

Chapter 24: Carbohydrates

[Sections: 24.1–24.10]



Carbohydrates definition

- naturally occurring compounds derived from carbon, oxygen and hydrogen
- the net molecular formula comes from each carbon having an equivalent of water, hence, hydrates of carbon

glucose = $C_6H_{12}O_6$ = 6 carbons and 6 water molecules (6 x H_2O)

- commonly referred to as "sugars" or "saccharides" (driving from *saccharum*, which is latin for sugar)

simple carbohydrates

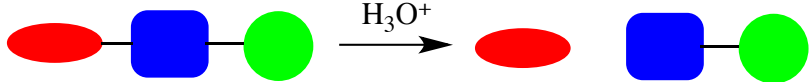
- carbohydrates that CANNOT be hydrolyzed to simpler carbohydrates



"monosaccharides"

complex carbohydrates

- carbohydrates that CAN be hydrolyzed to simpler carbohydrates



"trisaccharide"

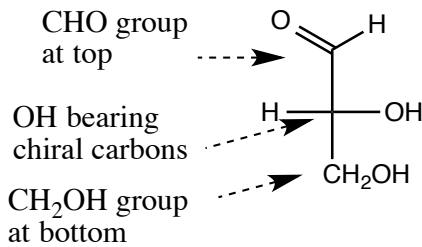
"monosaccharide"

"disaccharide"

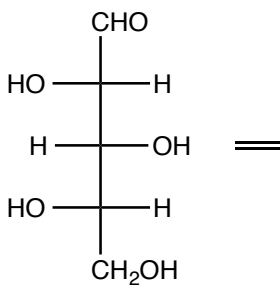
Monosaccharides: polyhydroxy aldehydes and ketones

