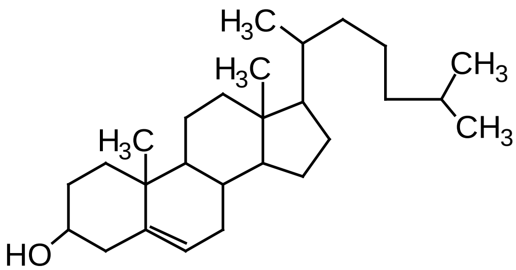
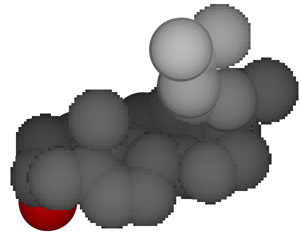
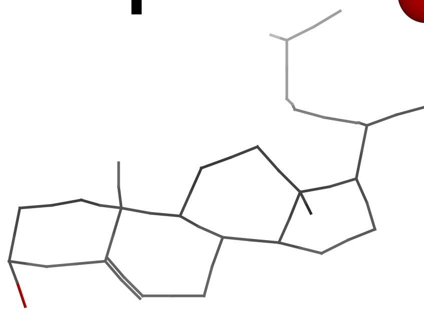


15

Lipids





Views of Cholesterol

CHAPTER SUMMARY

15.1 The Nature of Lipids

Lipids can best be defined as biomolecules which are **soluble to a great extent in nonpolar solvents**. In contrast to carbohydrates, proteins and nucleic acids, lipids do not have polymeric forms. By virtue of their **hydrophobic nature** they aggregate into large complexes, held together to a significant degree by nonpolar interactions.

The structures of lipids are quite varied: triacylglycerols (fats and oils), waxes, phospholipids, sphingolipids, steroids, eicosanoids, fat soluble vitamins, and pigments. Some lipids are **simple** in structure while others are more **complex**. Among these molecules are those which are esters in nature and therefore **saponifiable** in aqueous base. Others are **nonsaponifiable**. Many are **completely nonpolar** while others are **amphipathic**, that is, they have a polar/nonpolar nature.

15.2 Waxes - Simple Esters of Long-Chain Alcohols and Acids

Waxes are functionally the simplest of the lipids and are probably the most nonpolar.

15.3 Fats and Oils - Triesters of Glycerol

Fats and oils are triesters of glycerol and long-chain fatty acids. The fatty acids are usually **10-24 carbons** in length; they can be

saturated or **cis-unsaturated.** Saturated triacylglycerols have high melting points and are commonly called fats. Cis-unsaturation leads to a dramatic lowering of melting point and the presence of a liquid, or oil, at room temperature. **Short-hand notations** can be written for the fatty acids which indicate the number of carbons/ number of double bonds/ positions of double bonds from the carboxyl end of the molecule; for example, linoleic acid would be $C_{18:2}{}^{\Delta 9,\,12}$. Another way to describe unsaturated fatty acids denotes the position of the first double bond from the alkyl end of the molecule; for example, linoleic acid would be ω6.

CONNECTIONS 15.1 Errors in the Metabolism of Fatty Acids - Lorenzo's Oil

15.4 Reactions of Fats and Oils

A. Addition Reactions

The double bonds are subject to addition reactions such as **iodination** and **hydrogenation.**

The conversion of the double bonds in oils to single bonds leads to an increase in viscosity. Margarine is the product of hydrogenation of naturally occurring oils.

B. Oxidation Reactions

Oxidative cleavage at double bonds, the process of rancidification, is undesirable in foods because of the bad taste of the oxidation products. Oxidation can also lead to **polymerization** or cross-linking of fatty acid chains. This exothermic process is useful in terms of setting a finish on paints and dangerous if it occurs with combustible materials in an enclosed space.

C. Saponification

The ester bonds in fats and oils can be hydrolyzed in the presence of base to produce **soaps** which are the sodium salts of fatty acids. Soap making is an ancient process which has changed little over millenia.

15.5 Soaps and Detergents

A. Structure of Soaps

A soap molecule has a nonpolar, alkyl end and a polar, salt end. Because of this dual polarity, it is called amphipathic. This hydrophobic/hydrophilic nature is essential to the function of such molecules.

