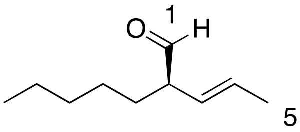
CHEM 261 Notes **Dec 8, 2017**

REVIEW:

An example of naming aldehydes is given with the below structure:



(2R,3E)-2-pentylpent-3-en-1-al

Find the parent name of the longest, most functionalized chain. In this case it is 5 carbons long and therefore is a pentane.

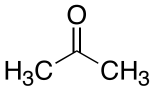
There is a trans double bond present in the molecule at position 3. You then drop the –*ane* ending, replacing it with *–ene* to give pent-3-ene.

Since the molecule is an aldehyde, you then drop the -*e* ending, replacing it with *–al* for the name to become pent-3-en-1-al.

There is also a pentyl group at position 2, making the molecule 2-pentylpent-3-en-1-al. There is also stereochemistry to take into account. The double bond is in the trans geometry and the aldehyde group is in the R configuration. Putting the overall name together gives (2R,3E)-2-pentylpent-3-en-1-al.

KETONE Nomenclature

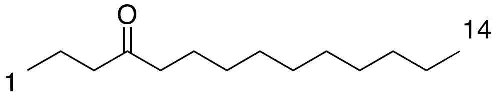
Ketones are named by substituting the *–e* ending of the parent alkane and replacing it with *–one*. The numbering of the hydrocarbon starts from the end of the chain that gives the carbonyl group the lowest number. Other substituents are named using prefixes and numbered to indicate their position relative to the start of the chain. A common name for the simplest ketone (acetone) is given below along with its systematic name.



acetone

or 2-propanone *or* propan-2-one

An example of naming ketones is given with the structure below:

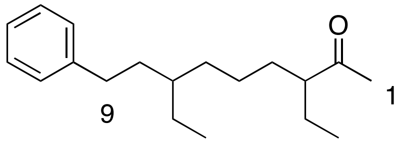


4-tetradecanone

or tetradecan-4-one

The first step in naming this compound is to find the parent name of the longest chain, which in this case is 14 and therefore is a tetradecane. When numbering this compound, you start from the left hand side to give the carbonyl the lowest number. You then drop the *–e* ending, replacing it with *–one* to give 4-tetradecanone.

The below structure is a sex pheromone from the crocodile.



3,7-diethyl-9-phenyl-2-nonanone

The first step in naming this structure is to identify the longest chain, which is 9 and therefore is a nonane.

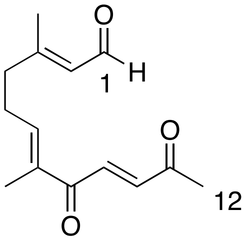
Since the carbonyl group is at the 2 position, you then drop the *–e* ending, replacing it with *–one* to give 2-nonanone.

At the 3 and 7 positions are ethyl groups, which are written as prefixes to give 3,7-diethyl-2-nonanone.

Also present is a phenyl group at the 9 position, to give the final name as 3,7-diethyl-9-phenyl-2-nonanone.

In this molecule there are also two stereogenic centers at the 3 and 7 positions but no information is given on the configuration of these centers. There are four possible stereoisomers for this company, but only one is likely to be biologically active.

Another naming example involves gyrinal (shown below) from the water boatman beetle (*Corixa* species), which is an anti-microbial agent and is toxic to fish and other predators.



Gyrinal *or*
3,7-dimethyl-8,11-dioxo-2E,6E,9E-dodecantrienal

The longest chain is 12 carbons and therefore a dodecane. This molecule is an aldehyde giving the parent name dodecanal.

Gyrinal has three trans double bonds at the 2,6 and 9 positions giving 2E,6E,9E-dodecatrienal.

Methyl groups are present at the 3 and 7 positions to give 3,7-dimethyl-2E,6E,9E-dodecatrienal.

Also present in gyrinal are two other carbonyl groups. Since this compound is being named as an aldehyde (which takes priority over ketones), the two carbonyl groups are named as oxo groups. Since the carbonyl groups are at the 8 and 11 positions the final name for gyrinal is 3,7-dimethyl-8,11-dioxo-2E,6E,9E-dodecantrienal.

