Polyols:

If more than one hydroxyl group is present, a prefix is added to the “ol” :

2 OH’s	diol (glycol)
3 OH’s	triol
4 OH’s	tetraol
5 OH’s	pentaol

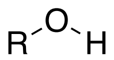
Physical Properties of Alcohols

- The hydroxyl group is a very polar group. This allows small alcohols (methanol, ethanol, propanols) to be miscible with water (if the number of C < 4) as they are good hydrogen bond donors *and* acceptors.
- Soluble in H_2O, as the #C increases, the solubility decreases.
- Alcohol densities are usually $\rho < 1.0$ g/cm^3.
- They have high boiling and melting points, again due to their hydrogen bonding capabilities.

Look at the following comparisons:

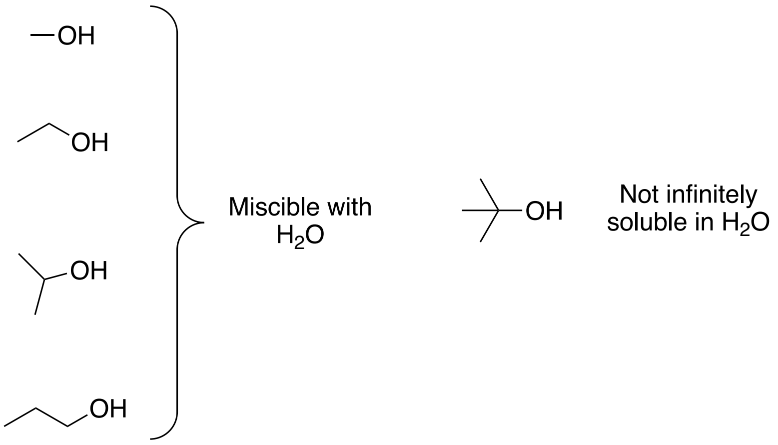
Name	Methanol	Ethane	Ethanol
Formula	CH_3OH	CH_3CH_3	CH_3CH_2OH
Molecular Weight (g/mol)	32	30	46
Boiling Point (° C)	65	-89	78.5
State (at room temp)	liquid	gas	liquid

Ethane has almost the same molecular weight as methanol. However, the boiling point is much lower than methanol. Methanol molecules like to stick together via H-bonding while ethane molecules interact with each other via hydrophobic interactions.



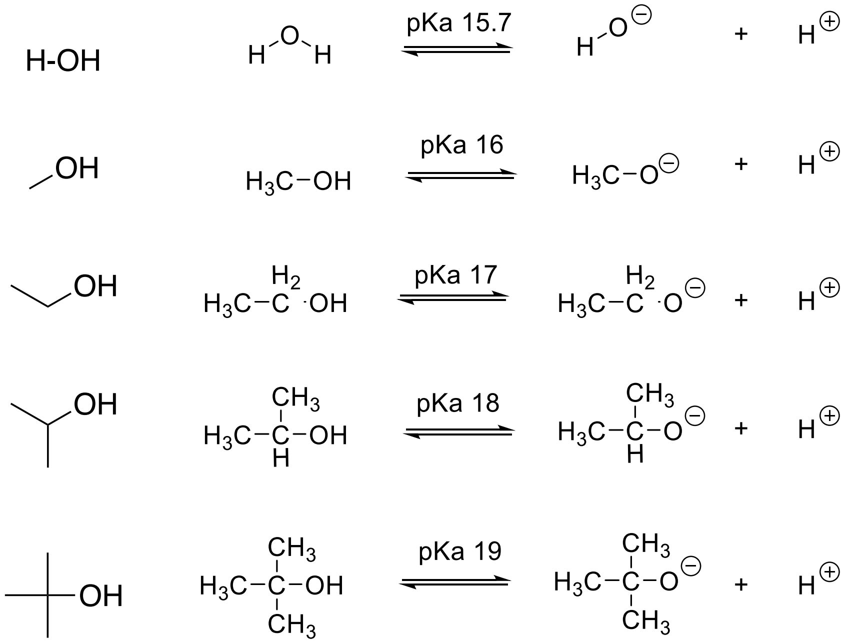
O-H bond - easy to break
R-O bond - hard to break; always needs a strong acid to break and can proceed either S_N-1 / S_N-2, or E1 / E2