aldose

polyhydroxy aldehydes

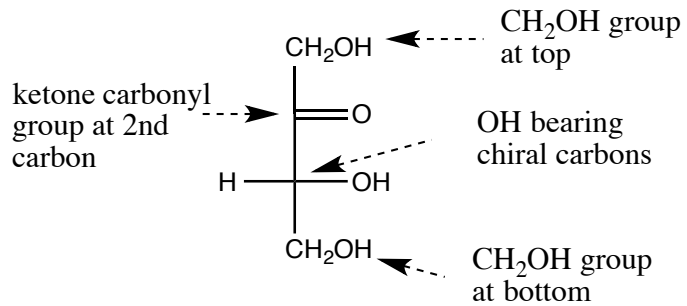


3 carbons in length =

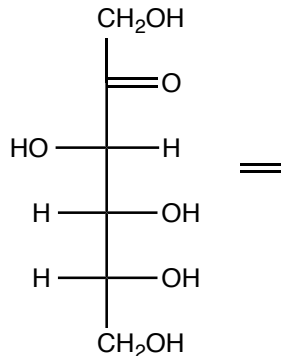


ketose

polyhydroxyketones

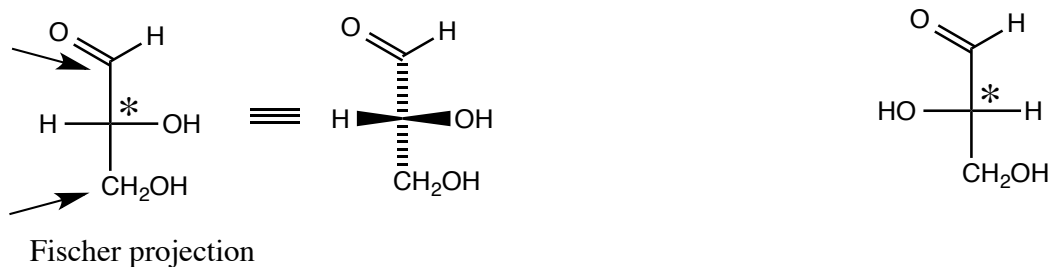


4 carbons in length =



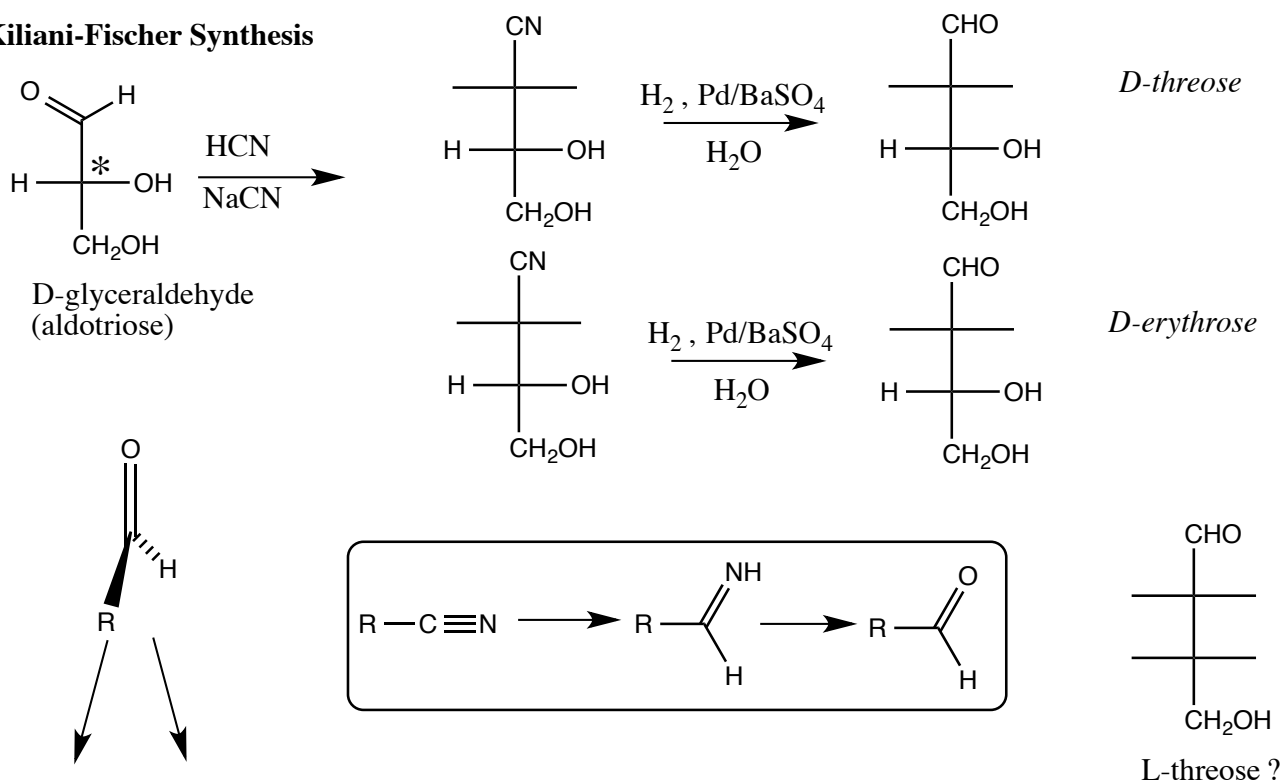
- "ose" ending implies a carbohydrate
- most common in nature are aldopentose, aldohexose, ketopentose, ketohexose
- each of these are examples of monosaccharides

The simplest aldoses: D- and L-glyceraldehyde



- *D*-glyceraldehyde (the *R* enantiomer) rotates a plane of polarized light in the dextrorotatory (+) direction in a polarimeter while *L*-glyceraldehyde is levorotatory (–)
- **remember:** we cannot predict whether any given enantiomer is (+) or (–) without either: i) conducting an experiment with a polarimeter, or ii) knowing the direction that light is rotated by the other enantiomer
- *D*-glyceraldehyde is naturally-occurring, while *L*-glyceraldehyde is not!
- All naturally-occurring monosaccharides derive from *D*-glyceraldehyde

Kiliani-Fischer Synthesis



- Kiliani-Fischer synthesis produces two new monosaccharides with one additional carbon atom
- two stereoisomeric products result. Type of stereoisomers =
- monosaccharide stereoisomers of this type are also called "epimers" because they differ ONLY in stereochemistry of a single stereogenic carbon atom
- both stereoisomers called "D" NOT because they are (+)-rotating[they are actually both levorotary] but because they derive from *D*-glyceraldehyde and have the *D*-stereochemistry at the bottom-most stereogenic carbon
- both are naturally occurring. *L*-sugars are NOT naturally-occurring!
- ALL naturally occurring sugars, both aldoses and ketoses, are *D*-sugars

