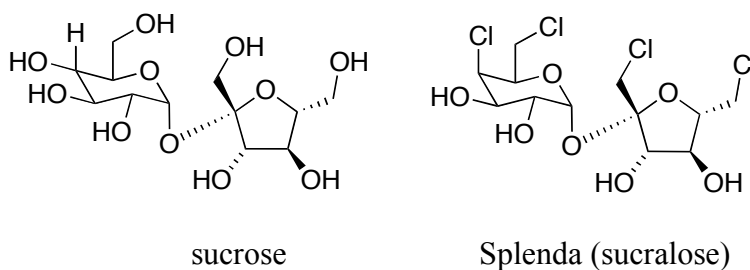


From Last Class

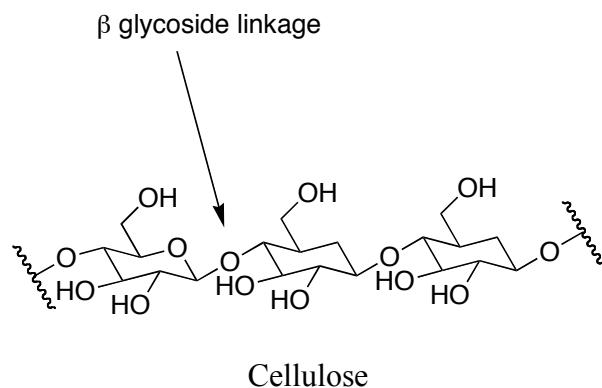
A question was asked last class about the structure of Splenda (also known as sucralose). Sucralose is a halocarbon and differs from sucrose in the following ways: it has an axial chlorine in the place of an equatorial alcohol and has all primary alcohols substituted as chlorines. Both are also non-reducing sugars and have an α -glycoside bond. Sucrose is assigned a sweetness rating of 100, whereas Splenda is 600x more sweet than sucrose.

**Polysaccharides**

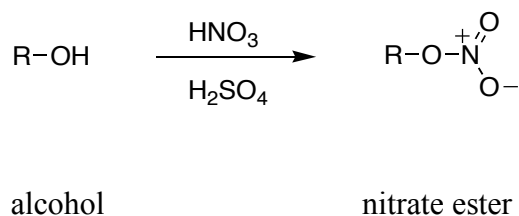
Polysaccharides are carbohydrates in which tens, hundreds, or even thousands of simple sugars are linked together through glycoside bonds. Most polysaccharides are not reducing sugars, and the two most widely occurring polysaccharides are cellulose and starch.

Cellulose

Cellulose consists of D-glucose units linked by a 1,4- β -glycoside bond as shown below (note: beta linkage). Several thousand glucose units are linked to form one large molecule. Nature uses cellulose primarily as a structural material to impart strength and rigidity in plants.

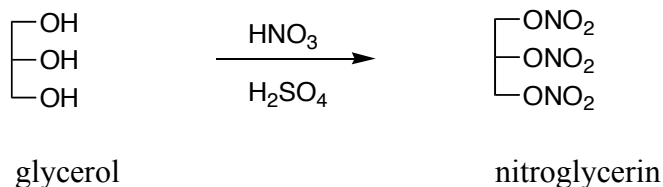


Cellulose also serves as a raw material for the manufacture of nitro-cellulose or commonly known as gun cotton. Gun cotton is an explosive, which when ignited, does not give off any black smoke. When an alcohol is treated with nitric acid and sulfuric acid, a nitrate ester is formed as shown below.



Similarly, when cellulose is reacted with nitric acid and sulfuric acid, gun cotton is formed. The true structure of gun cotton is not known because there are many possibilities for which alcohols get nitrated. Primary alcohols would be the first to be nitrated because they are less hindered followed by the secondary alcohols.