Miscibility of Alcohols with Water



*butanol is soluble in H_2O but not miscible

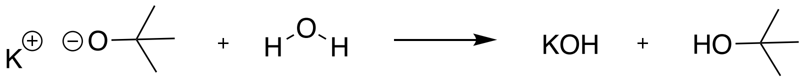
Acidity of R–OH



- pKa depends on conjugated base stability
- Harder to make a t-butoxide than methoxide. The alkyl group donates electron density to the C–O bond and destabilizes the negative charge (less favorable).

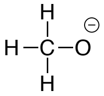
CH_3O-H methanol

$CH_3O^{\ominus}$ methoxide

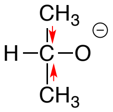


Stronger base — Stronger Acid — Weak base — pKa 19 weaker acid

Methoxide vs. Isopropoxide:



Methoxide
An alkoxide

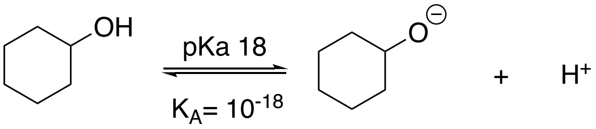


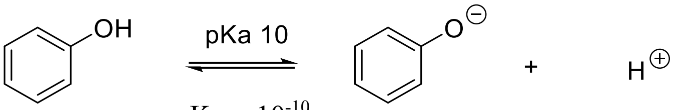
Isopropoxide
Less stable

Alkyl groups donate electrons through single bonds, destabilizing the negative charge (Inductive Effect), therefore, isopropoxide is less stable than methoxide

- Inductive effect – donation or withdrawal through single bonds

Conjugated/Aromatic R–OH



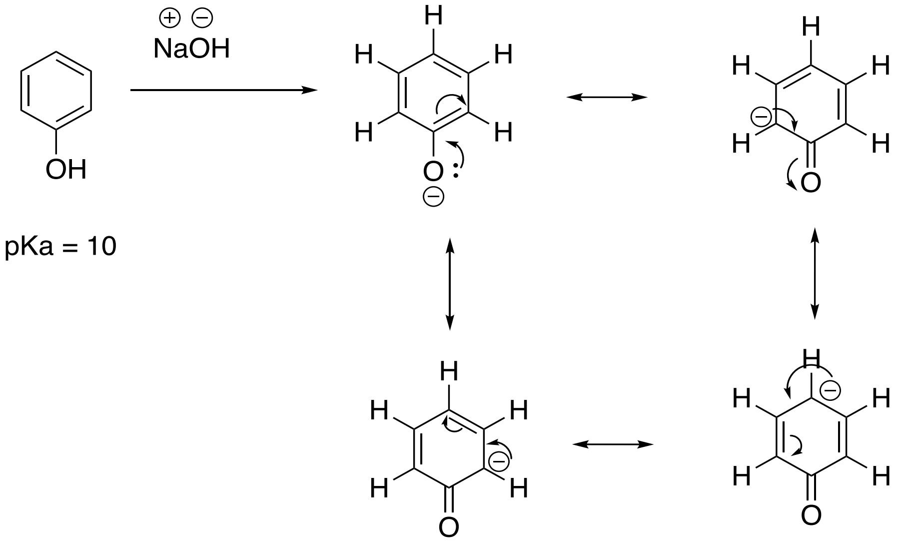


Phenol

$K_A = 10^{-10}$

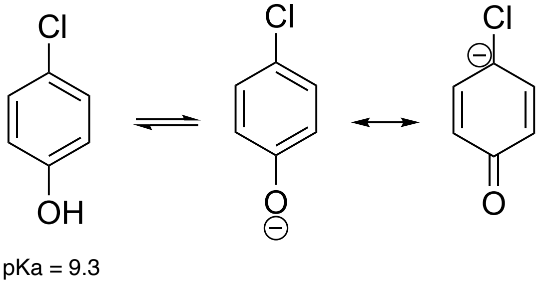
- More acidic than H_2O
- Resonance (resonance effect) takes electron density away from the O atom, resulting in stabilization of the negative charge.
- Resonance effect is strong through π system

