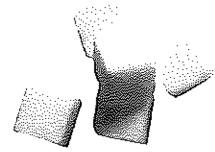
Chapter 24: Carbohydrates

[Sections: 24.1–24.10]



Carbohydrates definition

- *naturally occuring 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)*

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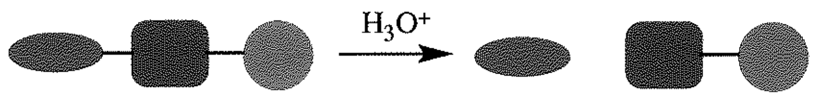
simple carbohydrates

- *carbohydrates that CANNOT be hydrolyzed to simpler carbohydrates*

"monosaccharides"

complex carbohydrates

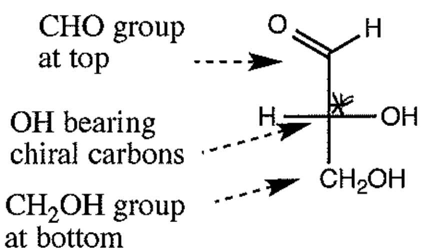
- *carbohydrates that CAN be hydrolyzed to simpler carbohydrates*



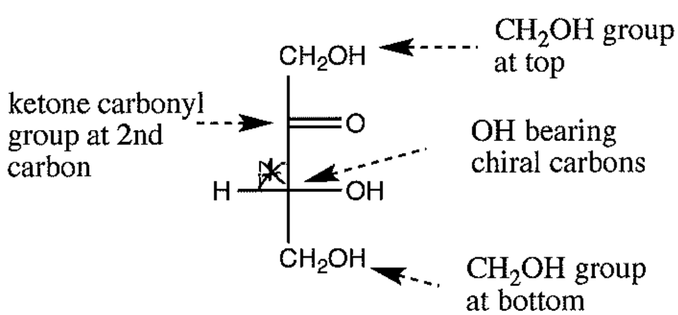
"trisaccharide" "monosaccharide" "disaccharide"

Monosaccharides: polyhydroxy aldehydes and ketones

aldose
polyhydroxy aldehydes

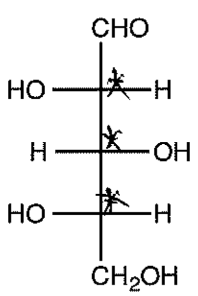


ketose
polyhydroxyketones

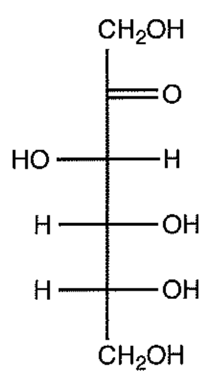


3 carbons in length = ALDOTRIOSE 3C

4 carbons in length = KETOTETROSE 4C

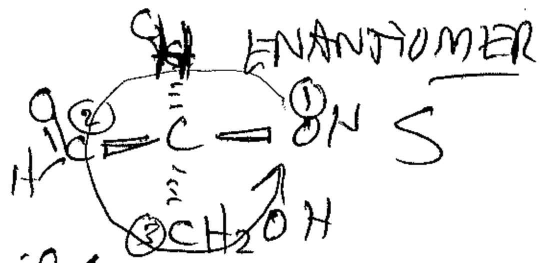


= ALDOPENTOSE 5C

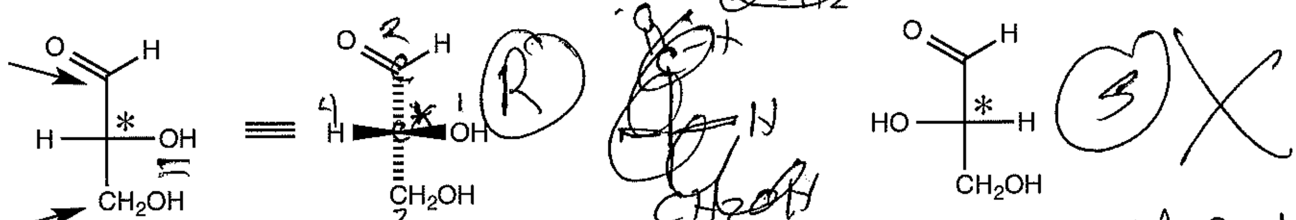


= KETOHEXOSE 6C

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



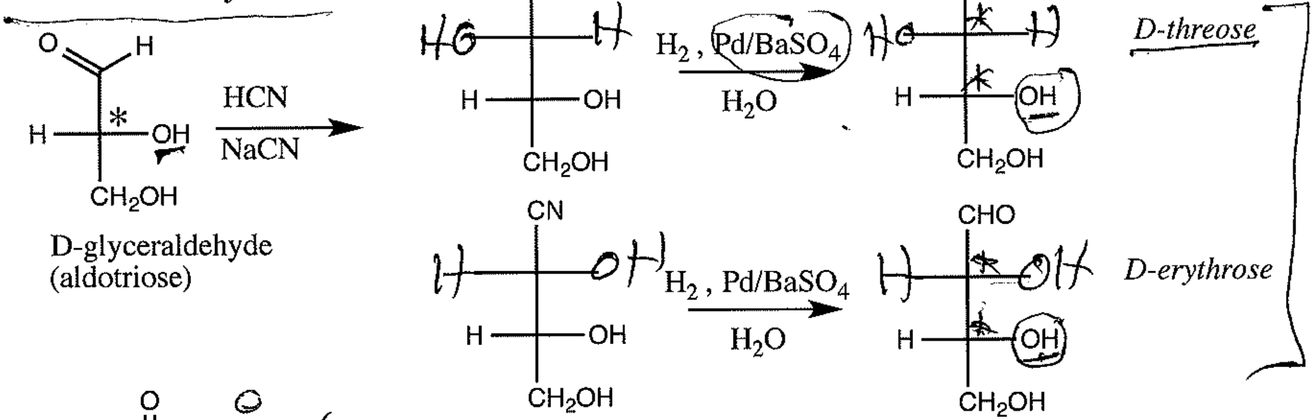
The simplest aldoses: D– and L-glyceraldehyde

