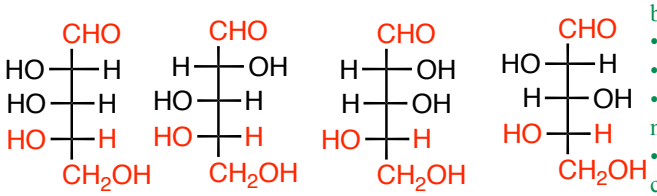
Problem Set Chapter 24

Organic Chemistry for Life Sciences: CHM 224

Name_____

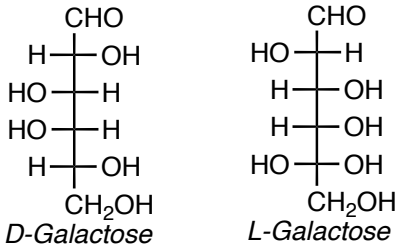
DUE: Wednesday March 20th in class

1. Draw Fischer projections for all of the non-naturally occuring aldopentoses



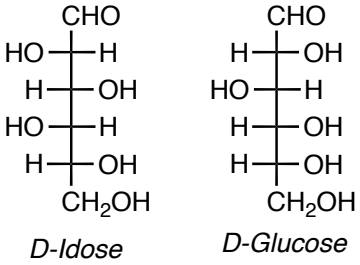
- ALL aldoses have a n aldehyde (CHO) group and a CH_2OH group at the bottom.
- aldo**pent**oses have 5 carbons
- non-natural have the bottom-most CHOH group with the OH on the left
- everything in red is therefore fixed in place by virtue of being a non-naturally occuring aldopentose (5-carbon chain ketone sugar)
- the OH group on the remaining carbons can be on either side of the main chain
- since there are 2 stereogenic carbons that are NOT fixed in place, we should be able to draw $2^n = 2^2 = 4$ stereoisomers

2. Draw the Fischer projection and provide the name for the *enantiomer* of D-Galactose (provided below):



- to draw the enantiomer, ALL stereogenic carbons must have inverted stereochemistry
- the CHO group and the non-stereogenic CH_2OH group can remain written in the same manner

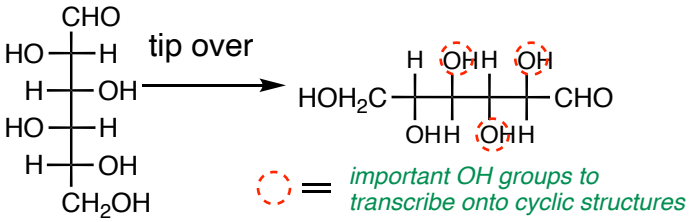
3. Which of the following terms correctly describe the relationship between D-Idose and D-Glucose (may be more than one):

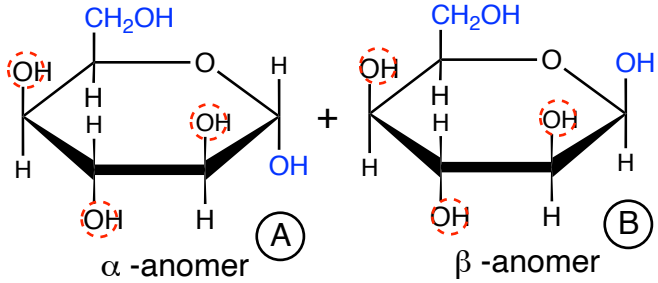


A. enantiomers NO! not ALL stereocenters are inverted
B. epimers NO! more than one stereocenters is inverted
C. anomers NO! anomers refer to cyclized structures
D. diastereomers YES! diastereomers are stereoisomers that are non-mirror images
E. stereoisomers YES! two structures differ only by how substituents are oriented in space

4. Draw the two pyranose rings that would be formed from D-iodose (structure in question 3):

HINT: https://youtu.be/2ectgHjUcV8



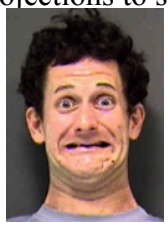


5. Label one of the two pyranose compounds drawn in question 4 as **A** and the other as **B**. Provide their ***complete*** names below:

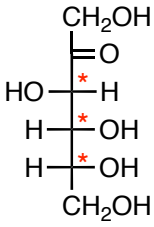
A: α-D-Idopyranose

B: β-D-Idopyranose

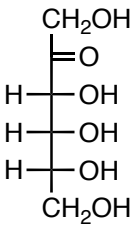
6. Jimmy says that 3 naturally-occurring epimers of D-fructose can be drawn. Is this true? Provide Fischer projections to support your answer.