B. Mechanism of Soap Action

The **cleaning action of soap** involves lowering the surface tension of water by disrupting hydrogen bonds at the surface and the formation of micelles within the volume of water present. **Micelles** are aggregrations of soap molecules arranged so that the hydrophobic “tails” are oriented towards each other away from the water solvent and the hydrophilic “heads” are pointed into the water.

C. Detergents

Detergents are amphipathic molecules which have enhanced solubility and biodegradability properties compared to soaps. Instead of having a sodium salt in the polar portion of the molecule, other ionic and polar groups are used giving rise to what are called "cationic", "anionic" and "nonionic" detergents.

15.6 Biolipids - Structures and Functions

A. Triacylglycerols

Triacylglycerols, or **TAGs**, are a major source of food energy for higher animals. The metabolism of TAGs gives us about 2.5 times the amount of chemical energy as does the metabolism of carbohydrates.

B. Phospholipids

This class of amphipathic lipids is very similar in structure to TAGs, but the polar portion is an ester of phosphoric acid. Schematically, **phospholipids** have this polar head plus <u>two</u> nonpolar tails.

C. Sphingolipids

While the overall structural scheme of a polar head and two nonpolar tails is also found in **sphingolipids**, this class of amphipathic lipids has its own unique set of distinguihing structures.

The main function of these two subclasses is to produce the semipermeable **lipid bilayer membrane** structure of the cell. The current model of a cell membrane is referred to as **fluid mosaic.** Proteins and cholesterol are also incorporated with the bilayer for purposes of stability, permeability, and cell recognition.

D. Steroids

A fused multiple-ring system is the structural framework for **steroids**. **Cholesterol** is the nonpolar, nonsaponifiable progenitor of the metabolic and gonadal hormones such as cortisol, testosterone and estrogen as well as the bile acids used for the intestinal absorption of fats and oils. Many toxins fit into this lipid subclass.

CONNECTIONS 15.2 RU-486

E. Eicosanoids

Eicosanoids in the form of prostaglandins, prostacyclins, thromboxanes, and leukotrienes are short-lived metabolites of fatty acids which affect a variety of tissues in the body.

F. Vitamins

Vitamins A, D, E, and K are called the **fat-soluble vitamins** and must be part of the diet for health and vigor.

G. Pigments

Many **pigments** found in algae, bacteria and plants, such as chlorophyll, are lipid in nature. These molecules help to convert light energy to metabolic energy by systems of conjugated bonds.

SOLUTIONS TO PROBLEMS

15.1 Structure and Reactions: Sections 15.2, 15.3

$$CH_3(CH_2)_{14}\overset{\overset{\displaystyle O}{\|}}{C}O(CH_2)_{29}CH_3 \xrightarrow{H_2O} CH_3(CH_2)_{14}COOH + HO(CH_{20})_{29}CH_3$$

$$CH_3(CH_2)_{24}\overset{\overset{\displaystyle O}{\|}}{C}O(CH_2)_{25}CH_3 \xrightarrow{H_2O} CH_3(CH_2)_{24}COOH + HO(CH_2)_{25}CH_3$$

15.2 Structure of Lipids

Fats and oils are simple, nonpolar and saponifiable.