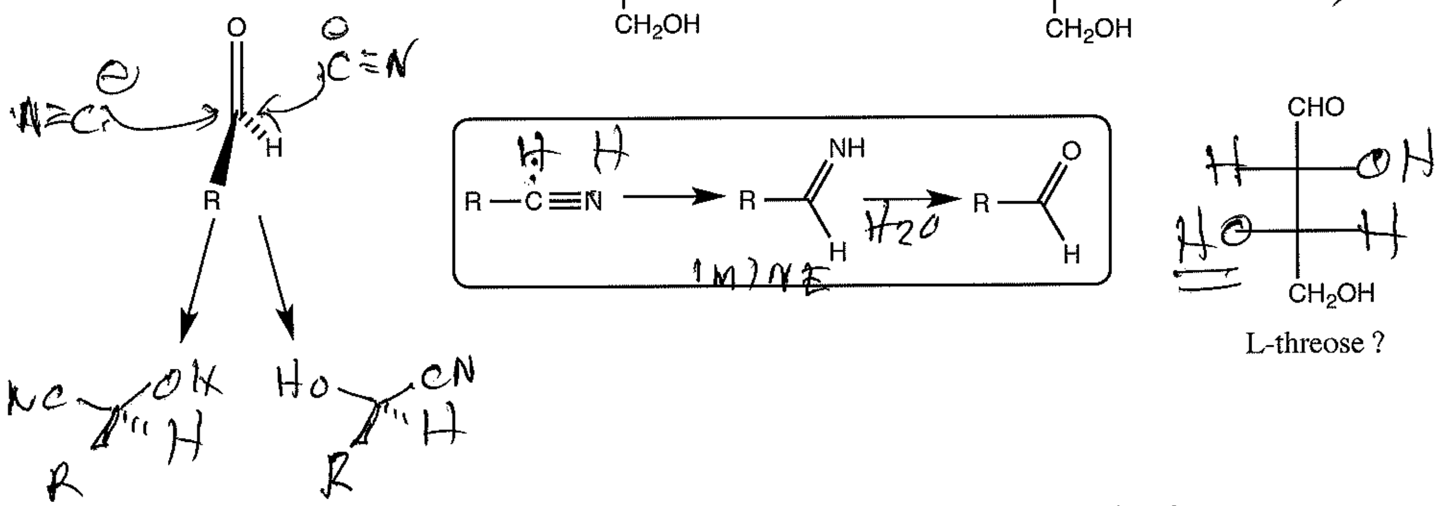


Fischer projection D-GLYCERALDEHYDE L-GLYCERALDEHYDE

- *D-gylceraldehyde (the R enantiomer) rotates a plane of polarized light in the dextroratory (+) direction in a polarimeter while L-glyceraldehyde is levoratory (–)*
- ***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-glceraldehyde is not!*
- *All naturally-occurring monosacharrides derive from D-glyceraldehyde*

Kiliani-Fischer Synthesis

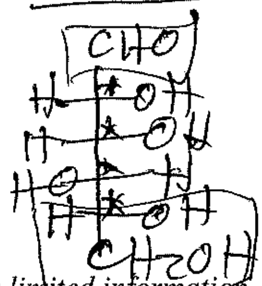




- *Kiliani-Fischer synthesis produces two new monosaccharides with one additional carbon atom*
- *two stereoisomeric products result. Type of stereoisomers =* DIASTEREOMERS
- *monosaccharide stereoisomers of this type are also called "epimers" because they differ ONLY in stereochemistry of a single stereogenic carbon atom*
- *both stereoisomers called "D" NOT because they are (+)-rotating [they are actually both levoratory] 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:*



