



27.71

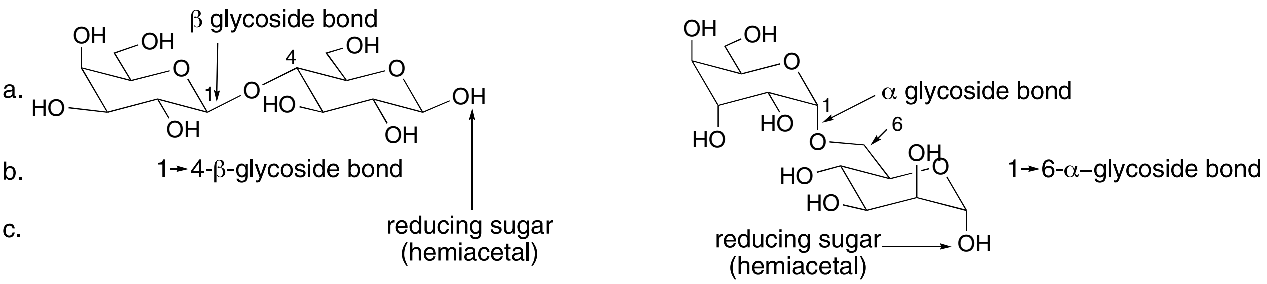


(Both anomers of **B** and **C** are formed, but only one is drawn.)



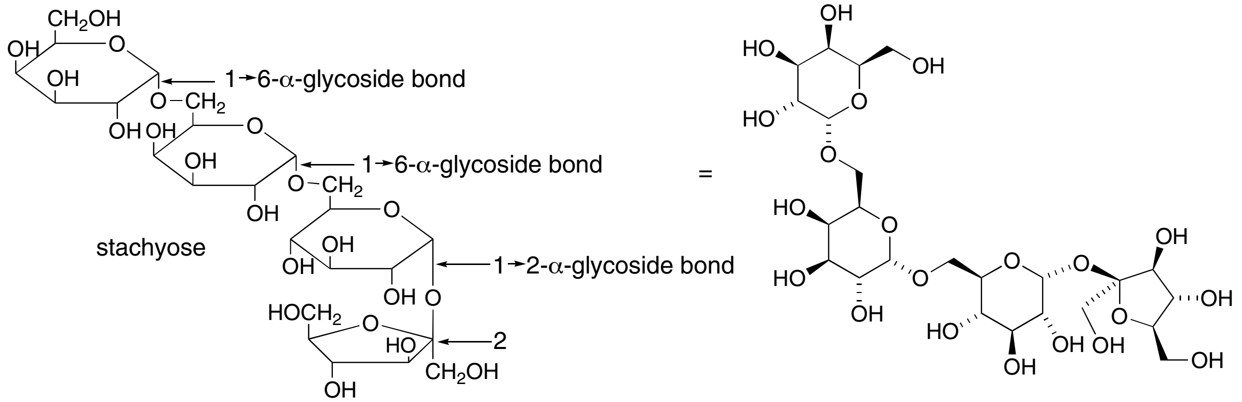
(Both anomers of **E** and **F** are formed, but only one is drawn.)

27.72

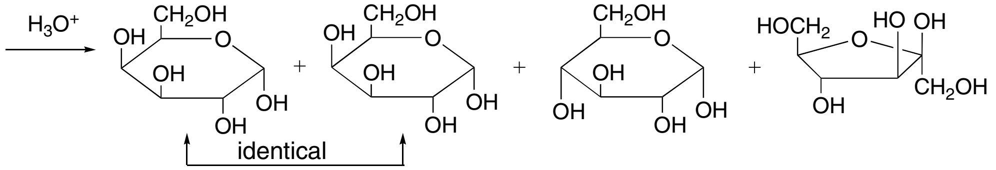


27.73

a and b.