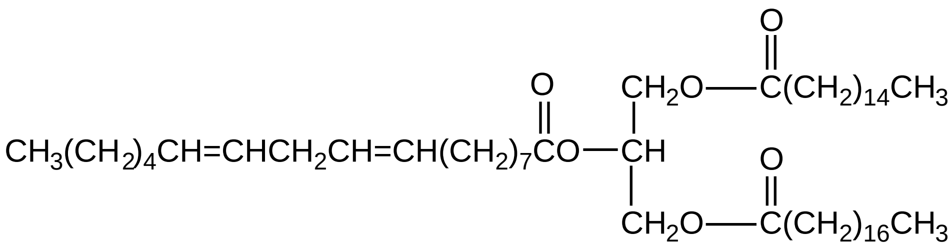
15.3 Structures: Section 15.3

a) $CH_3(CH_2)_{17}CH{=}CH(CH_2)_7COOH$

b) $CH_3(CH_2)_{15}CH{=}CHCH_2CH_2CH{=}CH(CH_2)_3COOH$

c) $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$

15.4 Structure: Section 15.3



15.5 Structure: Section 15.3

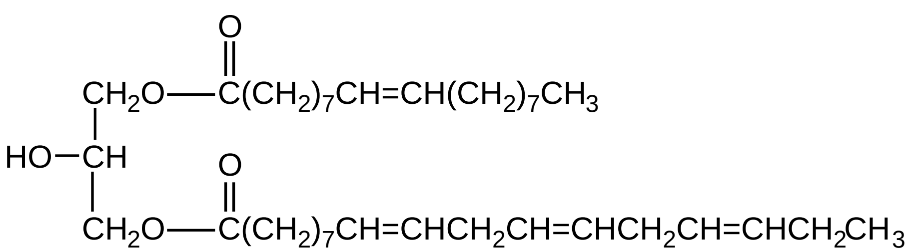
$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$ is erucic acid.

15.6 Reactions: Section 15.4

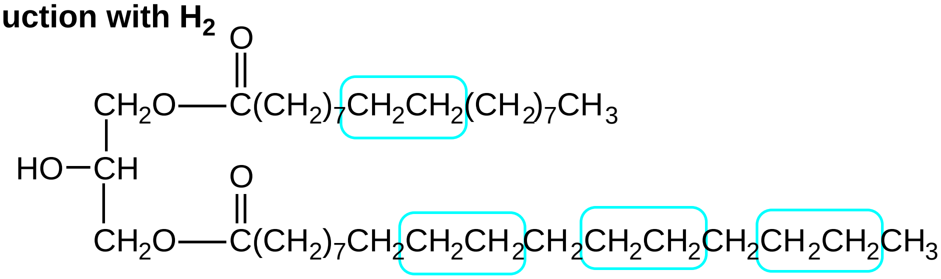
a) Trimyristin is saturated and therefore has an I_2 number of zero.
Triolein would have one double bond per fatty acid and 3 moles of I_2 would react with it.
Glyceryl oleopalmitostearate has only one double bond (oleo).
The order would be trimyristin < glyceryl oleopalmitostearate < triolein.