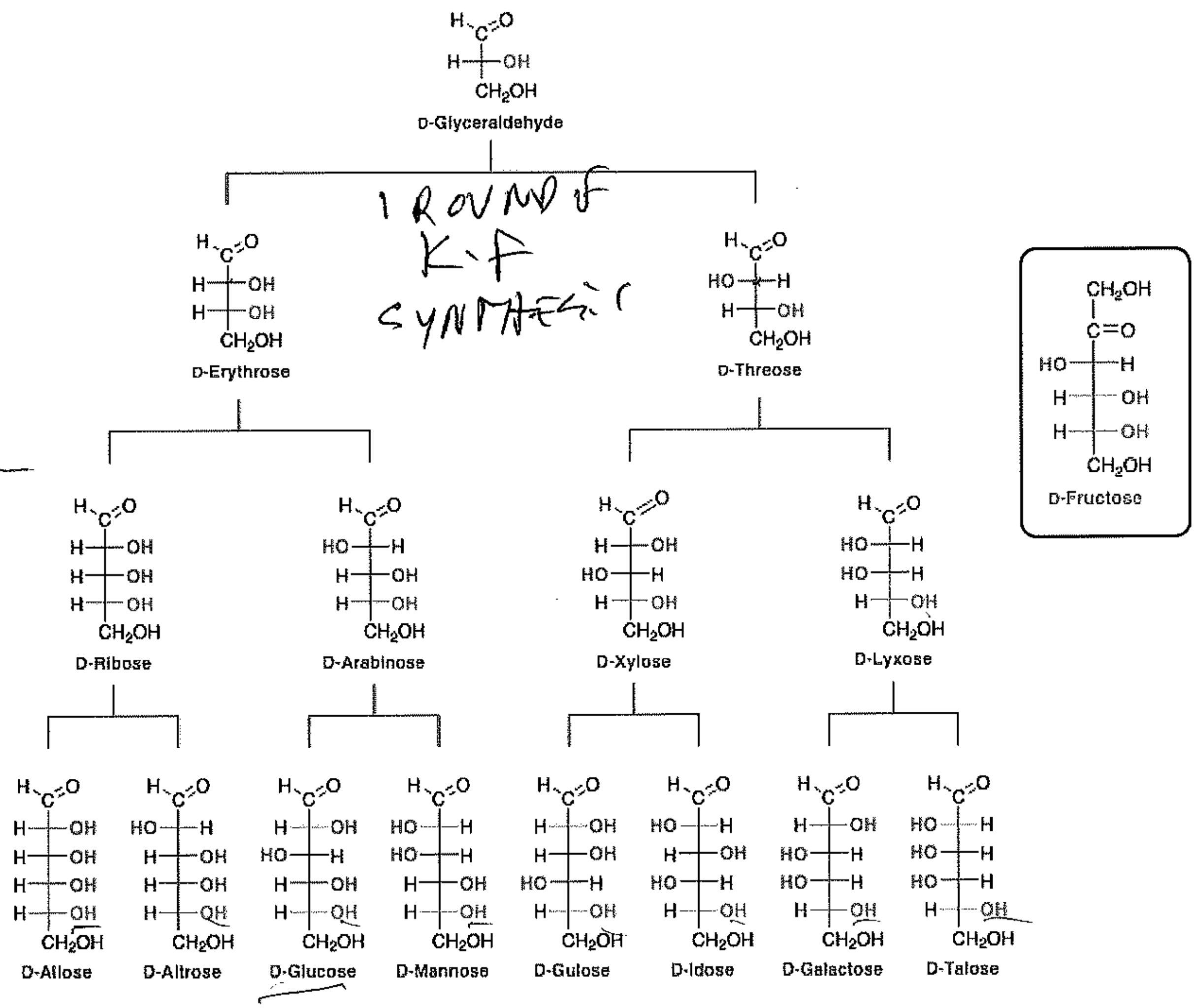
2^n n = # of stereogenic carbons

$2^4 = 2 \times 2 \times 2 \times 2 = 16$

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

Problems: 1, 2

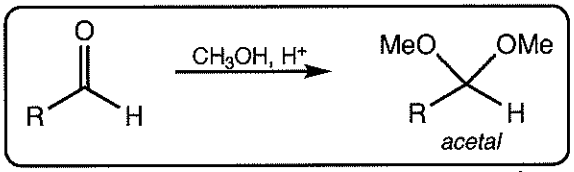
A more complete perspective and summary:

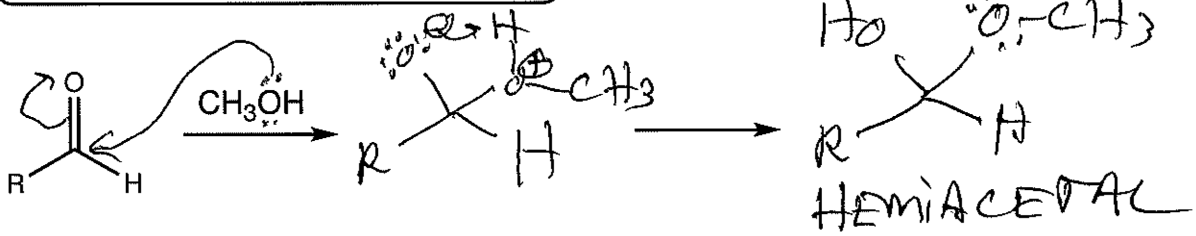


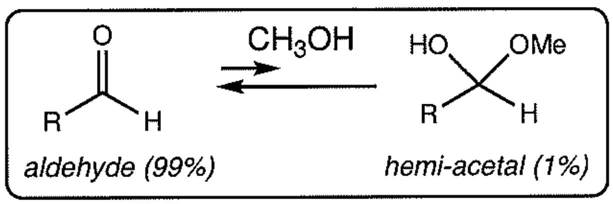
- *naturally-occurring monosaccharides, whether aldoses or ketoses, share in common the stereochemistry of the CHOH group at the stereogenic carbon nearest the bottom.*
- *D-glucose and D-fructose are particularly important sugars as far as human energy supplies are concerned*