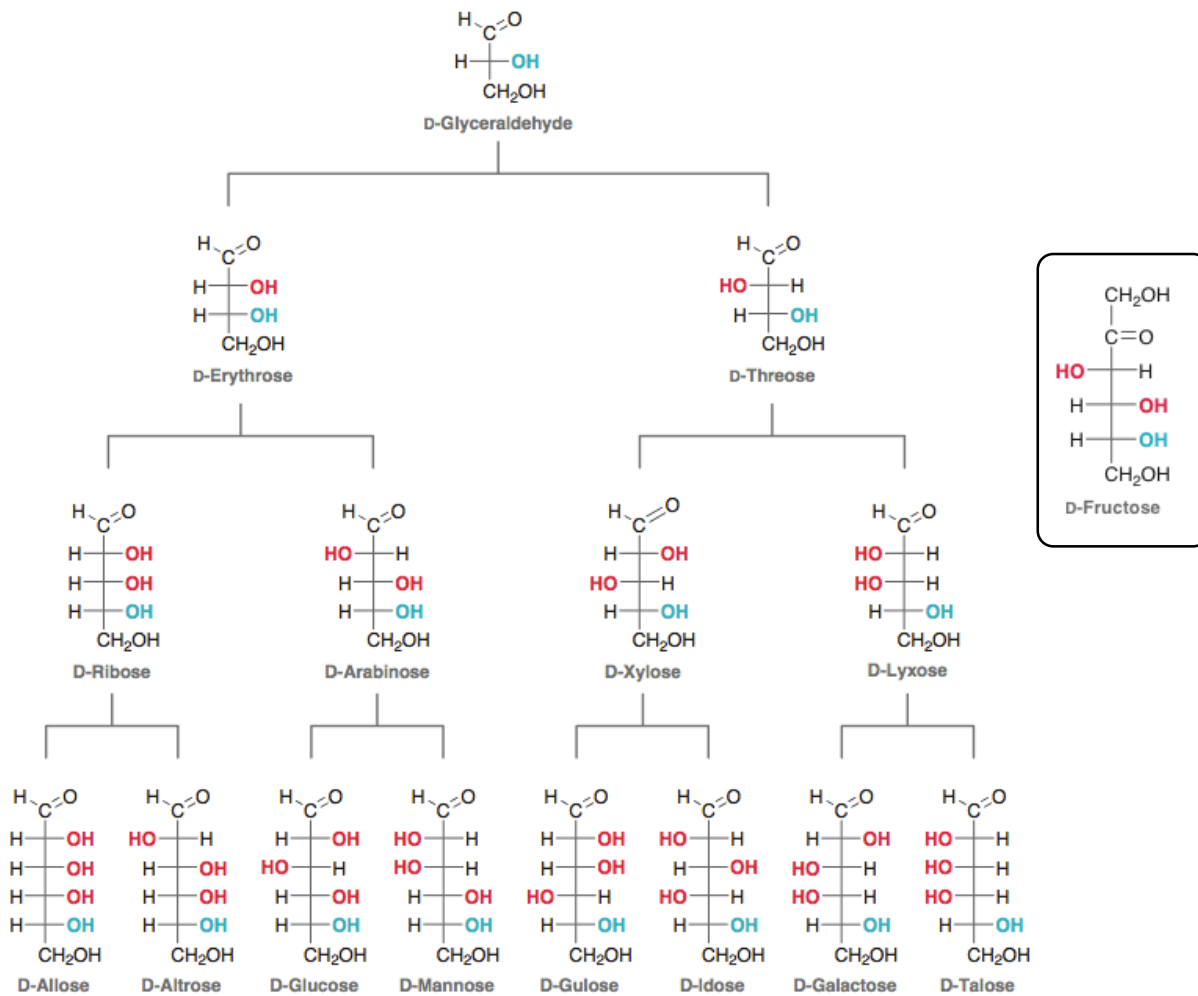
Glucose

- *Glucose is a naturally-occurring aldohexose. Given this information, draw as much of its structure as possible:*

- *given this limited information, how many possible stereoisomers could be drawn for glucose?*

Problems: 1, 2

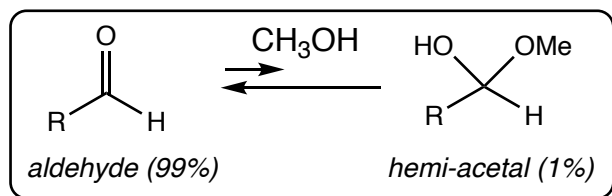
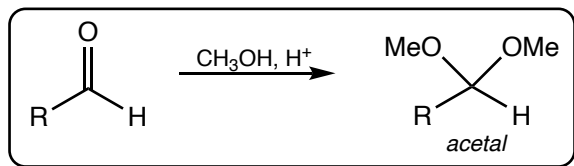
A more complete perspective and summary:



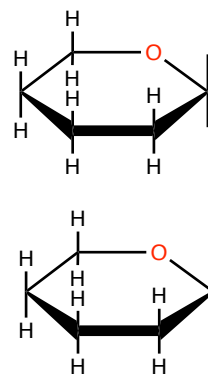
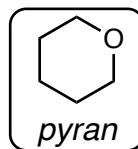
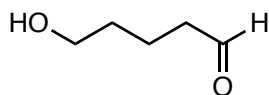
- *naturally-occurring monosaccharides, whether aldoses or ketoses, share in common the stereochemistry of the CHOH group at the stereogenic carbon nearest the bottom.*
- *D-glucose and D-fructose are particularly important sugars as far as human energy supplies are concerned*

Problems: 1–4

Acetals and hemi-acetals

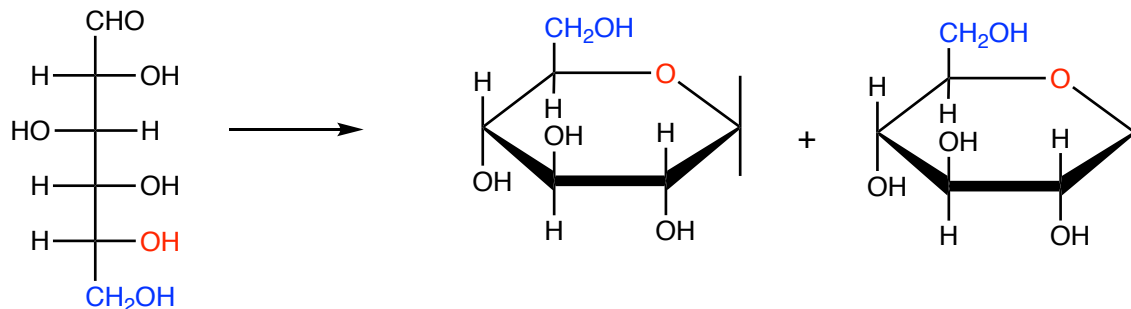


- in the absence of an acid catalyst, the reaction of an aldehyde with an alcohol cannot proceed past the hemi-acetal stage
- this is an equilibrium process that in ordinary cases heavily favors the starting aldehyde