b) Stearic < oleic < linoleic < linolenic

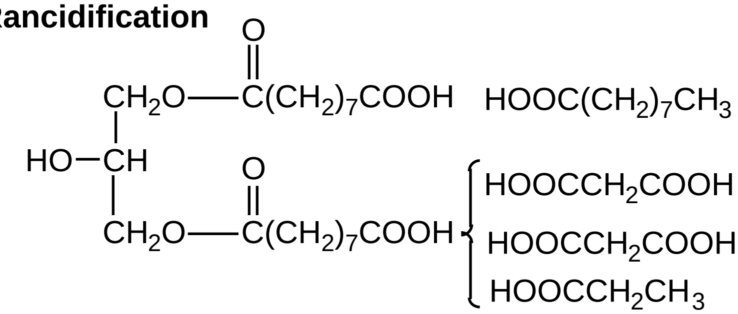
15.7 Soaps and Detergents: Section 15.5



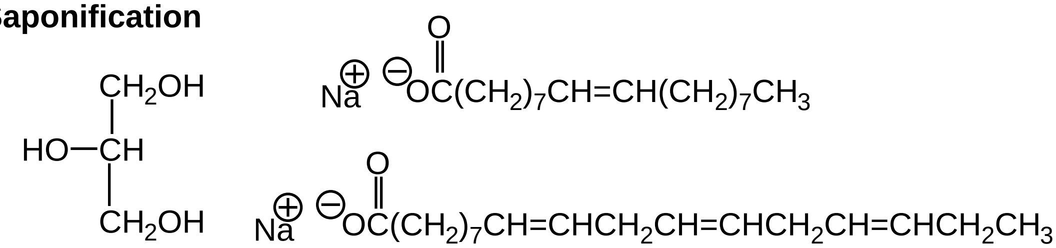
Reduction with H_2



Rancidification



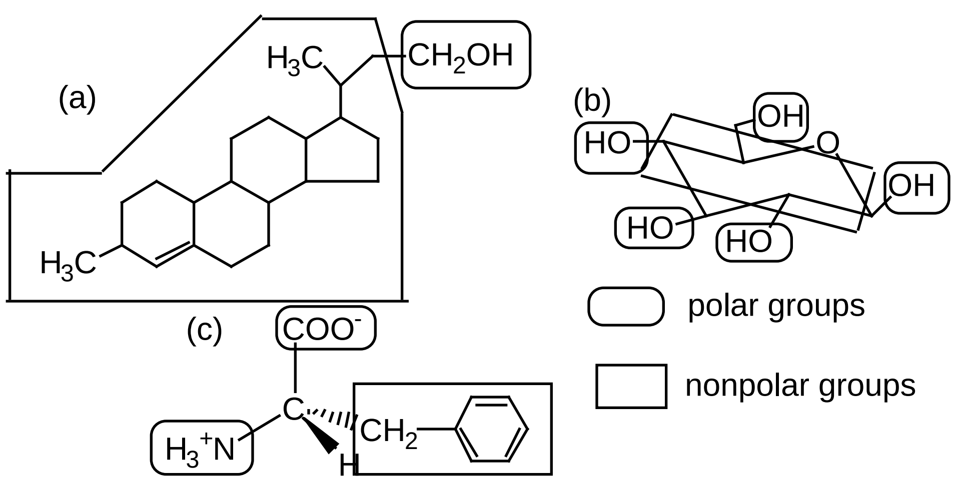
Saponification



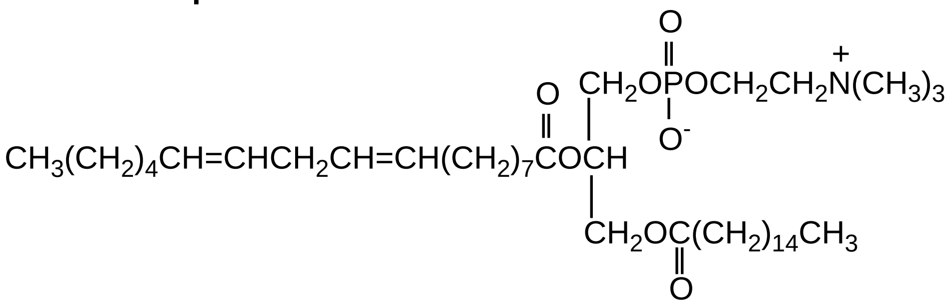
15.8 Reactions: Section 15.4

Margarines are semisynthetic and are not naturally-occurring. They are "organic" in the chemical meaning of the word, that is, they contain carbon. However, in the popular consumer vocabulary, since they are processed, they are not "organic" or natural.

