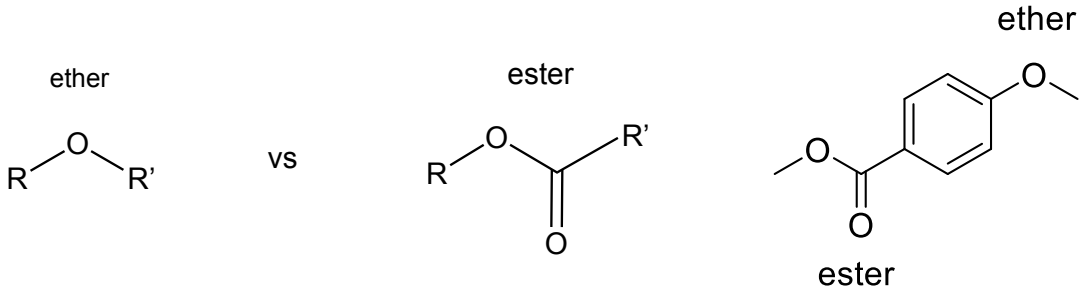
Ethers

- Unreactive to base
- Not miscible with H_2O

Recall:

Ethers are unreactive except in strongly acidic conditions (e.g. H_2SO_4) to undergo Substitution reactions (SN) or elimination reactions (E)

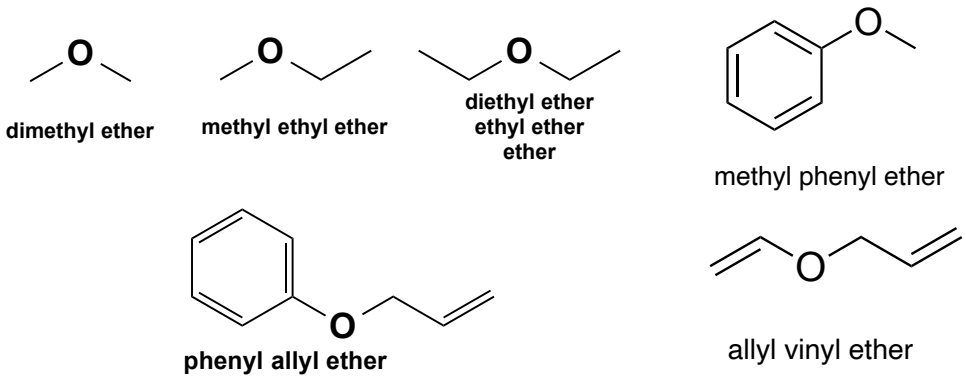
The difference between ester and ethers



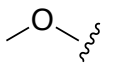
Nomenclature:

- In the absence of other functional groups, name the two alkyl groups attached to the O and add the word "ether"

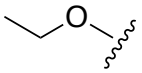
Examples:



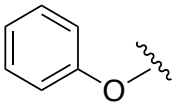
In the presence of other functional groups, name ethers as a group, drop "yl" and add "oxy" as seen below:



methoxy

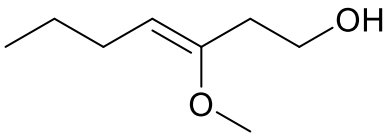


ethoxy



phenoxy

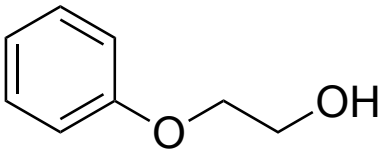
Example 1:



(Z)-3-methoxyhept-3-en-1-ol

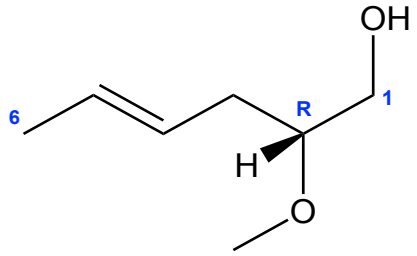
- Alcohol (-OH) takes priority over other functional groups
- Number the longest C chain so as to give the OH group the lowest number possible

Example 2:

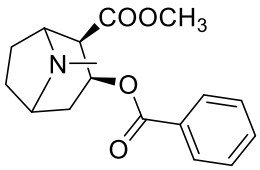


2-phenoxyethan-1-ol
or
2-phenoxy-1-ethanol

Example 3:



(E)-R-2-methoxyhex-4-en-1-ol



Cocaine (a ester, not ether)

Carbohydrates ($C_NH_{2N}O_N$)

sugars, saccharides

A familiar equation:

$$6\,CO_2 + 6\,H_2O \xrightarrow[photosynthesis]{h\nu} C_6H_{12}O_6 + 6\,O_2$$

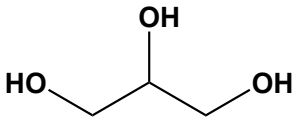
- about 4 x 10^{11} metric tons of carbon dioxide is converted into glucose by plants
- the process of photosynthesis only uses 0.02% of the suns total energy on Earth
- the sugar produced is known as D-glucose, shown below in a Fischer Projection

Nomenclature of Sugars

General formula of sugars: $C_NH_{2N}O_N$ *(approx.)*
The number of carbons is indicated as follows:

3 carbon sugar (C_3) – triose
4 carbon sugar (C_4) – tetrose
5 carbon sugar (C_5) – pentose
6 carbon sugar (C_6) – hexose

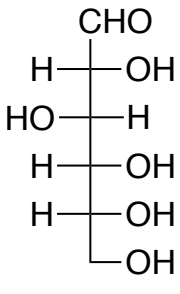
Example 1: Glycerol

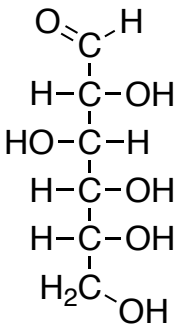


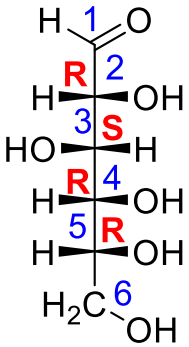
Triose

Example 2: D-Glucose

D-Glucose







D-Glucose is an Aldohexose

Aldo

Keto

The carbonyl group is indicated by the prefix:

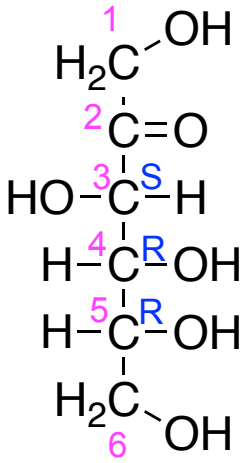
aldo – aldehyde
keto – ketone

Note: The sugar backbone is numbered such that the C=O is assigned the lowest number possible.

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 2: D-Fructose

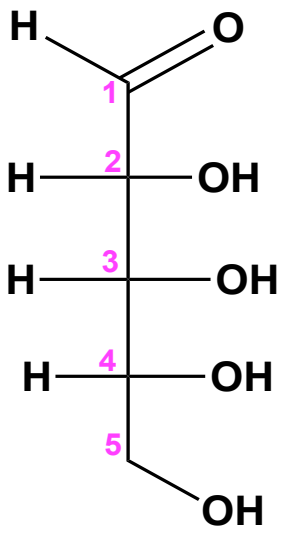


D-Fructose

Based on the above nomenclature, D-Fructose is a **ketohexose** (ketone, 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 3: D-Ribose



An aldopentose (aldehyde, 5 carbons long). At the highest numbered stereocentre (carbon 4) the stereochemistry is R.

