

## Chapter 12 Lecture Notes: Lipids and Membranes

### 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 **sphingophospholipid**.
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 used as: cell membrane components, energy storage compounds, insulation, signaling compounds, and hormones.

### Introduction to Lipids

**Lipids are not** defined by the presence of specific functional groups.

**Lipids are defined as** \_\_\_\_\_ **compounds that are** \_\_\_\_\_ **in** \_\_\_\_\_ **but soluble in nonpolar solvents.**

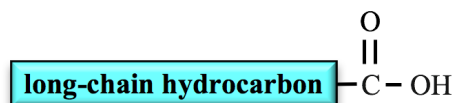
- *Biological compounds* are organic compounds that occur in *living* organisms.
- There are three *solubility classes* for biological compounds: **hydrophilic, hydrophobic, and amphipathic**.
  - Of these three classes, **hydrophobic and amphipathic** are **water-insoluble**.
    - Amphipathic molecules are **water-insoluble** because they do not dissolve when placed in water; they form *monolayers* and *micelles*.

You will be introduced to *seven classes of lipids* in this chapter:

- 1) **Fatty Acids**
- 2) **Waxes**
- 3) **Triglycerides**
- 4) **Steroids**
- 5) **Phospholipids**
- 6) **Glycolipids**
- 7) **Eicosanoids**

## Fatty Acids

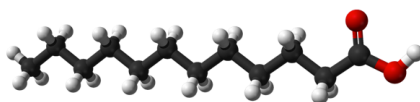
Fatty acids are \_\_\_\_\_ *acids* with \_\_\_\_\_ *-chain* hydrocarbon parts.



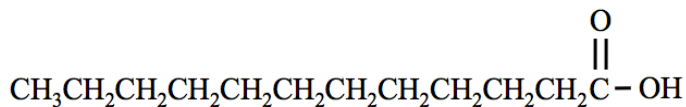
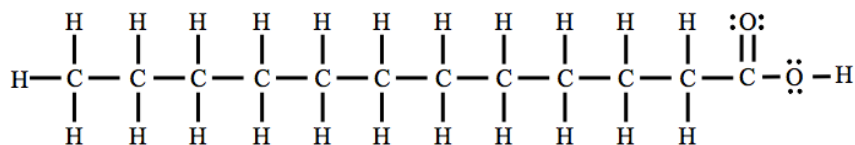
**general form of a fatty acid**

Fatty acids typically *contain between twelve and twenty carbon atoms*.

A specific example of a fatty acid is *lauric acid*.

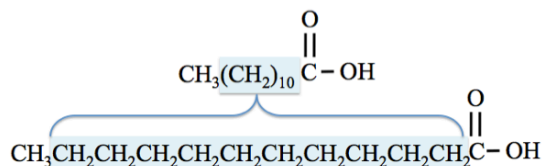


**lauric acid**



In order to save time when drawing structural formulas for large molecules such as fatty acids, an *abbreviated condensed structure* is used. Repeating units are shown in parenthesis with a subscripted number where the subscript is equal to the number of times that the structural unit *within the parenthesis* is repeated.

- For example, carbons that are single bonded to each other in a linear sequence, along with the hydrogens that are bonded to them, are abbreviated as  $(\text{CH}_2)_n$ , where **n** is equal to the number of times that the  $\text{CH}_2$  is repeated.



Fatty acids usually contain an \_\_\_\_\_ *number of carbon atoms* because they are made in nature by combining *two-carbon* molecules.

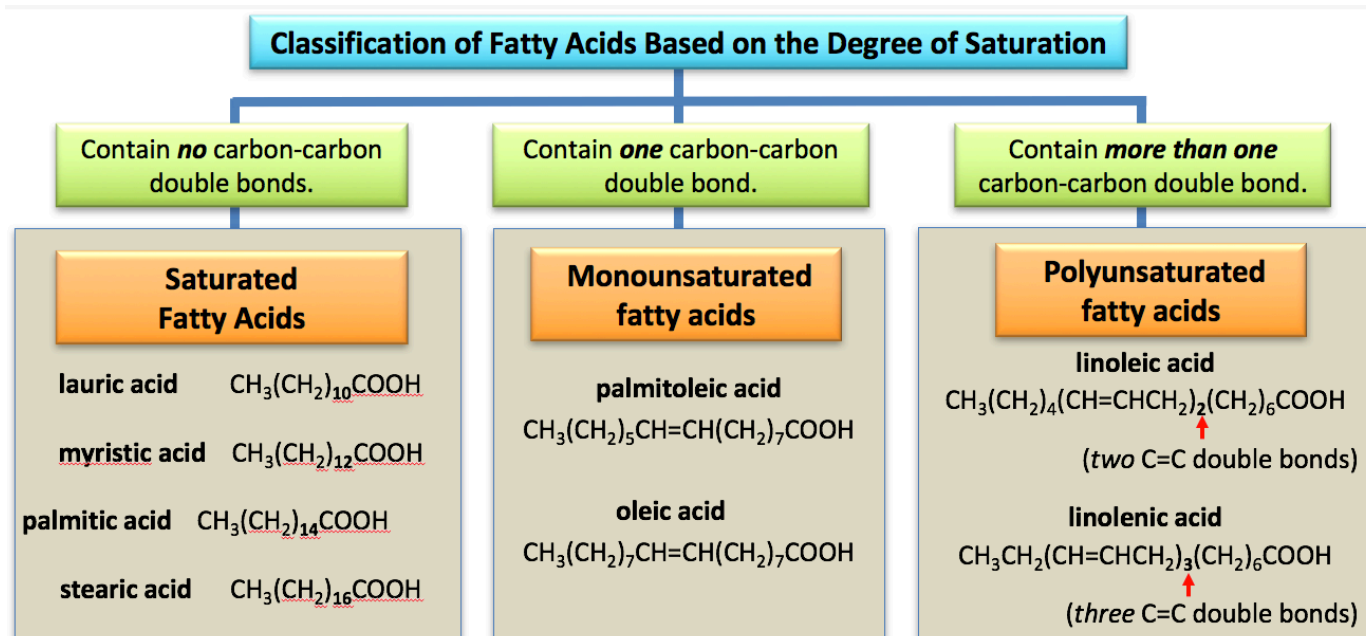
Fatty acids can differ from one another in the \_\_\_\_\_ **of carbon atoms** they contain, and in the **number of** \_\_\_\_\_ **bonds** they contain.

Some Fatty Acids that are Frequently Encountered in Biological Systems				
Number of Carbons	Number of Carbon-Carbon Double Bonds	Common Name	Condensed Structure	Major Source
12	0	lauric acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	coconut
14	0	myristic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	nutmeg
16	0	palmitic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	palm
16	1	palmitoleic acid	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	macadamia, animals
18	0	stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	animal fat
18	1	oleic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	olives
18	2	linoleic acid	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_2(\text{CH}_2)_6\text{COOH}$	safflower, soy
18	3	linolenic acid	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_6\text{COOH}$	flax, corn

## Classification of Fatty Acids

Fatty acids are classified as **saturated**, **monounsaturated**, or **polyunsaturated** based on the number of *carbon-carbon* double bonds they contain.

- **Saturated fatty acids** contain *no* carbon-carbon double bonds.
- **Monounsaturated fatty acids** contain *one* carbon-carbon double bond.
- **Polyunsaturated fatty acids** contain *more than one* carbon-carbon double bond.



## Classification of Fatty Acids

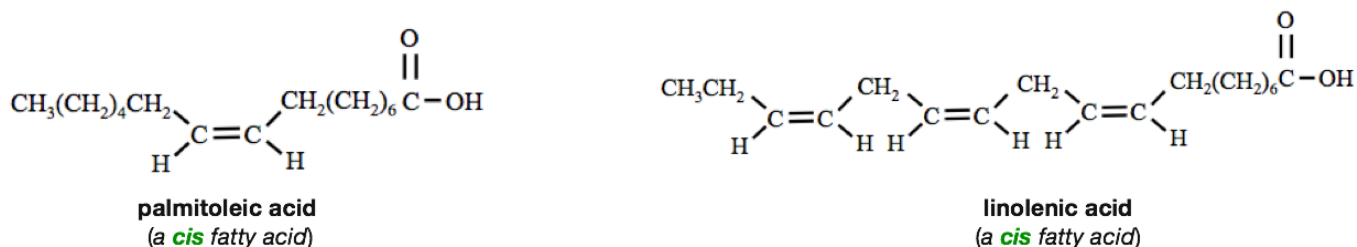
Another way in which fatty acids can be classified is by their \_\_\_\_\_.

They are categorized as either *cis* or *trans*, based on the stereochemistry of the carbon-carbon double bonds in their hydrocarbon parts.

- Fatty acids that contain **one or more** double-bonded carbons with the **trans geometry** are referred to as **trans fatty acids**.
- Fatty acids that contain **only** the **cis geometry** are called **cis fatty acids**.

Most of the fatty acids that are produced in nature are \_\_\_\_\_; the only known exceptions are the fatty acids produced by some bacteria.

- Examples of **cis fatty acids**:



## Omega Notation and Classification of Unsaturated Fatty Acids

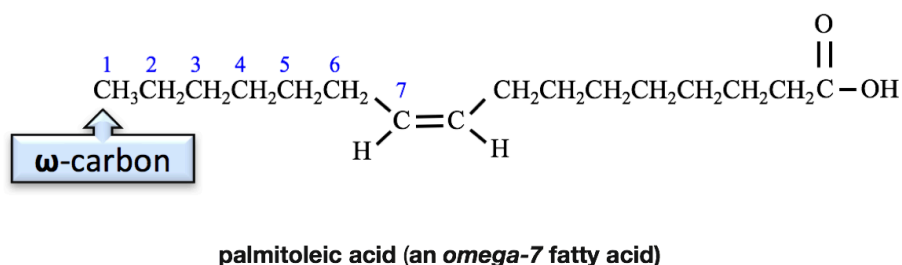
Although not used in IUPAC naming, **omega notation** is frequently seen in popular nutrition literature.

In omega notation, the carbon at the \_\_\_\_\_ of a fatty acid's hydrocarbon chain is designated as the "**omega carbon**" or "**ω-carbon.**"

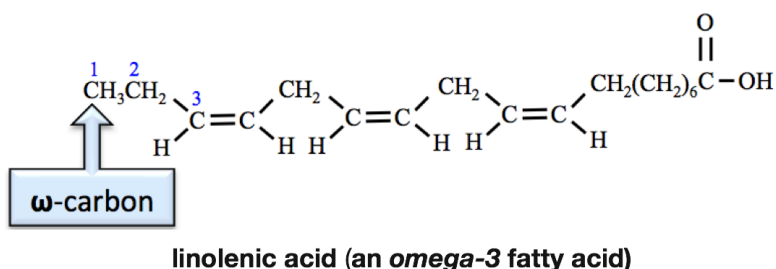
- Omega (ω) is the last letter of the Greek alphabet, making the omega designation appropriate for the "last" carbon in a fatty acid's hydrocarbon chain.

