Chapter 8 Lecture Notes: Lipids

Educational Goals

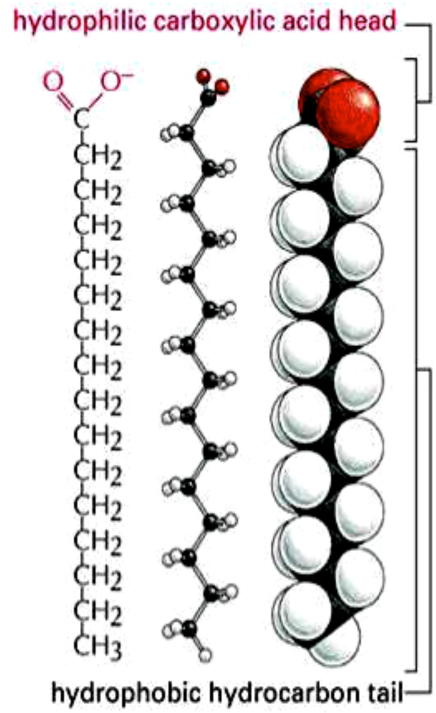
1. Know the *factors* that characterize a compound as being a **lipid**.
2. Describe the structure of **fatty acids** and explain how *saturated, monounsaturated, and polyunsaturated fatty acid* structures differ from one another.
3. Predict how the *number of carbons* and *the degree of unsaturation* affect the melting points of fatty acids.
4. Describe the *structure* of waxes, how they are made, and understand the *biological function* of waxes.
5. Describe the general ***structure of triglycerides*** and list their biological functions.
6. Describe the reaction involved in the *formation of triglycerides* from fatty acid residues and glycerol.
7. Describe three reactions in which *triglycerides are reactants*.
8. Explain how the structures of *saturated* and *unsaturated triglycerides* differ from one another.
9. Explain the difference in melting points of ***vegetable oils*** vs. ***animal fats***.
10. Distinguish **phospholipids** from **glycolipids**.
11. Distinguish **glycerophospholipids** from **sphingophospholipids**.
12. Distinguish **glyceroglycolipids** from **sphingoglycolipids.**
13. Identify the structural component that is common to all **steroids** and identify *three important members* of this class of lipids.
14. Describe the *structure and function* of **bile salts**.
15. Describe the *structure and function* of **lipoproteins**. List *five types* of lipoproteins.
16. Understand what is meant by the terms “total cholesterol,” “good cholesterol,” and “bad cholesterol” as they relate to lipid panel blood tests.
17. Understand the structural basis of the lipid class called **eicosanoids**.
18. Explain how *aspirin, ibuprofen, and acetaminophen* work to reduce fever, swelling, and pain.
19. Describe the *components and structure* of a ***cell membrane***.
20. Compare and contrast **passive transport** and **active transport**.
21. Compare and contrast **simple diffusion** and **facilitated diffusion**.

Lipids are a class of biomolecules that are______________________ ____________________________.

- This is ***not*** a classification based on functional groups.

Lipids are used as: cell membrane components, energy storage molecules, insulation, and hormones.

Fatty Acids



______________ ______________ are carboxylic acids that typically contain between 12 and 20 carbon atoms.

Fatty acids usually have an ***even*** number of carbon atoms because they are built from 2-carbon molecules.

Fatty acids differ from one another in the number of

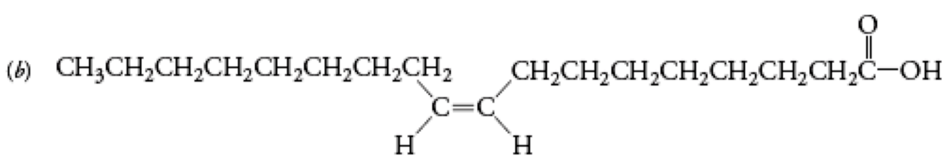
______________ atoms that they contain and in their number

of carbon-carbon_________________ ________________.

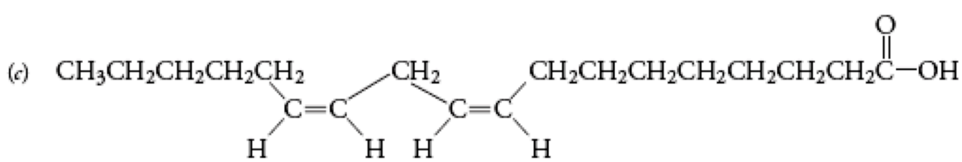
Saturated and Unsaturated Fatty Acids

Saturated Fatty Acids	⇐ **only single bonds**
Monounsaturated Fatty Acids	⇐ **one double bond**
Polyunsaturated Fatty Acids	⇐ **two *or* more double bonds**

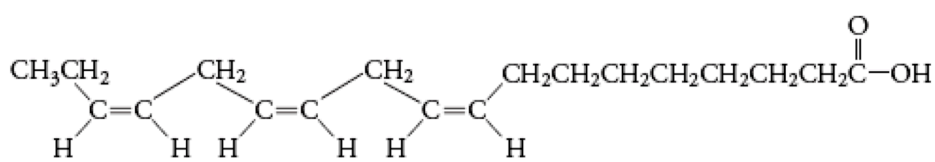
Stearic acid



Oleic acid

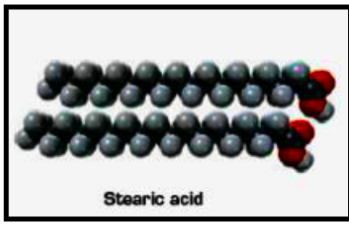


Linoleic acid



Linolenic acid

Interactions Between Fatty Acids: London Forces



Saturated fatty acid hydrocarbon tails interact through relatively strong London Forces.

- High Melting Point
- High Boiling Point

Cis double bonds in unsaturated fatty acids interact less efficiently (because of their shape) resulting in weaker London Forces.

- Lower Melting Point
- Lower Boiling Point

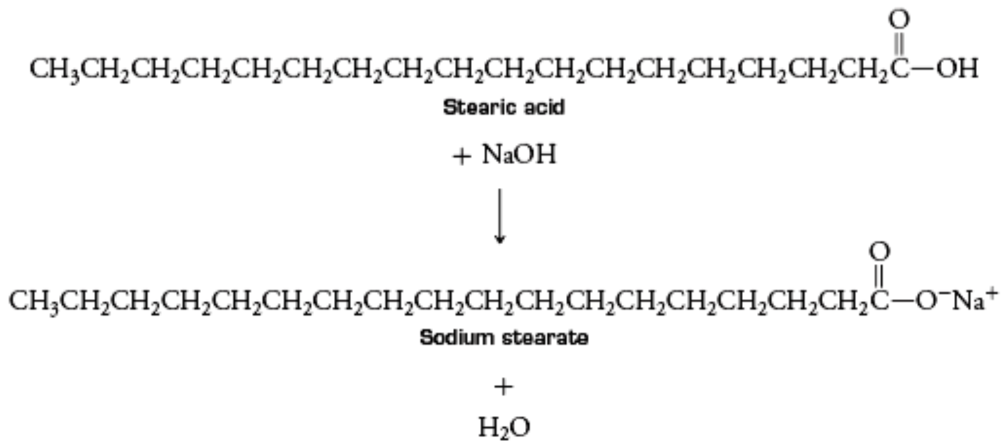
TABLE 8.1 Common Fatty Acids

Number of Carbon Atoms	Number of Double Bonds	Name	Formula	Melting Point (°C)	Source
12	0	Lauric acid	$CH_3(CH_2)_{10}CO_2H$	43	Coconut
14	0	Myristic acid	$CH_3(CH_2)_{12}CO_2H$	54	Nutmeg
16	0	Palmitic acid	$CH_3(CH_2)_{14}CO_2H$	62	Palm
16	1	Palmitoleic acid	$CH_3(CH_2)_5CH{=}CH(CH_2)_7CO_2H$	−0.5	Macadamia nuts
18	0	Stearic acid	$CH_3(CH_2)_{16}CO_2H$	69	Lard
18	1	Oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$	13	Olives
18	2	Linoleic acid	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6CO_2H$	−9	Safflower
18	3	Linolenic acid	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6CO_2H$	−17	Flax

Think about it: Explain why stearic acid had a higher melting point than lauric acid.

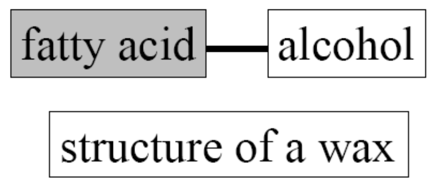
Linolenic acid has a lower melting point than linoleic acid. Explain why.

Fatty acids become ____________________when they lose their hydrogen to become carboxylate ions.

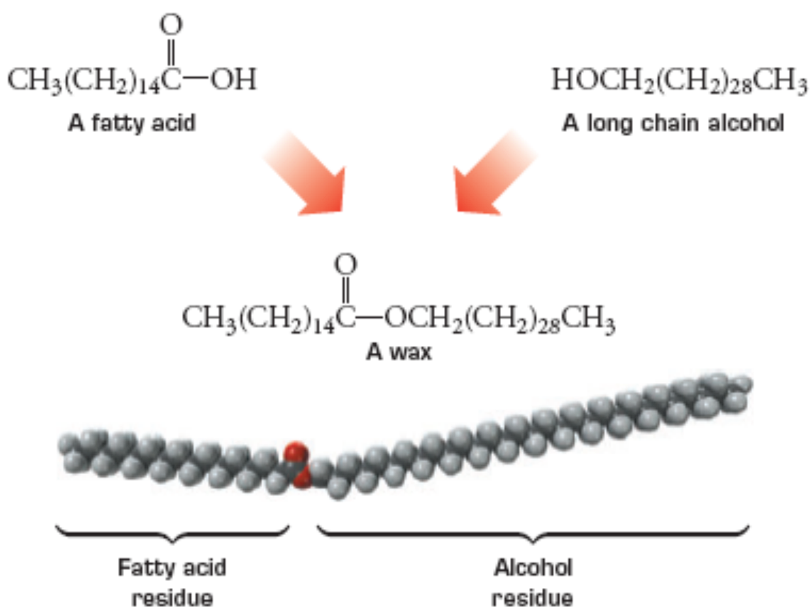


Waxes

Waxes are hydrophobic _______________ produced by combining **fatty acids** with **long-chain alcohols**.