Problems: 1–4

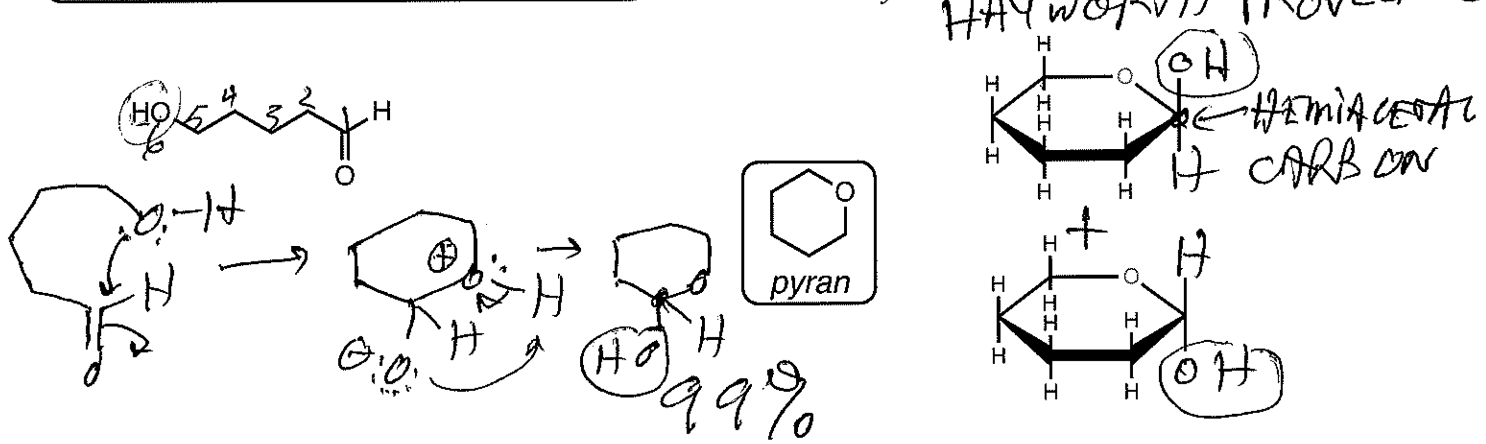
Acetals and hemi-acetals





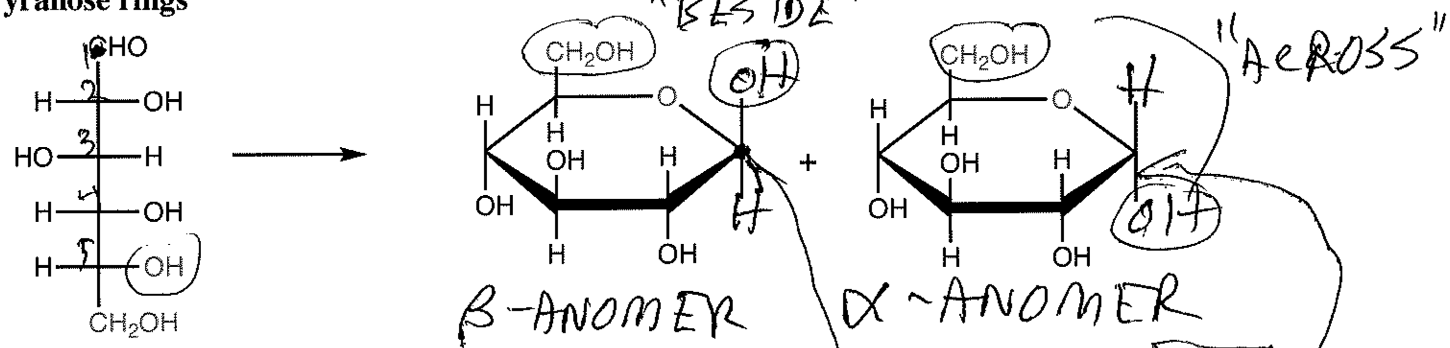


• in the absence of an acid catalyst, the reaction of an aldehyde with an alcohol cannot proceed past the hemi-acetal stage
• this is an equilibrium process that in ordinary cases heavily favors the starting aldehyde



• 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*

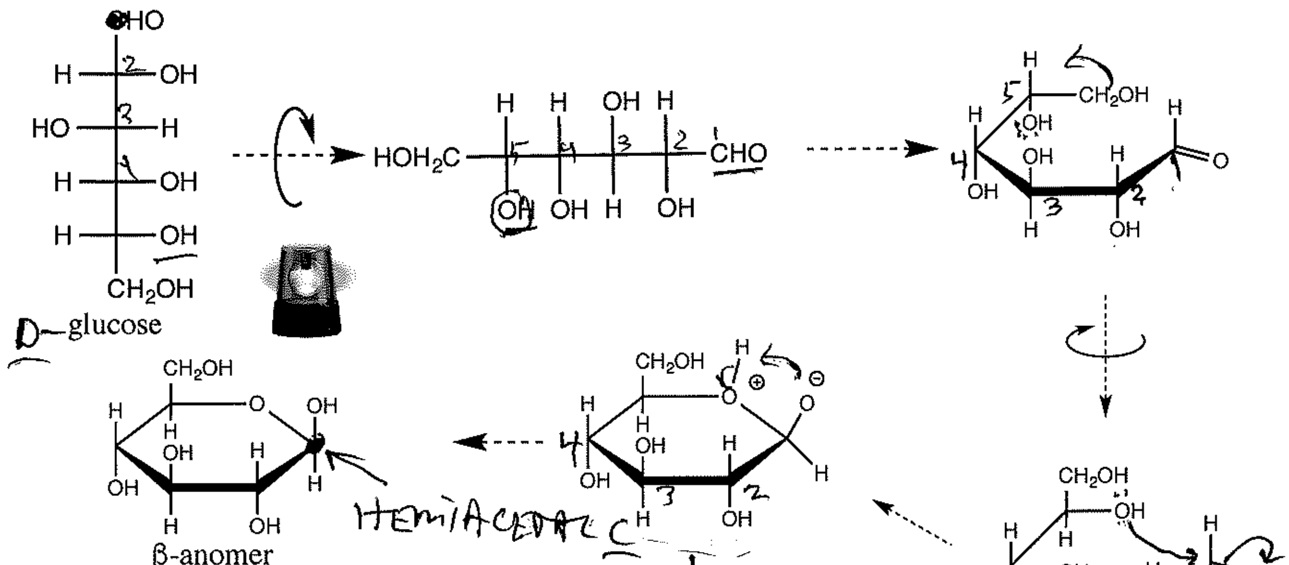
Pyranose rings



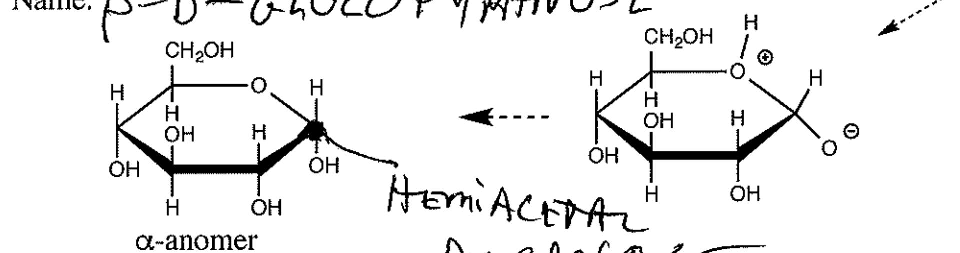
• upon closure to form the 6-membered pyranose ring, two different stereoisomers (called anomers) are formed, based on the stereochemistry of the OH group at the hemi-acetal linkage (or anomeric carbon)
• when pyranoses are drawn in this conventional manner, the α-anomer has the OH group pointing down (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

HEMIACETAL CARBON

predicting the structure of, and naming, pyranose rings:

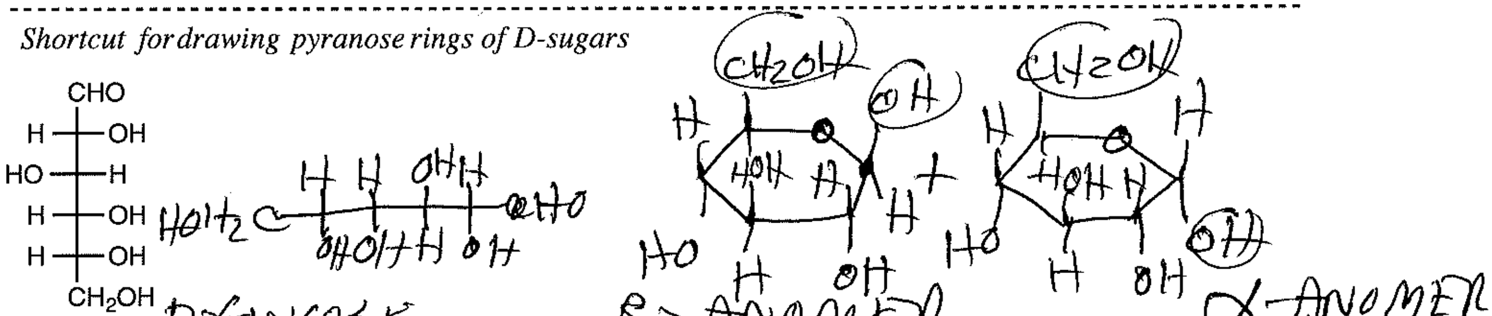


Name: β-D-GLUCOPYRANOSE



Name: α-D-GLUCOPYRANOSE

Shortcut for drawing pyranose rings of D-sugars



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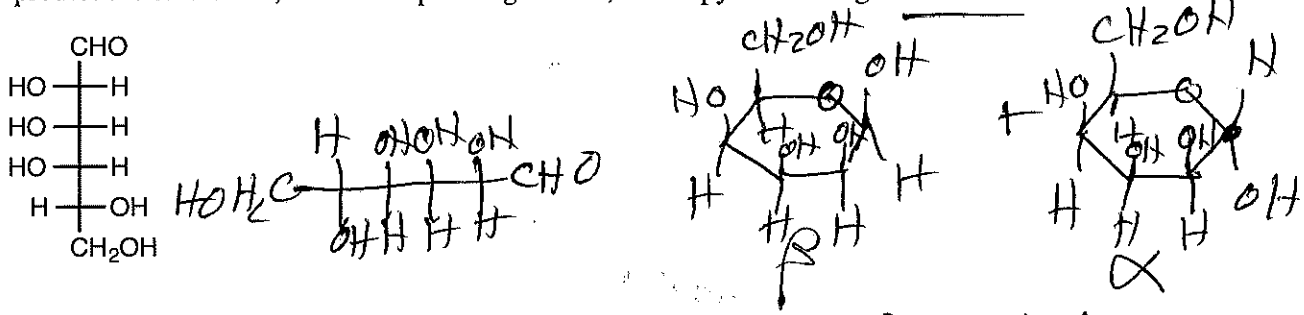
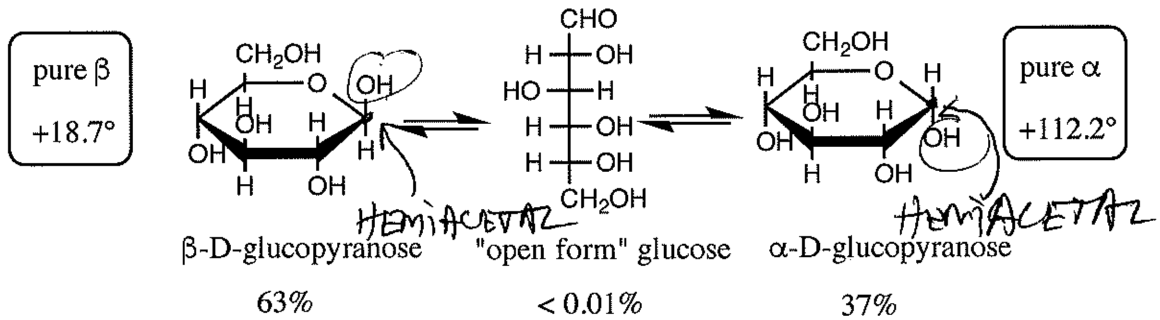
predict the structures, and corresponding names, of the pyranose rings of D-talose:



β-D-TALOPYRANOSE
α-D-TALOPYRANOSE

Mutarotation

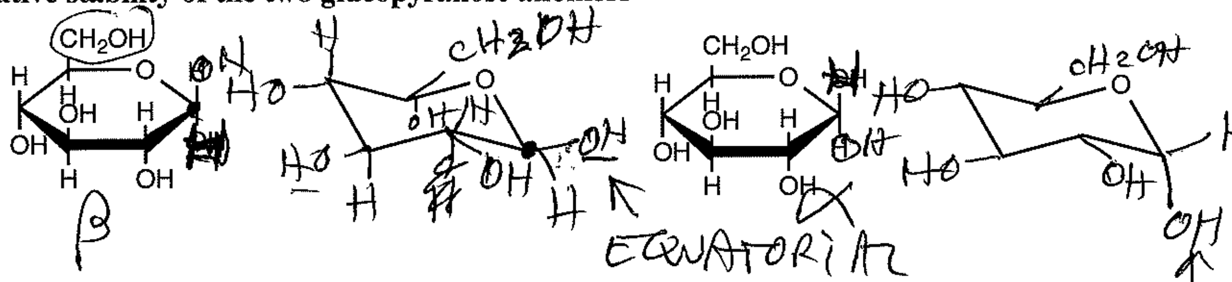
- *the two anomers of glucose can be separated and purified*
- *the β-anomer has [α] = +18.7°, the α-anomer has [α] = +112.2°*
- *no matter which isomer is started with, however, upon sitting in aqueous solution the final optical rotation from the polarimeter = +52.6° which is somewhere in between the 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*