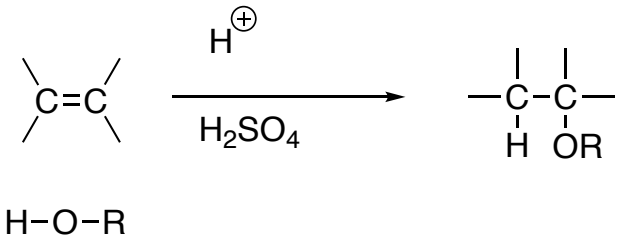
The name of this is D-ribose (found in RNA! – deoxyribose is in DNA)

These sugars can cyclize (form rings)

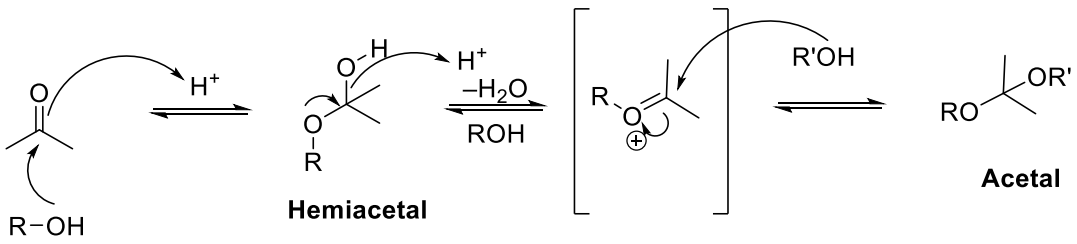
- 6-ring sugar is a pyranose
- 5-ring sugar is a furanose

Hemiacetal and Acetal Formation

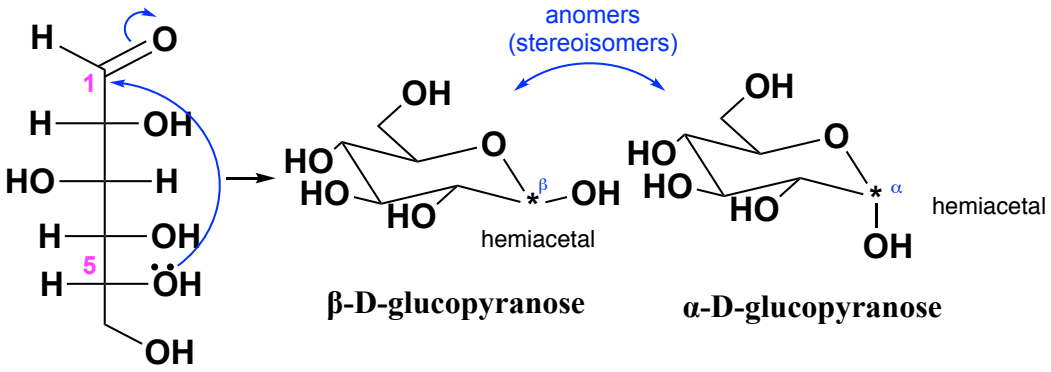
Recall addition reaction across a double bond (i.e., ether formation)



Similarly, addition reactions can be done on carbonyls (Ketones and Aldehydes) in the presence of an acid catalyst:

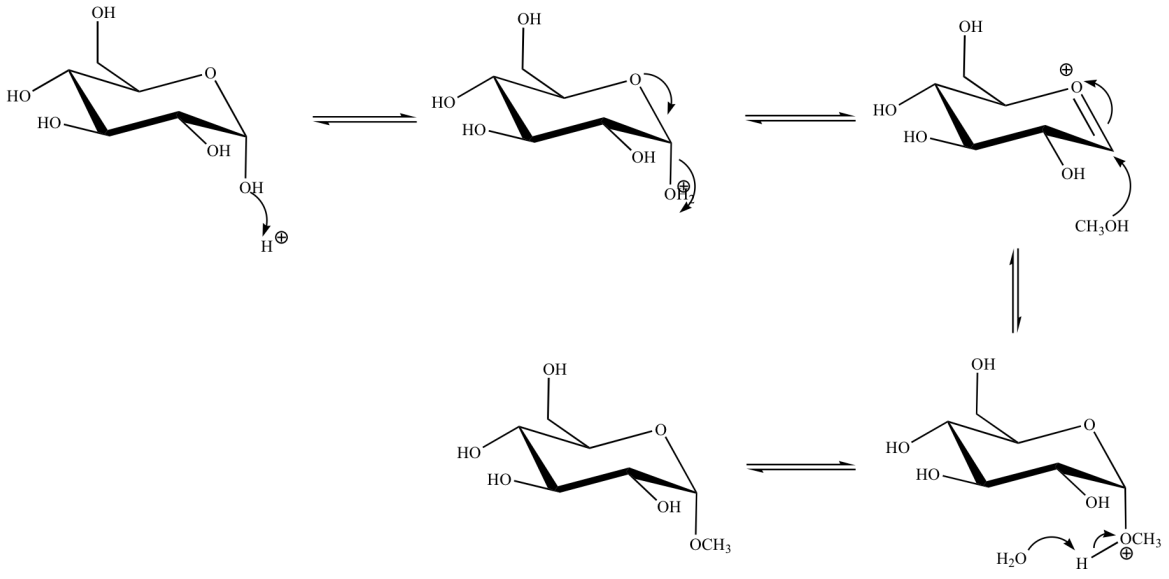


Example 4 - Glucose

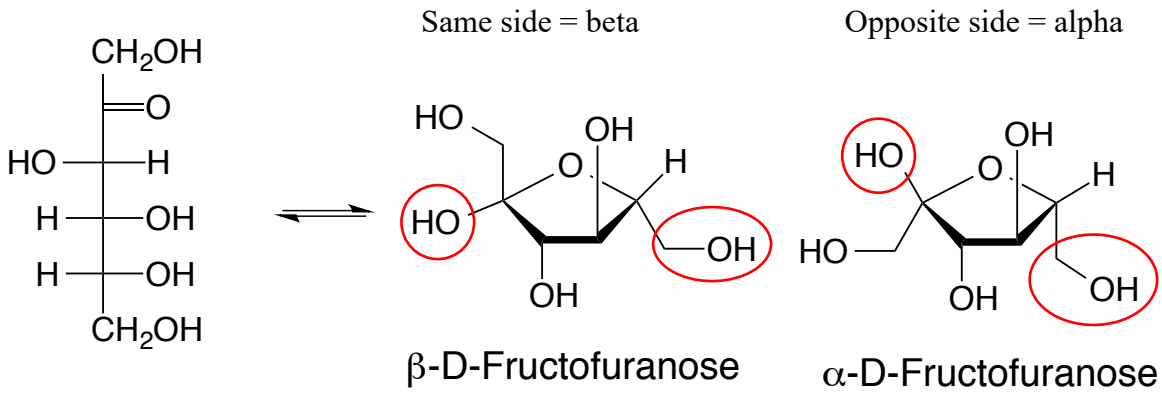


- This is a favored reaction. The sugar interconverts between the linear (or open) and ring form but the ring form (hemiacetal) is generally more favored.
- If OH at the anomeric carbon (C with 2 oxygens attached) is on same side of ring as CH_2OH then the configuration called **β (beta)** – if on opposite side it is **α (alpha)**
- For glucose, the alpha and beta anomer are present in the same amount. However, for other sugars, the alpha anomer is generally more favored.
- 6-Membered sugar rings are called pyranose
- 5-Membered sugar rings are called furanose