*Unsaturated* fatty acids are put into omega notation classes by the position of the **first double bond** that occurs, **counting from the omega carbon**.

**Example:** If a carbon-carbon double bond in a fatty acid occurs at the **seventh** carbon, counting from the **omega carbon**, then it is classified as an **omega-7** fatty acid (or ω-7 fatty acid).



An example of an **omega-3** fatty acid is linolenic acid.



**Understanding Check:** Use the structures in the table shown in the video to give the *omega notation* classification of:

- a) oleic acid
- b) linoleic acid

## Properties of Fatty Acids: Melting Points of Fatty Acids

All fatty acids are attracted to each other through hydrogen bonding, dipole-dipole interactions of their carboxyl groups, and through London forces.

The melting points of fatty acids are related to the \_\_\_\_\_ of their hydrocarbon part - as are, in general, the melting points of all organic compounds.

The larger the nonpolar hydrocarbon part, the stronger the \_\_\_\_\_ *forces* and the higher the melting point.

Number of Carbons	Common Name	Condensed Structure	Melting Point (°C)
12	lauric acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	43
14	myristic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	54
16	palmitic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	62
18	stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	69

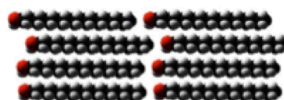
Another factor that influences the melting points of fatty acids is their *degree of saturation*.

The more carbon-carbon \_\_\_\_\_ *bonds* that are present in a fatty acid, the \_\_\_\_\_ the melting point.

The inability of rotation around double bonds prevents less saturated molecules from getting as close to each other as is possible for more highly saturated molecules. The strength of London forces - and all other noncovalent interactions - are distant dependent; the closer the particles are to each other, the stronger the attractive force.

If two fatty acids have the same number of carbon atoms but differ in degree of saturation, molecules of the fatty acid with more carbon-carbon double bonds cannot pack as close to each other as the molecules of the more saturated fatty acid, and will therefore have a lower melting point than the more saturated fatty acid.

**Example:**



**Stearic Acid**



18 carbons

**no** C=C double bonds  
melting point = 69 °C



**Linolenic Acid**



18 carbons

**three** C=C double bonds  
melting point = -17 °C

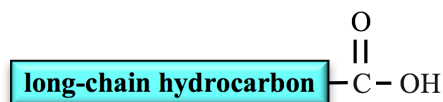
**Understanding Check:** Which fatty acid would you expect to have the higher melting point, oleic acid or palmitoleic acid?

**Understanding Check:** Which fatty acid would you expect to have the higher melting point, oleic acid or linoleic acid?

## Properties of Fatty Acids: Water Solubility of Fatty Acids

Fatty acids are \_\_\_\_\_ and therefore *do not dissolve in water*.

- This is because they contain eleven or more carbon atoms in their *hydrocarbon part*.

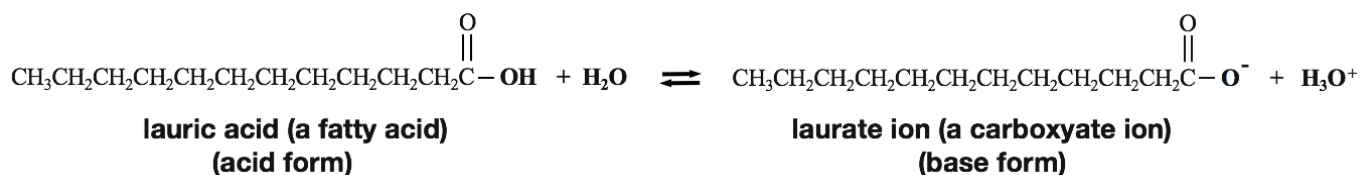


general form of a fatty acid

## Properties of Fatty Acids: Formation of Carboxylate Ions from Fatty Acids

Fatty acids, *like all carboxylic acids*, will react with water to produce their corresponding \_\_\_\_\_ *ion* forms (**base forms**).

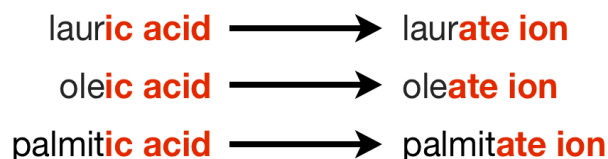
- Example:** Lauric acid and its corresponding carboxylate ion (laurate ion).



In previous chapters, you learned that the relative amounts of a conjugate pair's *acid form* and *base form* that are present in an aqueous solution depends on the pH of the solution *and* the  $\text{pK}_a$  of the particular acid (as described by the Henderson-Hasselbalch Equation). The  $\text{pK}_a$  of carboxylic acids (including fatty acids) is about **5**. Since the physiological pH in cells, blood, and intercellular solutions is *greater than 5*, the *carboxylate form* of fatty acids are predominant in these solutions ( $\text{pH} > \text{pK}_a$ ).

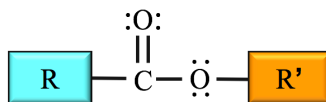
Carboxylate ions are named by replacing the “-ic acid” suffix of the *fatty acid* name with “-ate ion.”

- Examples:**



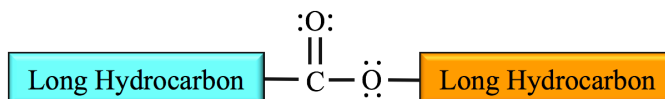
## Waxes

Waxes are members of the \_\_\_\_\_ family of organic compounds.



general form of an ester

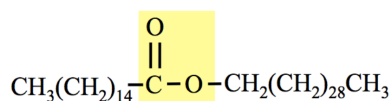
Waxes are *esters* with *relatively* \_\_\_\_\_ *hydrocarbon parts*.



general form of a wax

Waxes are produced by plants and animals.

- Insects use wax to contain their larvae and store food or pollen. Examples of waxes are the esters in beeswax.
- Beeswax is a mixture of compounds, of which about 80% are waxes. The condensed and skeletal structural formulas for the *most abundant wax* molecule found in beeswax are shown below.



Waxes are *hydrophobic* because of their large and nonpolar hydrocarbon parts.

- Sheep secrete a wax called *lanolin* which protects their wool and skin from the environment and helps shed water from their coats.
- Plants secrete waxes which help them control hydration and evaporation.

Examples of Esters Found in Waxes

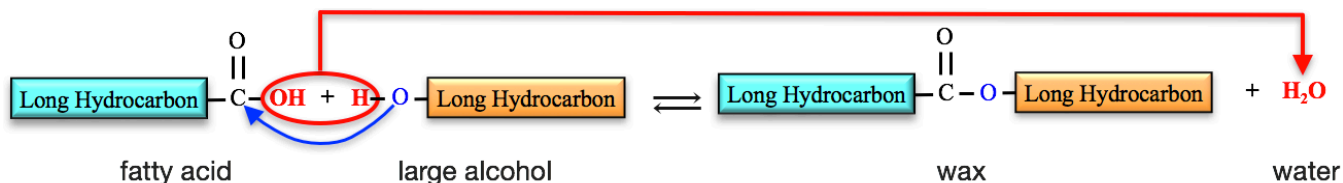
Common Name	Most Abundant Ester	Source	Uses
beeswax	$\text{CH}_3(\text{CH}_2)_{13}\text{COOCH}_2(\text{CH}_2)_{27}\text{CH}_3$	honeycomb	candles, shoe polish, wax paper
carnauba wax	$\text{CH}_3(\text{CH}_2)_{24}\text{COOCH}_2(\text{CH}_2)_{27}\text{CH}_3$	Brazilian palm	furniture, car, and floor wax
insect wax	$\text{CH}_3(\text{CH}_2)_{24}\text{COOCH}_2(\text{CH}_2)_{27}\text{CH}_3$	insects	shoe polish
spermaceti	$\text{CH}_3(\text{CH}_2)_{30}\text{COOCH}_2(\text{CH}_2)_{14}\text{CH}_3$	whale's head	lubricant
jojoba wax	$\text{CH}_3(\text{CH}_2)_{18}\text{COOCH}_2(\text{CH}_2)_{18}\text{CH}_3$	jojoba bush	candles, cosmetics, soap additive

## Formation of Waxes

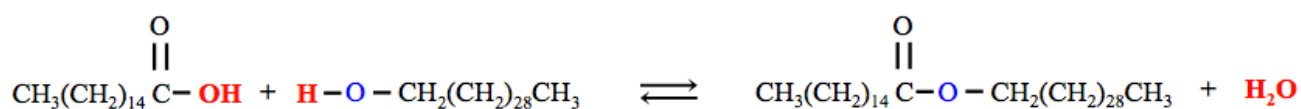
In chapter 9, you learned that in *esterification*, carboxylic acids react with alcohols to form esters.

*Waxes* are formed by the *esterification* reaction of *fatty acids* with *large alcohols*.

- In this reaction, the **OH** from the fatty acid and an **H** from the alcohol are removed, and then combined to form **H<sub>2</sub>O**. The oxygen (**O**) and hydrocarbon that was originally part of the alcohol, forms a new bond to the fatty acid's carbonyl carbon.

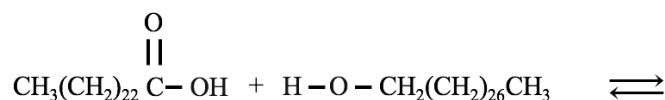


A specific example of the formation of a wax molecule in an esterification reaction is shown below.



### Understanding Check

Draw the condensed structure of the wax that is produced in the reaction shown here.



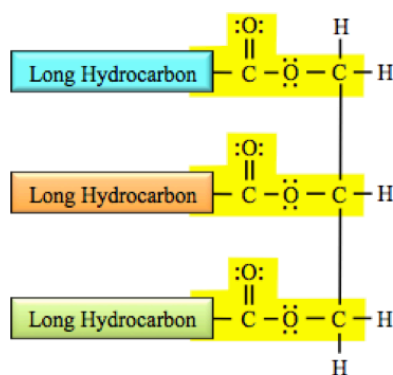
## Triglycerides

### The Structure of Triglycerides

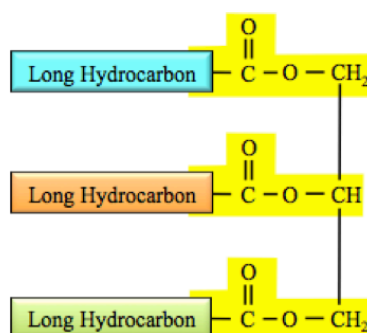
**Triglycerides** - also referred to as *triacylglycerides* - are **triesters**.

- The reason for this classification is that they contain **three** **-type bonds**.

