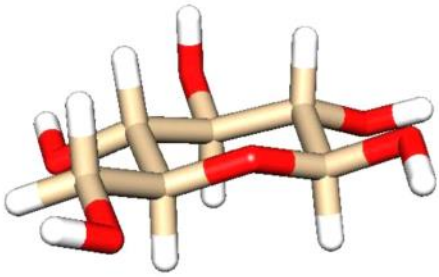
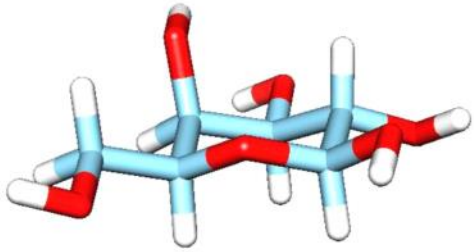
Carbohydrates

1. The 3D structure of glucose and galactose are shown.



D-glucose



D-galactose

a. Is the axial or equatorial position more stable in the chair conformation?
axial points up/down - groups could clash if they are too big. It is small, so it is favorable in axial position

b. What do you notice about the orientation of the OH and H groups in glucose? Are they in the axial or equatorial position?
all equatorial & all axial

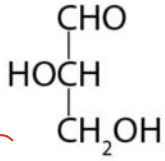
c. How does this differ from galactose?
one of the OH (on C4) is axial

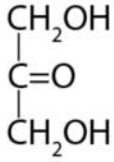
d. Which monoshaccharide do you think is more stable? Briefly justify your answer.
glucose because OH are larger groups + need the maximum space

e. Based on your answer, why do you think that sugars with more than one stereoisomer away from glucose are not very common?
because that puts 2 OH groups in the axial position - these two have a strong potential to sterically clash

2. Glyceraldehyde and dihydroxy acetone are shown.
   a. Are these carbohydrates? How do you know?

Yes, $C_3(H_2O)_3$
Mostly on H_2O per carbon





   b. What is the main difference between glyceraldehyde and dihydroxy acetone? Be specific – use chemical terms (i.e. think functional groups).

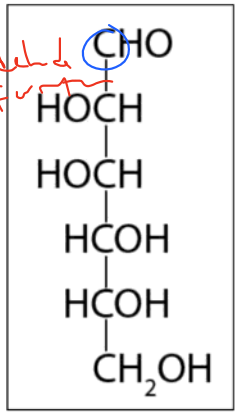
glyceraldehyde is an aldehyde on C1
dihydroxy acetone is a ketone with the carbonyl on C2

c. What is the difference between an aldose and a ketose?

aldose - contains an aldehyde

Ketose - contains a Ketone

3. The Hawthorn projection (linear form) of D-mannose is shown.



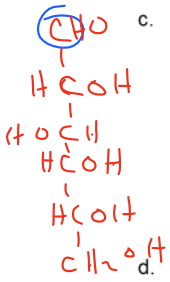
a. How do you know that this is the D isomer of mannose?

The stereocenter that is furthest from the aldehyde is in the D-configuration

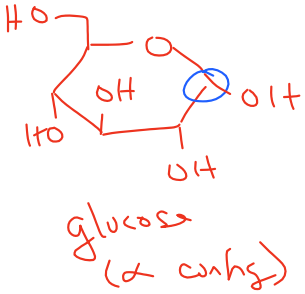
b. Is mannose an aldose or a ketose?

aldose

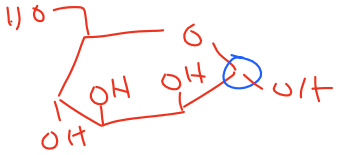
c. Draw the Hawthorn projection of D-glucose (the C2 epimer of mannose).



d. The cyclical form of glucose and mannose.