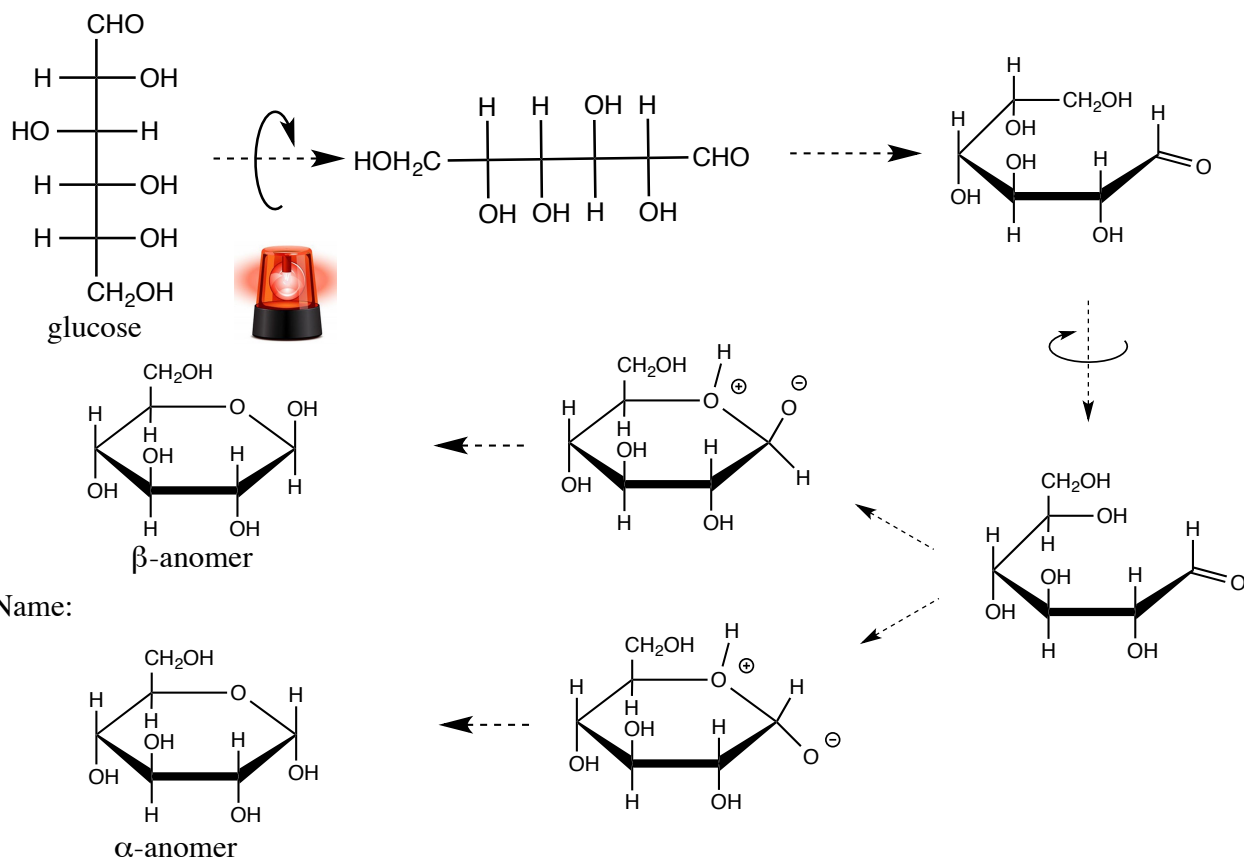
- however, if a molecule contains **BOTH** the alcohol group for the reaction **AND** the aldehyde group, formation of the hemi-acetal is strongly favored when a **stable** 5- or 6-membered ring can be formed

Pyranose rings

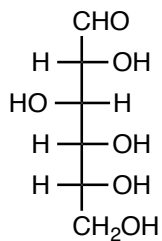


- upon closure to form the 6-membered pyranose ring, two different stereoisomers (called anomers) are formed, based on the stereochemistry of the OH group at the hemi-acetal linkage (or anomeric carbon)
- when pyranoses are drawn in this conventional manner, the α -anomer has the OH group pointing down (trans to the CH_2OH group) and the β -anomer has the OH group pointing up (cis to the CH_2OH group)
- the stereochemistries of the other OH groups are defined by the stereochemistries in the monosaccharide

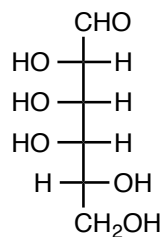
predicting the structure of, and naming, pyranose rings:



Shortcut for drawing pyranose rings of D-sugars

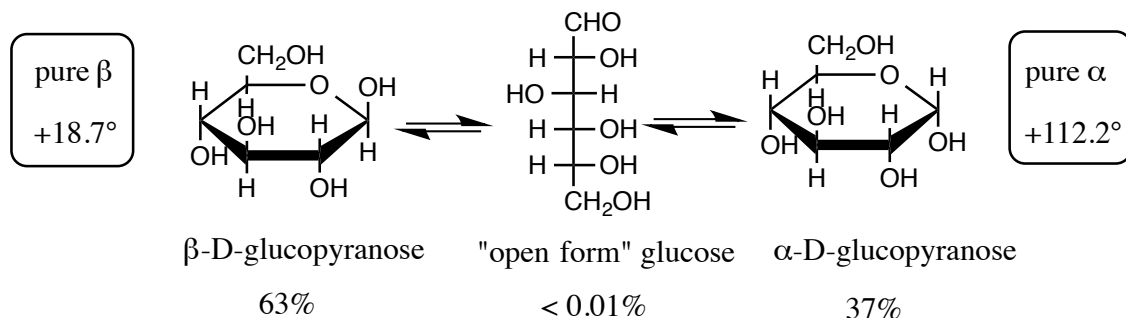


predict the structures, and corresponding names, of the pyranose rings of D-talose:



Mutarotation

- the two anomers of glucose can be separated and purified
- the β -anomer has $[\alpha] = +18.7^\circ$, the α -anomer has $[\alpha] = +112.2^\circ$
- no matter which isomer is started with, however, upon sitting in aqueous solution the final optical rotation from the polarimeter = $+52.6^\circ$ which is somewhere in between the readings of either pure compound
- this results from the fact that each ring is in equilibrium with the "open form" and hence in equilibrium with the other anomer as well
- the result is a mixture of the two anomers with a net resulting optical rotation