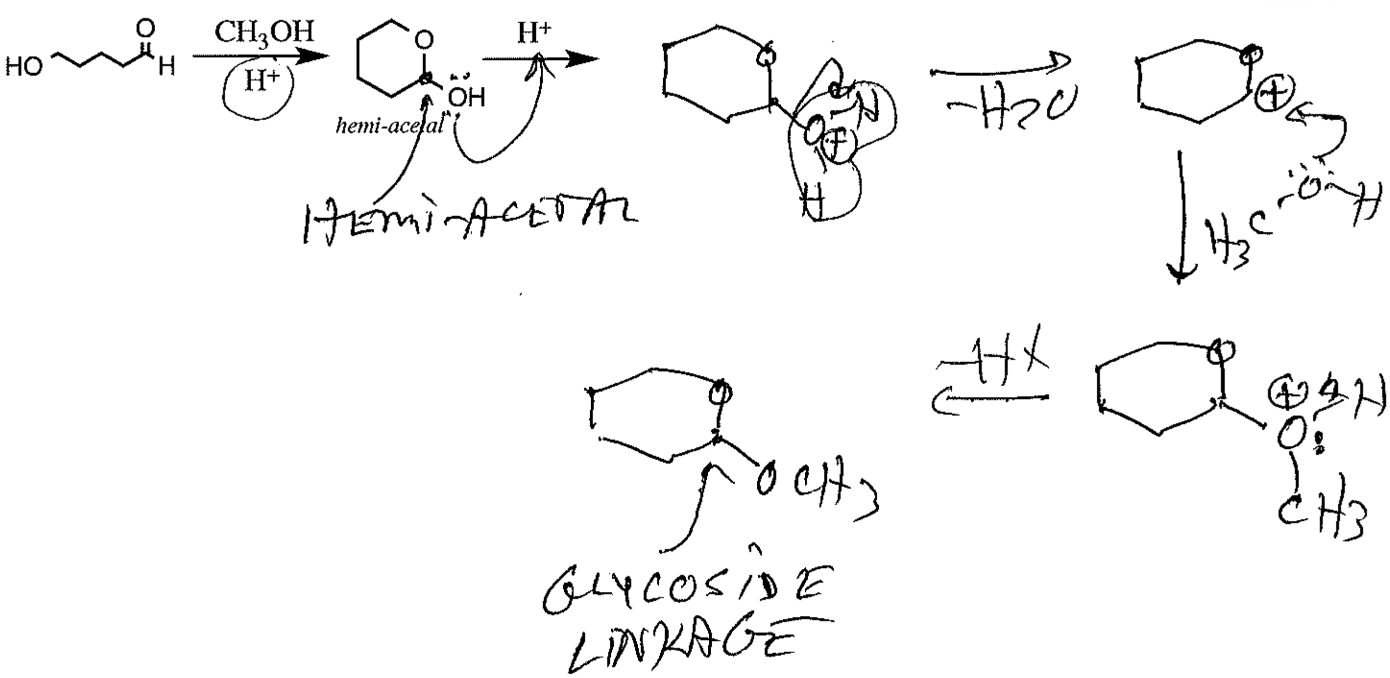
[ANOMERS "DIASTEREOMERS" ALSO "EPIMERS"]

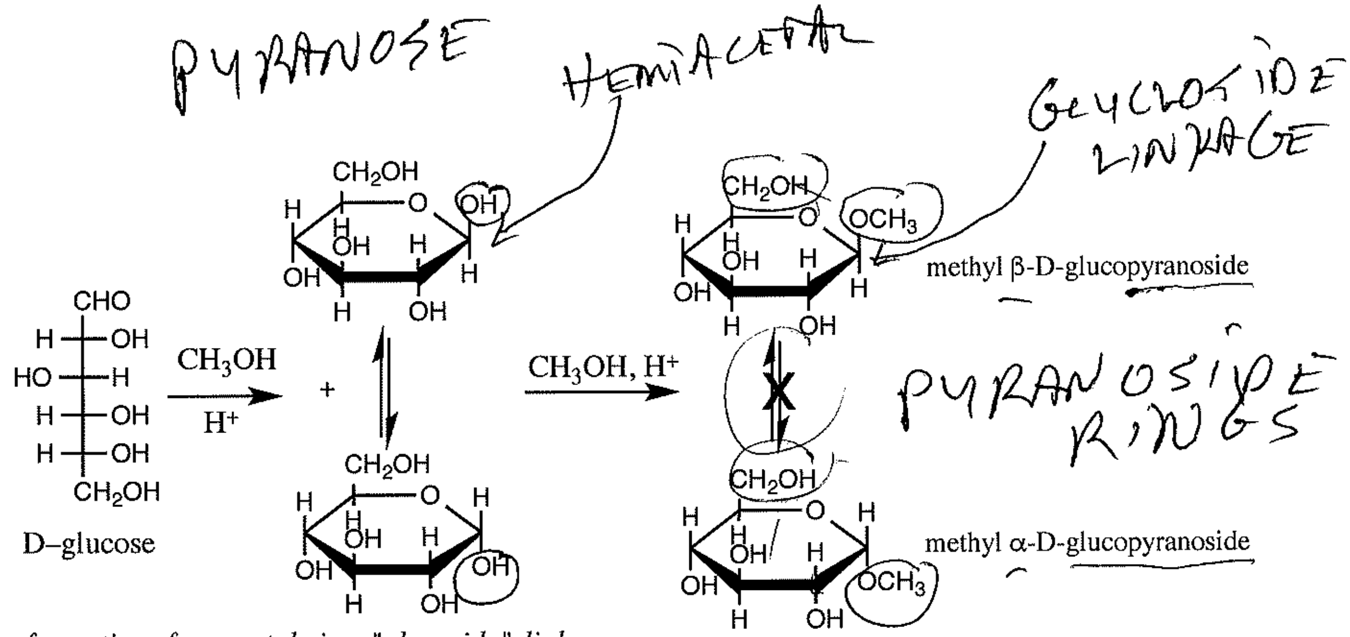
- *the interconversion of one anomer with the other in this way is known as "mutarotation"*