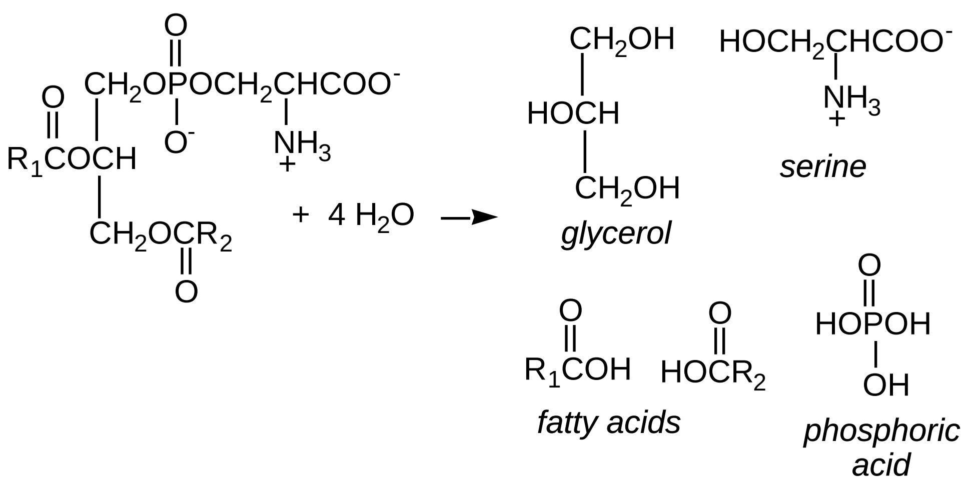
15.9 Nature of Lipids: Section 15.1



15.10 Biolipids - Structure: Section 15.6

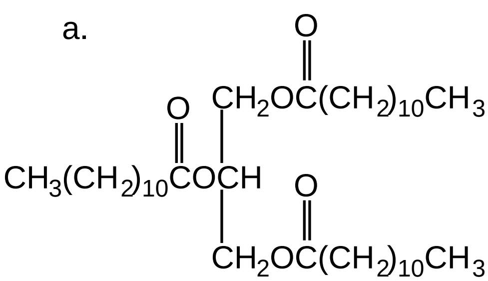


15.11 Biolipids - Structure: Section 15.6

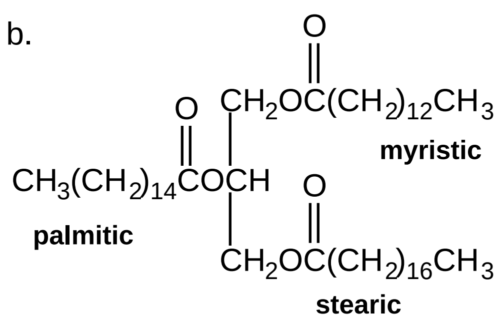


15.12 Structures of Fats and Oils: Section 15.3

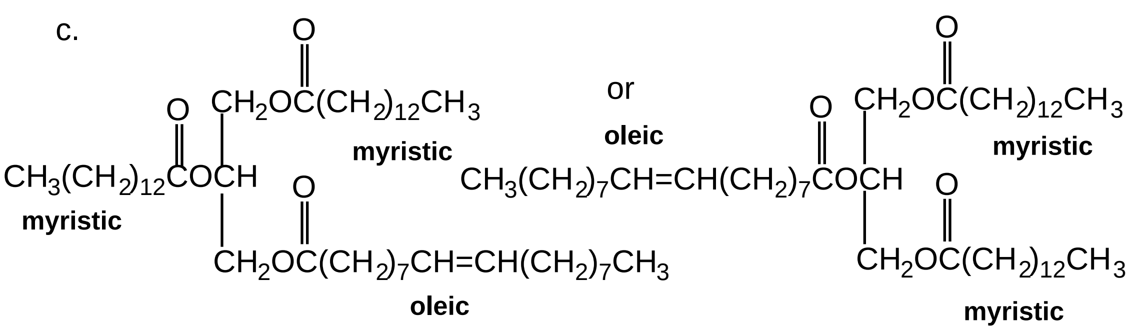
a.



b.

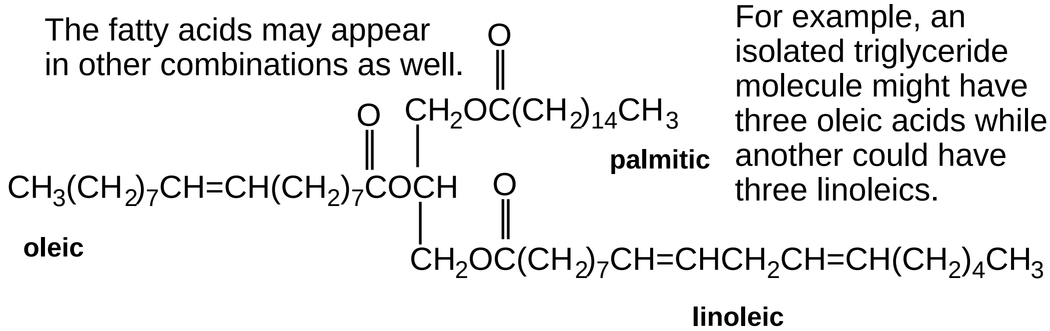


c.



d. The fatty acids may appear in other combinations as well.

For example, an isolated triglyceride molecule might have three oleic acids while another could have three linoleics.

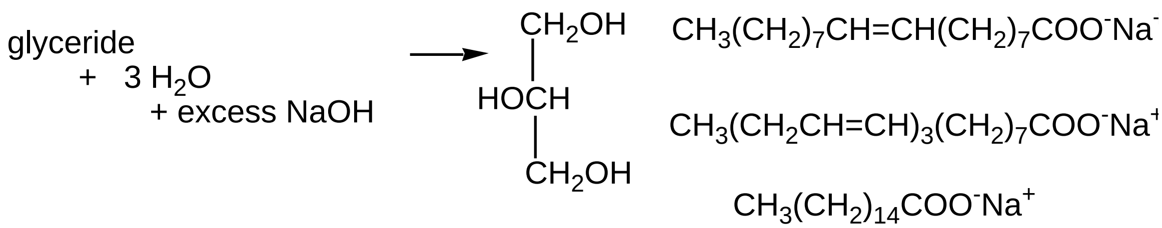


e. Same as for part d.