Example: Beeswax



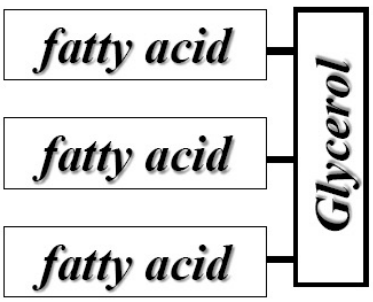
Beeswax is an ***ester*** formed by combining palmitic acid with a 30-carbon alcohol

TABLE 8.2 Key Esters Found in Some Waxes

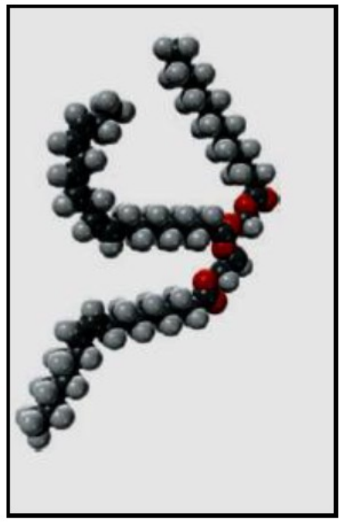
Name	Formula	Source	Use
Beeswax	$CH_3(CH_2)_{14}CO_2CH_2(CH_2)_{28}CH_3$	Honeycomb	Candles
Carnauba wax	$CH_3(CH_2)_{24}CO_2(CH_2)_{28}CH_3$	Palm	Furniture wax
Insect wax	$CH_3(CH_2)_{24}CO_2(CH_2)_{48}CH_3$	Insects	Polish

Triglycerides

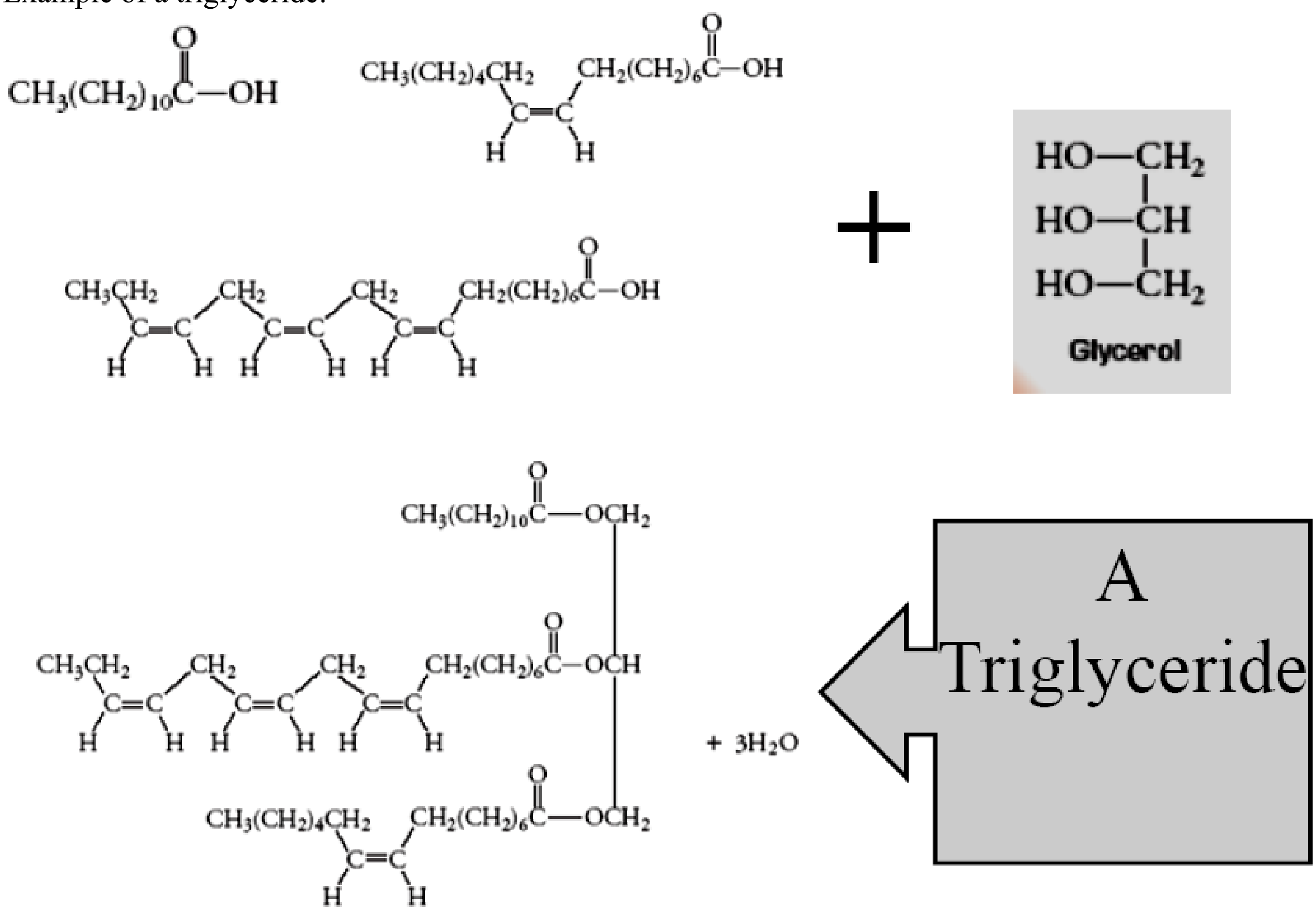
Animal fats and vegetable oils are ________________________ (or triacylglycerides), in which three ***fatty acid*** residues are joined to ***glycerol*** by ester bonds.



structure of triglyceride



Example of a triglyceride:



Saturated vs. Unsaturated Triglycerides

We classify triglyceride molecules as either ***saturated*** or ***unsaturated*** using the same criteria as we used for fatty acids.

- Saturated triglyceride molecules ***do not*** contain ___________________________ double bonds.
- Unsaturated triglyceride molecules contain ______ _____ ______ carbon-carbon double bonds.
    - Unsaturated triglycerides are often further subcategorized as either **monounsaturated** or **polyunsaturated**.
        - *Monounsaturated* triglycerides contain only ***one*** carbon-carbon double bond.
        - *Polyunsaturated* triglycerides contain ***two or more*** carbon-carbon double bond.

Solid vs. Liquid Triglycerides

Just like *fatty acids*, triglycerides with higher degrees of _____________ (***less*** carbon-carbon double bonds) are more flexible and can pack closer to each other than less saturated triglycerides.

The melting points of triglycerides ___________________ with the degree of saturation.

Since animal fats have a relatively ***high*** *degree of saturation*, they are solid at room temperature

Vegetable oils and fish oils have a ***lower*** *degree of saturation* than animal fats, and are therefore ***liquid*** at room temperature (consider olive and corn oil).

Use the table of fatty acids to draw a saturated triglyceride molecule.

The primary biological roles of triglycerides in animals are:

- energy storage
- the production of energy when metabolized
- provision of fatty acids for the production of other lipids
  insulation

Important Reactions of Triglycerides

- **Catalytic Hydrogenation**
  - triglyceride (C=C) + H_2/Pt → more saturated triglyceride

- **Oxidation**
  - triglyceride + O_2 → small organic molecules

- **Saponification**
  - Hydrolysis of the ester group in the presence of hydroxide (OH^-)

Catalytic Hydrogenation

- This is reaction is the same reaction that we saw for the reduction of an alkenes to alkanes in chapter 6!!!
- When enough H_2 is supplied, an unsaturated triglyceride is converted to a saturated triglyceride.

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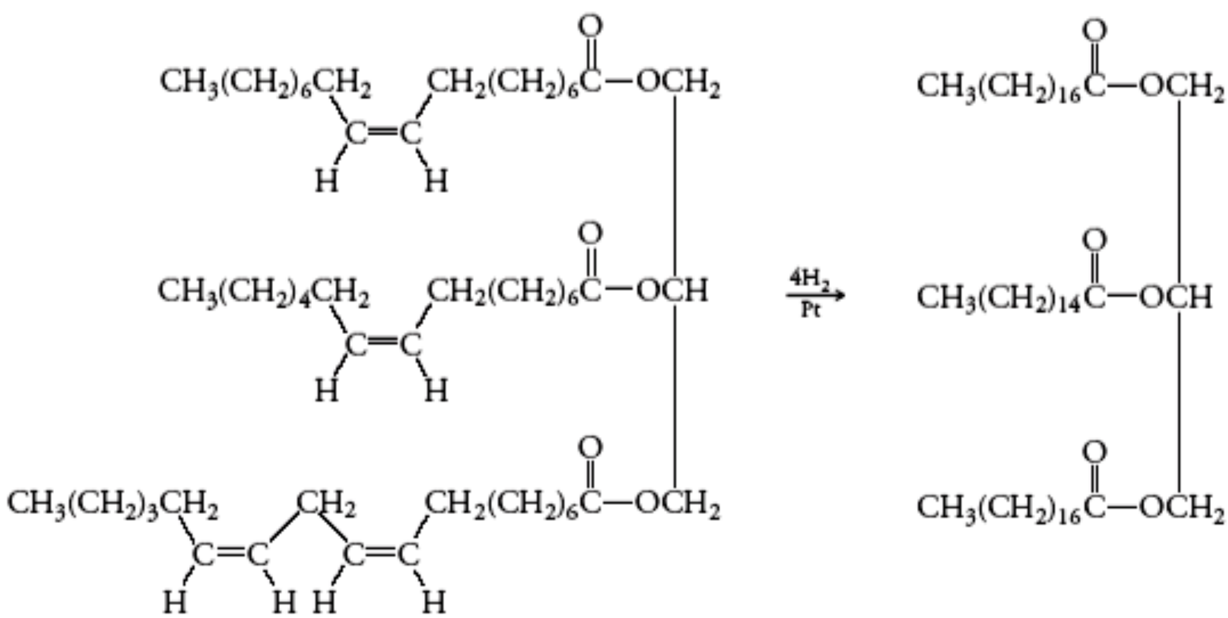
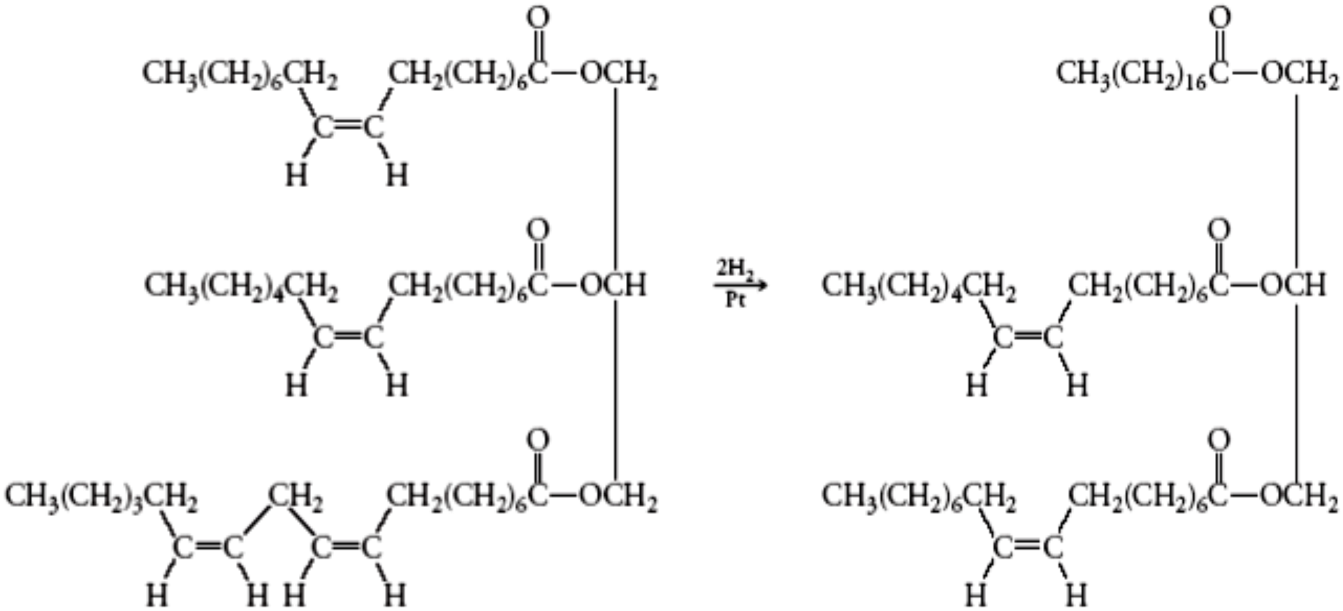


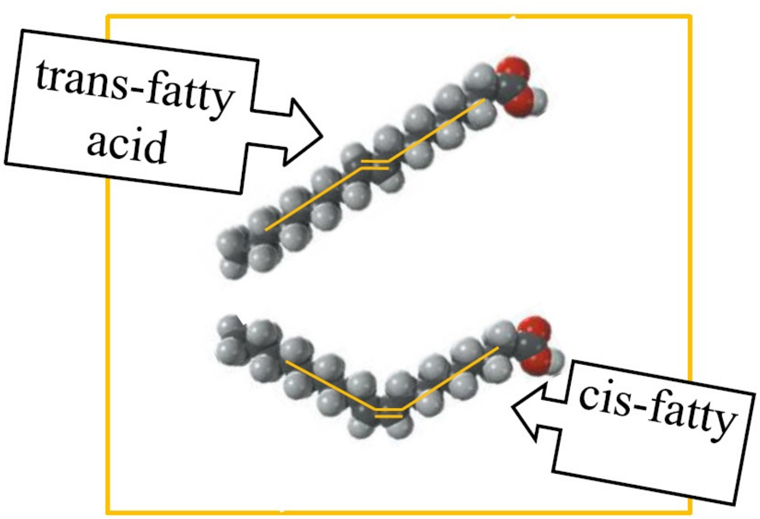
Example: Partial Hydrogenation

When H_2 is limited, only some of the carbon-carbon double bonds are removed.