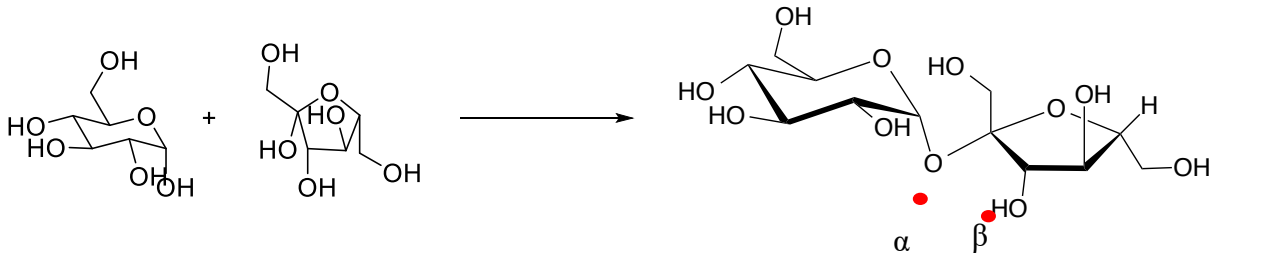
Example 4 - Glucose



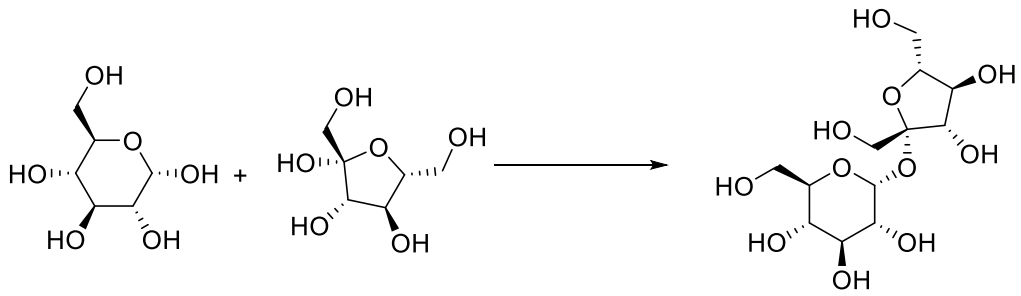
Example 5 - Fructose



Example 3 - Table Sugar (Sucrose):



α–D-Glucopyranosyl-β–D-Fructofuranoside



- Has 2 anomeric carbons
- Non-reducing sugar since it contains an acetal group and does not contain hemiacetals, aldehydes, or alpha-hydroxy ketone

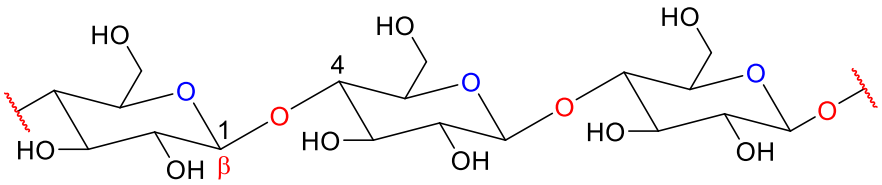
- Can be broken down by the body to glucose and fructose monomer

Monosaccharides – simple sugars such as glucose and fructose – can't be converted to smaller sugars by chemical reaction (i.e., hydrolysis)

Polymers of Sugars

- **Disaccharide:** sugars that are composed of 2 monosaccharide units
- **Trisaccharide:** sugars that are composed of 3 monosaccharide units
- **Tetrasaccharide:** sugars that are composed of 4 monosaccharide units
- **Oligosaccharides:** sugars that are composed of 3 to 10 monosaccharide units
- **Polysaccharides:** long chain of carbohydrates containing more than ten (> 10) monosaccharide monomers.

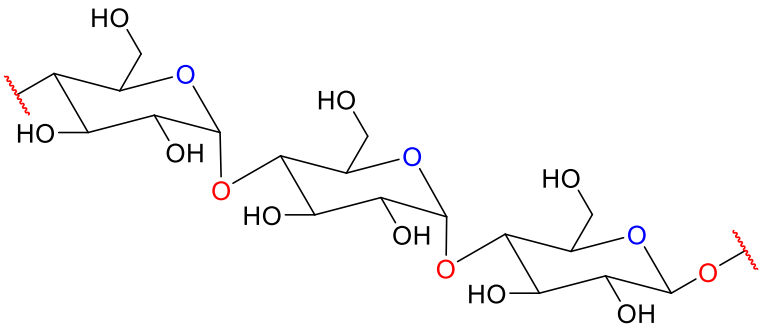
Cellulose



β-(1→4)-D-Glucopyranoside polymer (Cellulose)

- Cellulose is a polysaccharide composed of D-glucose monomers linked via **β-1,4 glycosidic linkages**.
- Cellulose is a main component of cotton and paper
- Cellulose is also a raw material for producing cellulose nitrate which is the major component of smokeless powder used as a propellant in ammunition of firearms and artillery.
- β-linkages cannot be digested by most mammals