Example 1: Phenol

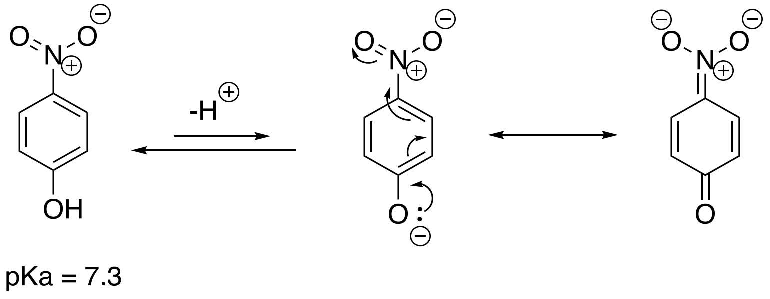


The alkoxide of phenol is a conjugated anion and is therefore much more acidic

Example 2: *p*-Chlorophenol

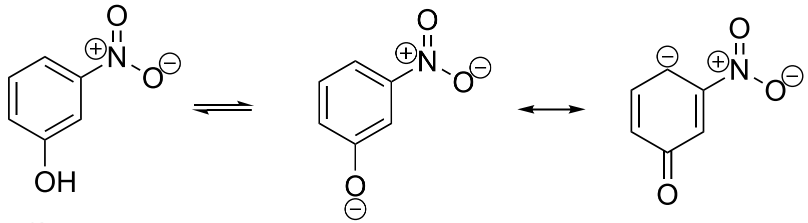


Example 3: *p*-Nitrophenol



p-Nitrophenol is more acidic than phenol because on top of the resonance forms that phenol contains, *p*-nitrophenol also contains the above extra resonance form, making the proton on the alcohol even more acidic.