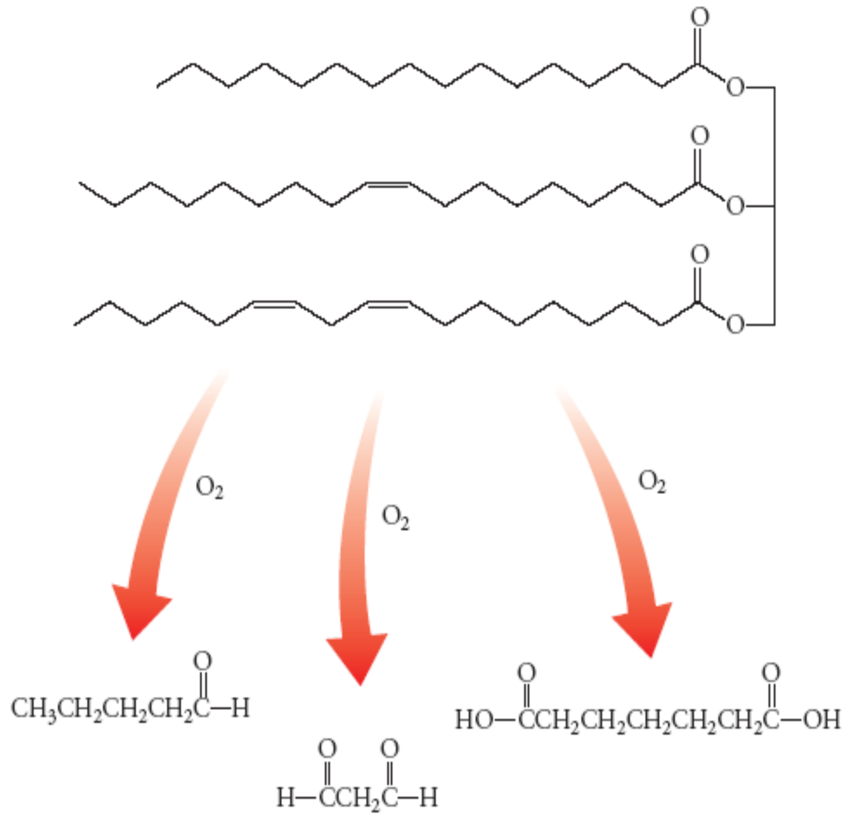
Catalytic Hydrogenation:
Partially Hydrogenated Vegetable Oil

- Many foods contain ***partially hydrogenated vegetable oil***.
- Partial hydrogenation will yield some __________________ fats.



Oxidation of Triglycerides:

Triglyceride + O_2 → Small organic molecules

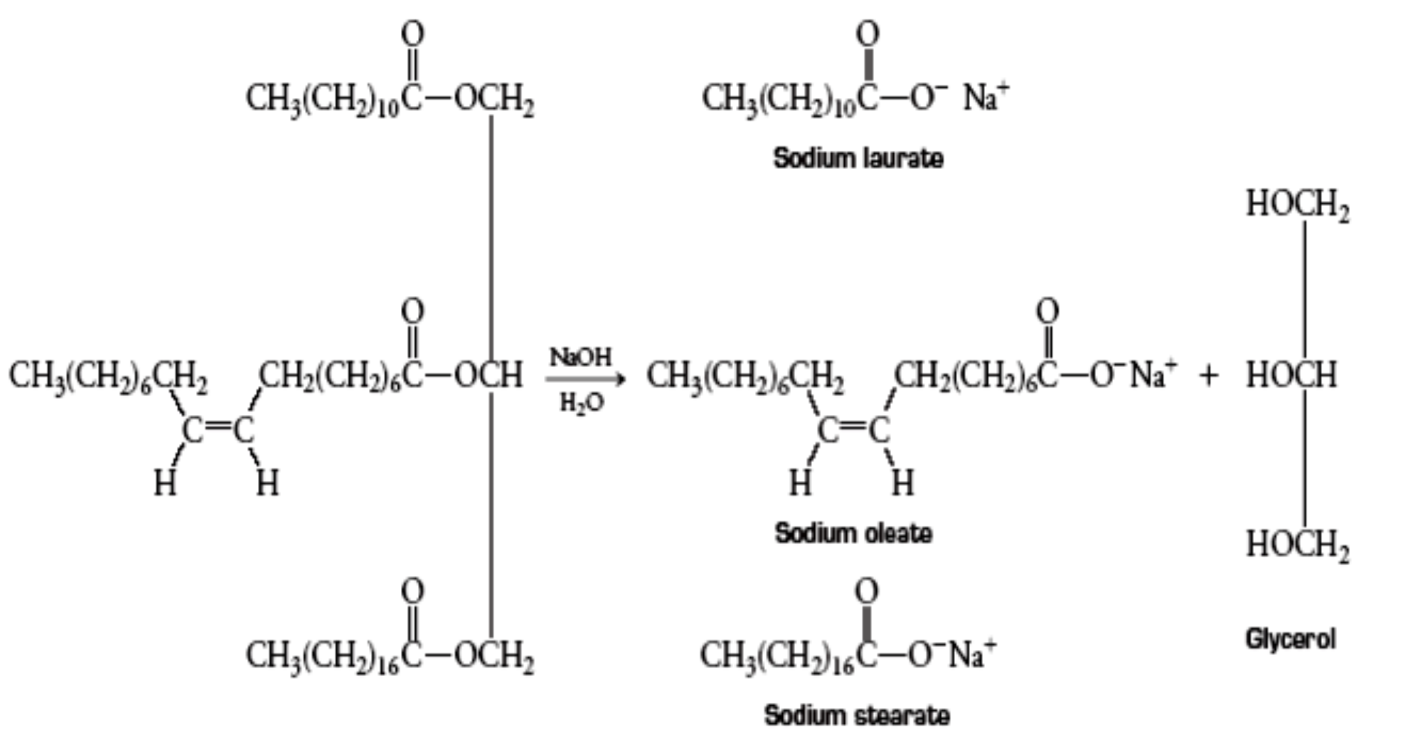


- The ***products*** of triglyceride oxidation ***smell very bad***.
  - *ex*: rancid butter
- Refrigeration helps because is slows the rate of oxidation.
- Tightly closed containers help because they limit the supply of oxygen

Saponification

_____________________________ of ester group in the presence of hydroxide (OH^-).

- Converts triglycerides into fatty acid salts (soap) and glycerol.



Phospholipids and Glycolipids

Phospholipids and Glycolipids are the Amphipathic Lipids Commonly Found in Membranes

Membranes are

____

________________of

amphipathic lipids.

- They are also referred to as **lipid bilayers**.

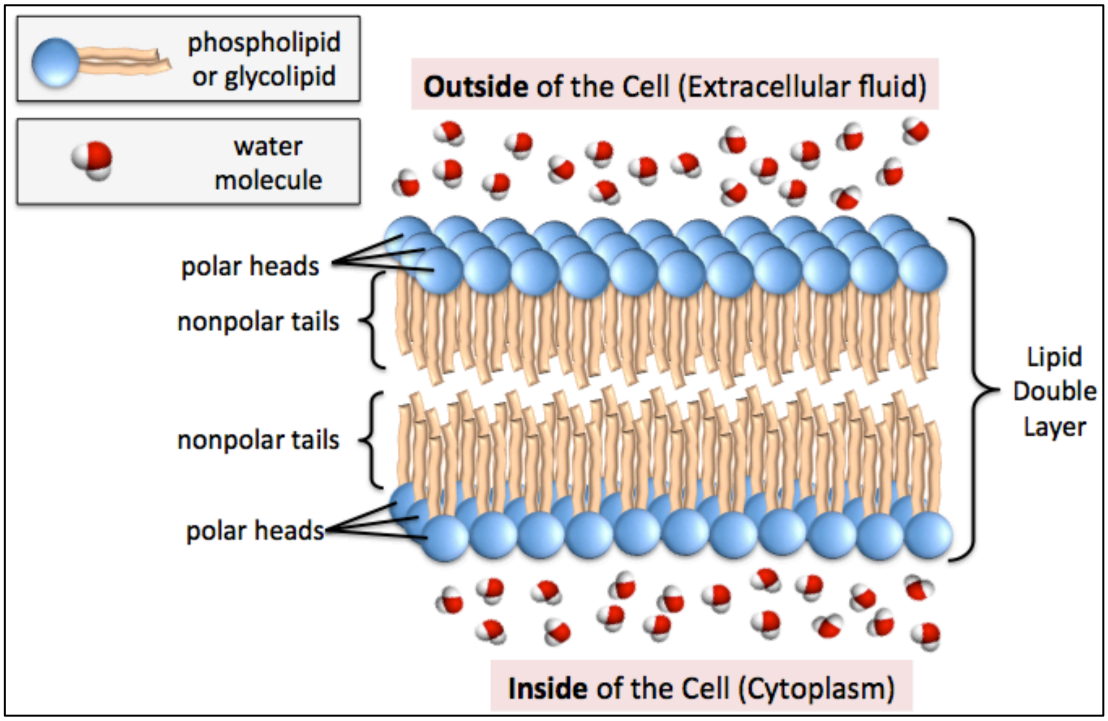
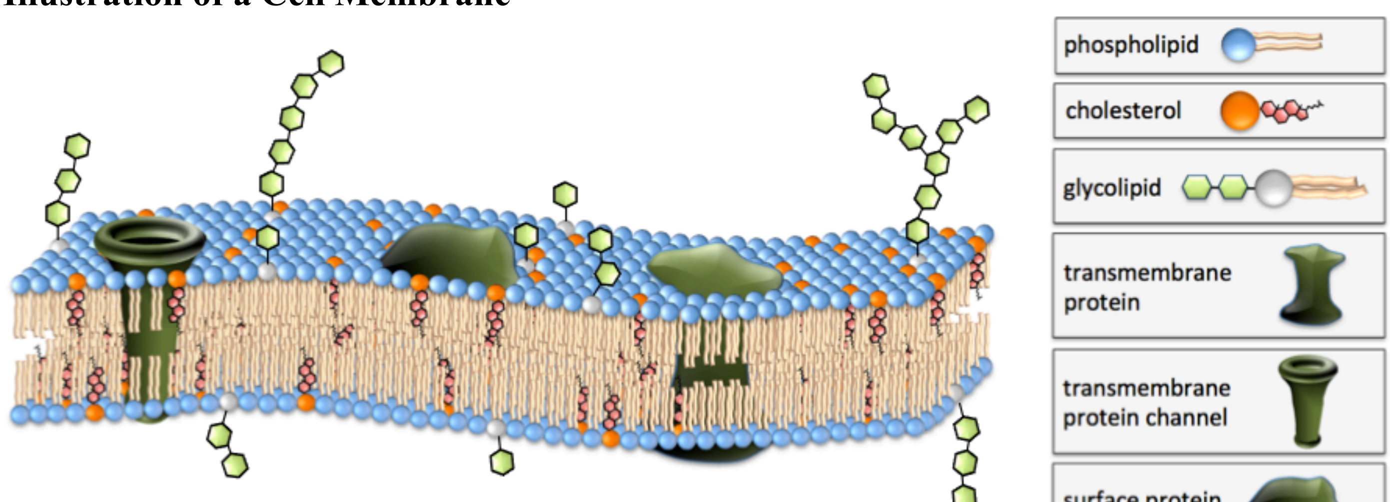
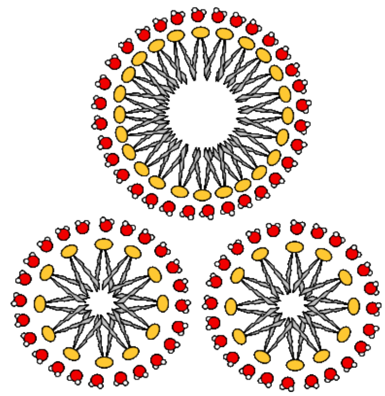


Illustration of a Cell Membrane



Phospholipids

Because they are amphipathic, phospholipids are effective as ***emulsifying agents***, compounds that make or stabilize emulsions.