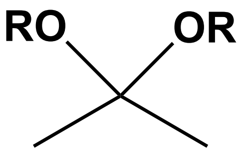
Physical Properties of Carbonyl Containing compounds

Carbonyl containing compounds are more polar than alkanes but less polar than alcohols. Generally good solvents for organic compounds.
Aldehydes are generally insoluble in water (except small compounds such as acetone, formaldehyde, acetaldehyde, etc). They have dipoles and are hydrogen bond acceptors, but not hydrogen bond donors.

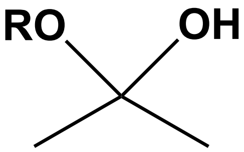
Reactions of Carbohydrates

Names to know:

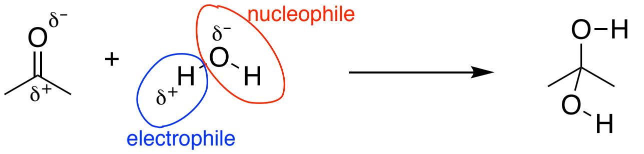
acetal



hemiacetal

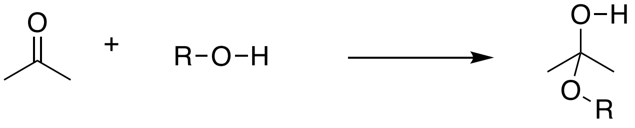


Hydration



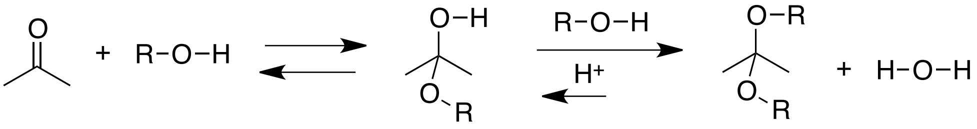
(a hydrate)

Hemiacetal Formation



(a hemiacetal)

Acetal Formation



(an acetal)

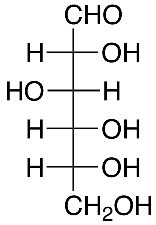
CARBOHYDRATES

- sugars, saccharides

A familiar equation:

$$6\ CO_2 + 6\ H_2O \xrightarrow[\text{photosynthesis}]{hv} C_6H_{12}O_6 + 6\ O_2$$

Approximately 0.02% of the sun's energy is used on this planet for photosynthesis in which organisms convert carbon dioxide (CO_2) and water (H_2O) to D-glucose ($C_6H_{12}O_6$) and oxygen (O_2). About 4 x 10^{11} metric tons of carbon dioxide are converted to glucose annually by plants, and glucose (as a subunit) is the most abundant organic compound on the planet. Learn the structure of D-glucose shown below.



Glucose (also called dextrose)

Carbohydrates occur in every living organism. The sugar in starch in food and the cellulose in wood, paper, and cotton, are carbohydrates. Modified carbohydrates form part of the coating in living cells, other carbohydrates are found in the DNA that carries genetic information, and still others are used in medicine.

The term carbohydrate is used to refer to a broad class of polyhydroxylated aldehydes and ketones commonly called sugars. Carbohydrates are also known as saccharides.

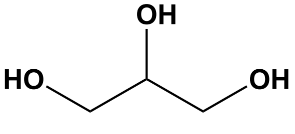
Nomenclature

General formula of sugars: $C_NH_{2N}O_N$ *(approx.)*

The number of carbons is indicated as follows:

3 carbon sugar – triose
4 carbon sugar – tetrose
5 carbon sugar – pentose
6 carbon sugar – hexose

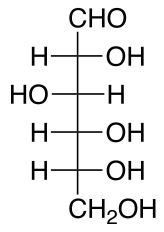
Remember glycerol? It is a triose.



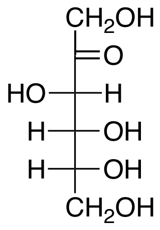
The location of the carbonyl group is indicated by the prefix:

aldo – aldehyde (at the end of the carbon chain)
keto – ketone (in the middle of the chain)

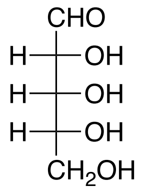
Carbohydrates can further be classified as either aldoses or ketoses. The –ose suffix is used to identify the carbohydrate, and the aldo- and keto- prefixes identify the nature of the carbonyl group. For example, glucose is an aldohexose, a six carbon aldehyde sugar; fructose is a ketohexose, a six carbon keto sugar; and ribose is an aldopentose, a five carbon aldehyde sugar. The most commonly occurring sugars are either aldopentoses or aldohexoses.