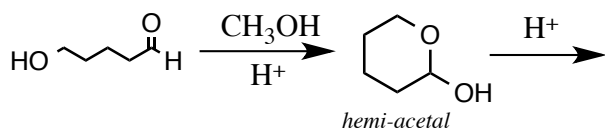


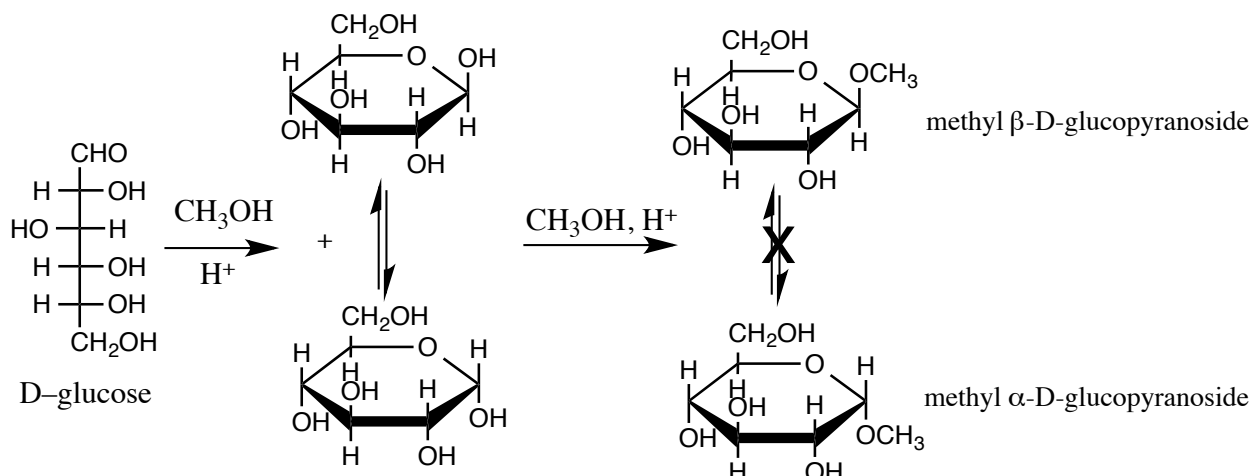
- the interconversion of one anomer with the other in this way is known as "mutarotation"

Relative stability of the two glucopyranose anomers



Glycoside formation

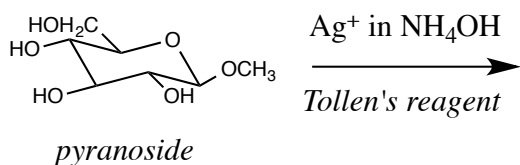
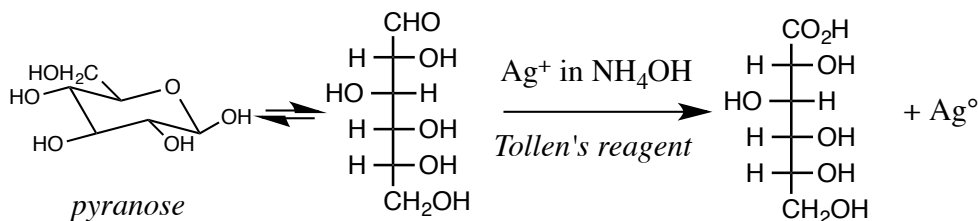




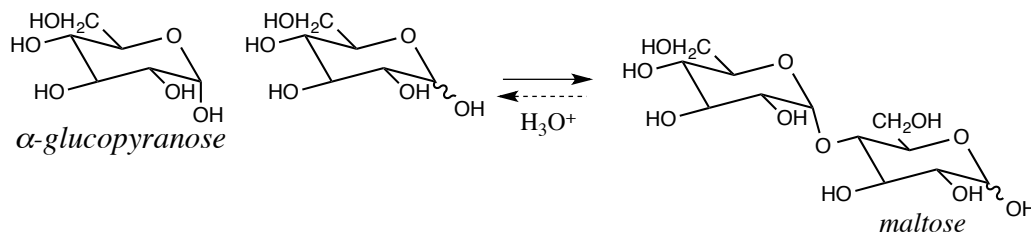
- formation of an acetal via a "glycoside" linkage
- when formed from a sugar molecule it is called a "pyranoside" since it comes from glucopyranose
- in the absence of an acid catalyst, the anomeric carbon of pyranosides is locked in place
- pyranosides will not undergo mutarotation under neutral conditions