Relative stability of the two glucopyranose anomers



Glycoside formation

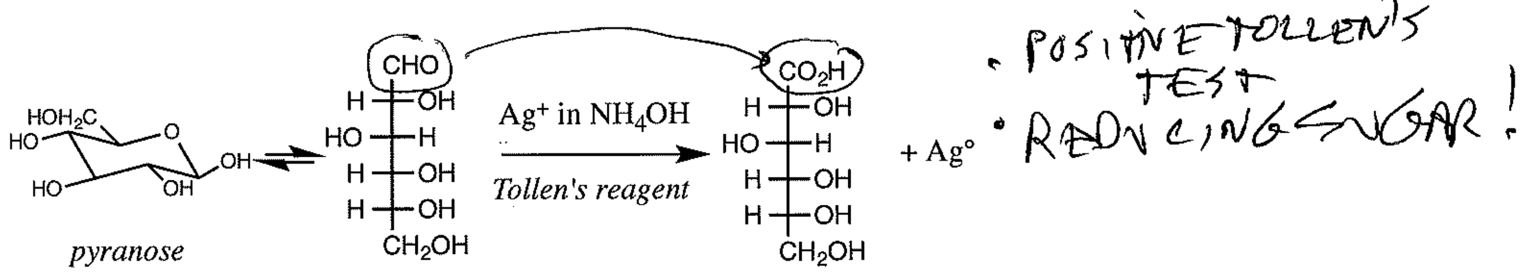


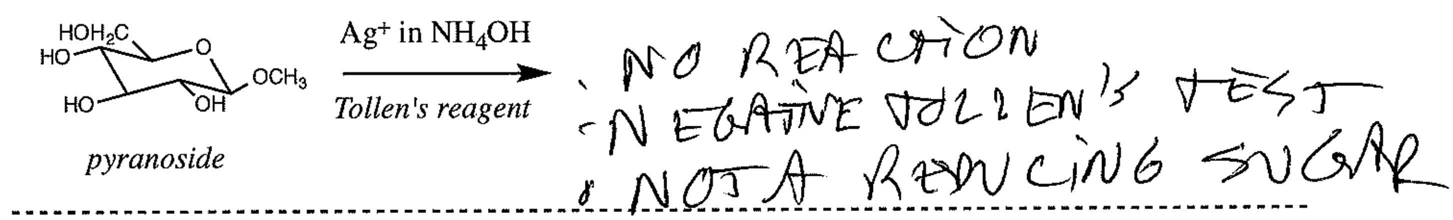


- *formation of an acetal via a "glycoside" linkage*
- *when formed from a sugar molecule it is called a "pyranoside" since it comes from glucopyranose*
- *in the absence of an acid catalyst, the anomeric carbon of pyranosides is locked in place*
- *pyranosides will not undergo mutarotation under neutral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

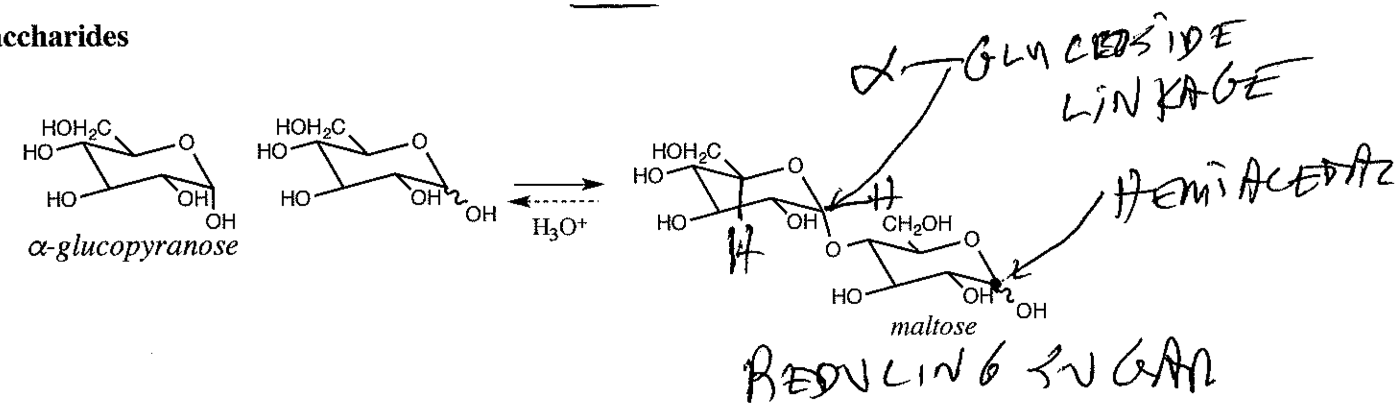
Problems: 6

Reducing sugars: Distinguishing between pyranose and pyranoside molecules.

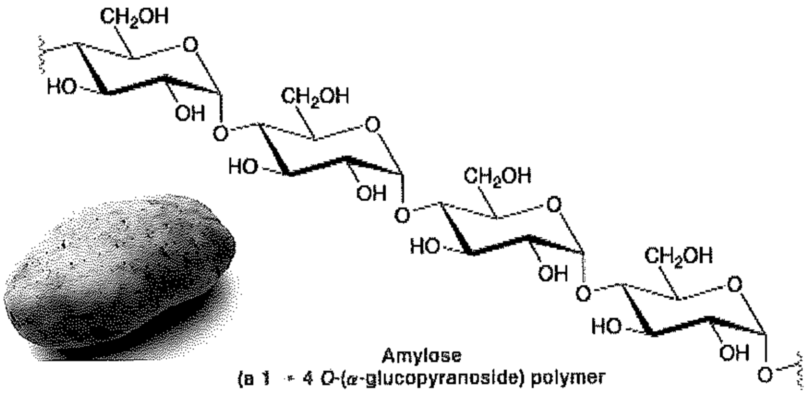




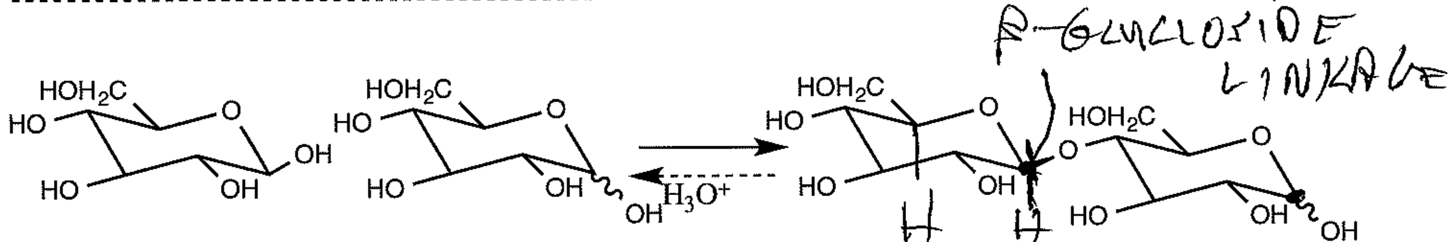
Disaccharides



- *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 mutatorate*



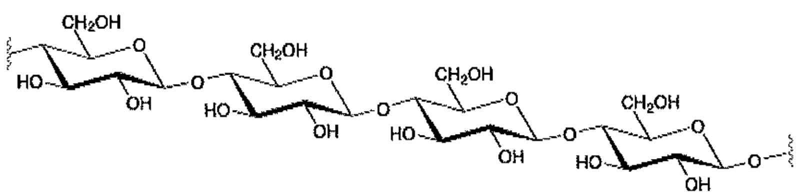
- *amylose is a polysaccharide made up of thousands of repeating glucose units*
- *all of the units are connected by the α-glycoside link*
- *amylose is a major consituent of starches in foodthat humans rely upon for food/energy*
- *more complex branched polymers (glycogen) are formedby the body as a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