Example 4: *m*-Nitrophenol

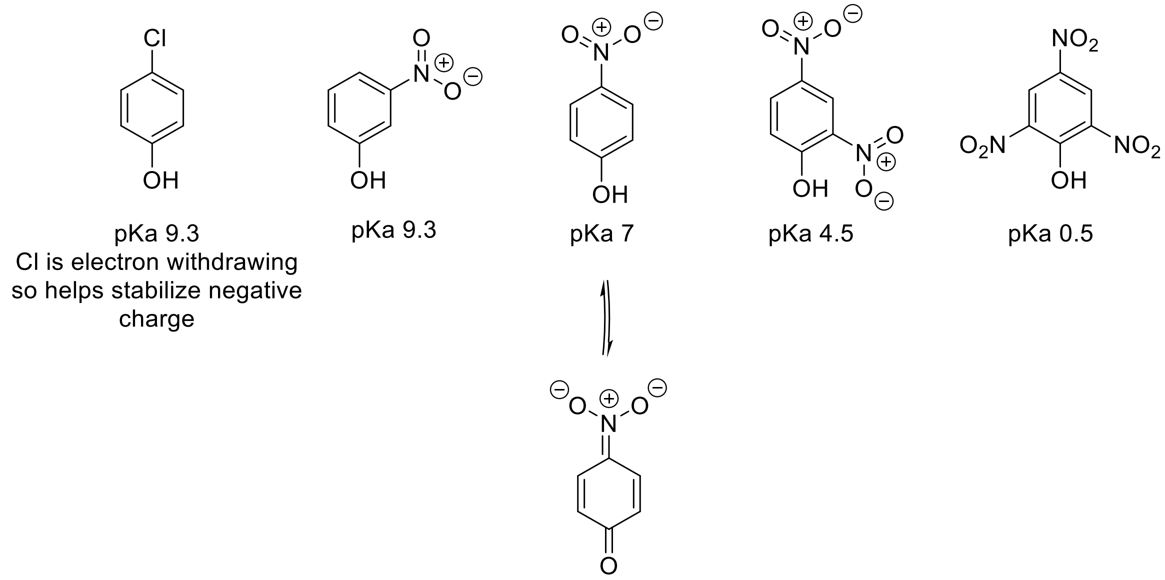


pKa = 9.3

not stabilized
except by induction

Less acidic than *p*-nitrophenol because there is less stabilization of the negative charge. The negative charge is not conjugated with the nitro group double bond.

More examples:



pKa 9.3
Cl is electron withdrawing
so helps stabilize negative
charge

pKa 9.3

pKa 7

pKa 4.5

pKa 0.5

- As you get more resonance possibilities, the negative charge is more spread out across the molecules, and is more stabilized, resulting in lower pKa (more acidic).

Ethers

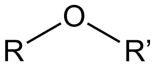
- Unreactive to base
- Not miscible with H_2O

Recall:

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

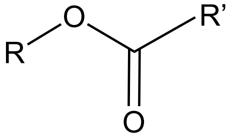
The difference between ester and ethers

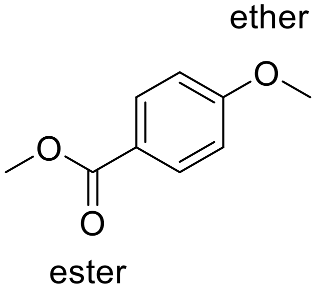
ether



vs

ester

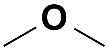




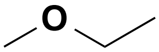
Nomenclature:

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

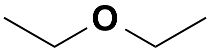
Examples:



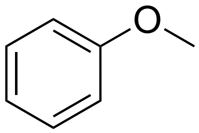
dimethyl ether



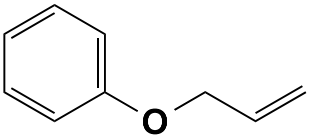
methyl ethyl ether



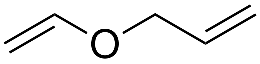
diethyl ether
ethyl ether
ether



methyl phenyl ether

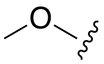


phenyl allyl ether

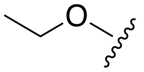


allyl vinyl ether

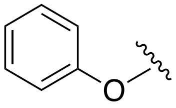
In the presence of other functional groups, name ethers as a group, drop “yl” and add “oxy” as seen below:



methoxy

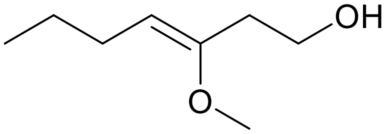


ethoxy



phenoxy

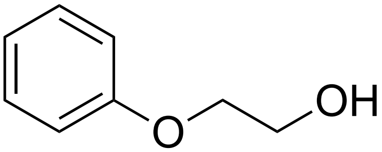
Example 1:



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

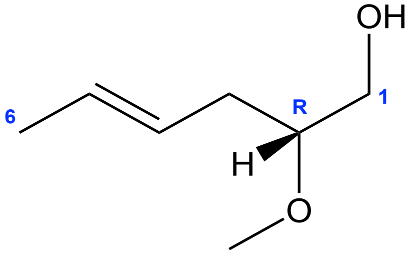
- Alcohol (-OH) takes priority over other functional groups
- Number the longest C chain so as to give the OH group the lowest number possible

Example 2:



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

Example 3:



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

Carbohydrates ($C_NH_{2N}O_N$)

sugars, saccharides

A familiar equation:

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

- 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

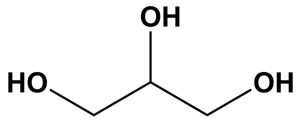
- the sugar produced is known as D-glucose, shown below in a Fischer Projection

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

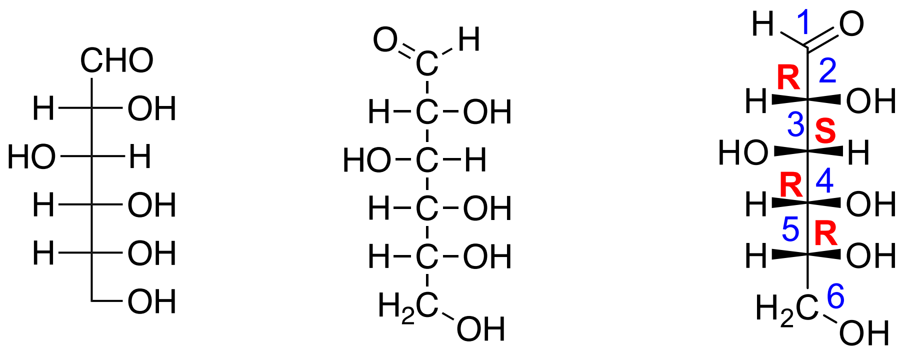
Example 1: Glycerol



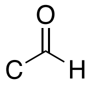
Triose

Example 2: D-Glucose

D-Glucose



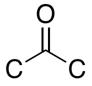
D-Glucose is an Aldohexose



Aldo

The carbonyl group is indicated by the prefix:

aldo – aldehyde
keto – ketone



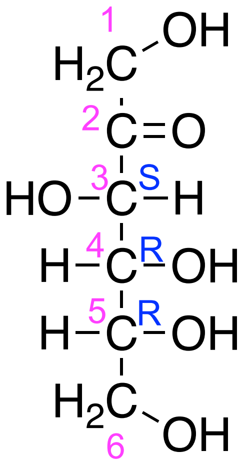
Keto

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

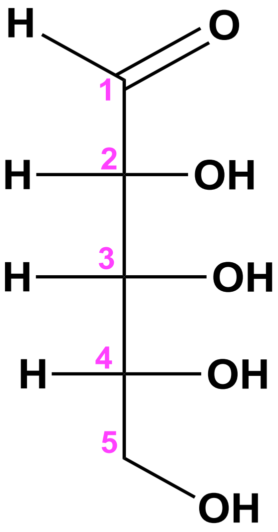


D-Fructose

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.

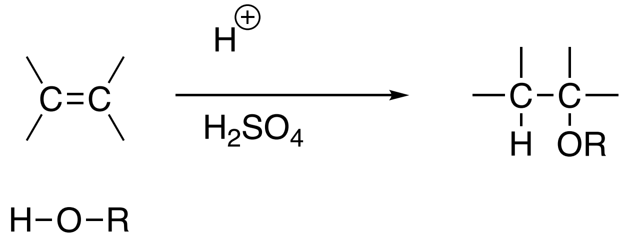
The name of this is D-ribose (found in RNA! – deoxyribose is in DNA)

These sugars can cyclize (form rings)

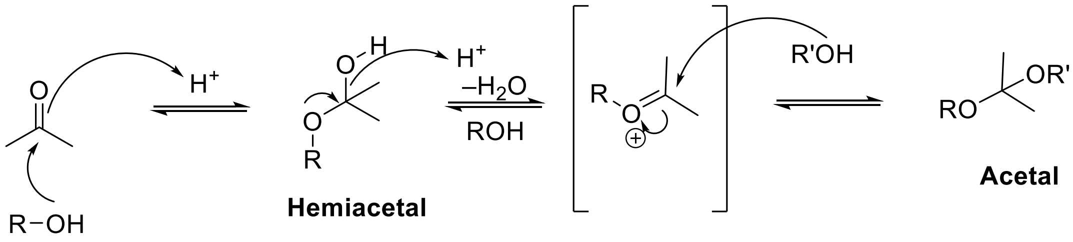
- 6-ring sugar is a pyranose
- 5-ring sugar is a furanose