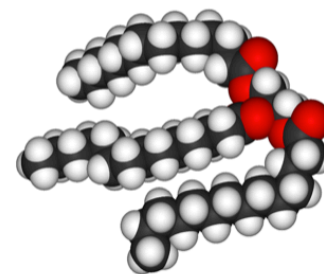
The triglyceride bonding pattern can be seen in the line bond, condensed, and space-filling structures shown here. The ester bonding patterns are highlighted in yellow.



line bond structure



condensed structure

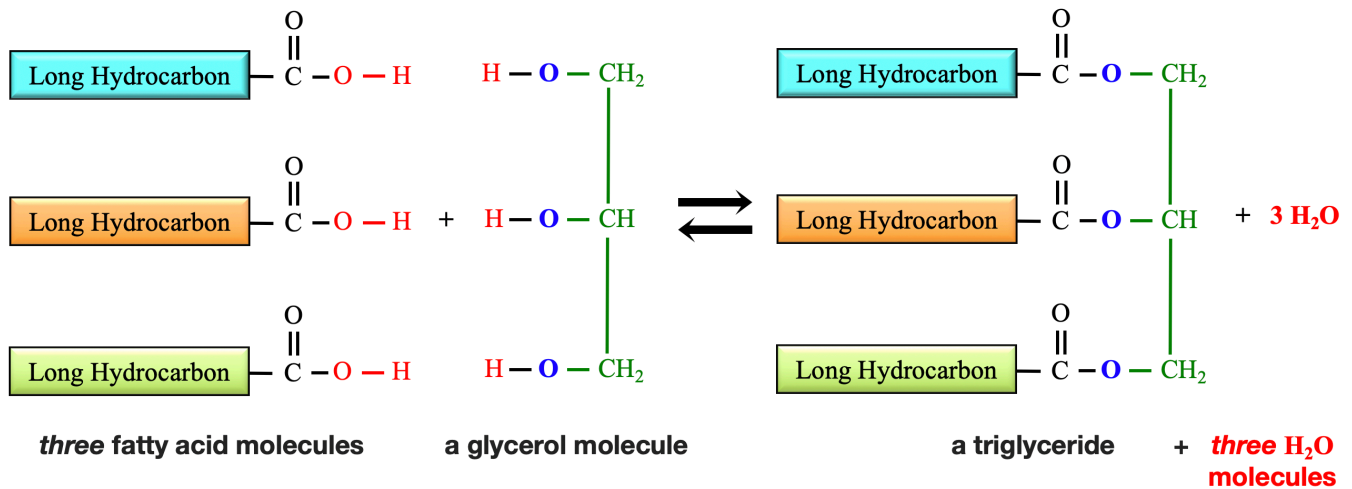


space-filling model



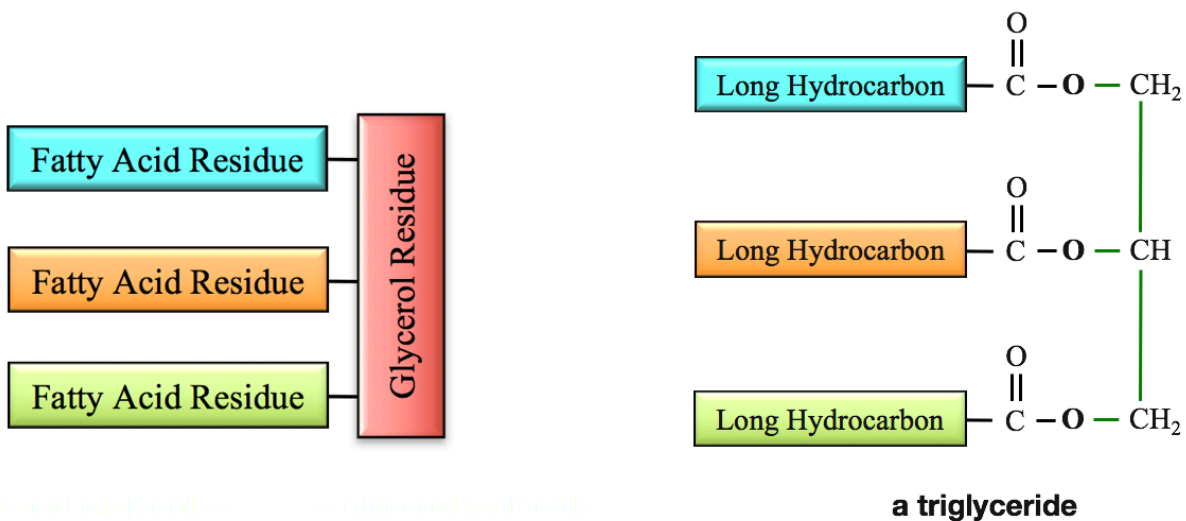
## The Formation of Triglycerides

*Triglycerides* are formed in the esterification reaction of **three fatty acid molecules** with \_\_\_\_\_ (an alcohol with three hydroxyl groups – a *triol*).



When molecules from particular organic families - such as the three fatty acids and glycerol in the formation of a triglyceride - react to form a large molecule, or when a large molecule is broken down to form them, they are often referred to as “\_\_\_\_\_.”

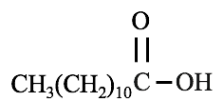
- For example, a *triglyceride* contains **three fatty acid residues** and a **glycerol residue**.



The part that was originally from glycerol – the glycerol residue - is sometimes called the “**glycerol backbone**.”

### Understanding Check

Draw the *condensed* structure of the triglyceride that is formed from the esterification reaction of *three* lauric acid molecules and a glycerol molecule.



**lauric acid**

### Classification of Triglycerides: Fat vs. Oil

The terms “fat” and “oil” can each have multiple meanings and, worse, are often used ambiguously. In the most general sense, the term “*oil*” is defined as any nonpolar, viscous liquid.

In the context of *triglycerides*:

- The term “\_\_\_\_\_” is generally used for a triglyceride that is \_\_\_\_\_ *at room temperature*.
- The term “\_\_\_\_\_” is generally used for a triglyceride that is \_\_\_\_\_ *at room temperature*.

Our use of the term “fat” in this context should not be confused with the common practice using the term “fat” for adipose tissue in humans and animals. Adipose tissue is composed of cells that store triglycerides.

Solid triglycerides made by *animals* are referred to as **animal fat**.

- Animal fat can be separated from other animal parts in a process called **rendering**. Fat from *pigs* is used in food products and is called **lard**. Fat from *chickens* that is used in food products is called **schmaltz**. Fat from *beef and sheep* is called **tallow**, and is used primarily for producing soap and in animal feed. Fat from *milk* is called **butterfat**, **clarified butter**, or **ghee**. The food product that is commercially marketed as “butter” contains about 80% fat, 15% water, and 5% protein and other substances. Butterfat is usually, but not always, made from *cow’s milk*.

#### Important Roles of Triglycerides in Animals:

- Energy storage
- Production of **ATP**
- Provision of fatty acids for the production of other lipids
- Insulation

Liquid triglycerides that are made by plants are referred to as **vegetable oils**. Vegetable oils are used for cooking and in food products, biofuels, cosmetics, and soaps. Evidence of human purification of vegetable oils goes as far back as 4000 years ("*4,000-year-old 'kitchen' unearthed in Indiana*". *Archaeo News*. January 26, 2006).

Some Vegetable Oils and Their World Consumption, Primary Uses, and Sources

Vegetable Oil	Worldwide Consumption (metric tons)	Primary Uses and Sources
palm oil	41.3	cooking oil, biofuel (from palm fruit mesocarp pulp)
soybean oil	41.3	cooking oil
canola oil	18.2	cooking oil (comes from a variety of rapeseeds)
sunflower oil	9.9	cooking oil, biodiesel (from sunflower seed)
cottonseed oil	5.0	food products
palm kernel oil	4.8	cooking oil, food products (from palm seed)
peanut oil	4.8	cooking oil
coconut oil	3.5	cooking oil and soap making
olive oil	2.8	cooking oil, cosmetics, soaps, fuel for traditional oil lamps (from whole olives)

Worldwide Consumption data is from the US Department of Agriculture for 2007/2008

**Fish oil** is purified from tissue and belly cavities of oily fish, such as sardines, herring, anchovies, salmon, trout, tuna, and mackerel. Some fish, such as shark and cod, have significant amounts of oil stored in their liver.

In nutritional labeling, **all triglycerides, whether from plants or animals, solid or liquid**, are often grouped together and called “**fat**” or included in the “**total fat**” category.

Sample label for Macaroni & Cheese

Nutrition Facts	
Serving Size 1 cup (228g)	
Servings Per Container 2	
Amount Per Serving	
<b>Calories</b> 250	Calories from Fat 110
% Daily Value*	
<b>Total Fat</b> 12g	<b>18%</b>
Saturated Fat 3g	15%
Trans Fat 3g	
<b>Cholesterol</b> 30mg	10%
<b>Sodium</b> 470mg	20%
<b>Total Carbohydrate</b> 31g	10%
Dietary Fiber 0g	0%
Sugars 5g	
<b>Protein</b> 5g	
Vitamin A	4%
Vitamin C	2%
Calcium	20%
Iron	4%
* Percent Daily Values are based on a 2,000 calorie diet. Your Daily Values may be higher or lower depending on your calorie needs.	
	Calories 2,000 2,500
Total Fat	Less than 65g 80g
Sat Fat	Less than 20g 25g
Cholesterol	Less than 300mg 300mg
Sodium	Less than 2,400mg 2,400mg
Total Carbohydrate	300g 375g
Dietary Fiber	25g 30g

## Classification of Triglycerides: 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 \_\_\_\_\_ contain **carbon-carbon \_\_\_\_\_ bonds**.
- **Unsaturated triglyceride** molecules contain \_\_\_\_\_ **carbon-carbon double bonds**.
  - **Unsaturated triglycerides** are often further subcategorized as either \_\_\_\_\_ **unsaturated** or \_\_\_\_\_ **unsaturated**.
    - **Monounsaturated** triglycerides contain only \_\_\_\_\_ carbon-carbon double bond.
    - **Polyunsaturated** triglycerides contain \_\_\_\_\_ carbon-carbon double bonds.

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

- It is for this reason that the noncovalent interactions, and therefore the melting points of triglycerides increase with the degree of saturation.