Glucose
(an aldohexose)



Fructose
(a ketohexose)



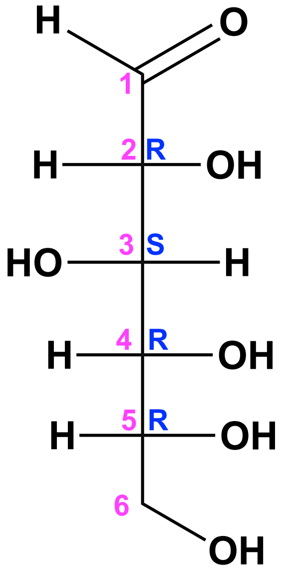
Ribose
(an aldopentose)

Additionally, an allocation of D or L is given to indicate the stereochemistry of the highest numbered (last) stereocentre.

D sugar – highest numbered stereocentre in *R* configuration.
L sugar – highest numbered stereocentre in *S* configuration.

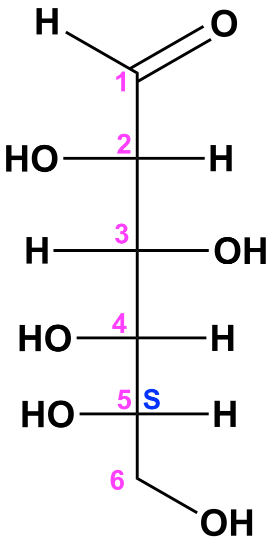
Example: **D-Glucose**

**know this structure*



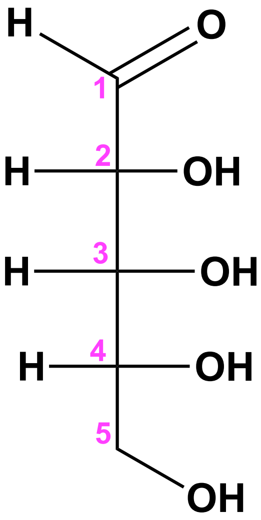
Based on the above nomenclature, D-glucose is an aldohexose (aldehyde, 6 carbons)
The above structure is labelled as "D" because the R configuration occurs at carbon 5 *(note that carbon 6 is not a stereocentre).*

Example: **L-Glucose**



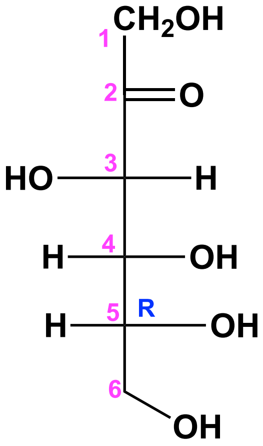
S configuration occurs at the highest numbered stereocentre (again at carbon 5), this is an L sugar. The sugar contains an aldehyde therefore this is an aldohexose. Turns out this is called L-glucose.

Example: **D-Ribose**



An aldopentose (aldehyde, 5 carbons long). At the highest numbered stereocentre (carbon 4) the stereochemistry is R. The name of this is D-ribose (found in RNA! – deoxyribose is in DNA)

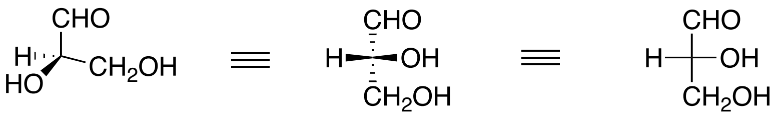
Example: **D-fructose**



Carbonyl is internal, therefore this is a ketone, and there are 6 carbons. This is a ketohexose. The R stereochemistry at carbon 5 designates this as a D sugar.

Configuration of Sugars: Fischer Projections

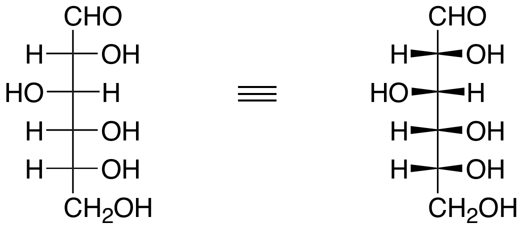
Fischer projections depict the stereogenic centers on a flat page surface. A Fischer projection is represented by two crossed lines, in which the horizontal line represents bonds coming out of the page, and the vertical lines represent bonds going into the page. By convention, the carbonyl is placed at or near the top of the Fischer projection. Shown below is the Fischer projection of (R)-glyceraldehyde.