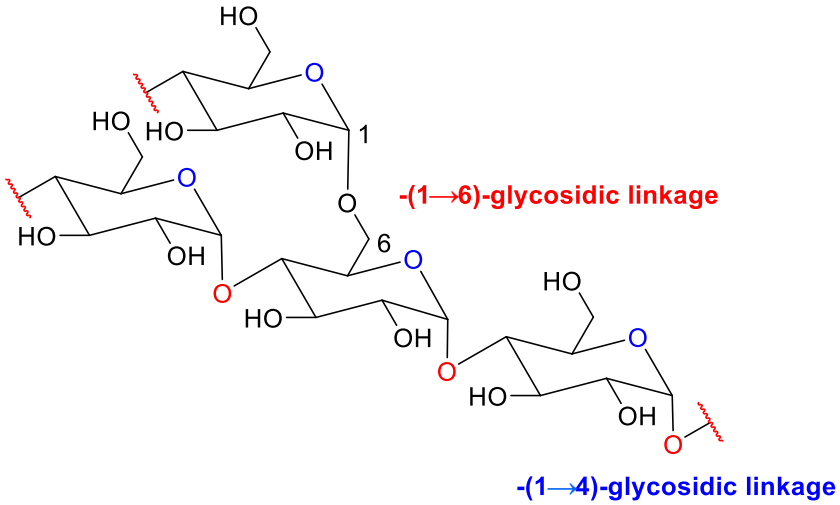
Starch (Amylose)



α-(1→4)-D-Glucopyranoside polymer (Amylose)

- Amylose (accounts for 20% of the weight of starch) is a polysaccharide composed of D-glucose units linked via α-1,4 glycosidic linkages

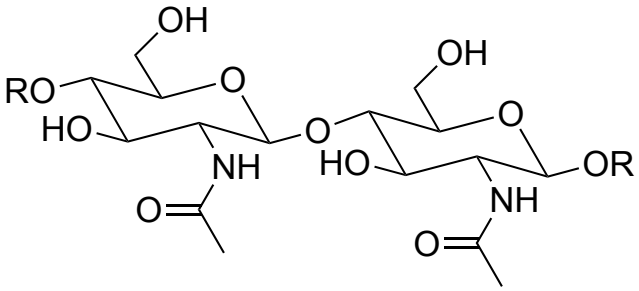
Starch (Amylopectin)



Amylopectin: α-(1→4) and α-(1→6) linked D-glucopyranoside polymer

- Amylopectin is the main component of starch (80% dry weight)
- Amylopectin is characterized by branching via α-(1→6)-glycosidic linkages in approximately every 25 glucose units along the main polymer chain.

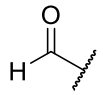
Chitin



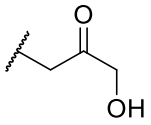
Other Examples and Information

Reducing Sugars

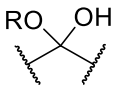
- Contains either an aldehyde, α-hydroxyketone, or a hemiacetal
- All aldoses are reducing sugars



Aldehyde



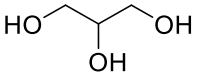
-Hydroxyketone



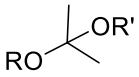
Hemiacetal

Non-reducing sugars

- Any sugars that do not contain any of the above functionality (i.e., glycerol) or an acetal group (i.e., sucrose)



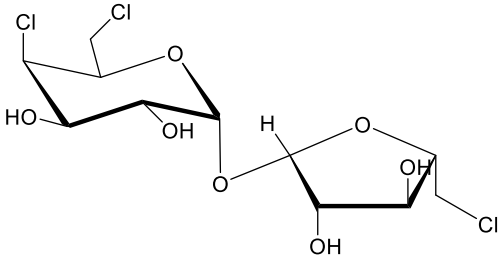
Glycerol
A Triose



Acetal

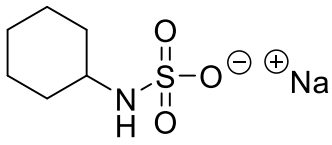
Artificial Sweeteners

Sucralose

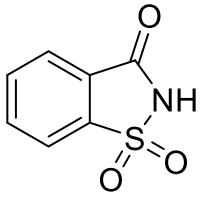


- Non-reducing sugar

Sodium Cyclamate



Saccharine



Aspartame