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

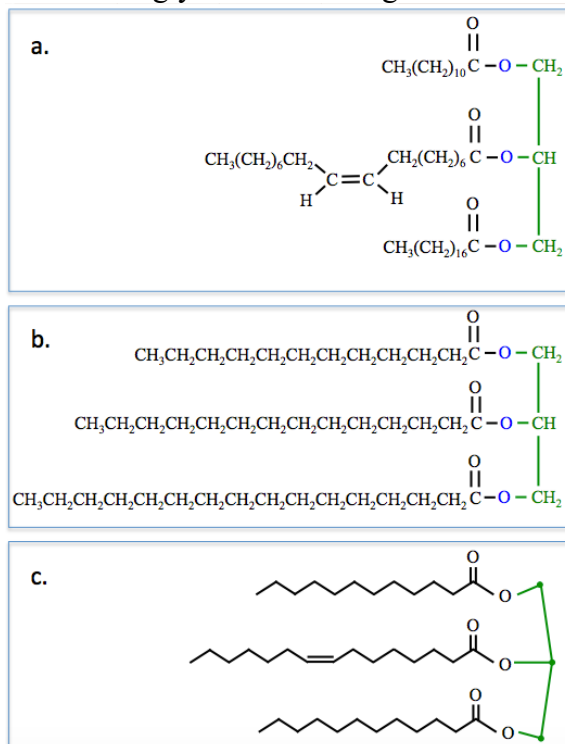
- Consider beef-fat or butter.

Vegetable oils and fish oils have a **lower degree of saturation** than animal fats, and are therefore **liquid** at room temperature.

- Consider olive or corn oil.
- Palm and coconut oil are *semi-solid* at room temperature because they contain a higher degree of saturation than the other vegetable oils.

### Understanding Check

Categorize each one of these triglycerides as being either **saturated** or **unsaturated**.



## Understanding Check

Using table of fatty acids shown below, draw the *skeletal structure* of a *saturated triglyceride*.

Some Fatty Acids that are Frequently Encountered in Biological Systems

Number of Carbons	Number of Carbon-Carbon Double Bonds	Common Name	Condensed Structure	Major Source
12	0	lauric acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	coconut
14	0	myristic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	nutmeg
16	0	palmitic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	palm
16	1	palmitoleic acid	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	macadamia, animals
18	0	stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	animal fat
18	1	oleic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	olives
18	2	linoleic acid	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_2(\text{CH}_2)_6\text{COOH}$	safflower, soy
18	3	linolenic acid	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_6\text{COOH}$	flax, corn

## Reactions of Triglycerides

### 1) Catalytic Hydrogenation

- unsaturated triglyceride +  $\text{H}_2 \rightarrow$  more saturated triglyceride

### 2) Oxidation

- triglyceride +  $\text{O}_2 \rightarrow$  small organic molecules

### 3) Hydrolysis/Saponification

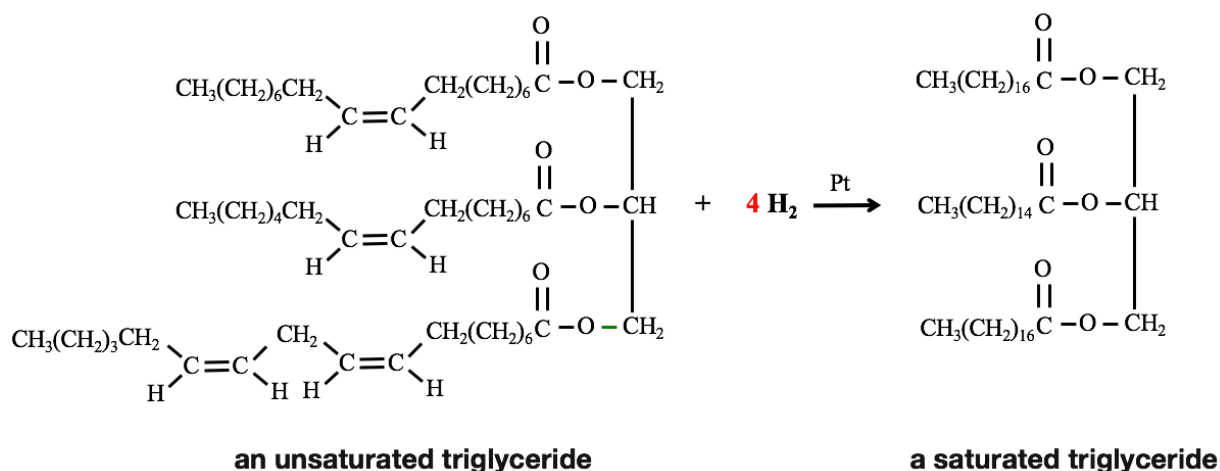
- hydrolysis of the ester group in the presence of hydroxide ( $\text{OH}^-$ )

## 1) Catalytic Hydrogenation

The *carbon-carbon* double bonds of triglycerides will react with hydrogen gas ( $H_2$ ) in the presence of a catalyst (at high temperatures). In chapter 6, you learned about the **hydrogenation** of an alkene's carbon-carbon double bonds. We were able to predict the product by "adding  $H_2$  across the carbon-carbon double bond." *We can do the same for triglycerides.*

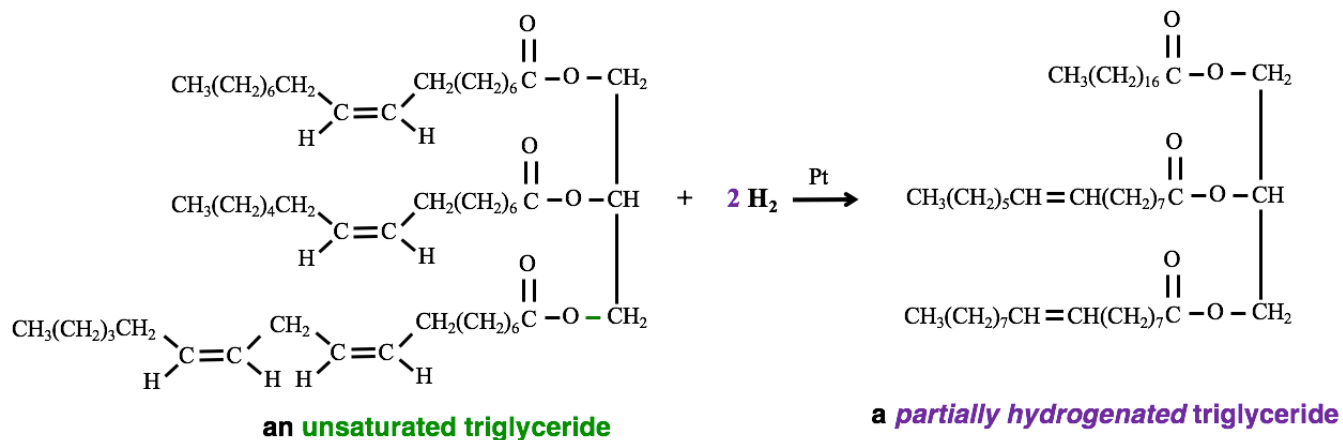
If enough  $H_2$  is supplied, the carbon-carbon double bonds in *unsaturated triglycerides* become \_\_\_\_\_; a *saturated triglyceride* is formed.

A hydrogen atom is added to each of the double-bonded carbons, thereby converting them into single bonds. The reaction must be done at a high temperature and on the surface of a *metal catalyst*. The catalysts used are typically platinum, palladium, rhodium, or ruthenium. An example of a chemical equation for *complete saturation* during a **catalytic hydrogenation reaction** is shown below.



If the amount of  $H_2$  is limited, or the chemical reaction time is reduced, then the triglyceride product will contain *some unreacted* carbon-carbon double bonds.

- We call this process \_\_\_\_\_ **hydrogenation**.
- **Example** of a *partial hydrogenation reaction*:



Note that the triglyceride reactant in this example contains **four** double bonds, however, only **two** moles of  $H_2$  were supplied, therefore only **two** of the carbon-carbon double bonds became saturated.

Triglycerides that are found in nature, with few exceptions, contain only *cis* fatty acid residues. Note that the **reactant** for the reaction shown above is drawn using *cis* configurations around *all of the carbon-carbon double bonds*.

The catalytic hydrogenation of vegetable oils is a very important reaction for the food industry.

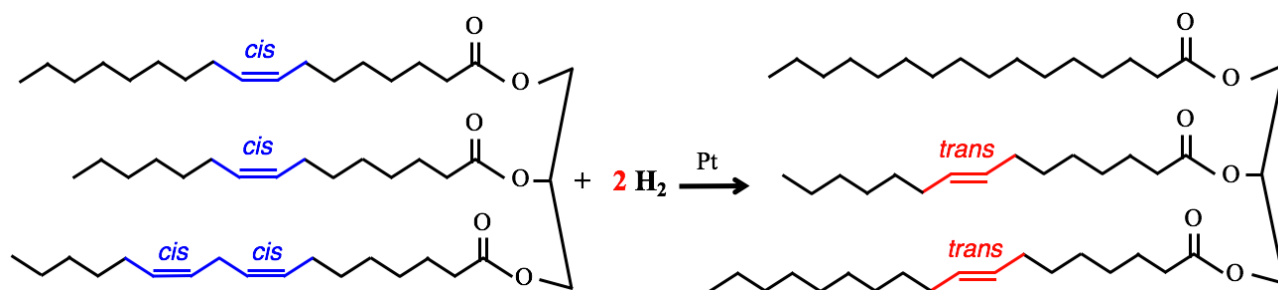
Solid triglycerides are advantageous in baking because of the texture that is achieved when they are mixed with flour. Animal fat - butter - can be used, however it is more expensive than vegetable oils.

The partial hydrogenation of vegetable oils produces what is referred to as **partially hydrogenated vegetable oil** or **shortening**.

*Margarine* and *Crisco* are examples of partially hydrogenated vegetable oil products.

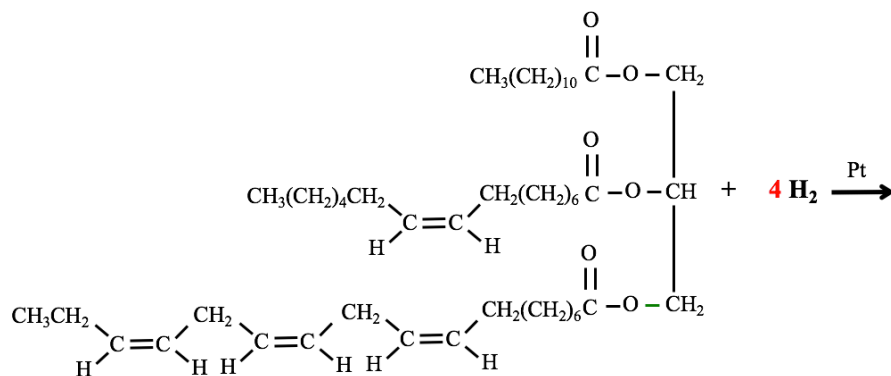
An undesirable consequence of *partial hydrogenation* is the formation of **trans fats** - fats containing one or more carbon-carbon double bonds that have the *trans* configuration.

- Many of the **unreacted cis** carbon-carbon double bonds are converted to the **trans** configuration.
- **Example:** The partial hydrogenation of a naturally-occurring unsaturated *cis*-triglyceride (vegetable oil) to a partially hydrogenated *trans*-triglyceride.



The product is a partially hydrogenated vegetable oil molecule, which typically contains one or more **trans** fatty acid residues.