(R)-glyceraldehyde

Fischer projection of (R)-glyceraldehyde

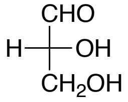
Another example is the Fischer projection of glucose. Glucose has four stereogenic centers stacked on top of one another, with the carbonyl placed near the top.



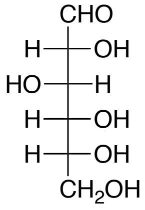
Fischer projection of Glucose

D, L Configuration of Sugars

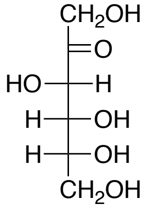
Glyceraldehyde has only one stereogenic center and therefore has two enantiomers (mirror image) forms. A D-sugar is defined as one that has R configuration at the stereogenic center with the highest number. L-sugars are those that have S-configuration at the stereogenic center with the highest number.



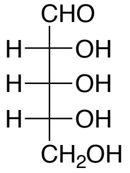
D-Glyceraldehyde



D-Glucose



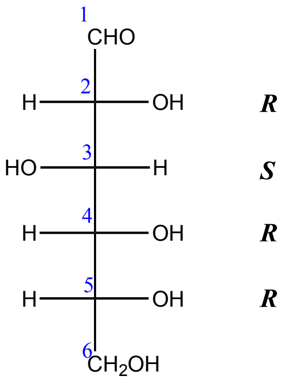
D-Fructose



D-Ribose

For example:

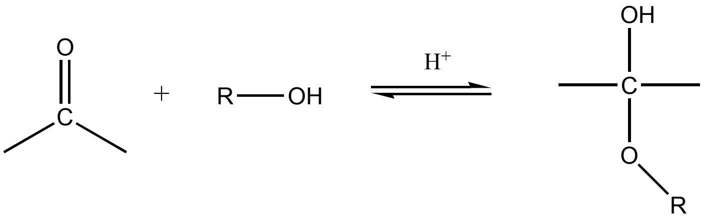
D-glucose has the structure shown below (you must know its structure). It is an aldohexose ("aldo" since it contains aldehyde functionality and "hexose" since it is a six carbon sugar, numbered on structure).



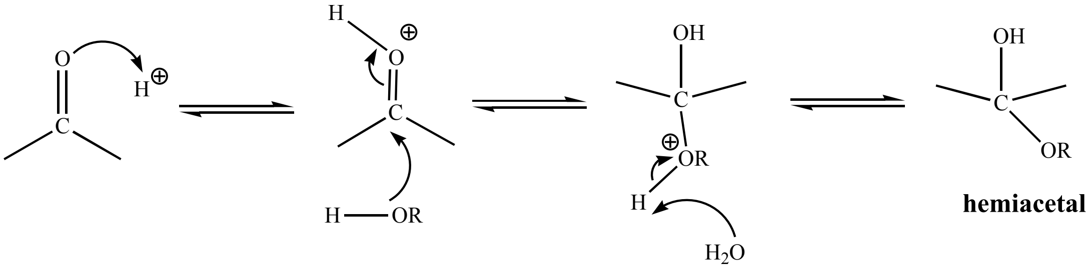
It contains 4 stereogenic carbons (C2, C3, C4 and C5). The highest numbered stereogenic center tells you whether it is a D (if it is R configuration at that stereogenic center) or an L (if it's S configuration at that stereogenic center) sugar. For glucose, the highest numbered stereogenic center is C5. It has an R configuration. By convention, it is designated as a "D" sugar. Configurations of other stereogenic centers are also shown next to the structure.

Carbohydrates- Hemiacetal Formation

You know from previous lectures that carbonyl compounds react with all kinds of nucleophiles. Hydration and hemiacetal formation are typical examples.