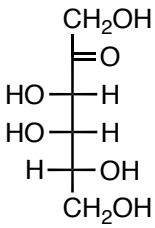


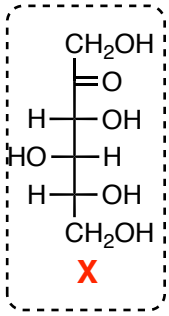
Jimmy



D-fructose





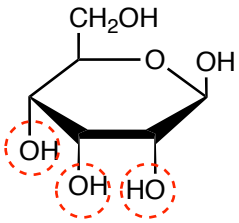


X

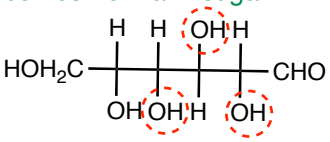
wrong again, Jimmy!!

- an epimer is a stereoisomer in which only a single stereogenic center of a molecule that contains multiple stereogenic centers is inverted (a special case of a diastereomer)
- since the epimers must be naturall-occurring the bottom most CHOH group must have the OH on the right side of the Fisher projection
- therefore, only two additional epimers can be drawn!
- note that the boxed compound is NOT an epimer of D-fructose because it differs at TWO stereogenic centers!!

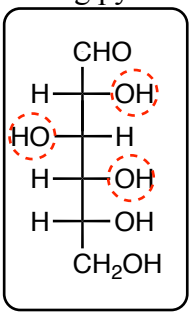
7. Draw the Fischer projection of the monosaccharide from which the following pyranose ring was formed:



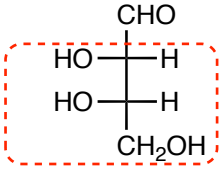
using the "tipped fischer projection" method in reverse, we can place the relative locations of the three indicated OH groups (circled). Plus, we know the remaining OH must be down because this comes from a D-sugar

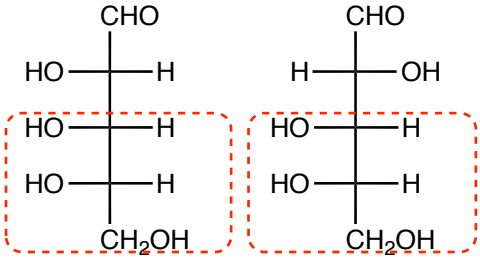


rotate into position



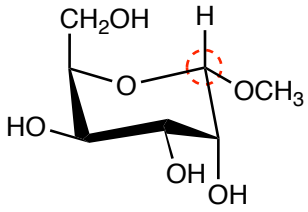
8. What will be the two aldopentoses formed from a round of Kiliani-Fischer synthesis upon the following sugar:





- a single round of K-F synthesis effectively converts the CHO group to an H-C-OH group with two different configurations and adds a new CHO group to the top of the molecule
- note that the bottom portion outlined in red remains the same for the two new aldoses

9. The following sugar is drawn in *"non-standard"format* ***so look carefully***. Answer the questions based on its structure:



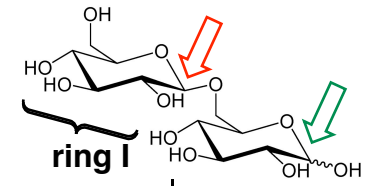
A. circle the acetal carbon **the acetal carbon is always the one connected to two oxygen atoms**

B. is this a reducing sugar? **NO, because it is a methyl pyranoside (full acetal) and not a pyranose ring (hemi-acetal)**

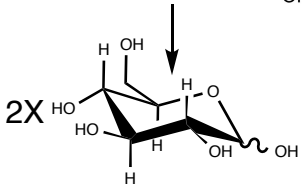
C. is this an a or b anomer? **the OCH_3 group is "across" (or trans to) the CH_2OH so it is a α-anomer**

D. does this sugar undergo mutarotation in neutral solution?
NO, because it is locked in place by the glycoside linkage

10. The structure of Gentiobiose is provided below. Which of the following are true (may be more than one answer):



ring I



2X

A. Gentiobiose is a complex carbohydrate
it is made of two sugar molecules, so it is "complex"

B. Gentiobiose will give a negative test with Tollen's reagent
the green arrow points to a hemiacetal carbon on the second ring (it is hemiacetal because it has an OH group!). any molecule with a hemiacetal linkage will give a positive Tollen's test

C. Ring I of Gentibiose is a β anomer
the red arrow points to a glycloside linkage on ring I. The C-O bond is in the equatorial position, meaning it is "cis" to the CH_2OH group. This means it is a β-anomer

D. Gentiobiose will undergo mutarotation in neutral solution
because this molecule has a hemiacetal linkage, it will undergo mutarotation

E. Hydrolysis of Gentiobiose will form two monosaccharides that are identical
hydrolysis of Gentiobiose will liberate two monosaccharides with identical stereochemistries, which means identical sugars