Hemiacetal and Acetal Formation

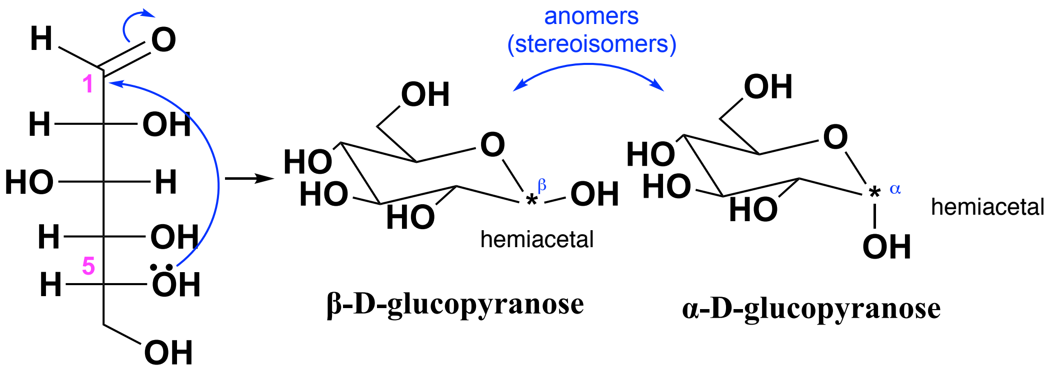
Recall addition reaction across a double bond (i.e., ether formation)