**Understanding Check:** Draw the *condensed structure* of the saturated triglyceride that is produced from the **complete hydrogenation** of the triglyceride shown here.



## 2) Oxidation of Triglycerides

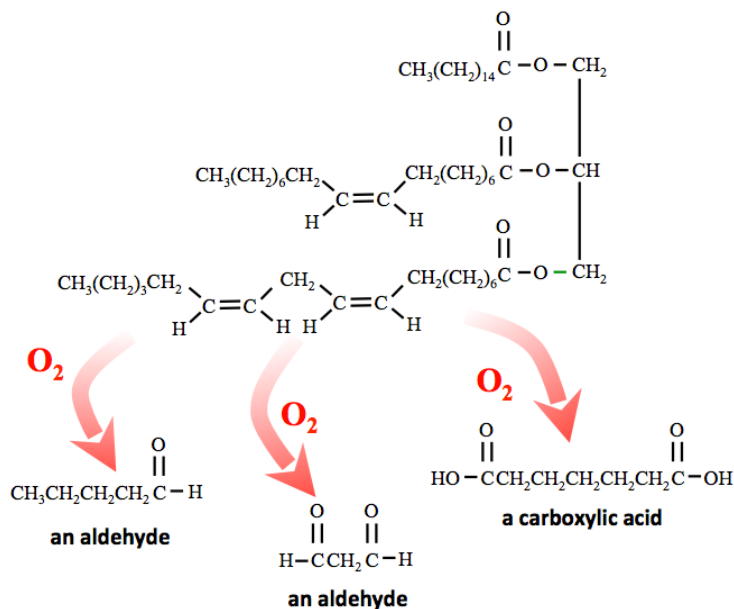
Triglycerides are oxidized by oxygen gas (O<sub>2</sub>) to form \_\_\_\_\_ and \_\_\_\_\_.

Prediction of the *specific* aldehydes and carboxylic acids that are produced is beyond the scope of this book, however a couple of typical aldehydes and a carboxylic acid that can be produced in this reaction are shown here (below, right).

Many of the aldehydes and carboxylic acids that are produced in this reaction have foul odors.

When triglyceride food products undergo this reaction, it is called “\_\_\_\_\_”; the food substances are said to become “**rancid**.”

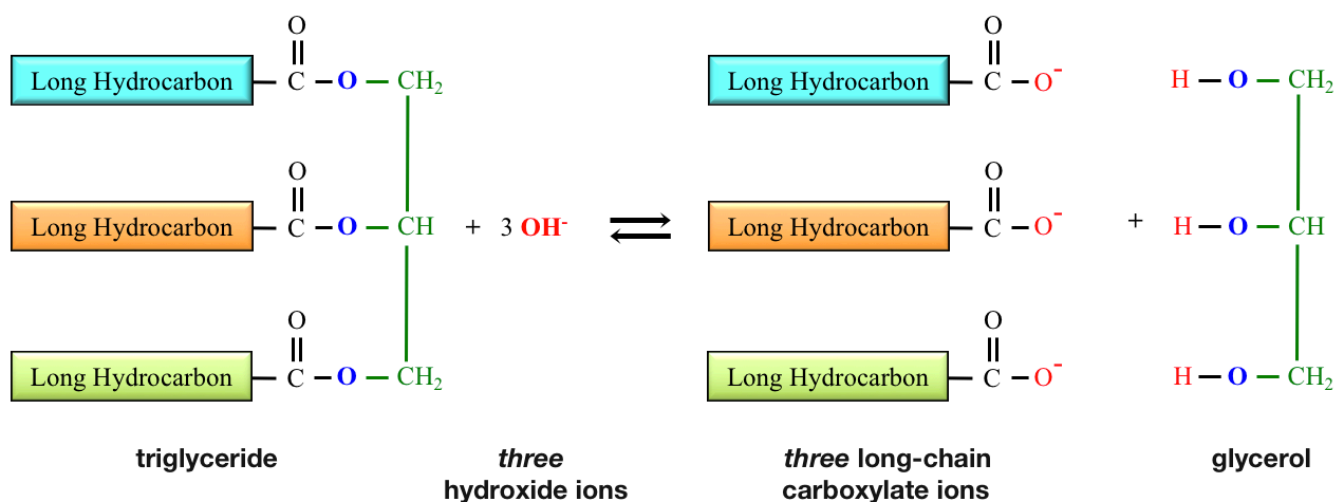
In order to prevent or slow the rancidification of foods, the oxygen supply can be limited by air-tight containers and packaging, and the food can be stored at low temperatures.



## 3) Saponification

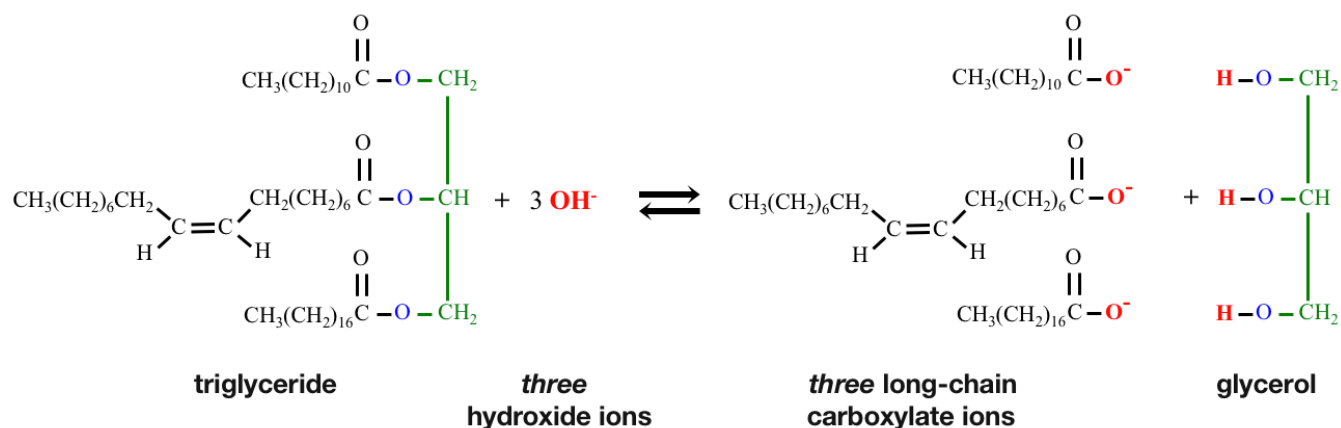
In the *saponification* reaction, a *triglyceride* reacts with *hydroxide ions* to produce \_\_\_\_\_ *long-chain carboxylate ions* and *glycerol* (an alcohol).

- The general form of this reaction is shown below.



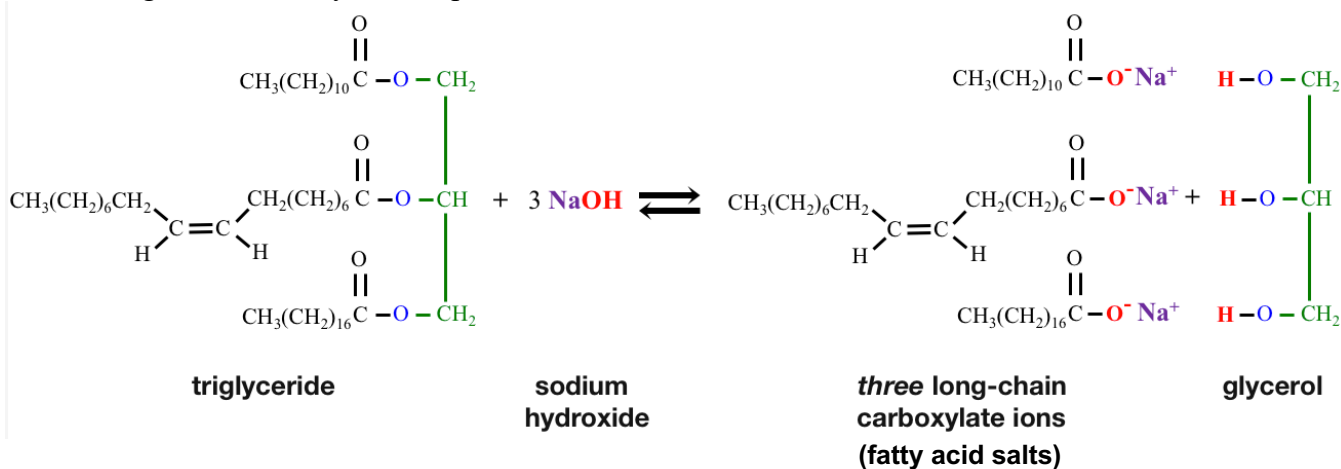


**Example of the hydrolysis of a *specific* triglyceride:**



The hydroxide ions in the saponification reaction come from hydroxide-containing ionic compounds, usually sodium hydroxide (**NaOH**) or potassium hydroxide (**KOH**).

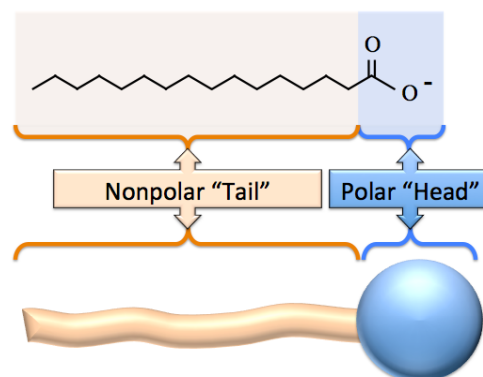
- When the cation of the hydroxide-containing compound is specified, it is often written after the long-chain carboxylate ion products as shown below:



When the  $\text{Na}^+$  or  $\text{K}^+$  cations are included in chemical equations, as shown above, be careful to avoid the **common misconception** of interpreting the negative sign of the carboxylate ion's *formal charge* for a covalent bond to the sodium or potassium ion.

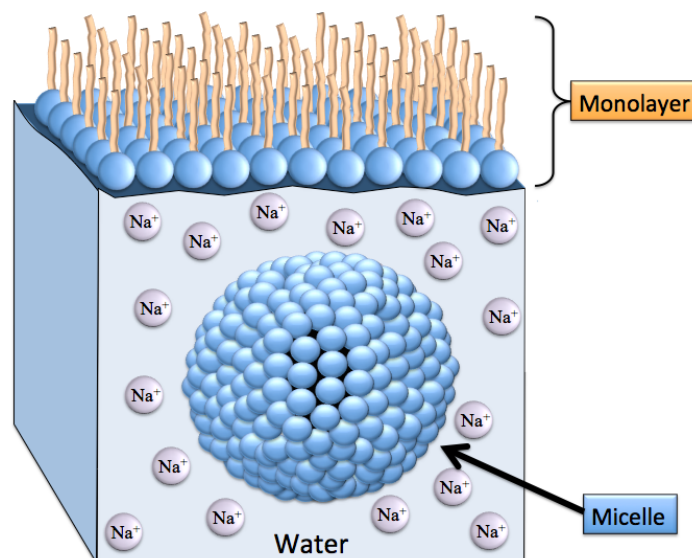
The compounds formed from the long-chain carboxylate anions and the  $\text{Na}^+$  (or  $\text{K}^+$ ) cations are **ionic** and are called \_\_\_\_\_.