β-glucopyranose

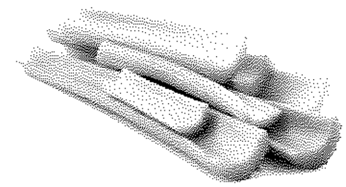
cellobiose

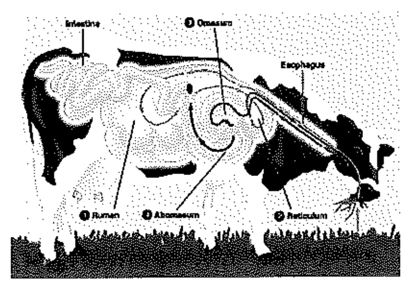
- *cellobiose is also a disaccharide and a complex carbohydrate (can be hydrolyzed)*
- *in cellobiose the β-gylycoside linkage is retained between the two sugars and is fixed*
- *the hemi-acetal linkage is still able to mutatorate*



Cellulose
(a 1 → 4 O-(β-glucopyranoside) polymer

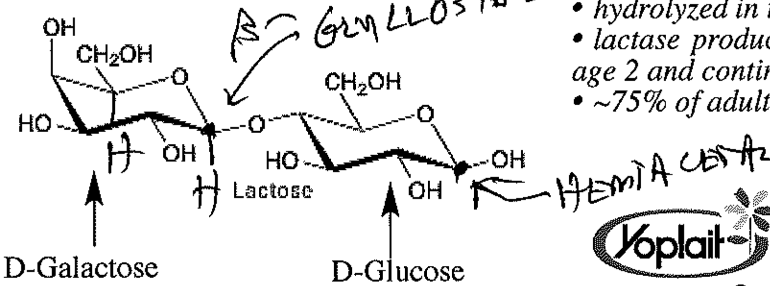
- *cellulose is a polysaccharide made of ~7,000 units on average of glucose*
- *all of the units are connected by the β-glycoside link*





- *humans have enzymes specific forhydrolysis of the α-glycoside link and can therefore hydrolyze starches like amylose to release the glucose forenergy*
- *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-glycosidee link but their stomachs contain microorganisms that DO produce the required enzymes so that cows are able to digest cellulose (e.g., grasses)*

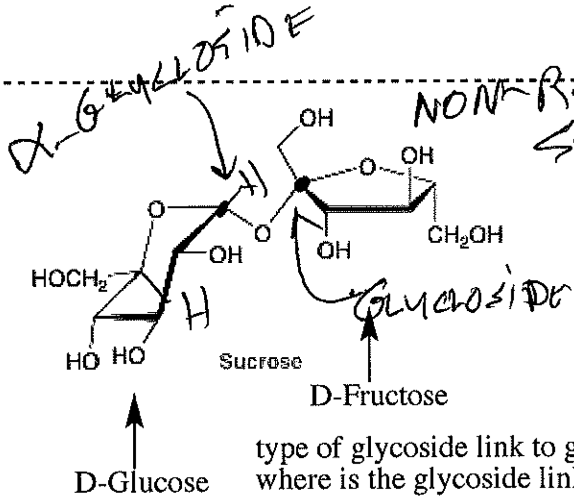
Some other interesting polysaccharides...



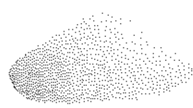
- *hydrolyzed in the body by an enzyme called lactase*
- *lactase production begins to decline for children past age 2 and continues*
- *~75% of adults have lactose intolerance*

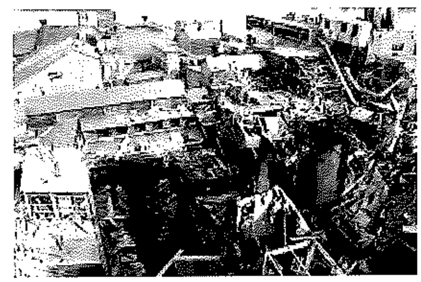
type of glycoside link? β

Yoplait Lactose Free

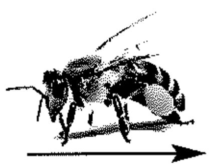


type of glycoside link to glucose? α
where is the glycoside link for fructose?

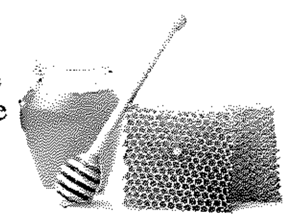




2008 Georgia sugar refinery explosion



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

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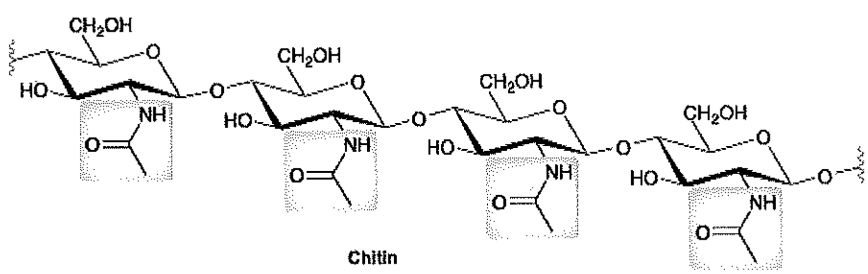

- *derivatized amino sugar*
- *similar structure to cellulose*
- *NH bonds allow for hydrogen bonding which increases the strength of strands*
- *main constituent of insect exoskeletons*