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



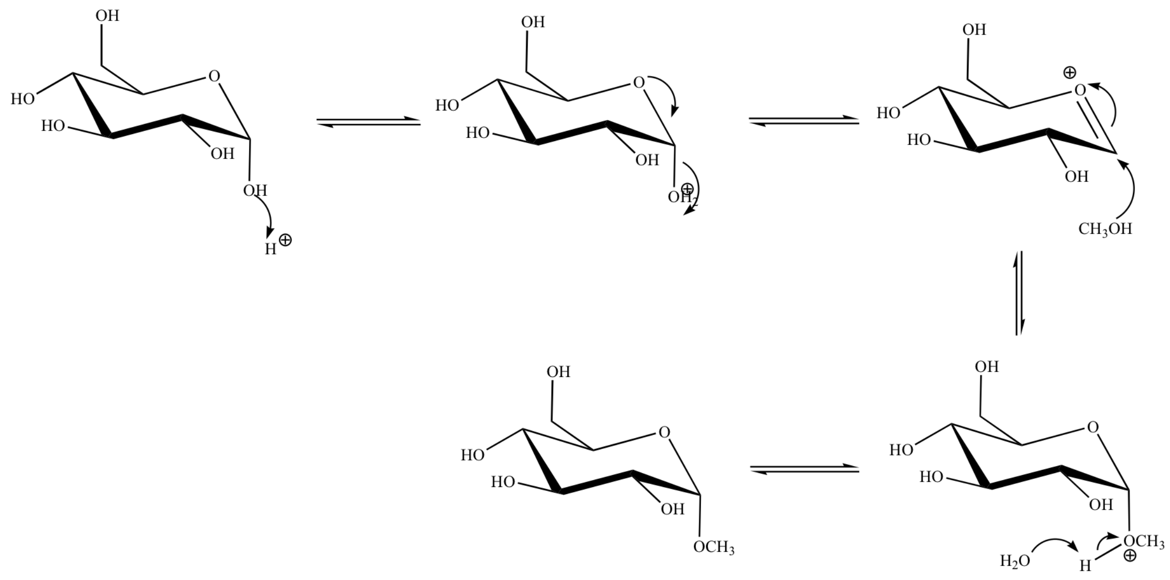
Example 4 - Glucose



β-D-glucopyranose α-D-glucopyranose

- 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

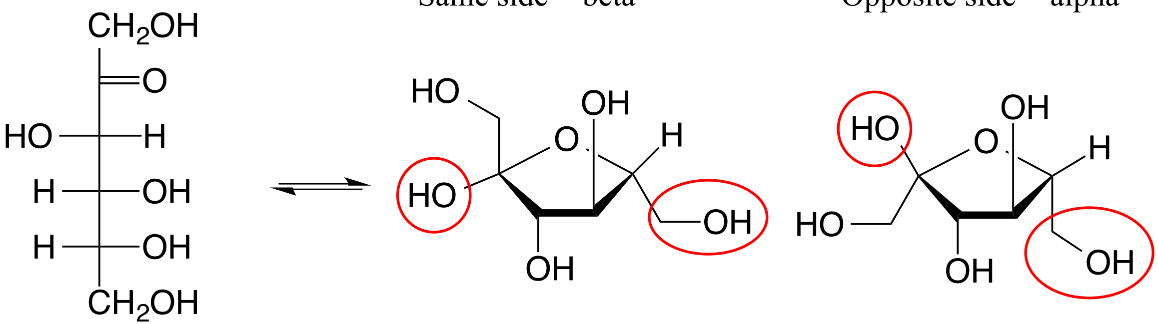
Example 4 - Glucose



Example 5 - Fructose

Same side = beta

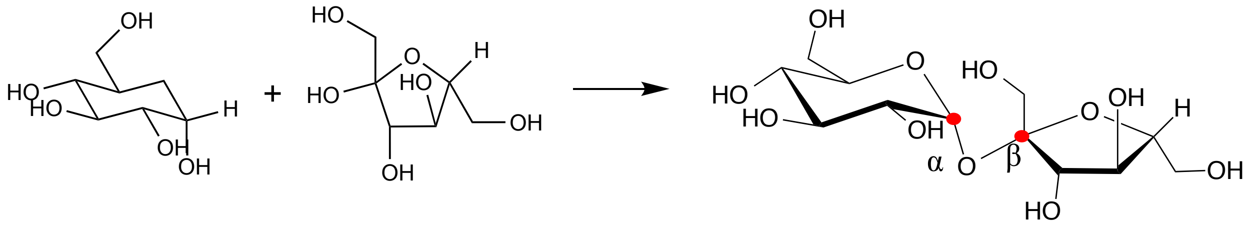
Opposite side = alpha



β-D-Fructofuranose

α-D-Fructofuranose

Example 3 - Table Sugar (Sucrose):



α–D-Glucopyranosyl-β–D-Fructofuranoside

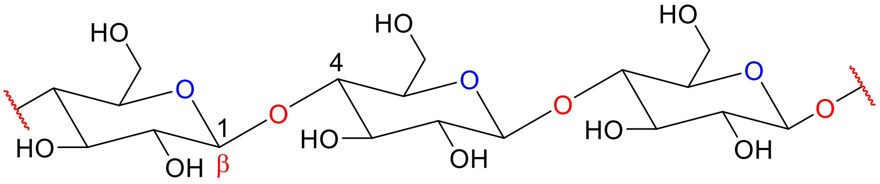
- Has 2 anomeric carbons
- Non-reducing sugar since it contains an acetal group and does not contain hemiacetals, aldehydes, or alpha-hydroxy ketone
- Can be broken down by the body to glucose and fructose monomer

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.