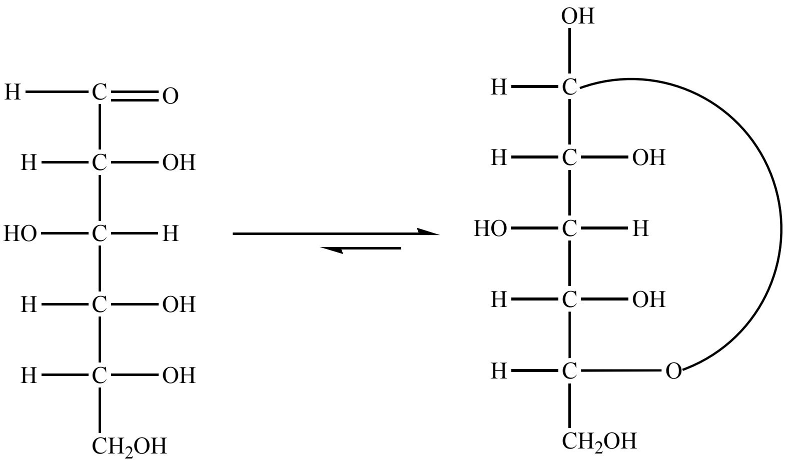
Mechanism (this should be a review from above):



In nature, formations of 5- and 6-membered rings are favored, and if possible, a molecule will form such a ring when it can.

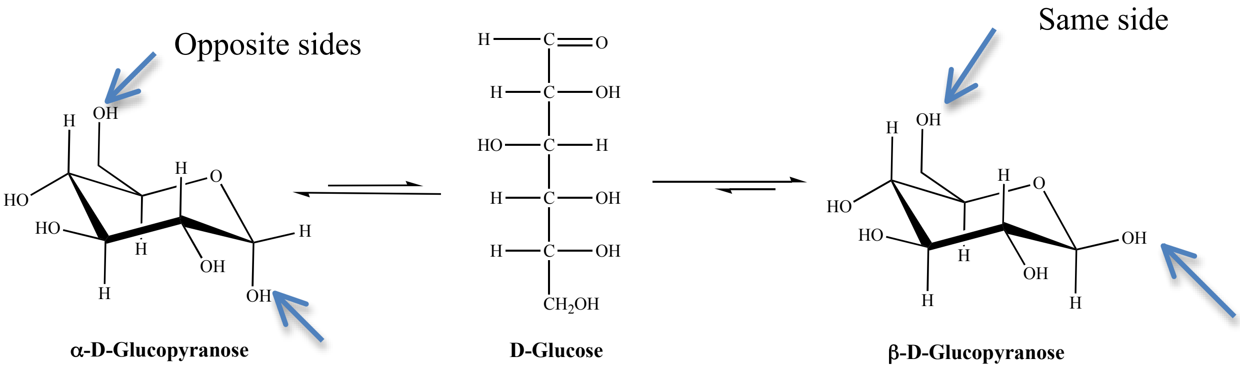
In sugars, the cyclic forms with 5-membered rings are called furanoses, and 6-member rings are called pyranoses. For most aldohexoses, the five membered furanose and six-membered pyranose can be formed. However, with D-glucose the six-membered pyranose usually predominates.

For example, glucose can react internally to form a hemiacetal (an intramolecular cyclization).



D-Glucose **hemiacetal**

The molecule exists predominantly in the cyclic form; however, it is still in equilibrium with a small amount of the acyclic form. The cyclic 6-membered rings exist in energy minimum chair forms (shown in figure below). This is also depicted in the handouts given.



Opposite sides

Same side

α-D-Glucopyranose **D-Glucose** **β-D-Glucopyranose**

The cyclic forms are indicated in the name by combining the simple name of the sugar with “furanose” or “pyranose” to indicate the size of the ring. Therefore, glucose in its 6-membered ring form is called glucopyranose.