The long-chain carboxylate ions that are produced are \_\_\_\_\_.



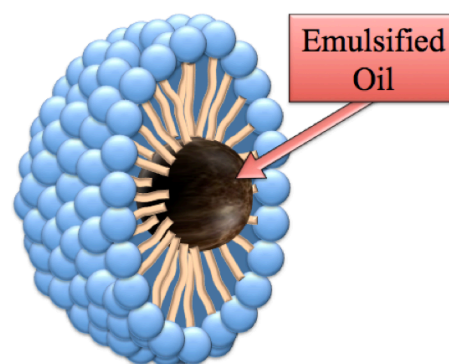
When *fatty acid salts* are formed or placed in water, **only** the cations,  $\text{Na}^+$  in our example, are solvated (dissolve).

The long-chain carboxylate ions form \_\_\_\_\_ and \_\_\_\_\_.



This is an important reaction because it is used to make *soap*.

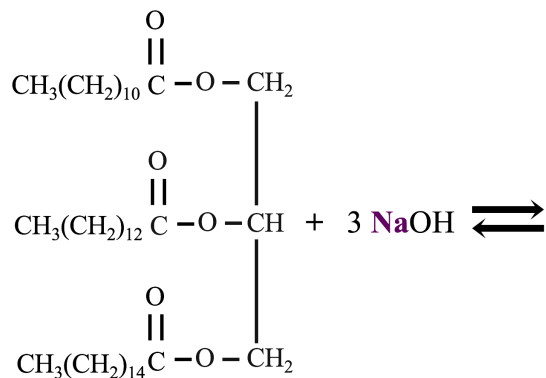
Because the long-chain carboxylate ions that are produced are **amphipathic**, they act as emulsifying agents to remove nonpolar molecules (i.e. grease or oil) from surfaces, including - very importantly - skin and clothing.



An illustration of an oil droplet emulsified by a long-chain carboxylate ion micelle.

### Understanding Check

Draw the *condensed structure* of the products for the saponification of the triglyceride shown below. Include the cations when drawing the fatty acid salts.

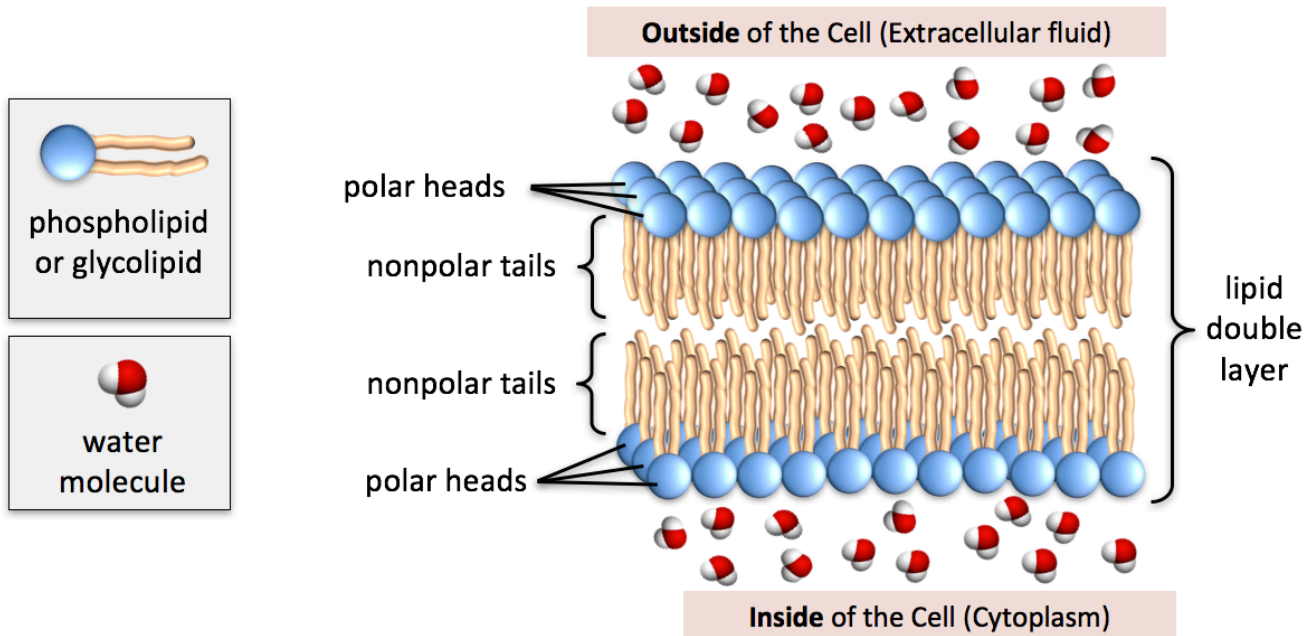


## Phospholipids and Glycolipids

**Phospholipids and glycolipids** are best known for their presence in biological membranes.

They are amphipathic compounds that contain a polar “head” group that is very hydrophilic, and hydrophobic nonpolar “tail” groups.

Phospholipids and glycolipids are found in nature as either monolayers, micelles, or in a layer that is two molecules-thick called a “*lipid bilayer*” or a “*lipid bilayer*.”



Note that the polar heads are oriented either toward the water that is inside the cell, or toward the water that is outside of the cell. The nonpolar tails in the top of the double layer are much more attracted to the nonpolar tails in the bottom of the double layer than to water or polar head groups. It is for this reason that the two monolayers have the tail-to-tail orientation. Later in this chapter, you will see that there are other components distributed throughout the lipid double layer of biological membranes, however, for simplicity, those other components are not included in the illustration (above).

Lipid double layer membranes not only occur as cell membranes, they also form specialized compartments within cells. For example, intracellular double layer membranes occur in liposomes and form the outer boundary of a cell’s nucleus.

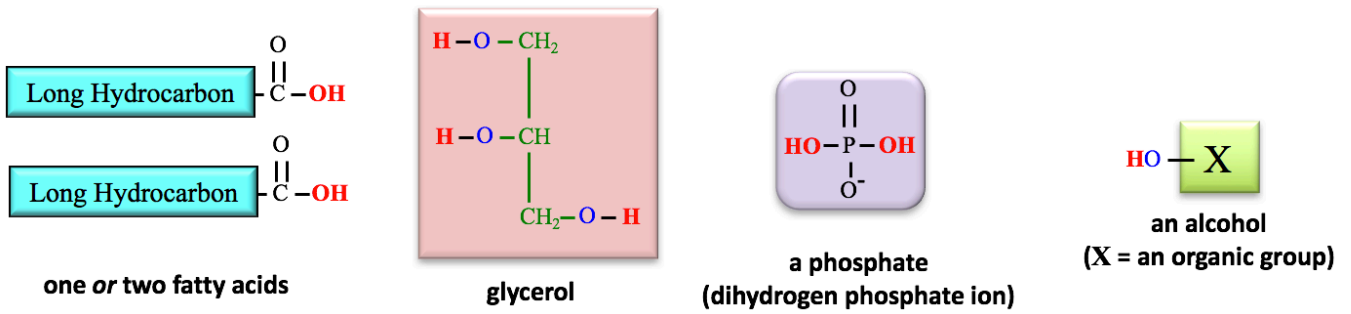
## Phospholipids

There are two main classes of **phospholipids**: \_\_\_\_\_ *phospholipids* and \_\_\_\_\_ *phospholipids*.

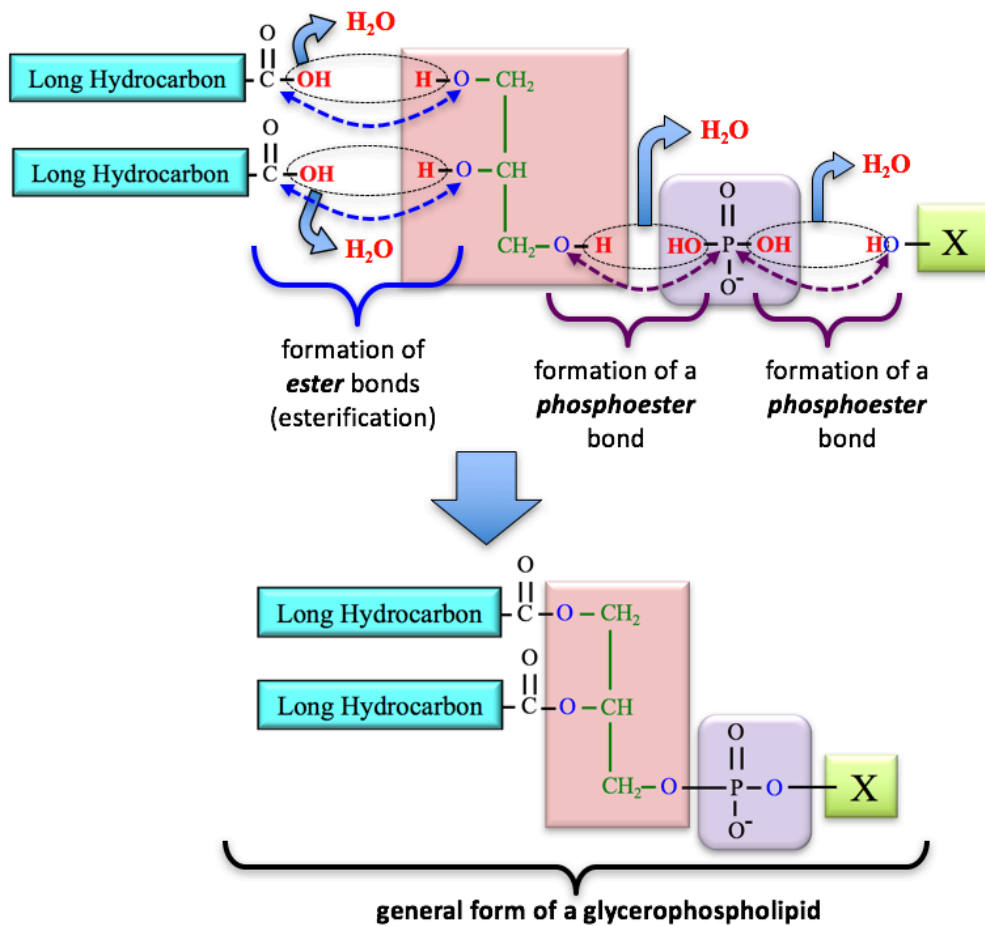
- Both of these classes contain a \_\_\_\_\_ residue in their structure, it is for this reason that they are called *phospholipids*.