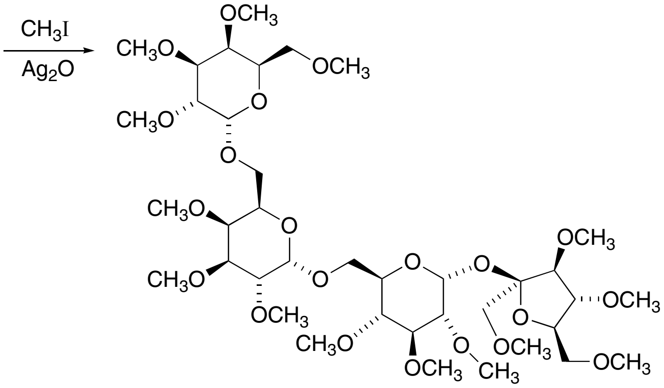
c.



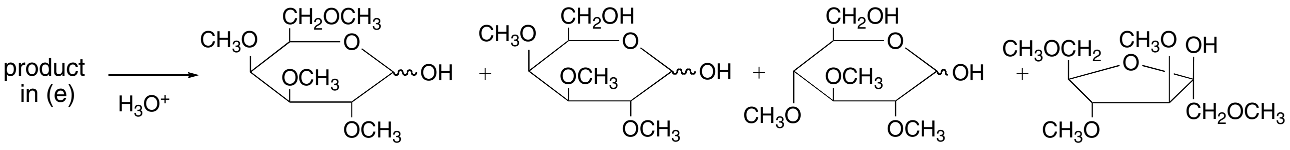
Two anomers of each monosaccharide are formed,
but only one anomer is drawn.

d. Stachyose is not a reducing sugar since it contains no hemiacetal.

e.

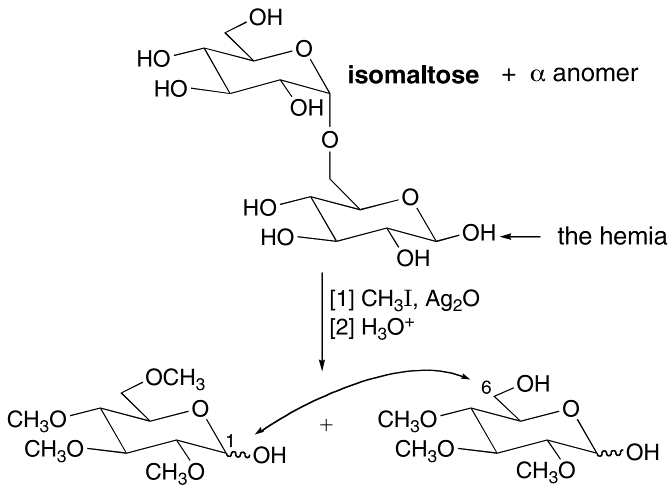


f.



Two anomers of each monosaccharide are formed.

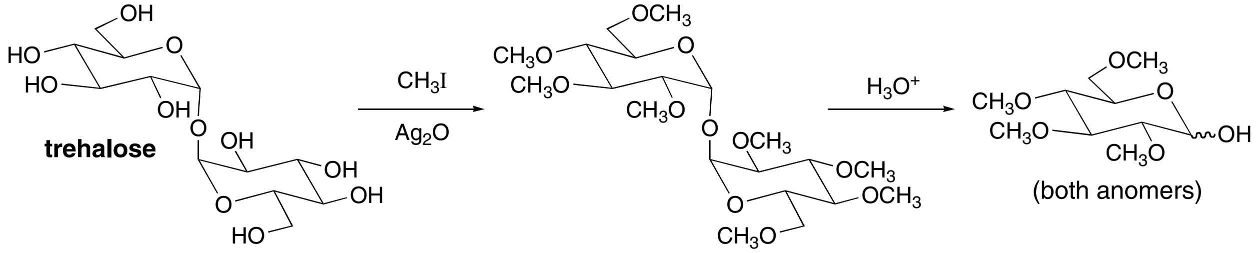
27.74



Isomaltose must be composed of two glucose units in an α-glycosidic linkage. Since it is a reducing sugar it contains a hemiacetal. The free OH groups in the hydrolysis products show where the two monosaccharides are joined.

(Both anomers are present.)