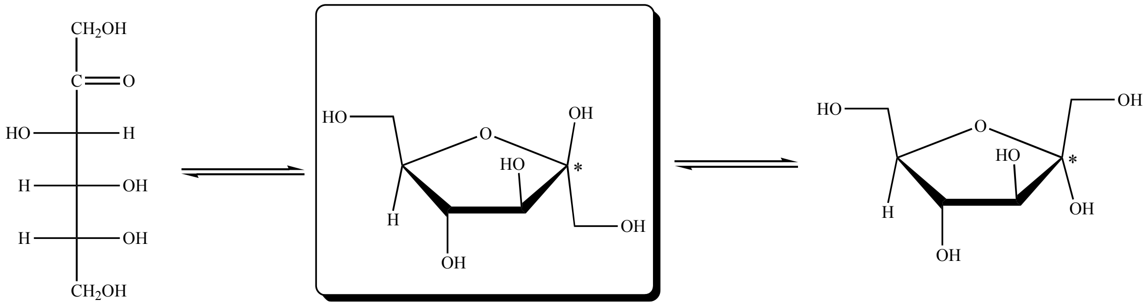
The intramolecular cyclization reaction creates a new stereogenic carbon that can be either R or S configuration, with OH group in equatorial or axial position. The terms ***α*** and ***β*** refer to position of OH at C1 relative to CH_2OH group of C6.

When the OH group attached to C1 is down relative to the CH_2OH group that is up (they are *trans* to each other), The configuration is ***α***. When they are on the same side (both are up), the configuration is ***β***.

The two stereoisomers are interconverting structural isomers called **anomers**. They differ only in stereochemistry at C1 position, which is known as the **anomeric carbon**.

The ***α*** and ***β*** anomers can equilibrate through the linear form.

Formation of a 5-membered ring is possible for D-glucose, but it exists predominantly as the 6-membered ring. Fructose, on the other hand, exists predominantly as 5-membered ring.



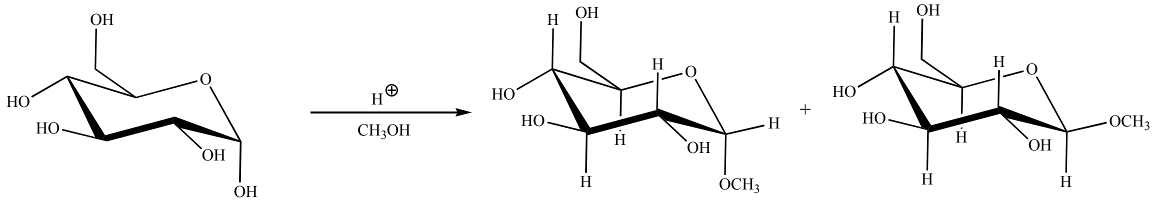
D-Fructose **D-β-Fructofuranose** **D-α-Fructofuranose**

D-fructose is a ketohexose ("keto" since it contains ketone). Its cyclized form, D-fructofuranose is a hemiacetal since the anomeric carbon (marked by asterisk) has a free OH group and a OR group attached. An easy way to find the anomeric carbon is to find a carbon with 2 oxygen atoms attached directly.

Is the fructofuranose highlighted in box an ***α*** or ***β*** *sugar?*

Answer: It is ***β***. The rule is to find the CH_2OH group (not on the anomeric carbon) and the OH substituent of the anomeric carbon, and see of they are on the same or opposite side. Since the OH group and the CH_2OH group are on the **same** side as each other, the ring is ***β***.