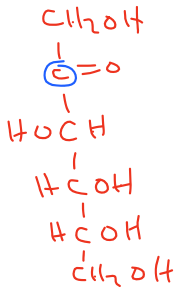


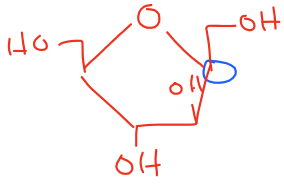
glucose (α anhy)



mannose

e. Fructose is the ketose equivalent of glucose. Draw the linear and cyclical form of fructose.



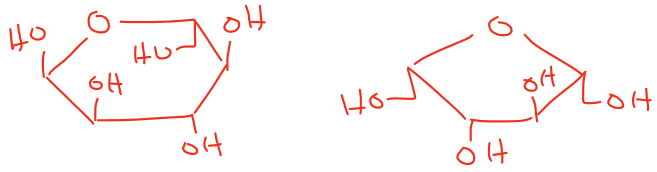


f. Circle the anomeric carbons on each of the cyclical forms of the sugars that you drew in parts a and f and label each as alpha or beta. Now circle the carbon on the Hawthorn projections. What do you notice? Which carbon in the linear form ends up as the anomeric carbon?

It is always the carbonyl carbon that becomes the anomeric carbon

g. The 3D structure of galactose is shown in problem 2. Galactose is a C_4_ epimer of glucose.

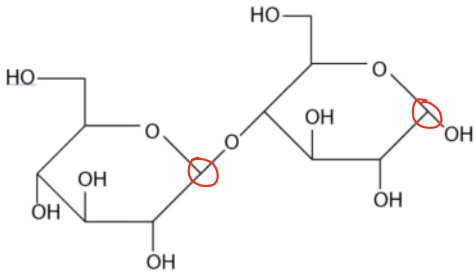
h. Sometimes you will need to be able to draw the anomeric carbon pointed left instead of right. To accomplish this, you need to draw the ring in reverse, but you also need to "flip" each OH group (what was up now goes down). Draw glucose and fructose with the anomeric carbon pointing left.

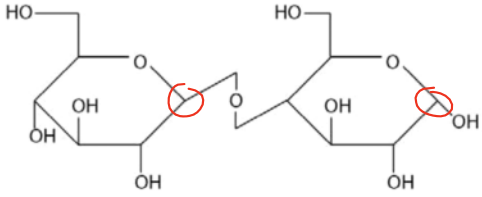


4. Carbohydrate monomers link together through glycosidic bonds. These bonds are the product of a condensation reaction between two alcohols.
   a. What is the product of a condensation reaction between ethanol (CH_3CH_2OH) and methanol (CH_3OH)?

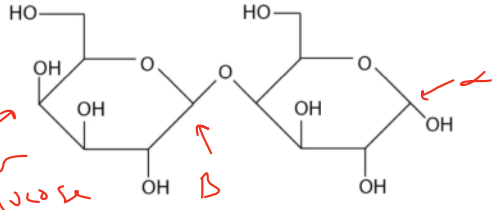
$CH_3CH_2OCH_3 + H_2O$

   b. Disaccharide names tell you everything that you need to know about how they are linked together. α-D-glucose (1→4) β-D-glucose means that a glycosidic bond is linking the anomeric carbon (C1) of β-D-glucose to C4 of α-D-glucose. This molecule is drawn below in two ways: on the left, the glycosidic linkage is drawn directly and the right image is a common representation of the glycosidic bond that allows the saccharide polymers to be drawn in a linear way while retaining the ability to identify the stereochemistry of the C1 and C4 carbons.





   c. Circle the anomeric carbons in the two structures above.
   d. Name the disaccharide shown here