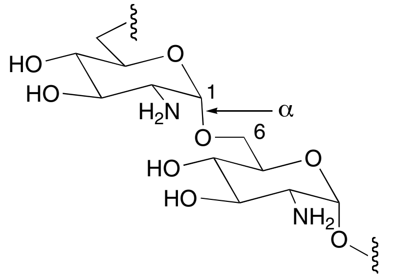
27.75



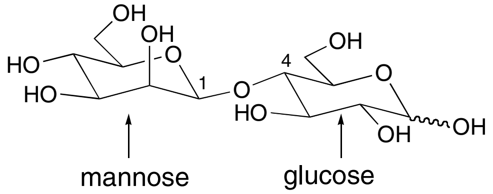
Trehalose must be composed of D-glucose units only, joined in an α-glycosidic linkage. Since trehalose is nonreducing it contains no hemiacetal. Since there is only one product formed after methylation and hydrolysis, the two anomeric C's must be joined.

27.76

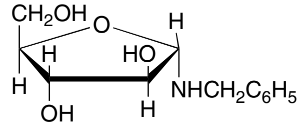
a.



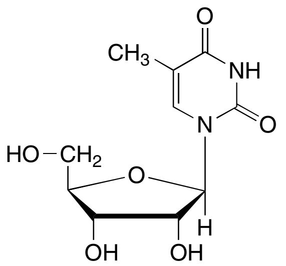
b.



c.