Problems: 6

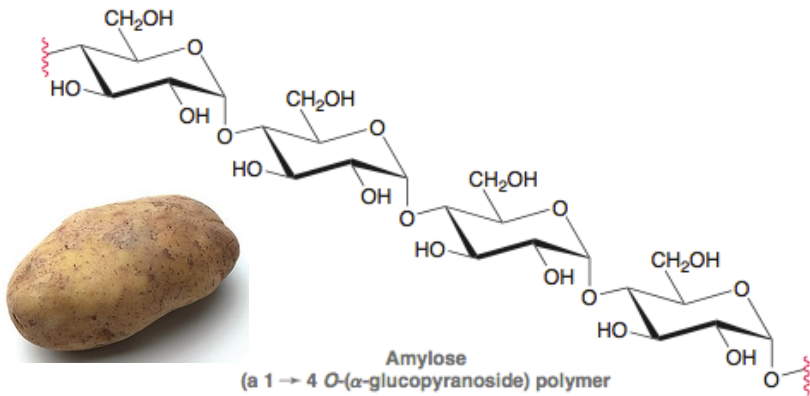
Reducing sugars: Distinguishing between pyranose and pyranoside molecules.



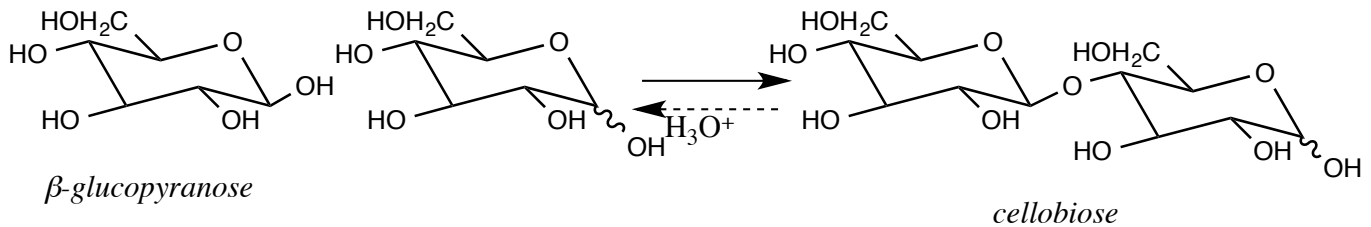
Disaccharides



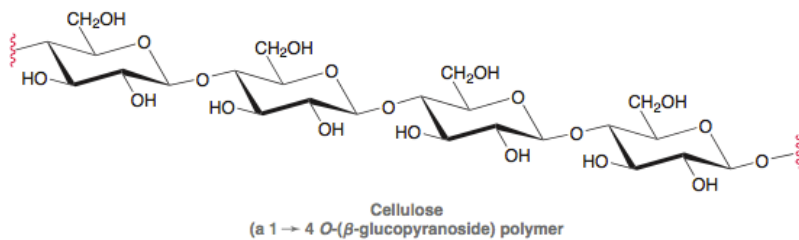
- maltose is a disaccharide and a complex carbohydrate (can be hydrolyzed)
- the two monosaccharides are connected via a "glycoside" linkage
- in maltose, the α -pyranoside linkage is retained between the two sugars and is fixed
- the hemi-acetal linkage, however, is still able to mutarotate



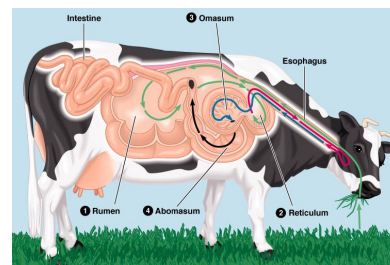
- amylose is a polysaccharide made up of thousands of repeating glucose units
- all of the units are connected by the α -glycoside link
- amylose is a major constituent of starches in food that humans rely upon for food/energy
- more complex branched polymers (glycogen) are formed by the body as a way of storing glucose for energy