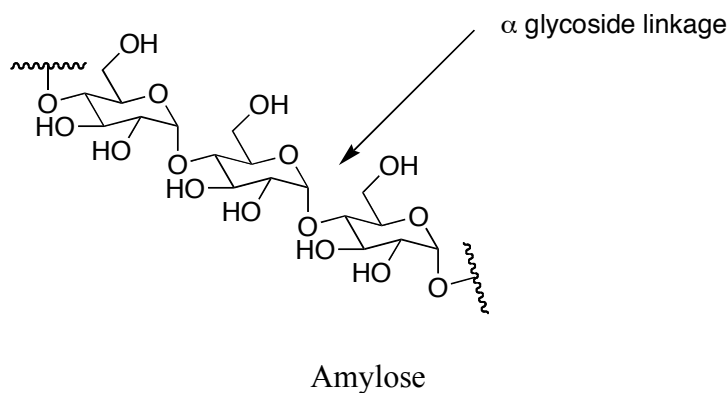
Nitroglycerin is another extremely explosive material. When glycerol is mixed with nitric acid and sulfuric acid, nitroglycerin is formed. This compound is very difficult to handle because of its explosive nature.



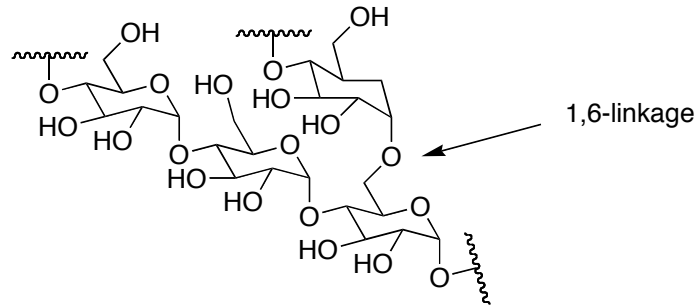
When 1% nitroglycerin is mixed with 99% diatom earth, it forms a mixture commonly known as dynamite. This was first discovered by A. Nobel and found to be a stable mixture for nitroglycerin.

Starch

Starch is a polymer of glucose in which the monosaccharide units are linked by a 1,4'- α -glycoside bond. Starch can be separated into two fractions: a fraction soluble in cold water, called amylopectin, and a fraction insoluble in cold water, called amylose. Amylose, which accounts for 20% by weight of starch, consists of several hundred glucose units linked together by a 1,4'- α -glycoside bond.



Amylopectin, which accounts for the remaining 80% of starch, is a far more complex structure. Unlike amylose and cellulose, which are linear structures, amylopectin contains 1,6'- α -glycoside bonds approximately every 12 glucose units. As a result, amylopectin has a very complex 3-D structure and is a highly branched molecule.

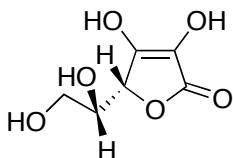


Amylopectin

Starch is digested by the human body in the mouth and stomach, by enzymes (glycosidases) that selectively hydrolyze the glycoside bonds and release individual molecules of glucose. These enzymes only hydrolyze the α -glycoside bond links in starch and leave the β -glycoside links in cellulose untouched. Thus, humans can digest starch in potatoes and grains but not cellulose in grass and wood.

Glycogen is a polysaccharide that serves the same energy storage purpose in animals as starch does in plants. Dietary carbohydrates that are not needed for immediate energy are converted by the body to glycogen for long-term storage. Like amylopectin in starch, glycogen contains a complex 3-D structure with both 1,4'- and 1,6'- linkages. Glycogen is much larger than amylopectin (up to 100,000 glucose units) and contains even more branches. The body converts glucose to glycogen for several reasons including: it is less reactive than glucose, it creates less osmotic pressure in the cell than glucose, and allows for the slow release of glucose into the body.

Ascorbic acid, commonly known as vitamin C, is an essential nutrient for humans, that is derived from a sugar. If humans do not obtain enough vitamin C, a disease known as scurvy develops in which the body tissues start to decompose. The symptoms include swollen and bleeding gums with loosened teeth, stiffness and soreness in joints, bleeding under the skin, and slow wound healing. This disease was very common among sailors on long sea voyages in which no fresh fruit was available.

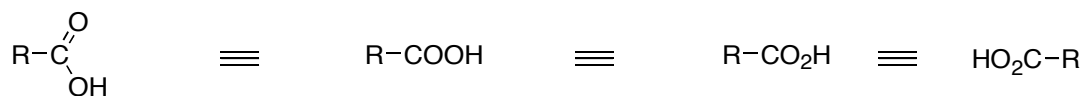


Ascorbic acid (Vitamin C)

Carboxylic acids and Derivatives

Carboxylic acids are very important compounds in nature and serve as building blocks for preparing related derivatives such as esters and amides.