# 1) Glycerophospholipids

Glycerophospholipids are made from the components shown here.



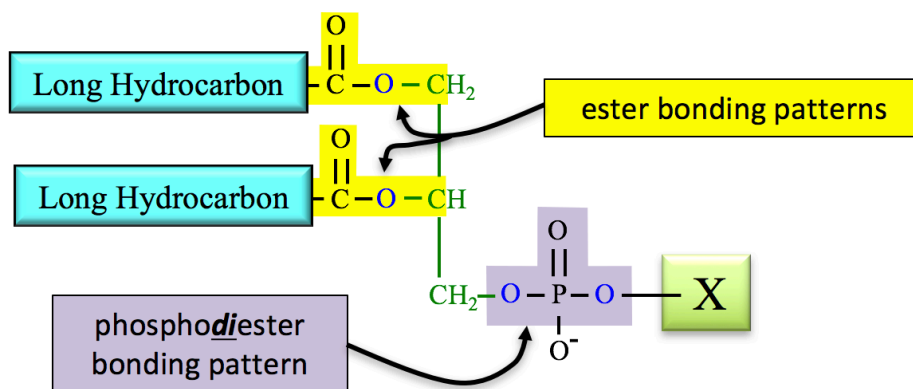
These components are bonded to each other by \_\_\_\_\_ *reactions* to form glycerophospholipids.



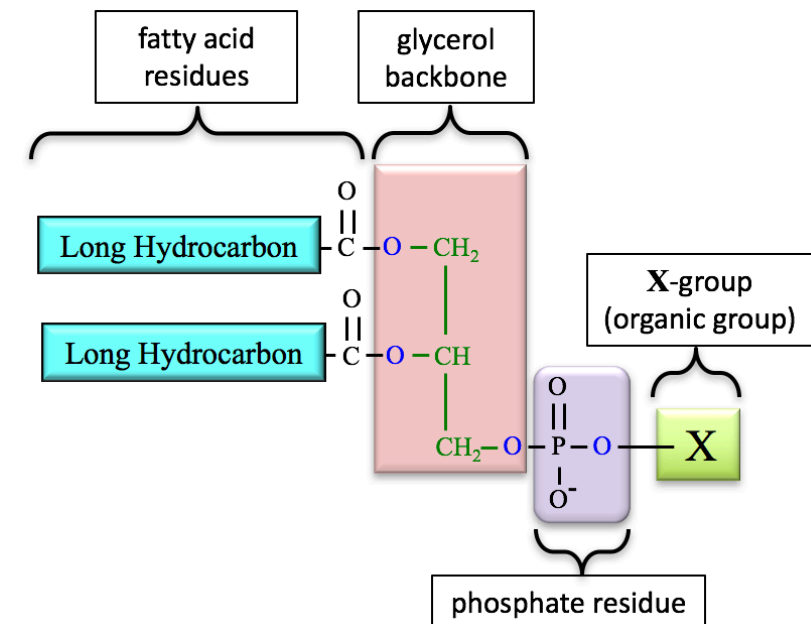
When **both OH's** of a phosphate form phosphoester bonds, the bonding pattern is called a **phospho** \_\_\_\_\_ bond.

Note the similarity in the way that a carboxyl group (COOH) of a fatty acid reacts with an alcohol, and the way that a phosphate reacts with an alcohol.

The **ester** and **phosphodiester** bonding patterns in a *glycerophospholipid* are highlighted and labeled in the structure shown below.



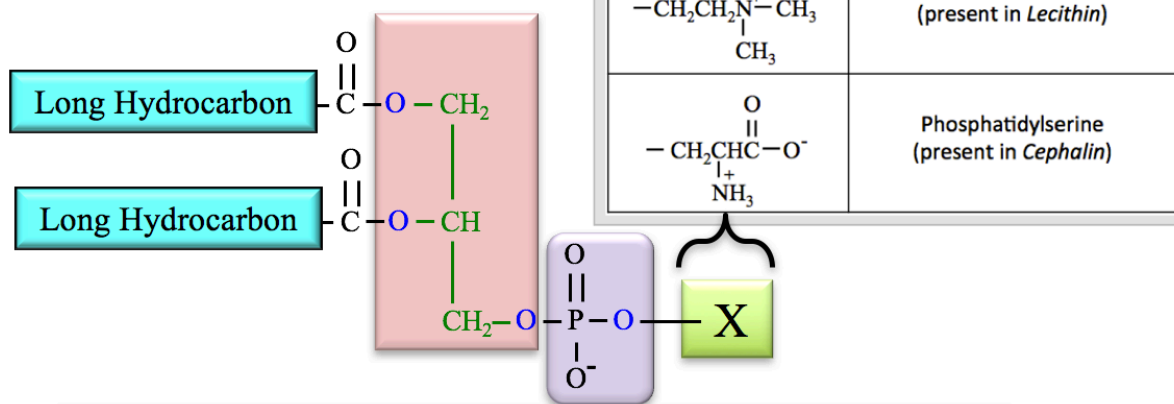
The various “residues” that make up a glycerophospholipid are labeled in the structure below.



The atoms that came from glycerol are referred to the “*glycerol* \_\_\_\_\_.”

The identity of the organic “X-group” varies.

The subclasses of glycerophospholipids are determined by the identity of their X-groups.



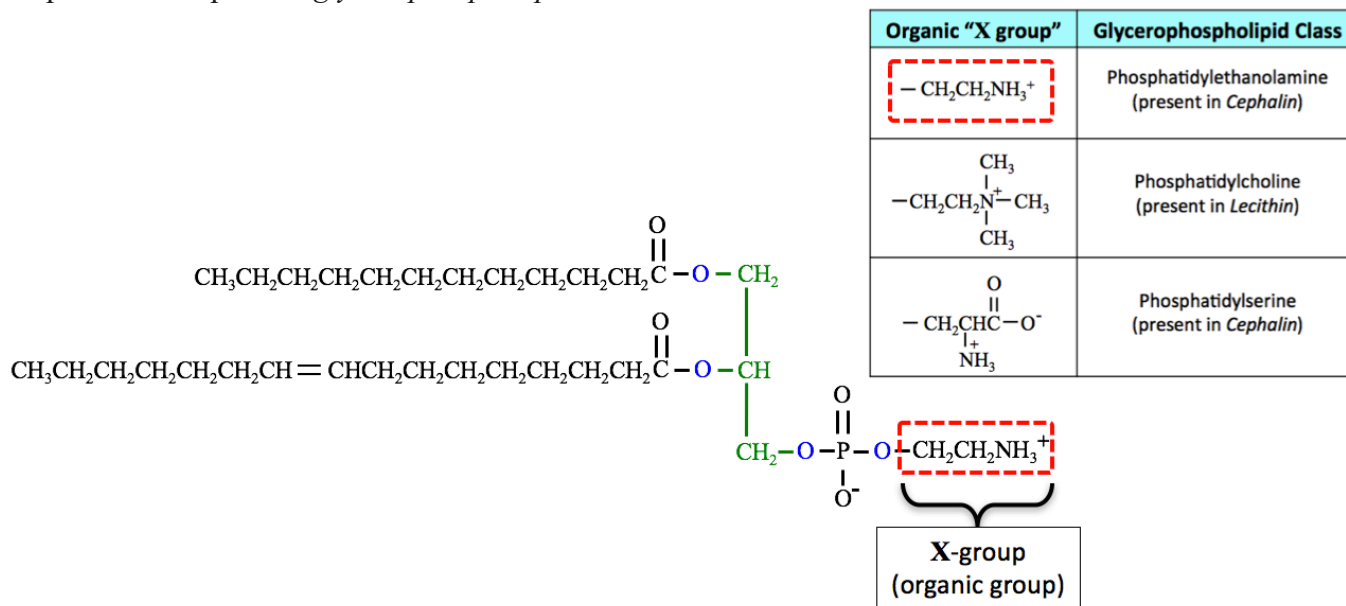
**Phosphatidylethanolamines** and **phosphatidylserines** are components of *cephalin*.

- Cephalin is found throughout the body, with especially large amounts present in the brain and nerve tissue.

**Phosphatidylcholines** are a component of *lecithin*.

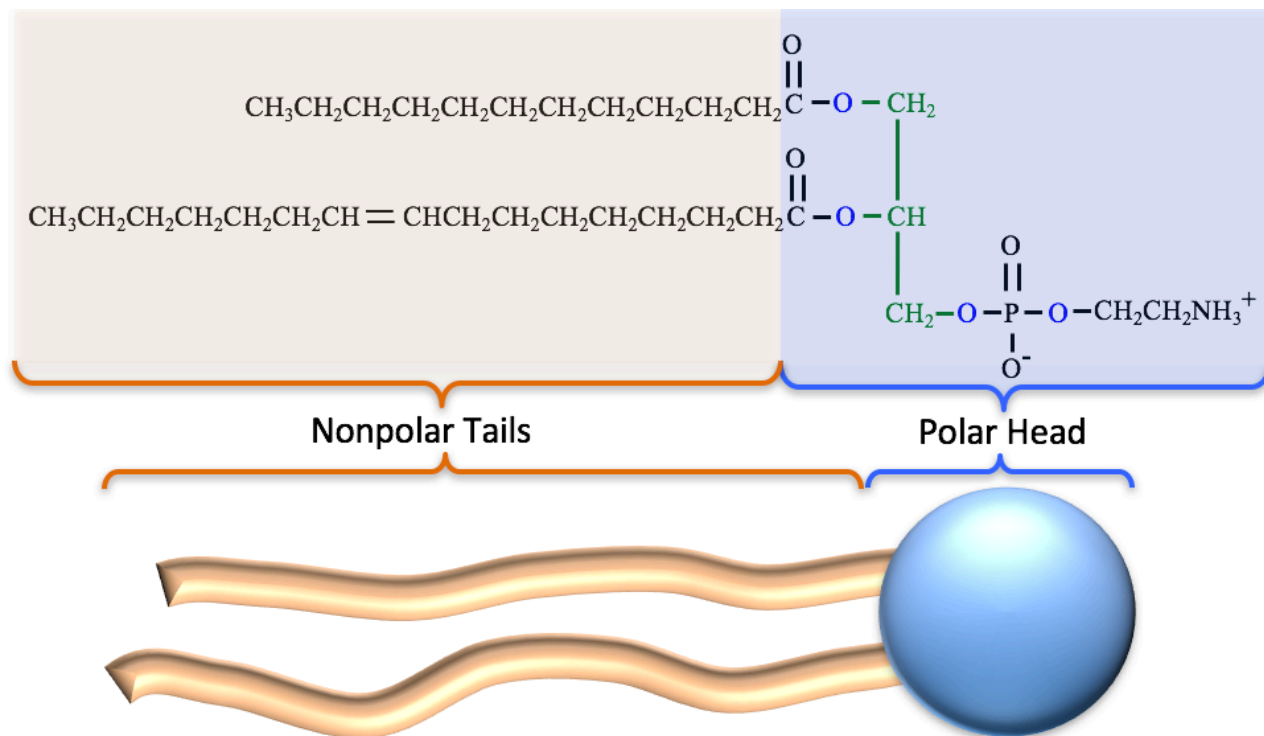
- Lecithin is a term for the yellow-brown fatty substances present in animal and plant tissues.