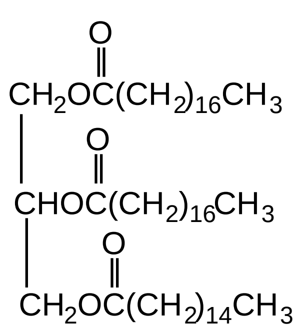
15.13 Reactions of Fats and Oils: Section 15.4

The following products will be formed with the glyceride in question:

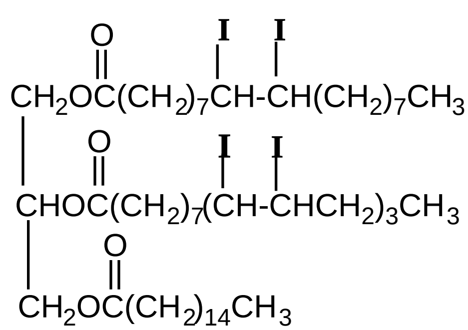
a.



b. hydrogenation



c. I_2/CCl_4



15.14 Reactions of Soaps: Section 15.4

a) $2\ CH_3(CH_2)_{16}COO^-Na^+ + Mg^{2+} \longrightarrow (CH_3(CH_2)_{16}COO^-)_2Mg^{2+} + 2\ Na^{1+}$

b) $3\ CH_3(CH_2)_{16}COO^-Na^+ + Fe^{3+} \longrightarrow (CH_3(CH_2)_{16}COO^-)_3Fe^{3+} + 3\ Na^{1+}$

c) $CH_3(CH_2)_{16}COO^-Na^+ + H^+ \longrightarrow CH_3(CH_2)_{16}COOH + Na^{1+}$

15.13 Structure of Fatty Acids: Section 15.3

a) $CH_3(CH_2)_5CH{=}CH(CH_2)_9COOH$ This is neither ω3 nor ω6. It is ω7.

b) $CH_3(CH_2CH{=}CH)_6(CH_2)_2COOH$ This is an ω3.

15.17 Structure of Fatty Acids: Section 15.3

a) $CH_3(CH_2)_3(CH_2CH{=}CH)_4(CH_2)_7COOH$

The first double bond would appear at position 9 from the carboxyl end.

b) $CH_3(CH_2)_3(CH_2CH{=}CH)_5(CH_2)_{10}COOH$

The first double bond would appear at position 12 from the carboxyl end.

c) $CH_3(CH_2)_3(CH_2CH{=}CH)_3(CH_2)_{12}COOH$

The first double bond would appear at position 14 from the carboxyl end.

15.17 Structures of Soaps and Detergents: Section 15.4

a) $CH_3(CH_2)_{14}CO_2^-Na^+$ would be an effective soap because it is the sodium salt of a long chain fatty acid.

b) $(CH_3(CH_2)_{16}CO_2^-)_2Ca^{2+}$ would be insoluble in water and so would not be effective as a soap.

c) $CH_3CH_2CO_2^-Na^+$ does not have a long nonpolar carbon chain and therefore could not make good micelles. It would not be an effective soap.

d) $CH_3(CH_2)_{14}CH_2N(CH_3)_3^+Cl^-$ would be a good detergent because it is a soluble ammonium salt with a long carbon chain.

e) $CH_3(CH_2)_{16}CH_3$ has no polar region, is not amphipathic, and therefore cannot have soap action.

f) $CH_3(CH_2)_{14}CO_2H$ is a neutral molecule. The protonated carboxyl end is not polar enough to counteract the long hydrocarbon chain.

g) $CH_3(CH_2)_{14}CH_2OSO_3^-Na^+$ should be a good detergent.