The general formula for a carboxylic acid includes a carbonyl and a hydroxyl group. The carboxylic acid can also be written in different ways and you should take note of these ways.

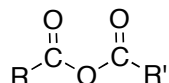


Many derivatives can be derived from carboxylic acids and below they are depicted in order of decreasing reactivity:

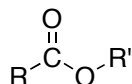
Acyl halides where X = F, Cl, Br, I



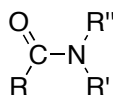
Anhydrides where R doesn't have to equal R'



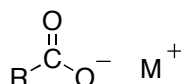
Esters where R doesn't have to equal R'



Amides where R doesn't have to equal R' or R''



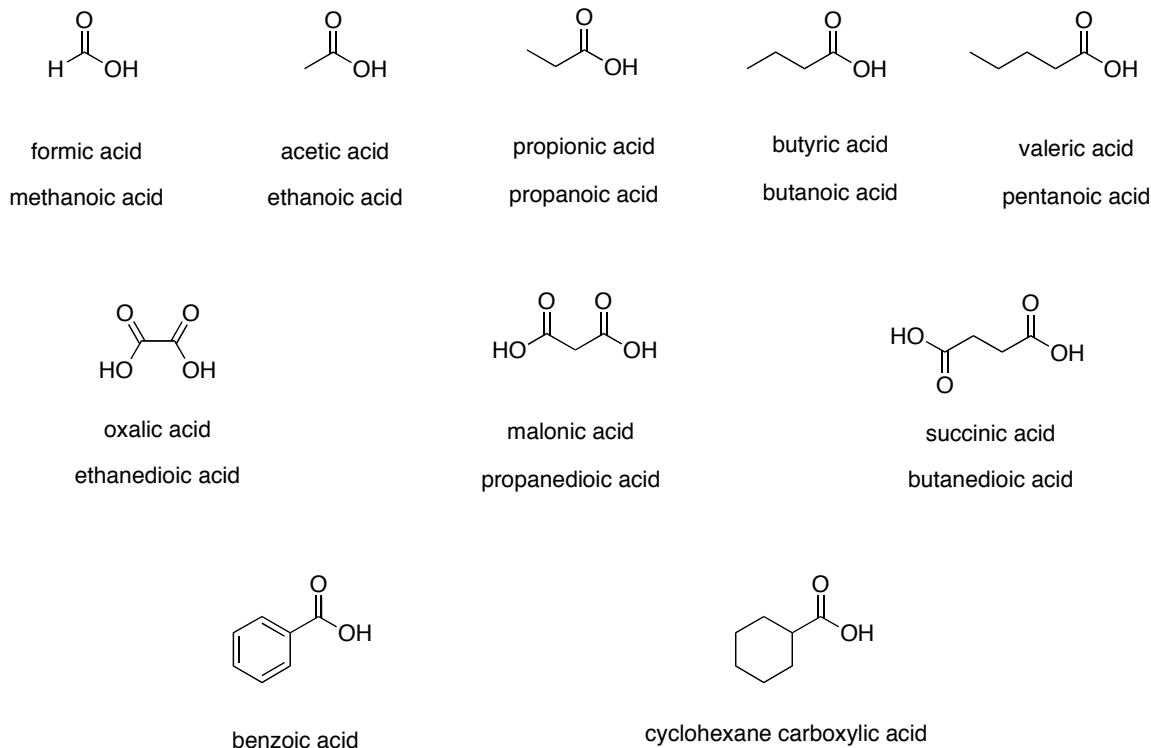
Carboxylate salts where M is a metal counter ion



Nomenclature of Carboxylic acids

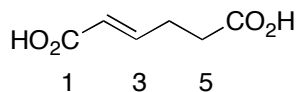
Carboxylic acids are derived from open chain alkanes and are systematically named by replacing the terminal “-e” of the corresponding alkane name with “-oic acid”. The carboxyl group is always numbered C1 in this system. Alternatively, compounds that have a –COOH group bonded to a ring are named with the suffix “-carboxylic acid”. In this system, the carboxylic acid carbon is attached to C1 and is not itself numbered in this system.