C4 epimer of glucose = Galactose

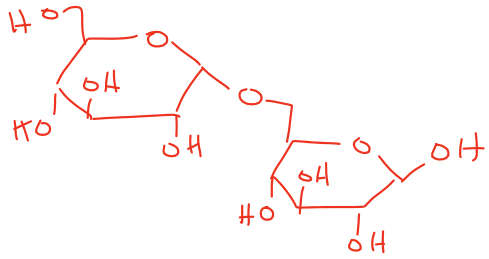
β

α

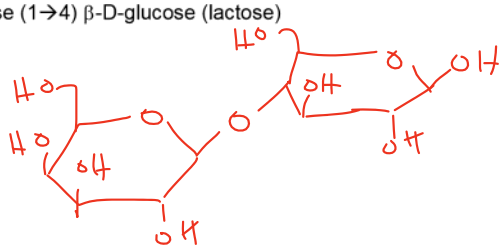
β-D-galactose (1→4) α-D-galactose

e. Sketch each of the following disaccharides:

α-D-glucose (1→6) β-D-glucose (this is part of the branching that occurs in starch and cellulose)

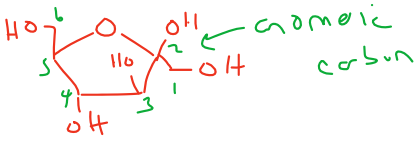


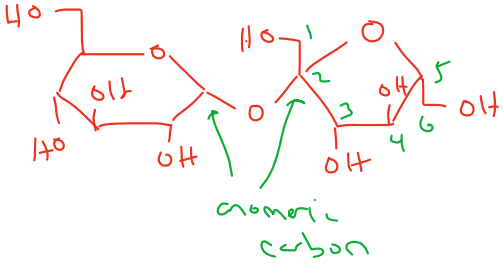
β-D-galactose (1→4) β-D-glucose (lactose)



α-D-glucose (1→2) β-D-fructose (sucrose – so table sugar)

anomeric carbon on left





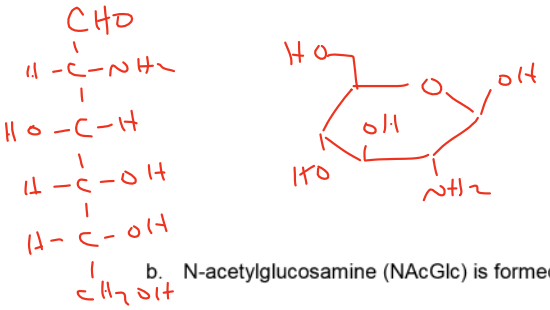
5. Monosaccharides are incredibly soluble in water (2.1 kg of sucrose will dissolve in 1L of water!). However, most polysaccharides are sparingly or not at all soluble in water. Why do you think this is?

monosaccharides dissolve really well in H_2O b/c of all of the H-bonds that form (every C has an OH). If polymers of these are not soluble, it must be because the OH are tied up in intramolecular H-bonds. (See pp 226-227 in your book)

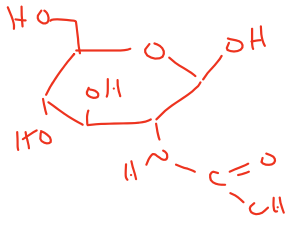
Based on your answer, propose a reason that corn starch can be used as a thickening agent in stew. It may help you to think about what happens to Jell-O (yep, a polysaccharide) when it gets heated up and then cooled back down.

Heating the starch breaks the intramolecular H-bonds and allows the starch to dissolve. As the solution cools, H-bonds are reformed. However, they now can form with H_2O + the starch polymers as well. Therefore, there is a new H-bond network that forms throughout the solution that is "thick"

6. Sugar modifications are an incredibly important part of sugar chemistry. For example, chitin, the principle component in the exoskeleton of crustaceans, insects, and spiders, is made from repeating units of β-N-acetylglucosamine linked through a (1→4) glycosidic bond.
   a. Glucosamine (yep, the glucosamine that you hear about when you hear ads about joint health) is a glucose molecule with an amine group substituted at the C2 carbon. Draw glucosamine.



   b. N-acetylglucosamine (NAcGlc) is formed when glucosamine is condensed with acetic acid. Draw NAcGlc.



   c. Draw the repeating disaccharide of chitin.