- An ________________ is a *colloid* formed by combining two liquids with an emulsifying agent such as a phospholipid.
    - For example, it is the lecithin (a phospholipid) present in egg whites that keeps mayonnaise, an oil-water emulsion, from separating.
    -

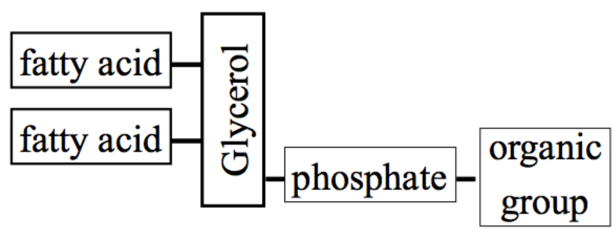
Phospholipids get their name from the fact that the phosphate ion (PO_4^{3-}) is one of the components used in their formation.

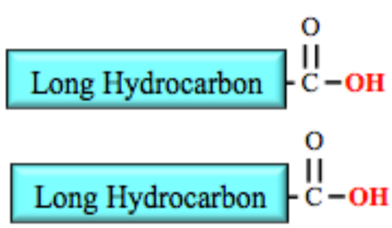
There are two classes of phospholipids:

1) glycerophospholipids
2) sphingophospholipids

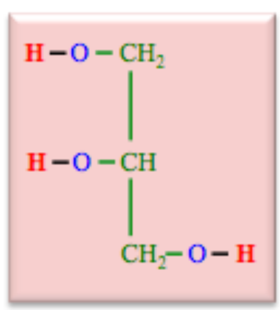
1) Glycerophospholipids

Glycerophospholipids are made by combining glycerol, two fatty acids, a phosphate group, and an alcohol.

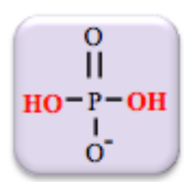




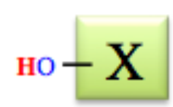
one *or* two fatty acids



glycerol

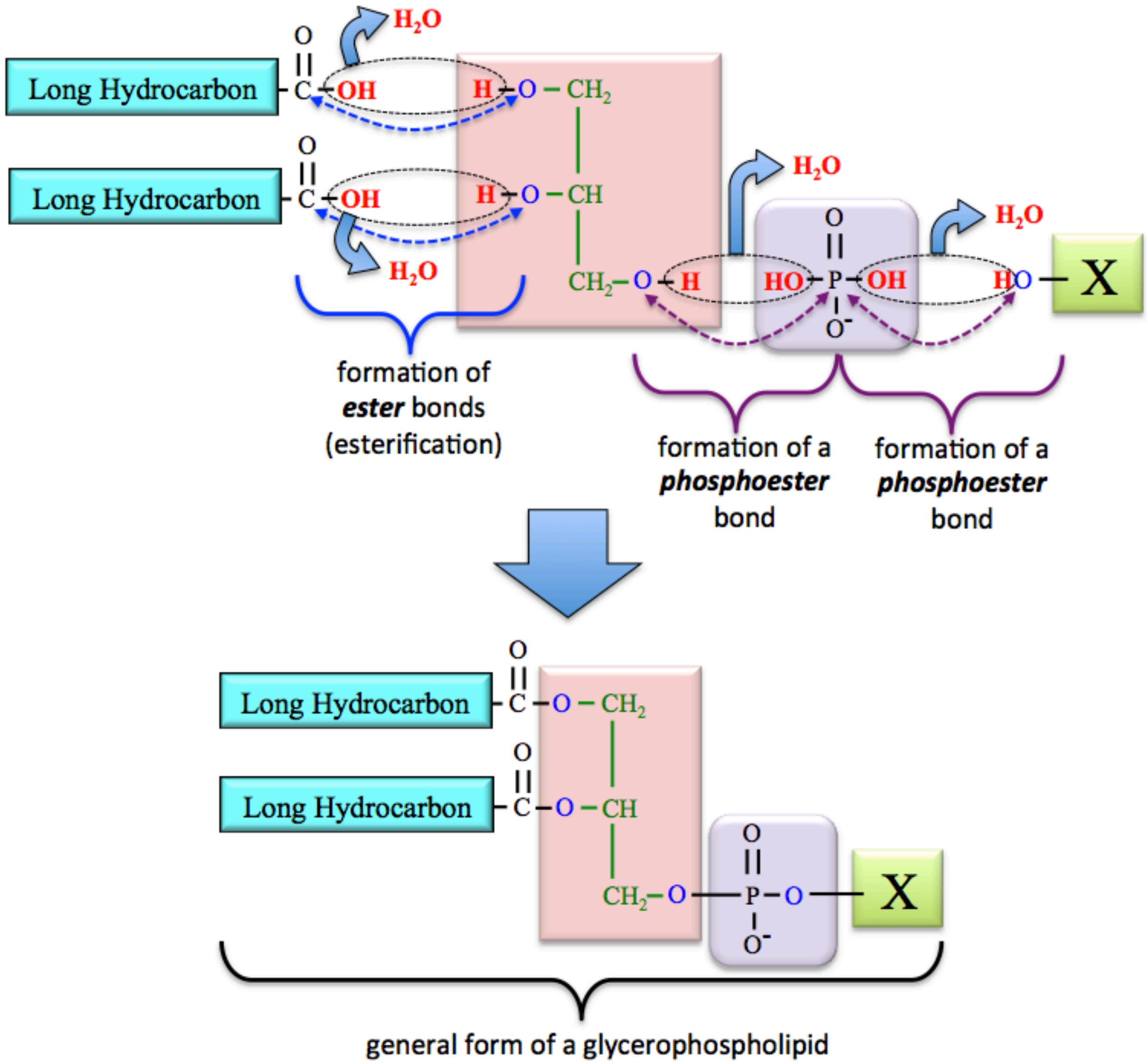


a phosphate
(dihydrogen phosphate ion)



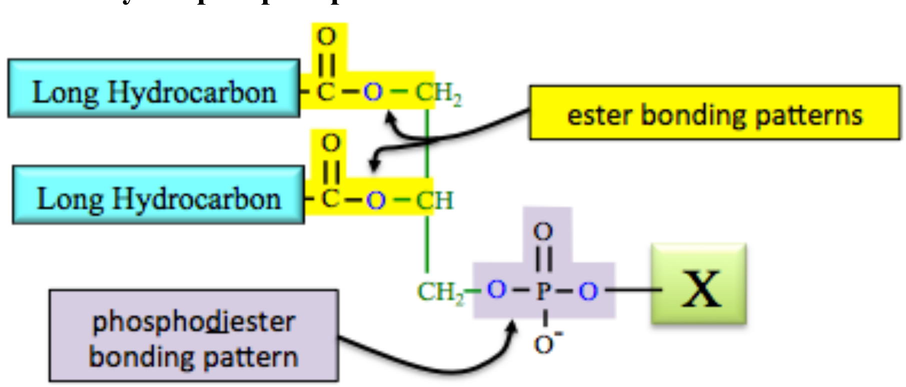
an alcohol
(X = an organic group)

The glycerol, fatty acids, phosphate group, and organic group combined as shown below:

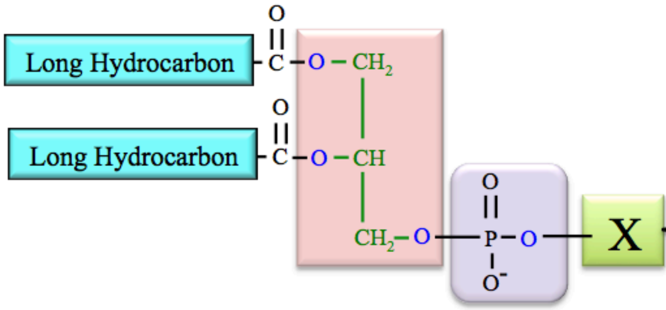


In glycerophospholipids, we refer to the glycerol residue (highlighted red above) as the "**glycerol backbone**."

Bonding Patterns in a Glycerophospholipid:

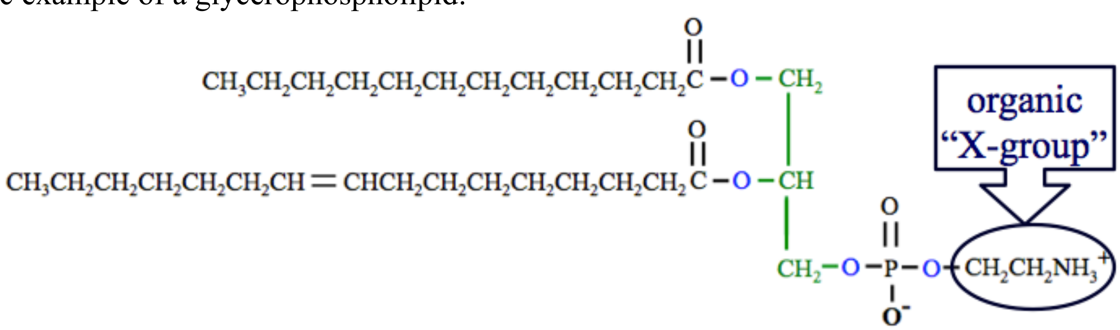


Glycerophospholipids are sub classified based on the identity of their organic "X group" as shown below.