Acetal formation

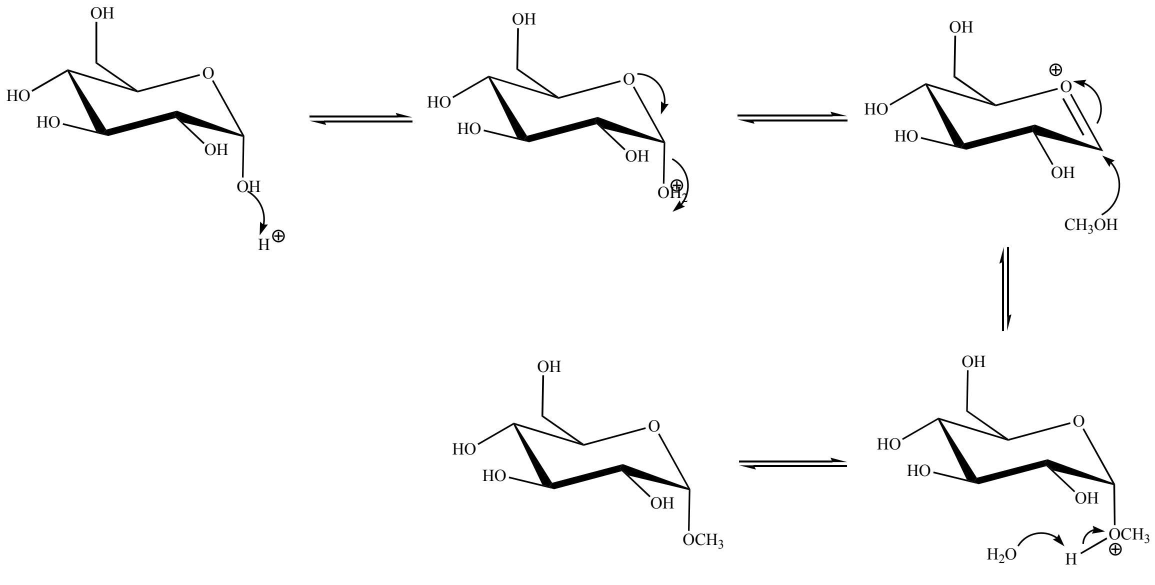


α-D-Glucopyranose **α-D-Glucopyranoside (favored)** **β-D-Glucopyranoside (minor)**

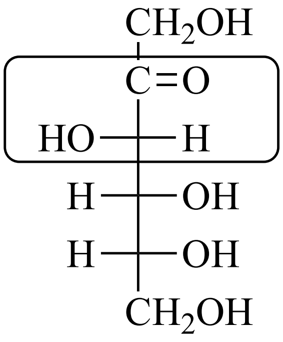
Treatment with dilute acid and alcohol converts only the OH at the anomeric position into an acetal called a glycoside. Specific glycosides are named by replacing the "ose" of the simple sugar's name with "oside". When glucopyranose is reacted, its product is called glucopyranoside.

The ***α*** anomer with the methoxy group in axial position is favored due to the anomeric effect (details about the anomeric effect is beyond the scope of this class).

Mechanism:



Example:



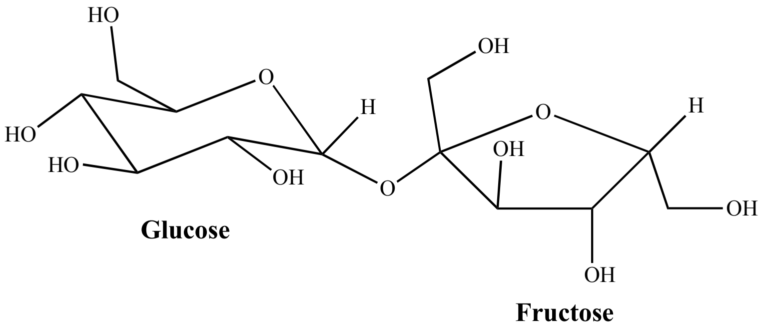
D-Fructose

Fructose is the sweetest sugar of all (sweetness index 180)

Is it a reducing or non-reducing sugar? **NOT DISCUSSED - Extra Material – Not on Exam**

It is reducing since it contains a α-hydroxyl ketone group in open form and the cyclized form is a hemiacetal at anomeric position.

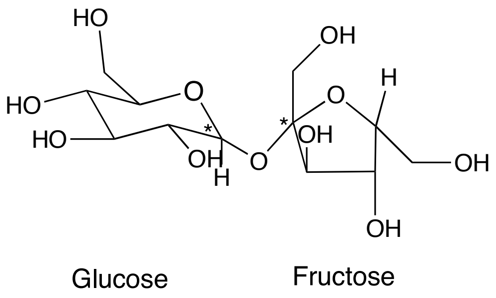
Example: a disaccharide



The structure shown is sucrose (table sugar). It is made up of a glucose and a fructose molecule (sweetness index 100)

Does this molecule have anomeric carbon?
Yes.

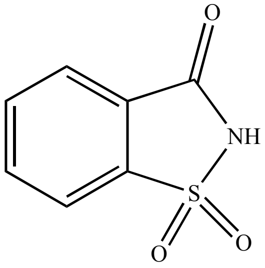
Identify the anomeric carbon. → They are highlighted with asterisks.



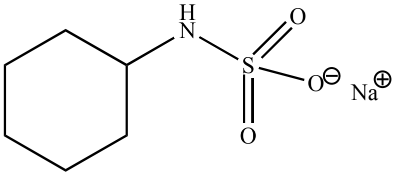
Are they acetals or hemiacetals?
They are acetals. In both cases, the carbon has two OR group attached. There is no free OH group.