15.18 Properties of Soaps and Detergents: Section 15.4

a) *polar* $CH_3(CH_2)_{14}COO^-Na^+$ *nonpolar*

b) *polar* $CH_3(CH_2)_{14}CH_2N(CH_3)_3^+Cl$ *nonpolar*

c) *polar* $CH_3(CH_2)_{14}CH_2OSO_3^-Na^+$ *nonpolar*

15.19 Consumer Chemistry

This should be carried out in the grocery and/or drug stores.

15.20 Properties of Fats and Oils: Section 15.3

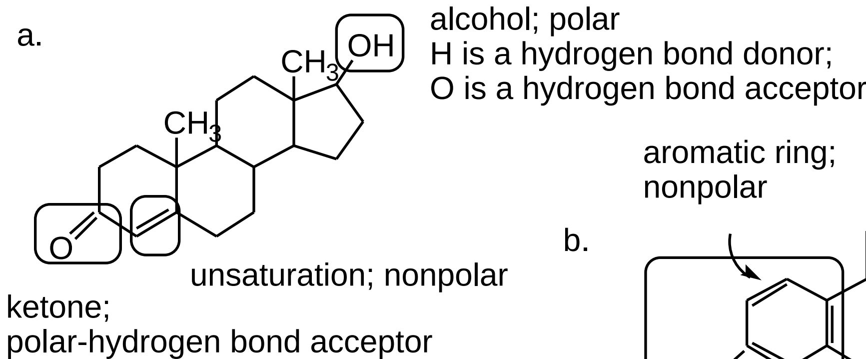
The melting point of a triglyceride decreases with an increase in double bonds or unsaturation. The iodine number is a measure of unsaturation. Therefore the higher the iodine number, the lower the melting point.

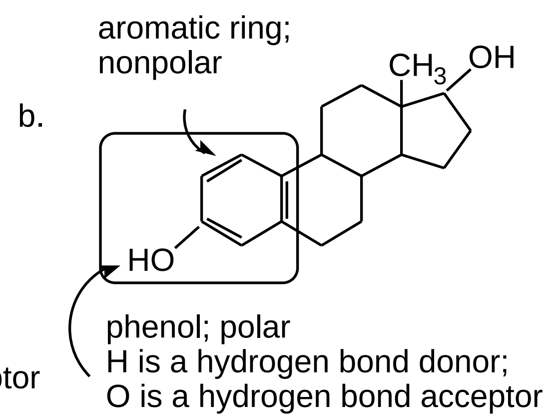
15.21 Structure: Section 15.4

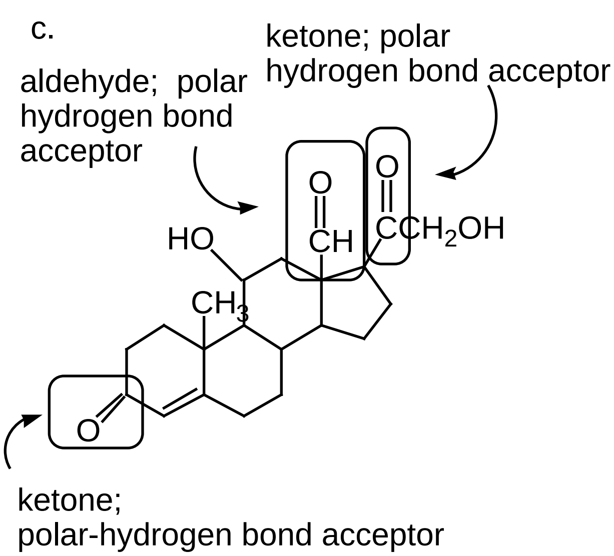
Detergents, phospholipids and sphingolipids are alike in that they are amphipathic molecules. In a polar solvent like water they will aggregate so that their nonpolar portions are away from the solvent.

They differ because phospholipids and sphingolipids have two nonpolar "tails" while detergents usually have only one. While detergents form micelles with one layer of molecules shaped into a sphere, the other two types form lipid bilayers such that a polar solvent can appear within and outside of the structure.