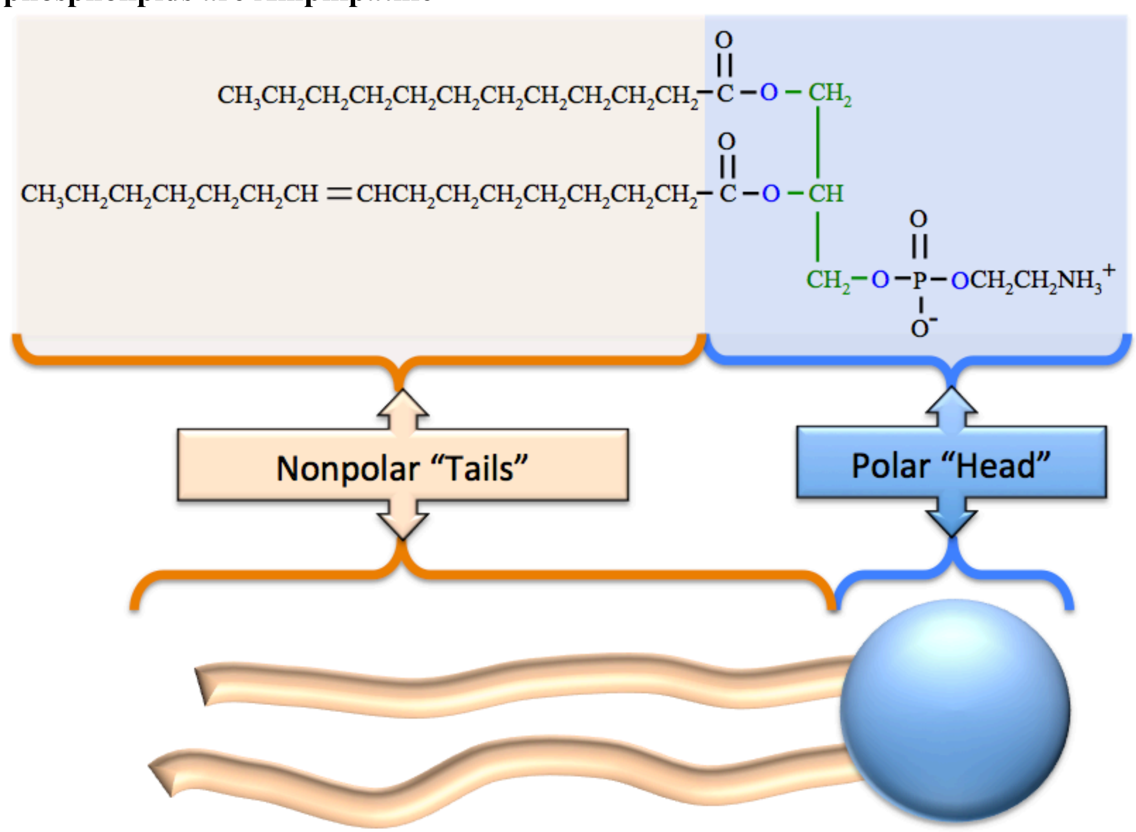
Organic "X group"	Glycerophospholipid Class
$-CH_2CH_2NH_3^+$	Phosphatidylethanolamine (present in *Cephalin*)
$-CH_2CH_2N^+(CH_3)_3$	Phosphatidylcholine (present in *Lecithin*)
$-CH_2CH(NH_3^+)C(=O)O^-$	Phosphatidylserine (present in *Cephalin*)

A specific example of a glycerophospholipid:



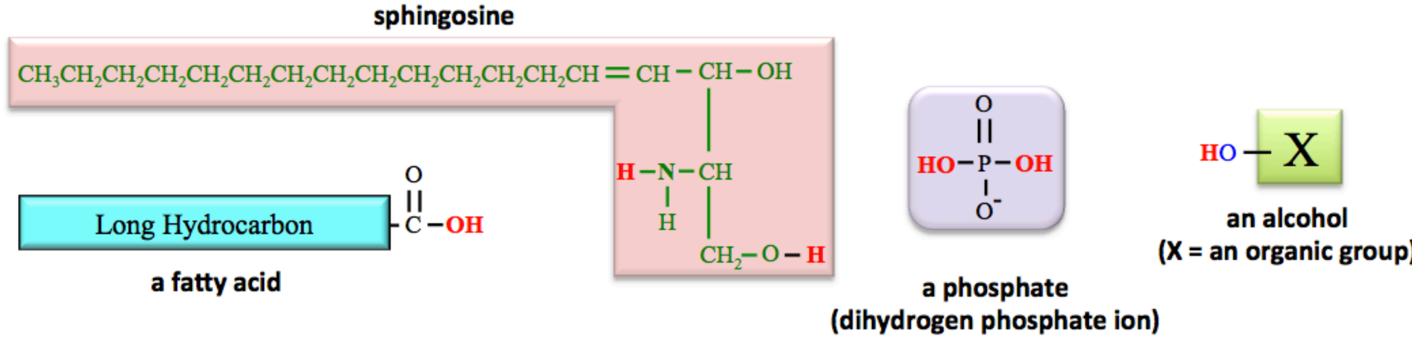
a phosphatidylethanolamine

Glycerophospholipids are Amphipathic

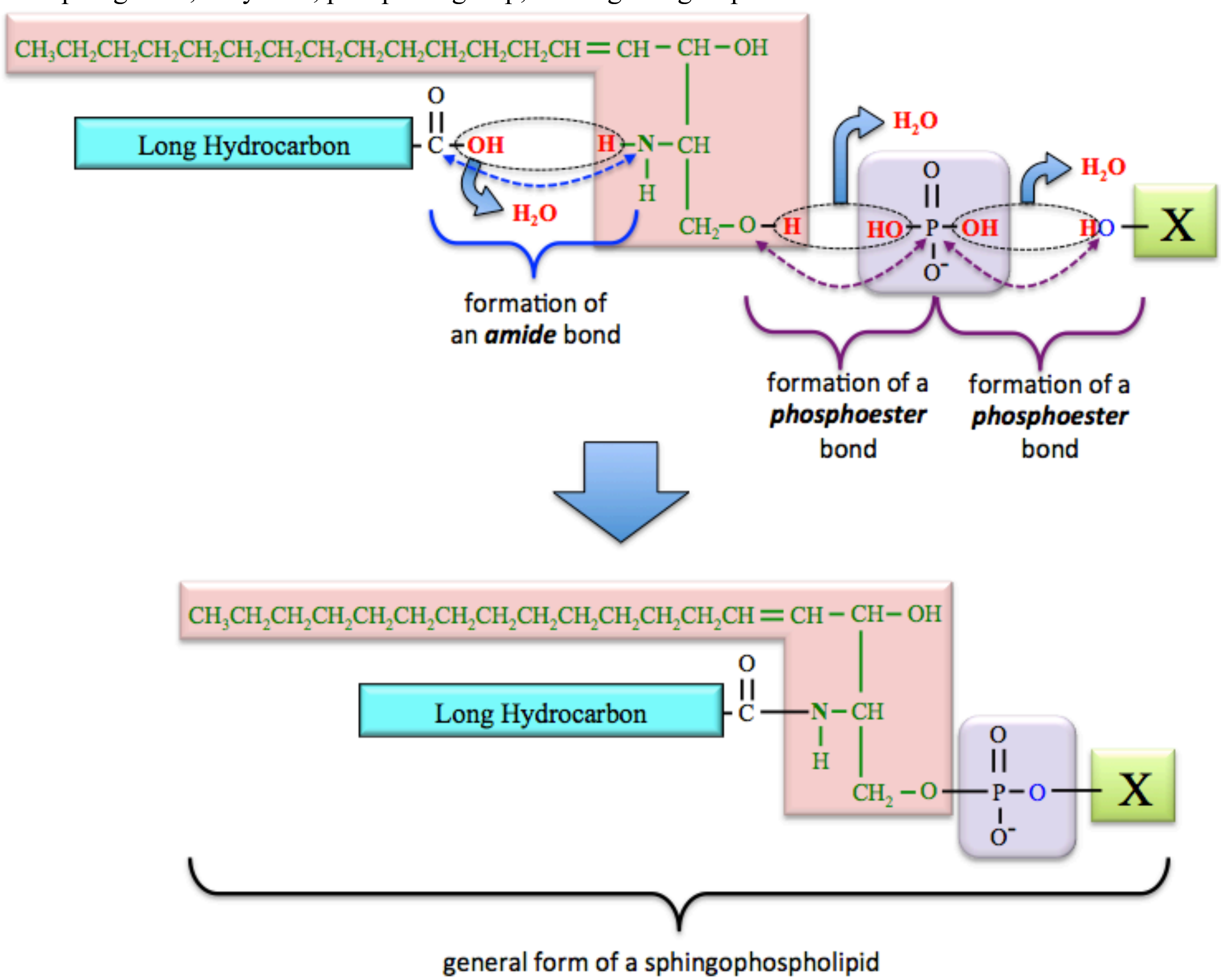


2) Sphingophospholipids

Sphingophospholipids are made by combining sphingosine, a fatty acid, a phosphate group, and an alcohol.

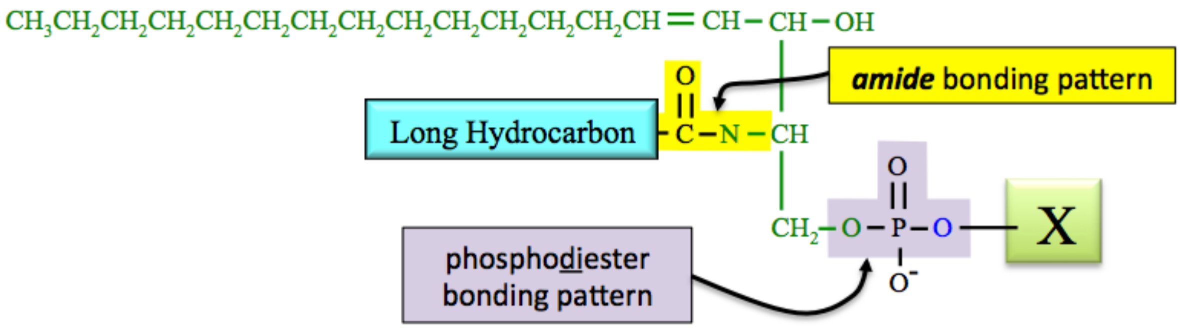


The sphingosine, fatty acid, phosphate group, and organic group combined as shown below:



In sphingophospholipids, we refer to the sphingosine residue (highlighted red above) as the "**sphingosine backbone**."

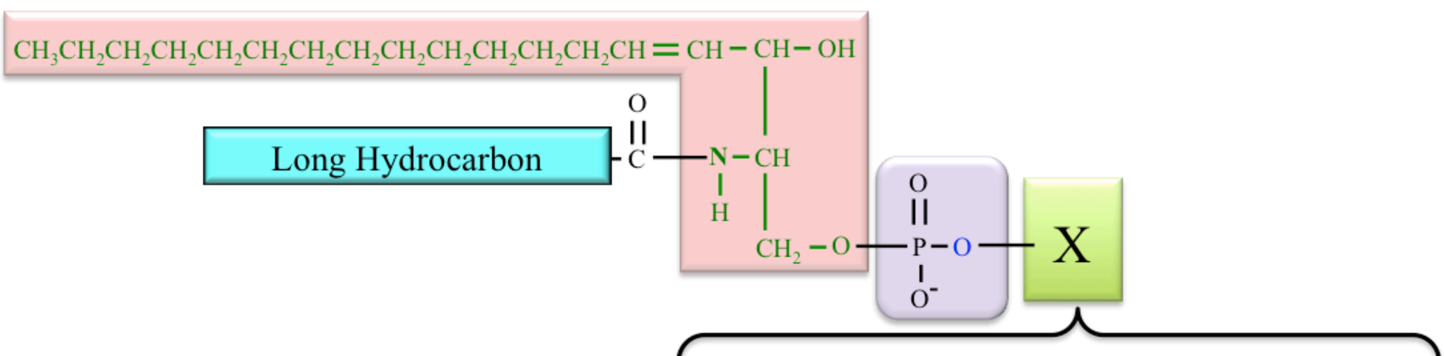
The General Form of a Sphingophospholipid:



What do you need to know about phospholipids?
How to distinguish sphingophospholipids from glycerophospholipids.

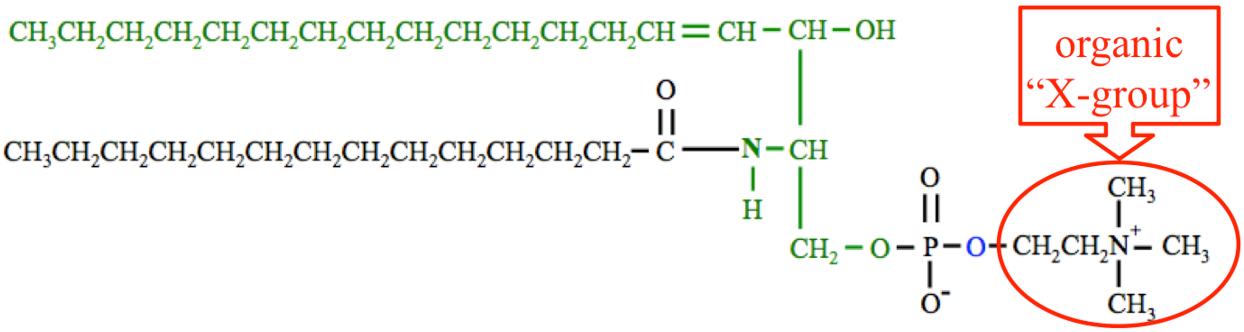
- Both have phosphate groups
- To identify sphingophospholipids, look for the sphingosine backbone and the amide bonding pattern.
- To identify glycerophospholipids, look for the glycerol backbone, the ester bonding pattern.