Is this sugar reducing or non-reducing?
Non-reducing since the anomeric carbons has acetal groups.

Some artificial sweeteners are shown below: **NOT DISCUSSED - Extra Material – Not on Exam**

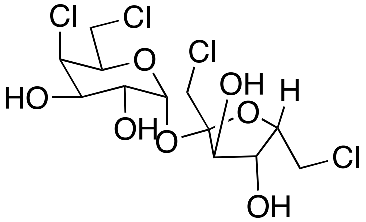


saccharin



sodium cyclamate

Although a small amount tastes a lot sweeter than sugars, these are suggested to be carcinogenic in very large doses.

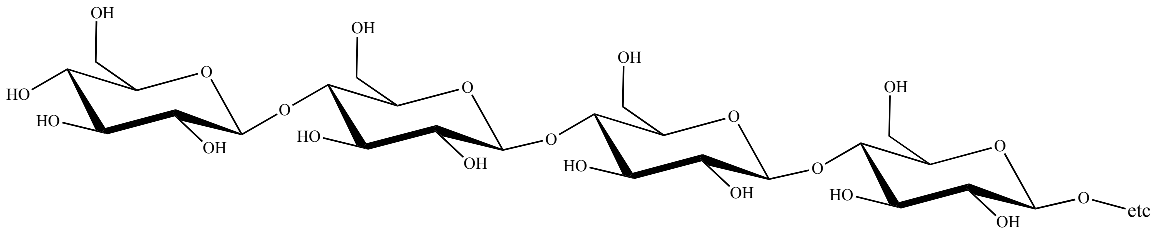


Splenda (sucralose)

Polysaccharides = polymers of sugars NOT DISCUSSED – Extra Material - Except Cellulose

Disaccharides = 2 sugar linked
Trisaccharides = 3 sugar linked
Tetrasaccharides = 4 sugar linked
Oligosaccharides = Polysaccharides

Example: Cellulose; β-(1,4) linked D-glucose polymer

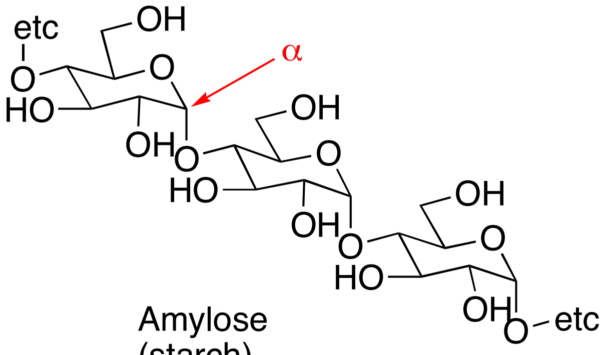


Cellulose is a polymer of simple repeating monosaccharide units (D-glucose).

Polysaccharides NOT DISCUSSED – Extra Material – Not on Exam

Many mammals cannot digest cellulose directly. Ruminants such as cows or goats have bacteria in their stomach to break it down to its simpler unit. The bacteria have a cellulose hydrolysis enzyme called cellulase which we do not have. Humans cannot metabolize β linkages.

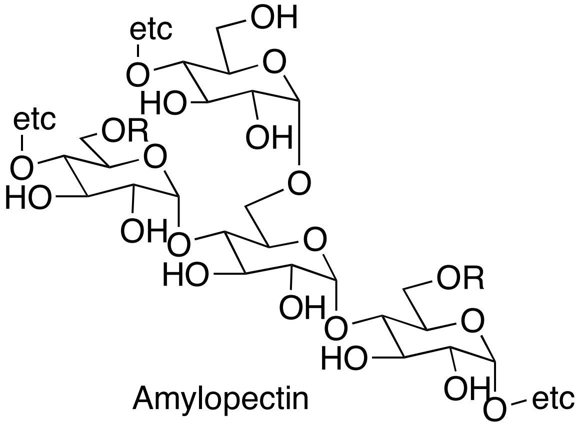
Example: Amylose; α-(1,4) linked D-glucose polymer



Amylose
(starch)

In contrast, amylose is a polysaccharide with α linkage between each monosaccharide units. Humans can digest amylose. Starch is comprised of approximately 20% amylose.

Example: Amylopectin



Amylopectin

Amylopectin is the other component in starch (~ 80%), which is similar to glycogen.