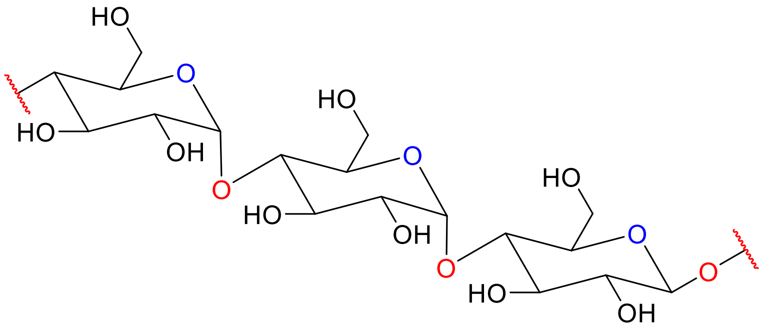
Cellulose



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

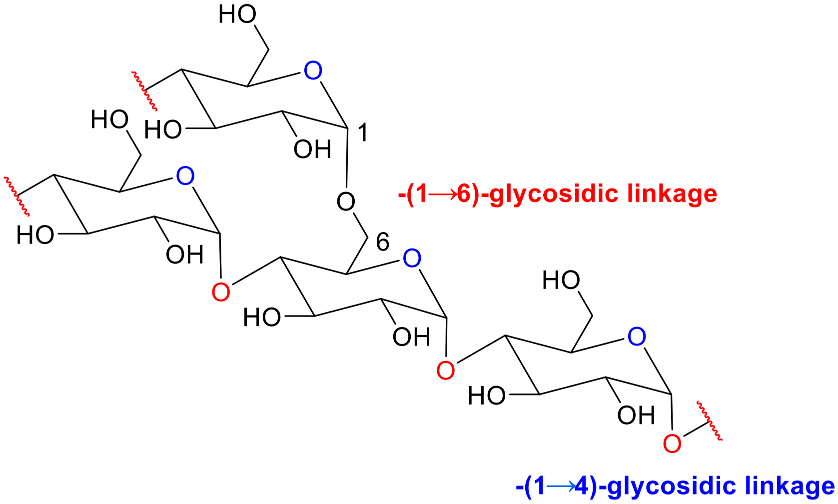
Starch (Amylose)



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

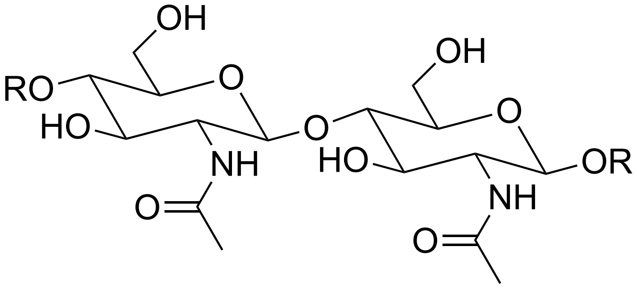
Starch (Amylopectin)



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.

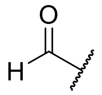
Chitin



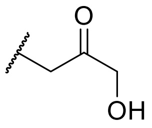
Other Examples and Information

Reducing Sugars

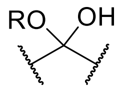
- Contains either an aldehyde, α-hydroxyketone, or a hemiacetal
- All aldoses are reducing sugars



Aldehyde



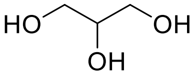
-Hydroxyketone



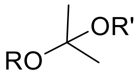
Hemiacetal

Non-reducing sugars

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



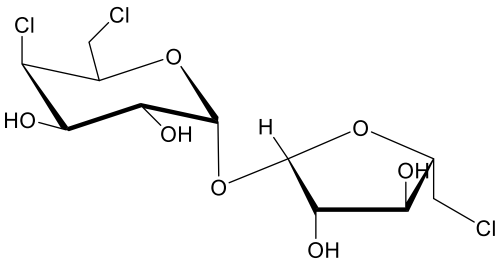
Glycerol
A Triose



Acetal

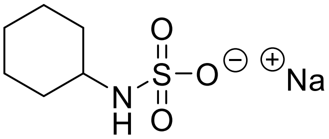
Artificial Sweeteners

Sucralose

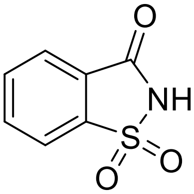


- Non-reducing sugar

Sodium Cyclamate



Saccharine



Aspartame