Sphingophospholipids are sub classified based on the identity of their organic "X group" as shown below.



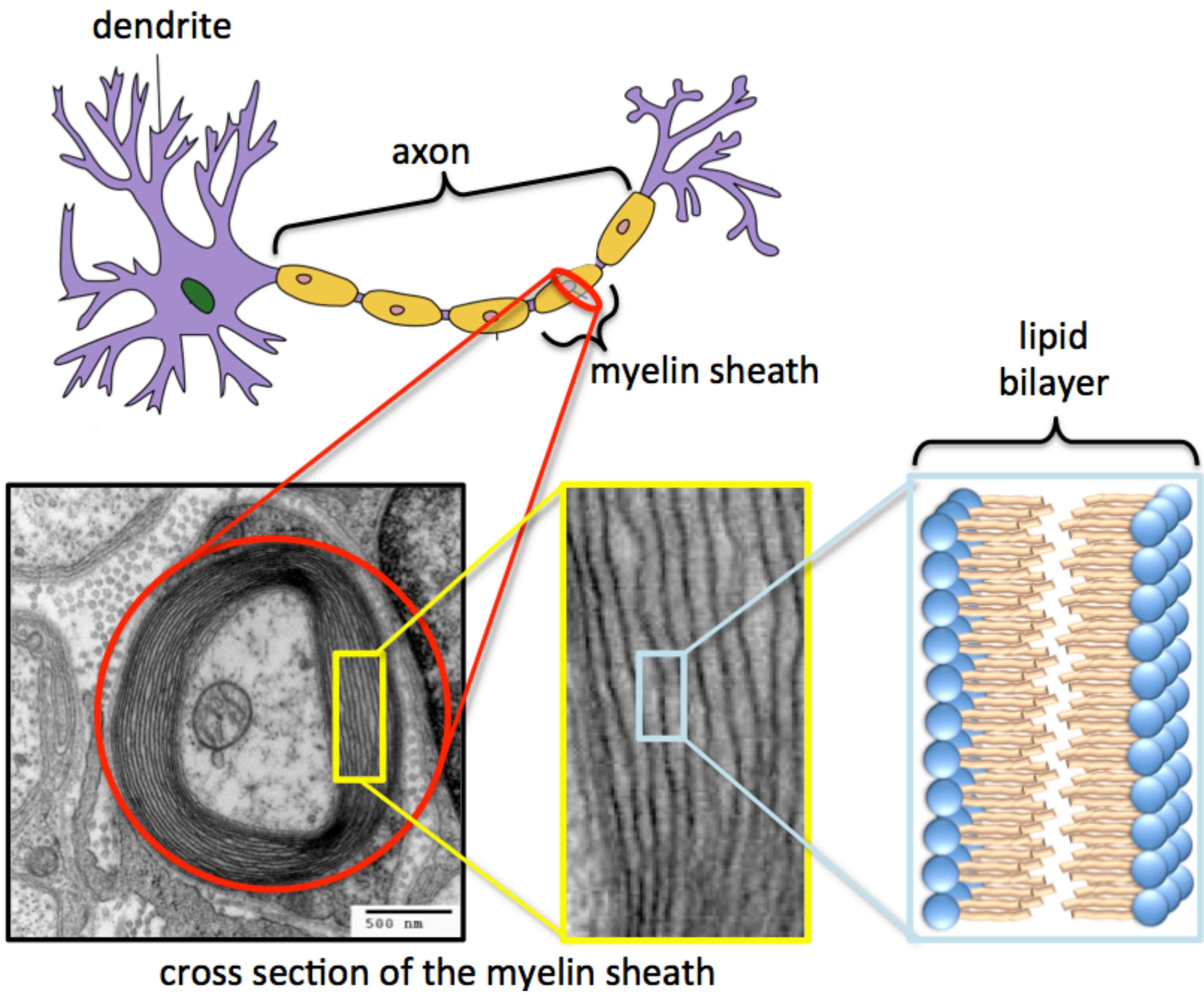
Organic "X-group"	Sphingophospholipid Class
$-H$	Ceramide
$-CH_2CH_2NH_3^+$ **or** $-CH_2CH_2N^+(CH_3)_3$	Sphingomyelin

A Specific Example of a Sphingophospholipid:

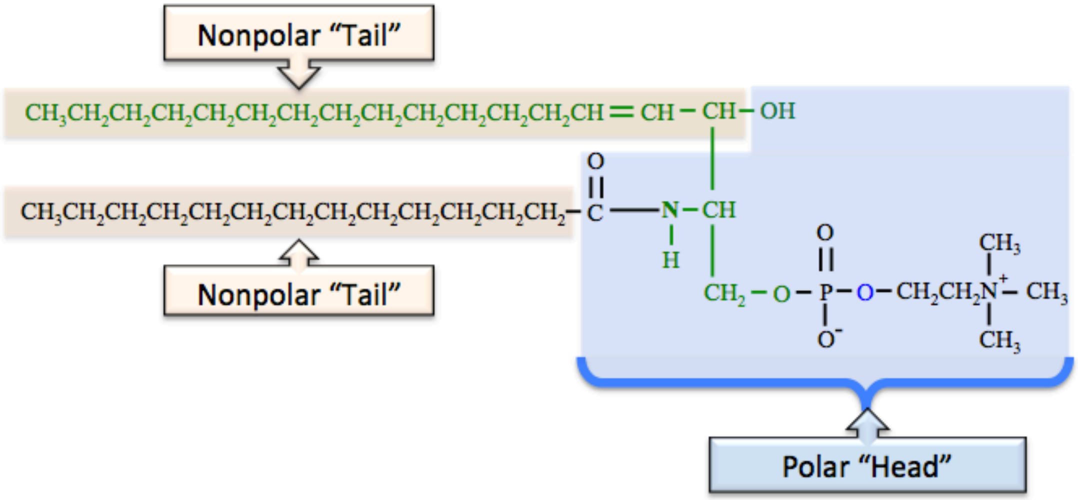


a sphingomyelin

Sphingomyelin is found in *myelin*, a bilayer that wraps around nerve cell axons.

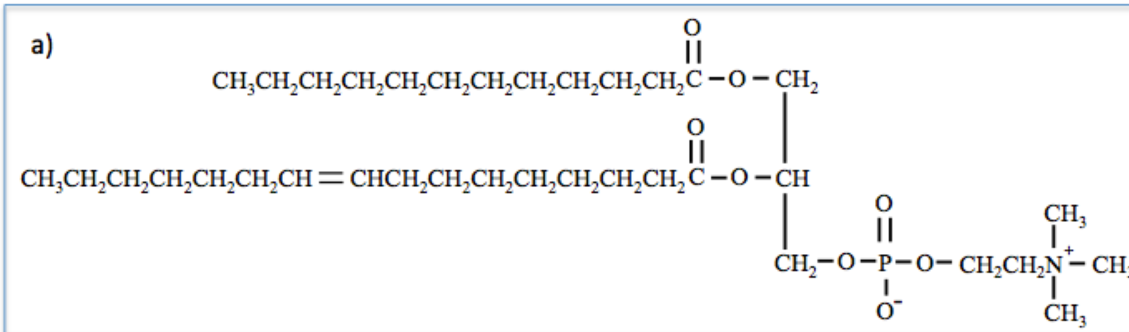


Sphingophospholipids are Amphipathic

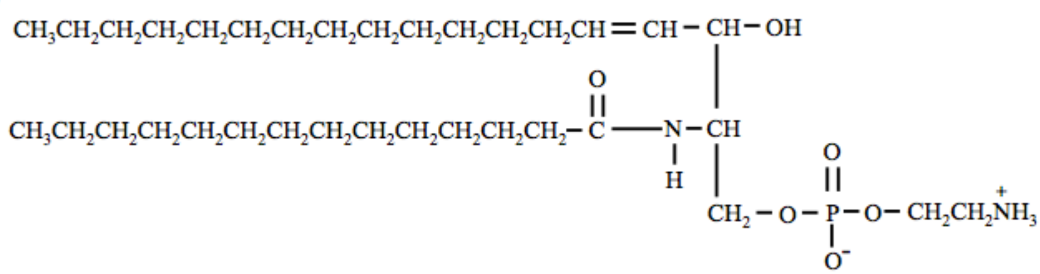


You try a problem: Categorize each of the following compounds as being either a ***glycerophospholipid*** or a ***sphingophospholipid***.

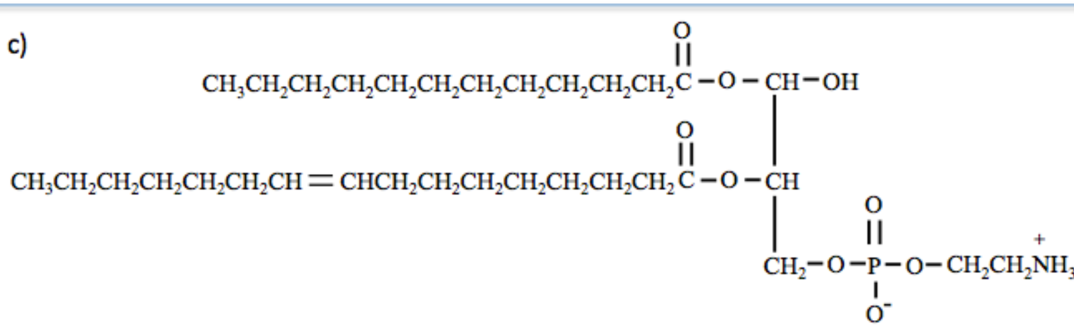
a)



b)



c)



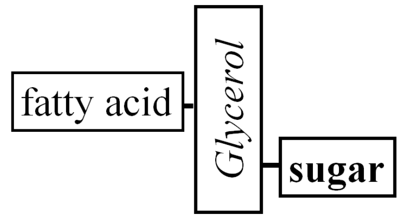
Glycolipids

Glycolipids are lipids that contain a sugar residue.

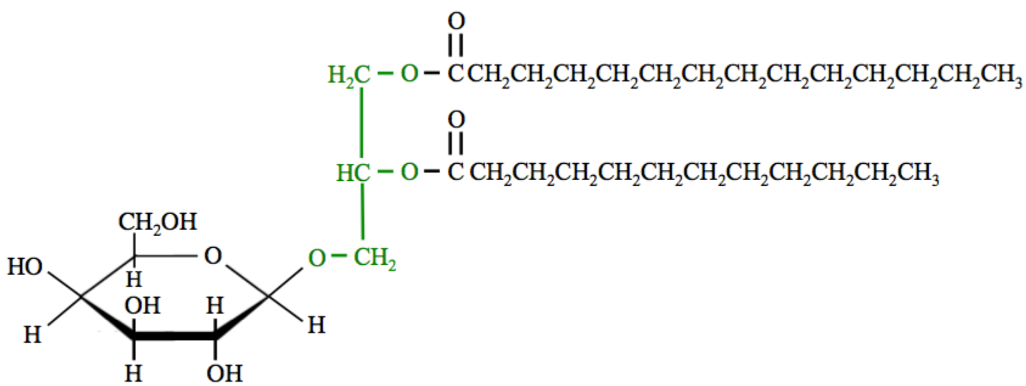
- NOTE: No phosphate groups
- The sugar can be a monosaccharide, oligosaccharide, or polysaccharide.