- cellobiose is also a disaccharide and a complex carbohydrate (can be hydrolyzed)
- in cellobiose the β -glycoside linkage is retained between the two sugars and is fixed
- the hemi-acetal linkage is still able to mutarotate

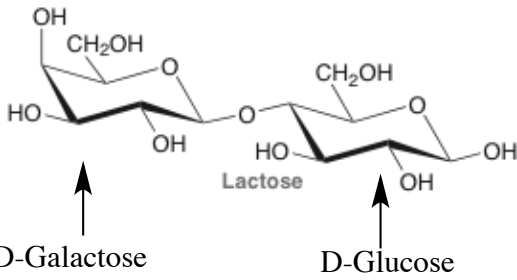


- cellulose is a polysaccharide made of ~7,000 units on average of glucose
- all of the units are connected by the β -glycoside link



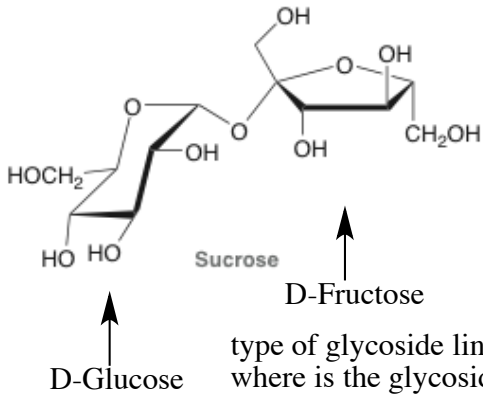
- humans have enzymes specific for hydrolysis of the α -glycoside link and can therefore hydrolyze starches like amylose to release the glucose for energy
- humans lack the enzymes necessary to hydrolyze the β -glycoside link and cannot, therefore, liberate the glucose from polysaccharides like cellobiose
- cows also do not naturally produce enzymes necessary to hydrolyze the β -glycoside link but their stomachs contain microorganisms that DO produce the required enzymes so that cows are able to digest cellulose (e.g., grasses)

Some other interesting polysaccharides...



type of glycoside link?

- hydrolyzed in the body by an enzyme called lactase
- lactase production begins to decline for children past age 2 and continues
- ~75% of adults have lactose intolerance



type of glycoside link to glucose?
where is the glycoside link for fructose?



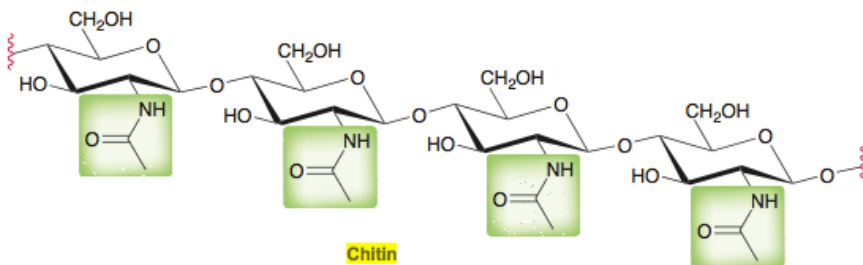
2008 Georgia sugar refinery explosion



- 31% glucose
- 38% fructose
- 17% water
- 7% maltose
- 1% sucrose



nectar: 90% water with a mixture of compounds comprised of 55% sucrose, 24% glucose, 21% fructose plus aroma chemicals and proteins



- derivatized amino sugar
- similar structure to cellulose
- NH bonds allow for hydrogen bonding which increases the strength of strands
- main constituent of insect exoskeletons



Chapter 24 *Essential Concepts*

1. Know the molecular formula for all carbohydrates and be able to differentiate complex from simple carbohydrates
2. Know the basic structure of all aldoses and all ketoses, understand how to name the structures, and how to determine if they are (D) naturally occurring or (L) non-naturally occurring.
3. Understand the sequence involved in the Kiliani-Fischer synthesis. Be able to predict products.
4. Know why sugars adopt ring structures, be able to form pyranose rings from a given D-aldoheptose sugar, and be able to assign proper names for the anomers.
5. Understand the process of mutarotation and why one anomer might be favored over another.
6. Be able to draw simple alkyl (typically methyl) pyranosides and assign names.
7. Know Tollen's reagent, why it is used, and what it determines about a sugar's structure.
8. Understand how complex carbohydrates are built up from simple carbohydrates. You should be able to pick out glycoside (acetal) versus hemi-acetal linkages.
9. Be familiar with some of the common complex carbohydrates discussed in class.