For historical reasons having to do with the fact that many carboxylic acids were among the first compounds isolated and purified, there are several common names given to these acids. These common names, along with the systematic names are given below where the common names are given first.



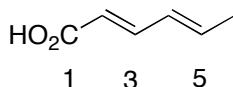
Naming examples

Below is an example of a molecule with two carboxylic acid groups. The first step to naming this compound is to find the parent alkane chain. Since it is a 6 carbon chain, it is a hexane. We then drop the “-e” and add “-oic acid” for the name to become hexanoic acid. Since there are two carboxylic acids present, the name becomes hexandioic acid. We notice that there is a double bond present in the molecule and therefore the name becomes hexendioic acid. The numbering of the chain should give the lowest number for the alkene, therefore the alkene is at C2 if you start numbering from the left, giving the name 2-hexendioic acid. Since the alkene is a trans double bond, the final name of this compound is 2E-hexendioic acid.



2E-hexendioic acid

Another naming example is given below. The first step is to find the parent alkane chain. This example once again has a 6 carbon chain and is a hexane. We then drop the “-e” and add “-oic acid” for the name to become hexanoic acid. There are two double bonds present in the molecule and therefore the name becomes hexadienoic acid. The numbering of the chain gives the carboxylic acid carbon C1 and therefore the alkenes are at C2 and C4 if you start numbering from the left giving the name 2,4-hexadienoic acid. Both alkenes are trans double bonds, therefore the final name for this molecule is 2E,4E-hexadienoic acid.

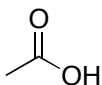


2E,4E-hexadienoic acid

Acyl Halide Nomenclature

Acid halides are named by identifying first the acyl group and then the halide. They are derived from open chain carboxylic acids and are systematically named by replacing the terminal “-ic acid” of the corresponding acid name with “-yl halide”. The carbonyl group is always numbered C1 in this system. Below are some examples of this naming system.

Acetyl chloride is derived from acetic acid. Firstly, the “-ic acid” is dropped and replaced with “-yl” then the halide is identified giving acetyl chloride. The systematic name would involve calling acetic acid, ethanoic acid. This would then give ethanoyl chloride.

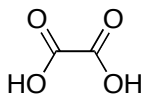


acetic acid

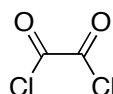


acetyl chloride

Oxalyl chloride is derived from oxalic acid. The “-ic acid” is replaced with “-yl” followed by identification of the halide to give oxalyl chloride.

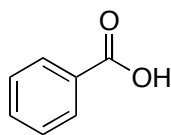


oxalic acid

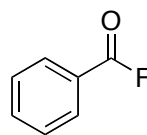


oxalyl chloride

Benzoyl fluoride is derived from benzoic acid. The “-ic acid” is replaced with “-yl” followed by identification of the halide to give benzoyl fluoride.



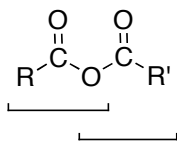
benzoic acid



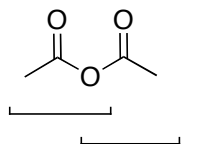
benzoyl fluoride

Anhydride Nomenclature

Symmetrical anhydrides of straight chain monocarboxylic acids are named by naming the two halves as acids then replacing the word “acid” with “anhydride”.



In the following example, a two carbon acid (acetic acid) is used in forming the anhydride. The “acid” is dropped and replaced with “anhydride” to give acetic anhydride. The systematic name would be ethanoic anhydride.

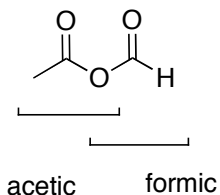


acetic acetic

acetic anhydride

If the anhydride is not symmetrical, both acids are named in alphabetical order and the “acid” suffix is replaced with “anhydride”.

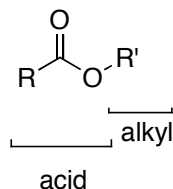
In the following example, the left side of the anhydride is derived from acetic acid and the right side from formic acid. By replacing the “acid” with “anhydride”, the name becomes acetic formic anhydride.