Glyceroglycolipids

In many cases the sugar and fatty acid residues are attached to a ***glycerol*** backbone, these are called glyceroglycolipids.



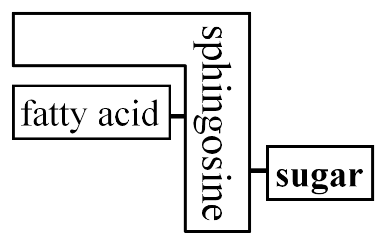
A Specific Example of a Glyceroglycolipid:



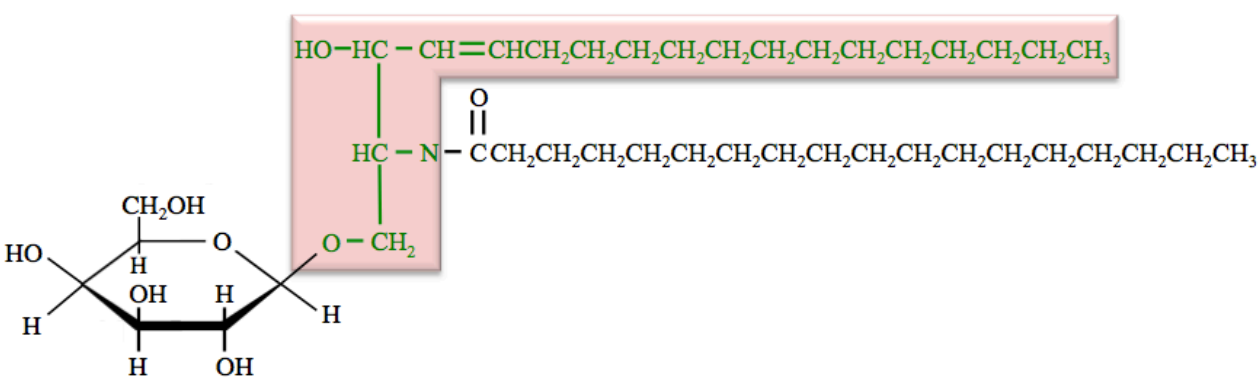
monogalactosyldiglyceride (MGDG)

Sphingoglycolipids

In many cases this sugar and fatty acid residues are attached to a ***sphingosine*** backbone, these are called sphingoglycolipids.



A Specific Example of a Glyceroglycolipid:

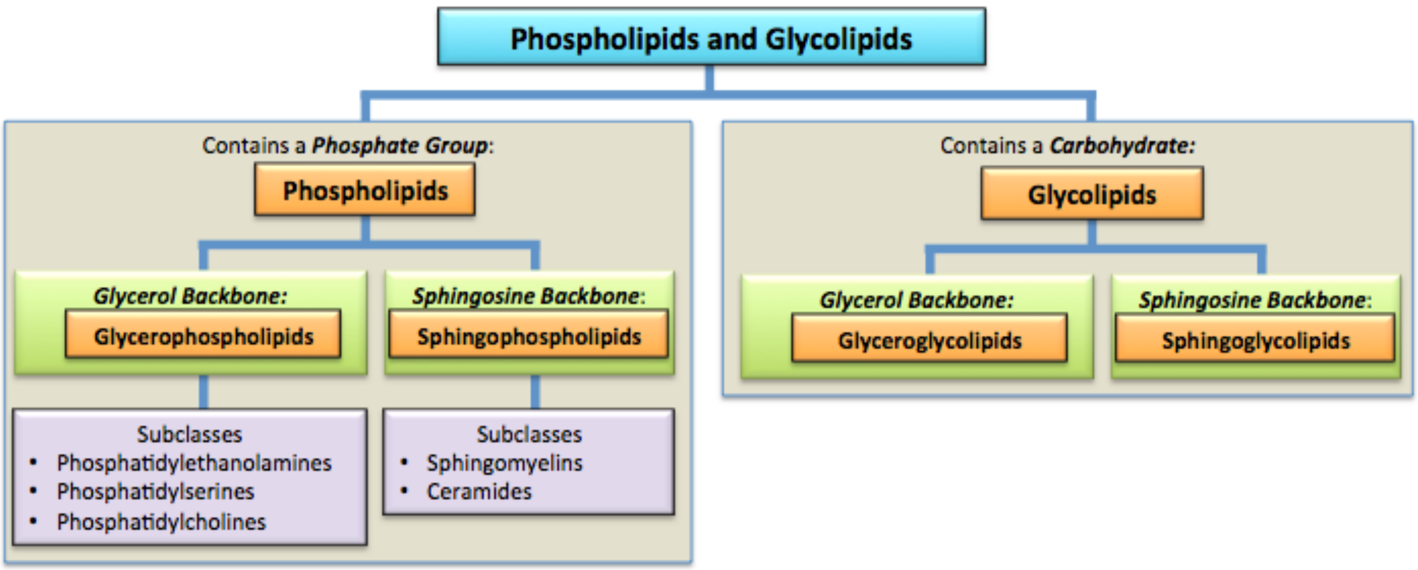


Glucosylceremide

Tay-Sachs Disease:

- **Hexosaminidase A Deficiency**
- **Sphingolipidosis**
- A gentic disorder, fatal in its most common variant known as **Infantile Tay-Sachs disease**.
    - TSD is inherited in a recessive pattern.
- The disease occurs when harmful quantities of a sphingoglycolipids accumulate in the nerve cells of the brain.

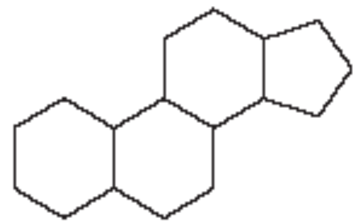
Summary: Phospholipids and Glycolipids



Steroids

__________________ are a class of lipids that share the same basic ring structure - three fused 6-carbon atom rings and one 5-carbon atom ring.

- There are three important types of steroids:
  - 1) cholesterol
  - 2) steroid hormones
  - 3) bile salts

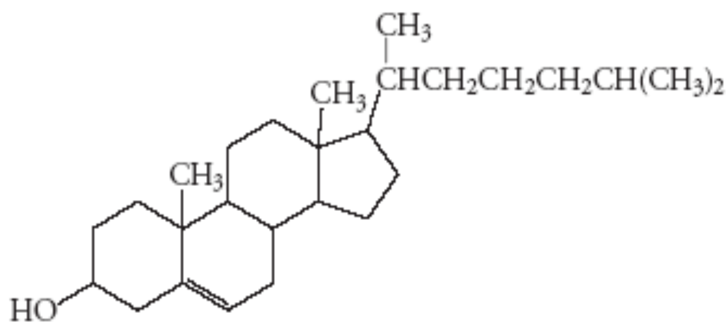


Ring structure of a steroid

1) Cholesterol

Cholesterol is the steroid found most often in humans and other animals.

Regardless of what you eat, your body will contain some cholesterol, because it is manufactured in the liver.



Cholesterol

In cholesterol, the nonpolar rings and hydrocarbon chain are hydrophobic and the -OH group, which makes up *a much smaller part of the molecule*, is hydrophilic.

Overall, this makes the molecule ***hydrophobic***.

The primary biological use of cholesterol is as the starting material for the biosynthesis of other

_______________.

Cholesterol is a component of cell membranes.

2) Steroid Hormones

Hormones, *molecules that regulate the function of organs and tissues*, come in a variety of forms.

- Some, such as sex hormones and adrenocorticoid hormones, are steroids.
- Steroid hormones are made from______________________.

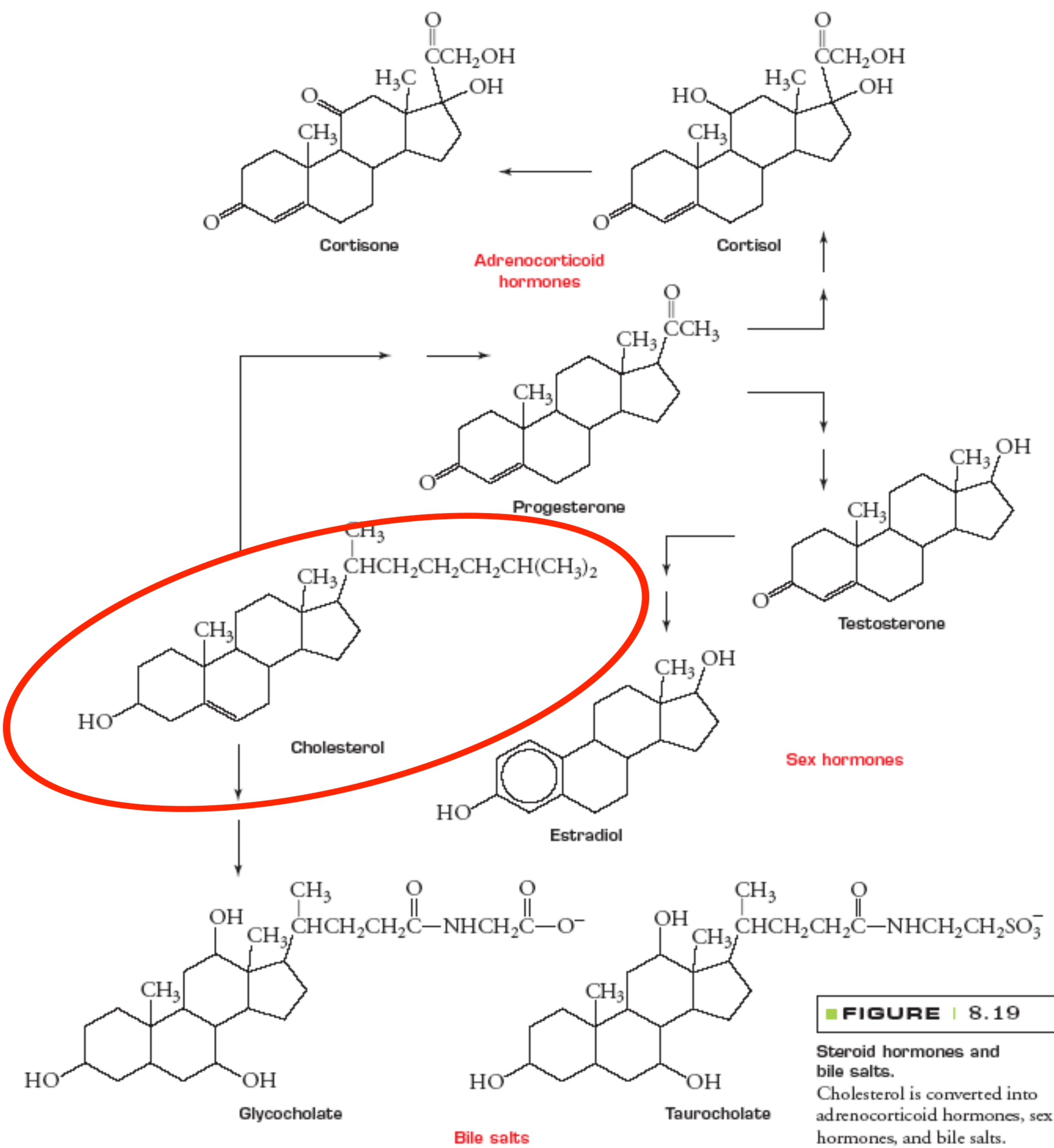


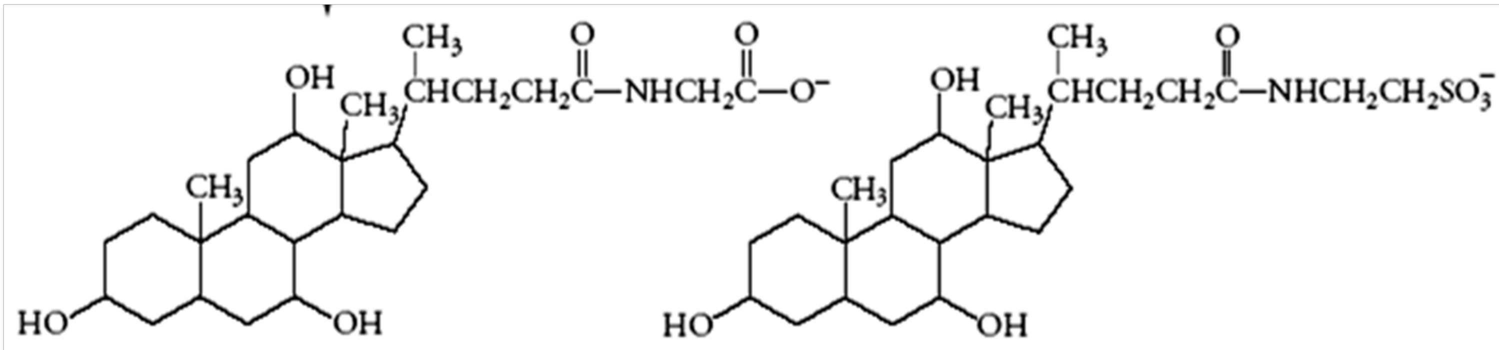
FIGURE 8.19

Steroid hormones and bile salts.
Cholesterol is converted into adrenocorticoid hormones, sex hormones, and bile salts.