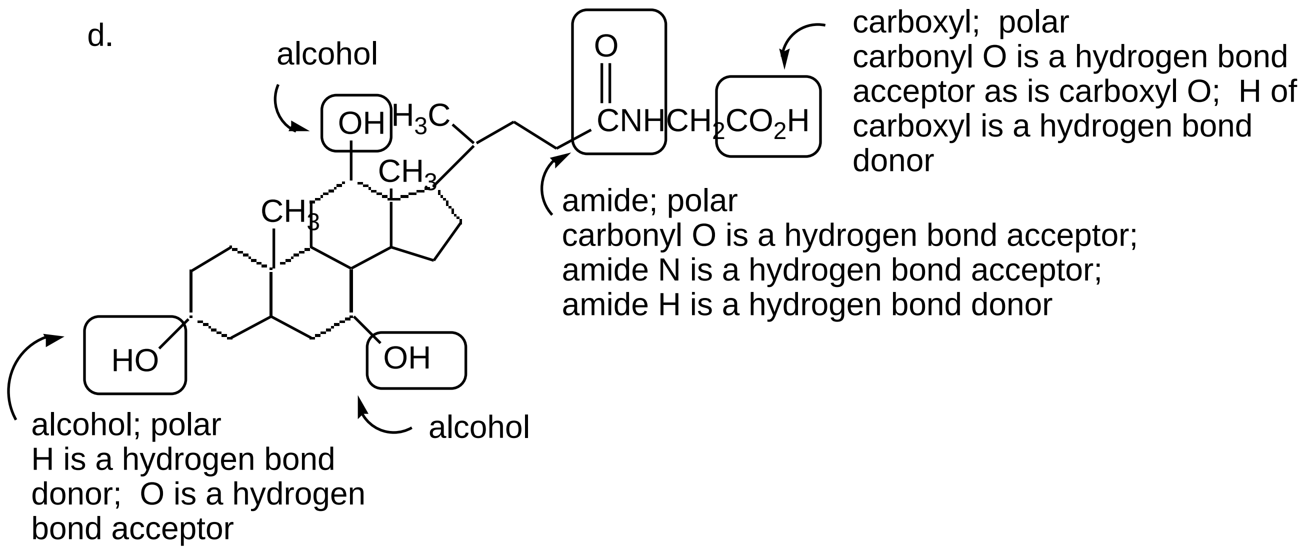
15.22 Structure of Biolipids: Section 15.6





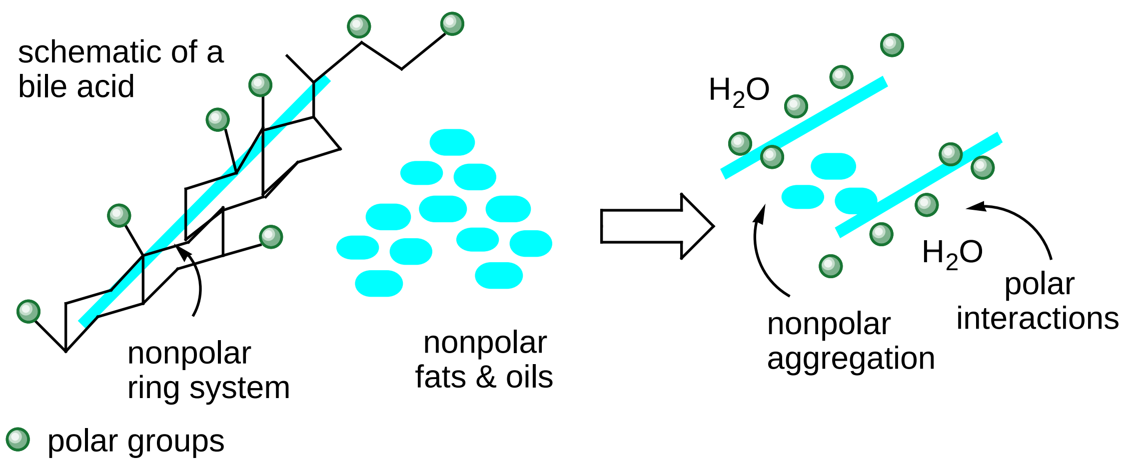


d.



15.23 Functions of Biolipids: Section 15.6

The acidic carboxyl and sulfonic acid portions of the bile acids are polar as are the alcohol groups rimming the steroid nucleus. The fused ring system is nonpolar. Therefore the bile acids are amphipathic and could form micelles which could engulf fats and oils in the intestines.



15.24 Structure of Biolipids: Section 15.6

chiral centers

There are 11 chiral centers, 2×10^3 optical isomers.