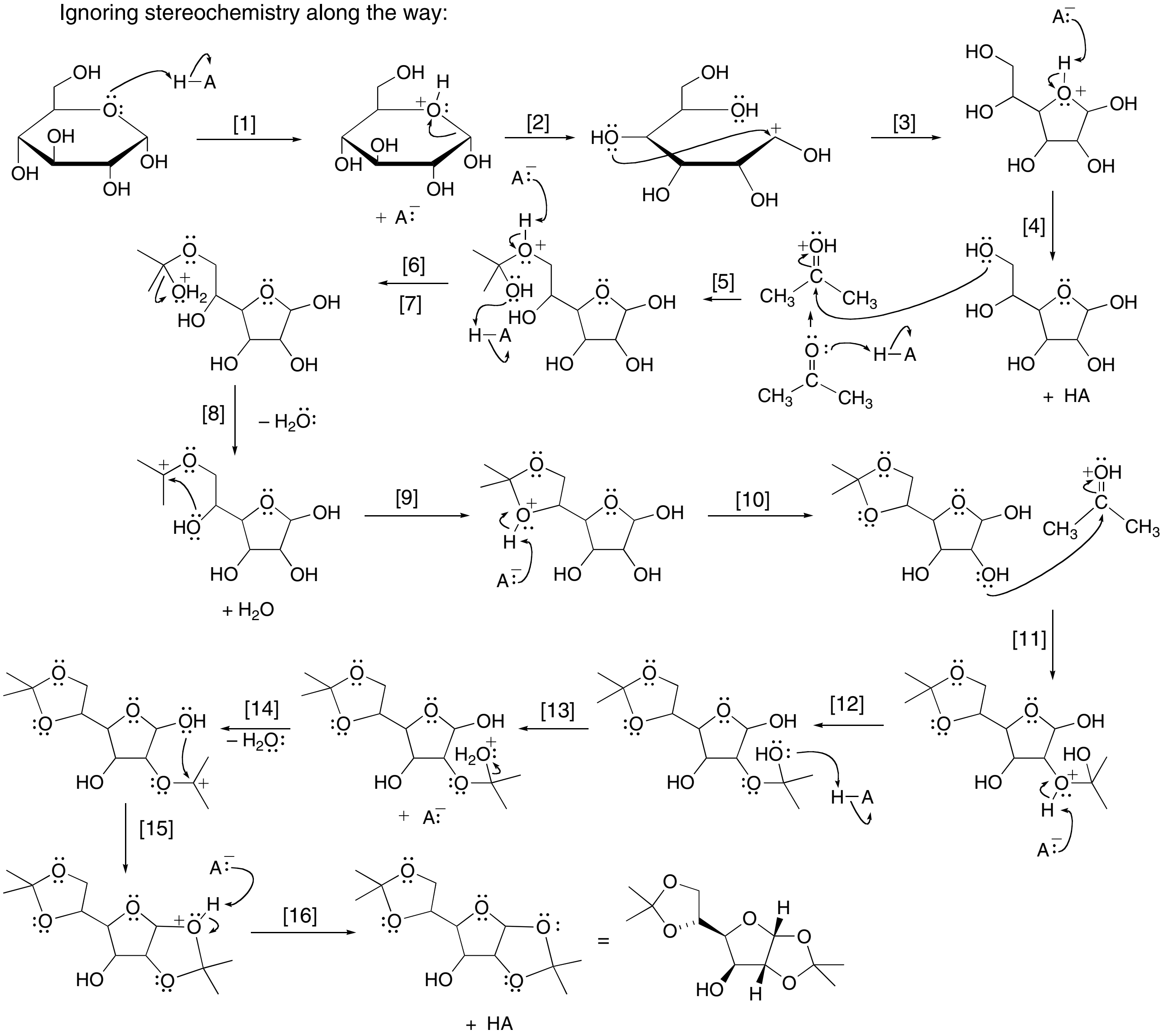


d.

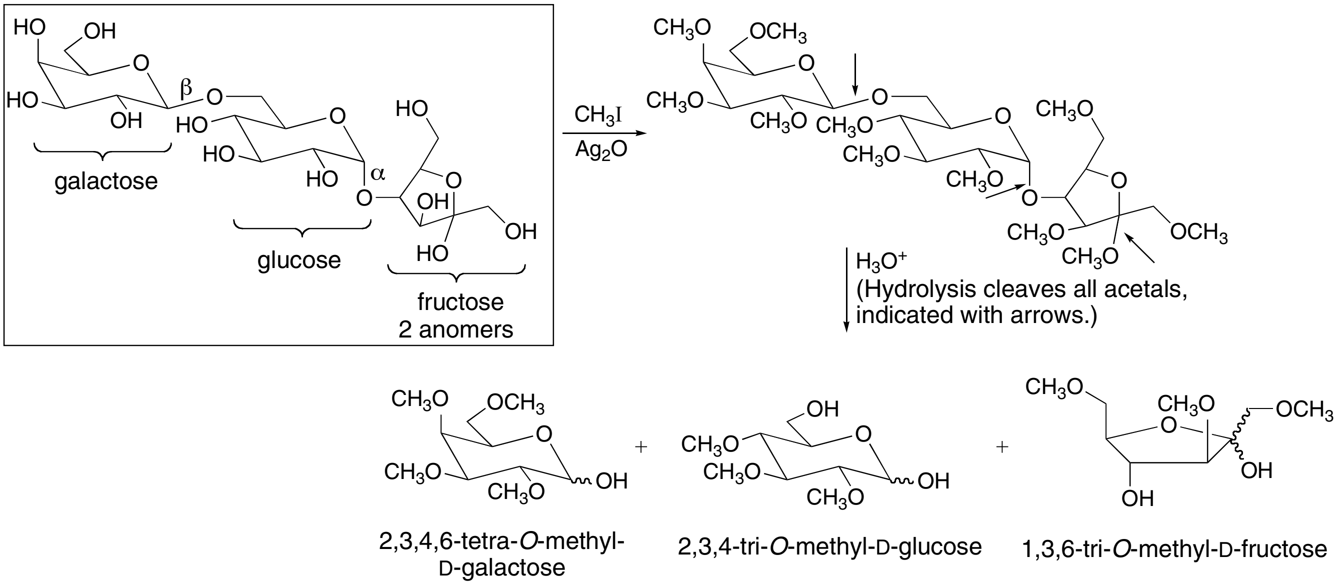


27.77

Ignoring stereochemistry along the way:



27.78 The hydrolysis data suggest that the trisaccharide has D-galactose on one end and D-fructose on the other. D-Galactose must be joined to its adjacent sugar by a β-glycosidic linkage. D-Fructose must be joined to its adjacent sugar by an α-glycosidic linkage.



(Both anomers of each compound are formed.)