3) Bile Salts

Bile salts, produced from cholesterol, are_______________________________.

- Glycocholate, taurocholate, and other bile salts are released from the gallbladder into the small intestine, where they aid digestion by forming ***emulsions*** with dietary lipids.



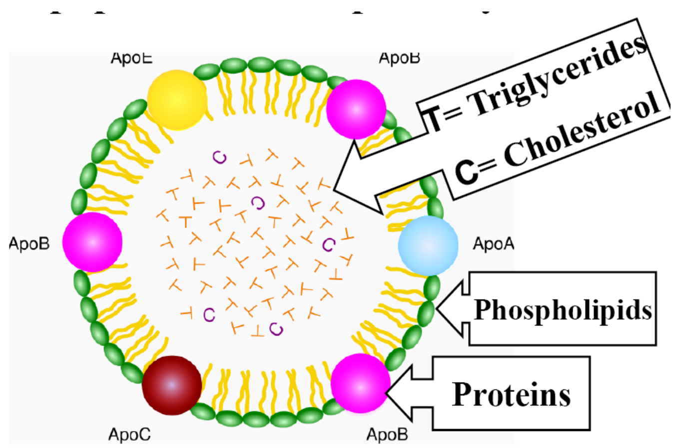
Glycocholate Taurocholate

How are *hydrophobic* lipids such as cholesterol and other molecules transported through the body in *aqueous* body fluids (such as blood)?

Answer:____

Lipoproteins

Example: Chylomicron



Classification of Lipoproteins

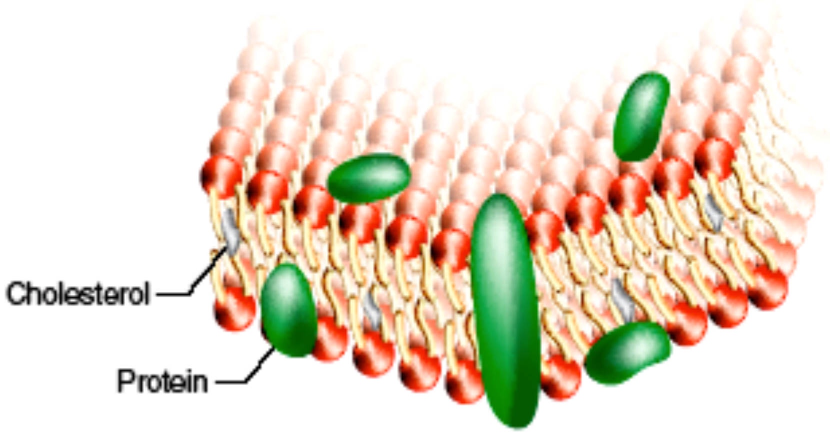
Lipoproteins are classified according to density.

- High protein to phospholipid ratio = high density.
- Low protein to phospholipid ratio = low density.

LDLs and HDLs

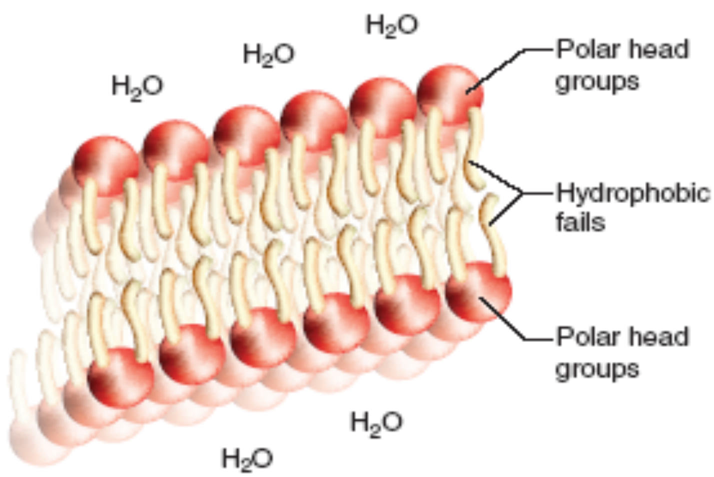
- The major function of **low density lipoproteins** (**LDLs**) is to transport cholesterol and phospholipids from the liver to the cells, where they are incorporated into membranes or, in the case of cholesterol, transformed into other steroids.
- **High density lipoproteins** (**HDLs**) transport cholesterol and phospholipids from the cells back to the liver.
  - Low HDL and high LDL levels in the blood are warning signs of atherosclerosis, the buildup of cholesterol-containing deposits in arteries.

Membranes



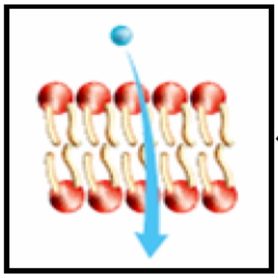
Membranes, barriers that surround cells or that separate one part of a cell from another, are a bilayer of amphipathic lipids - usually phospholipids, glycolipids, and cholesterol.

The lipids are arranged so that their hydrophilic heads interact with one another and with water at the surface of the membrane, and so that their hydrophobic tails interact with one another at the center of the membrane.

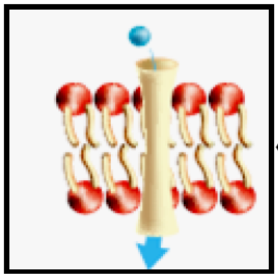


Movement Through Cell Membranes

2 Types of Passive Transport:

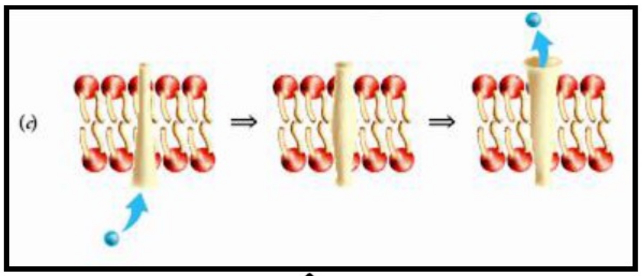


1) Diffusion:
Non-polar molecules diffuse across membranes moving from areas of higher to lower concentration.



2) Facilitated Diffusion:
Some polar molecules diffuse through a protein channel that spans the membrane

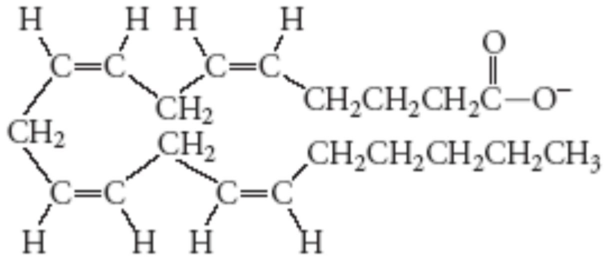
Active Transport:



Active Transport: Some molecules and ions are Transported across membranes in the direction of lower to higher concentration (requires energy).

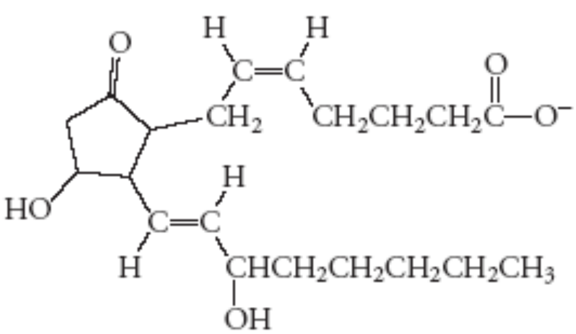
Eicosanoids

The "*eico*" prefix is from the Greek "*eicosa*," which means twenty. The lipids called **eicosanoids** are *signaling molecules* that contain twenty carbon atoms. They are derived from one of three, twenty-carbon polyunsaturate fatty acids (arachidonic acid, eicosapentaenoic acid, or dihomo-gamma-linolenic acid). Arachidonic acid, shown below, is the major precursor of eicosanoids.

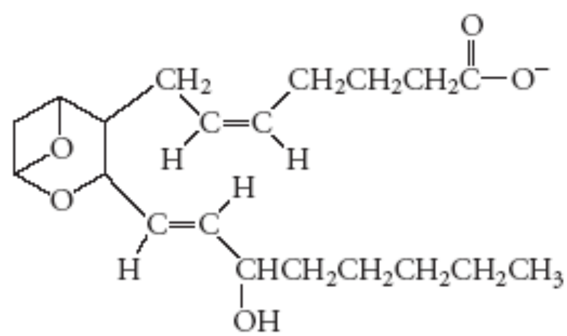


Arachidonic acid

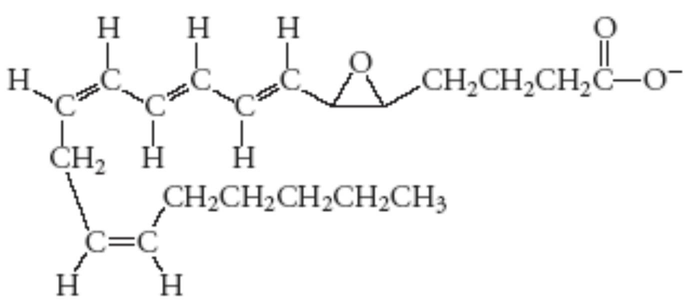
Arachidonic acid, eicosapentaenoic acid, or dihomo-gamma-linolenic acid undergo *reactions* that transforms them into the various classes of *eicosanoids* - such as ***prostaglandins***, ***thromboxanes***, ***leukotrienes***, and ***prostocyclin***. For example, arachidonic acid can be transformed into the three eicosanoids shown below.



PGE_2
(a prostaglandin)



Thromboxane A_2



Leukotriene A_4

FIGURE | 8.20

Eicosanoids.
Arachidonic acid, a polyunsaturated fatty acid, is converted into prostaglandins, thromboxanes, and leukotrienes.

Prostaglandins

- Prostaglandins have a wide range of biological effects:
  - causing pain
  - causing inflammation
  - causing fever
  - affecting blood pressure
  - inducing labor (PGE_2)

Thromboxanes and Leukotrienes

- Thromboxanes, such as thromboxane A_2, are involved in blood clotting.
- Leukotrienes, including leukotriene A_4, induce muscle contractions in the lungs and are linked to asthma attacks.
  - Some anti-asthma drugs block the production of leukotrienes.

Nonsteroidal Anti-inflammatory Drugs (NSAIDs)

- NSAIDs such as aspirin, acetaminophen, and ibuprofen reduce pain, fever, and inflammation by blocking the action of an enzyme involved in the conversion of arachidonic acid into prostaglandins and thromboxanes.
  - There are two forms of this enzyme:
    - COX-1 and COX-2