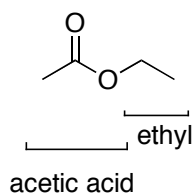
acetic formic anhydride

Ester Nomenclature

Systematic names for esters are derived by first giving the name of the alkyl group attached to the oxygen, and then identifying the carboxylic acid portion of the molecule. In doing so, the “-ic acid” is replaced with “-ate”. When naming, the C1 carbon is always the carbon attached to the oxygen in the alkyl chain and the carbonyl in the acid portion.

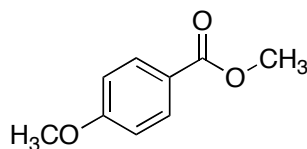


In the below example, the alkyl chain is identified as an ethyl group and the carboxylic acid is identified as acetic acid. Identification of the alkyl chain and dropping the “-ic acid”, replacing it with “-ate”, gives the name ethyl acetate. The systematic name for this compound would be ethyl ethanoate.



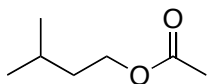
ethyl acetate

The following compound is a sex pheromone for dogs. When naming this molecule, first the alkyl chain is identified as a methyl group. The acid portion is a substituted benzoic acid. The methoxy group is in the 4 position and therefore the acid portion is 4-methoxybenzoic acid. Dropping the “-ic acid” and replacing it with “-ate” and identifying the alkyl chain gives the final name as methyl 4-methoxybenzoate.



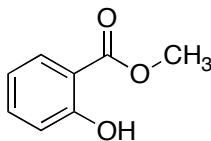
methyl 4-methoxybenzoate

The following compound is sweet smelling and is essence of banana. When naming this compound, first the alkyl chain should be identified. The longest chain is 4 carbons and therefore is a substituted butyl group. When numbering from the carbon attached to the oxygen, the methyl substituent is at C3 giving a 3-methylbutyl chain. The acid portion is identified as acetic acid. Dropping the “-ic acid” and replacing it with “-ate” and identifying the alkyl chain gives the final name as 3-methylbutyl acetate.



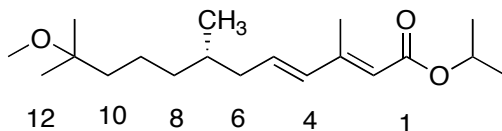
3-methylbutyl acetate

The following molecule has a common name methyl salicylate (essence of oil of wintergreen) and also has a nice aroma. When naming this molecule, first the alkyl chain is identified as a methyl group. When naming the acid portion, the acid takes priority over the phenol and is 2-hydroxybenzoic acid. Dropping the “-ic acid” and replacing it with “-ate” and identifying the alkyl chain gives the final name as methyl 2-hydroxybenzoate.



methyl 2-hydroxybenzoate

A more difficult example is the following growth inhibitor of fleas used in anti-flea powders on dogs and cats. When naming this compound, first the alkyl chain should be identified. The longest chain is 2 carbons and therefore is a substituted ethyl group. When numbering from the carbon attached to the oxygen, the methyl substituent is at C1 giving a 1-methylethyl chain. The acid portion of this molecule is a little more difficult. Firstly, we should identify the longest chain in the acid portion to get the parent alkane name. Since the longest chain is 12 carbons, it is a dodecane. Secondly, there are two trans alkenes in this molecule at the C2 and C4 positions when numbering starts at the carbonyl carbon to give dodeca-2E,4E-diene. The parent name for the acid would then be dodeca-2E,4E-dienoic acid. Since the molecule is an ester, dropping the “-ic acid” and replacing it with “-ate” gives the name dodeca-2E,4E-dienoate. Lastly is the naming of the substituents coming off the parent acid chain. At positions C3, C7, and C11 are methyl groups and at C11 is a methoxy group. The C7 methyl group is a stereogenic center and is in the S configuration. By combining the acid portion of the name and the alkyl portion, the final name for this molecule is isopropyl 11-methoxy-3,7S,11-trimethyldodeca-2E,4E-dienoate. Instead of isopropyl, one can call the alkyl part 1-methylethyl.



isopropyl 11-methoxy-3,7S,11-trimethyldodeca-2E,4E-dienoate