A specific example of a *glycerophospholipid* is shown below.



This particular glycerophospholipid is classified as a **phosphatidylethanolamine** because the X-group is  $-\text{CH}_2\text{CH}_2\text{NH}_3^+$ .

Glycerophospholipids have a *polar head* region and *nonpolar tails*, as depicted for the glycerophospholipid below.

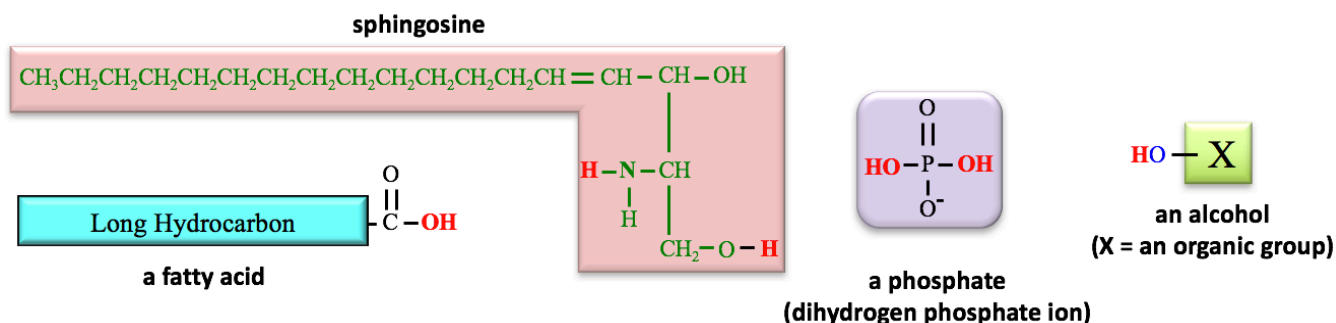


The *polar head* region is quite **hydrophilic**. This region is attracted to water through **dipole-dipole** interactions because it contains several “highly polar” bonds. It can **hydrogen bond** with water. The polar head is also attracted to water through **ion-dipole interactions** because of the *formal charge* on both an oxygen *and* a nitrogen. The hydrocarbon chains of the fatty acid residues make up the nonpolar tails.

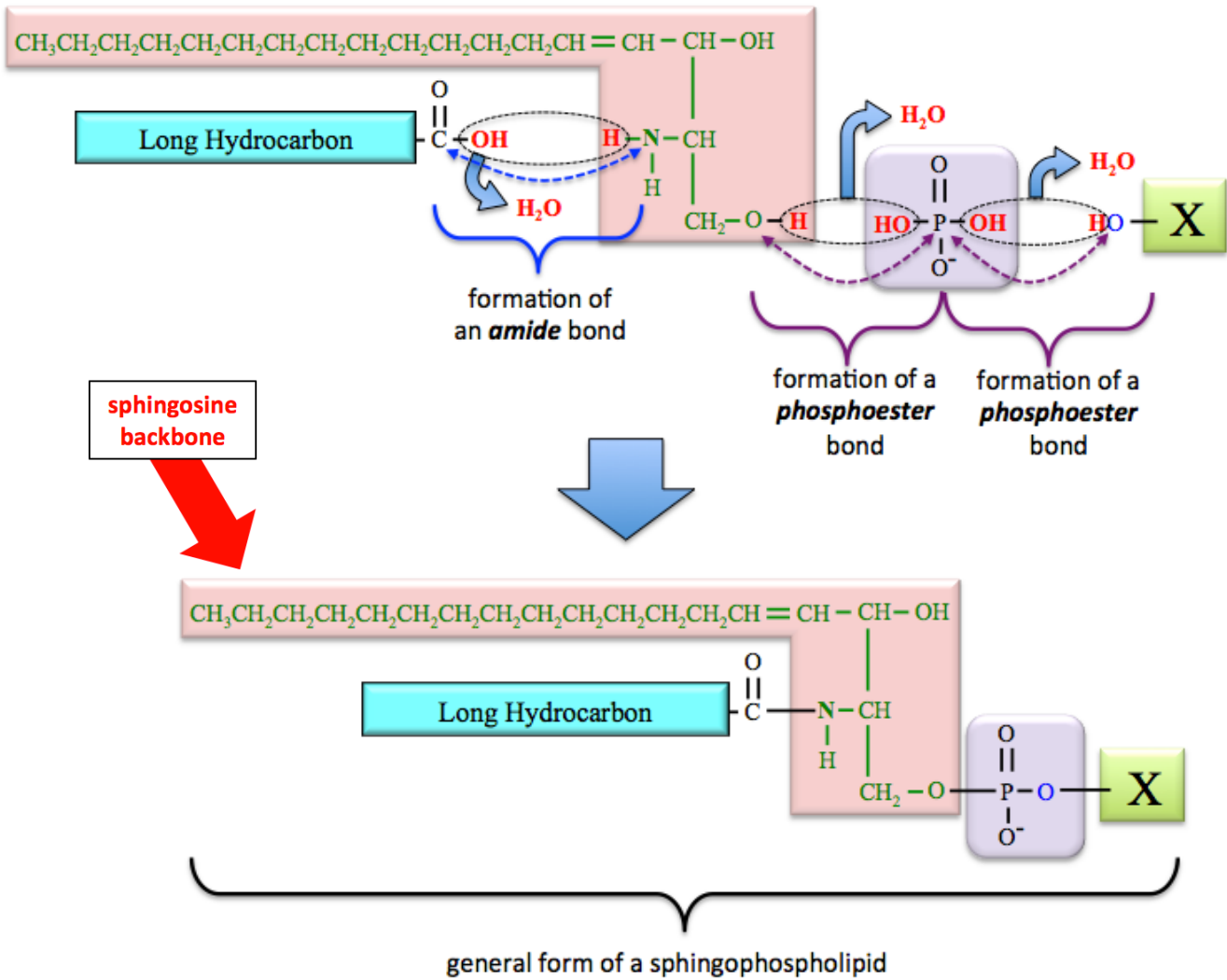
## 2) Sphingophospholipids

The difference between the two classes of phospholipids - *glycerophospholipids* and *sphingophospholipids* - is that **sphingophospholipids** have a “\_\_\_\_\_ **backbone**” instead of a *glycerol backbone*.

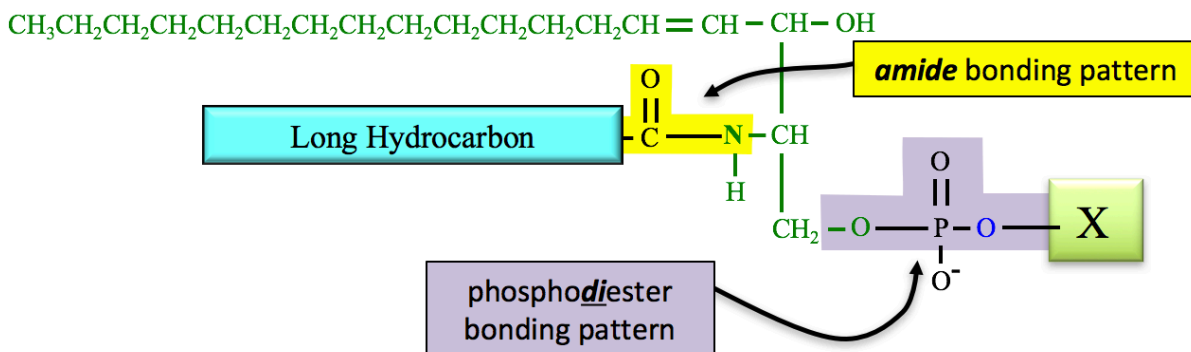
*Sphingophospholipids* are made from the components shown below.



Let's take a look at the bonds that are made in the formation of a *sphingophospholipid*.

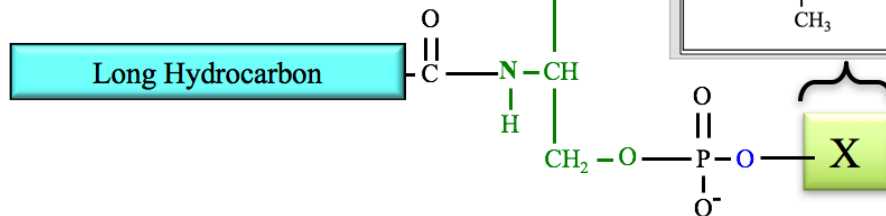


The *amide* and *phosphodiester* bonding patterns for a sphingophospholipid are indicated in the structure shown below.



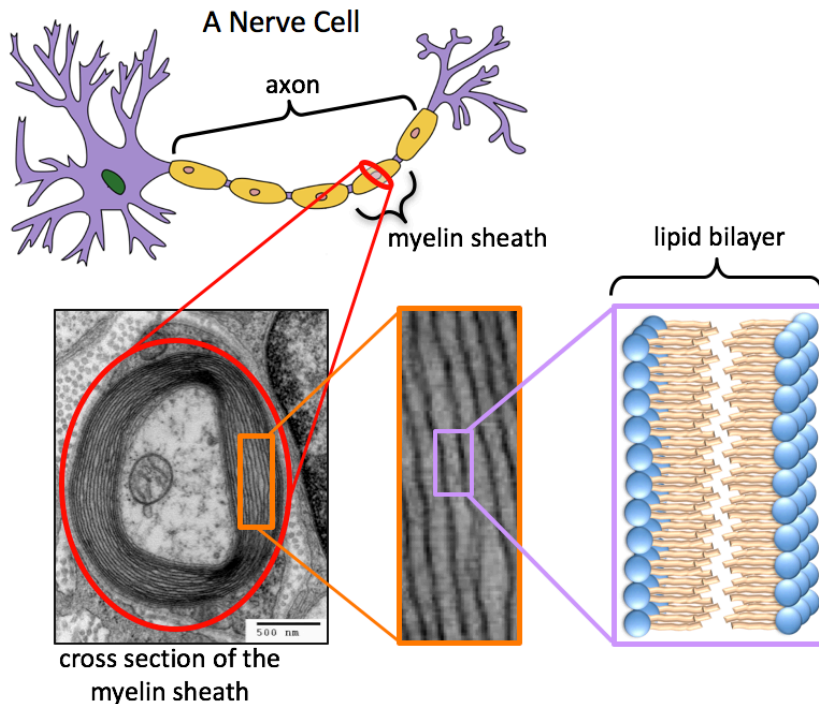


As was the case for glycerophospholipids, sphingophospholipids are classified based on their X-group.



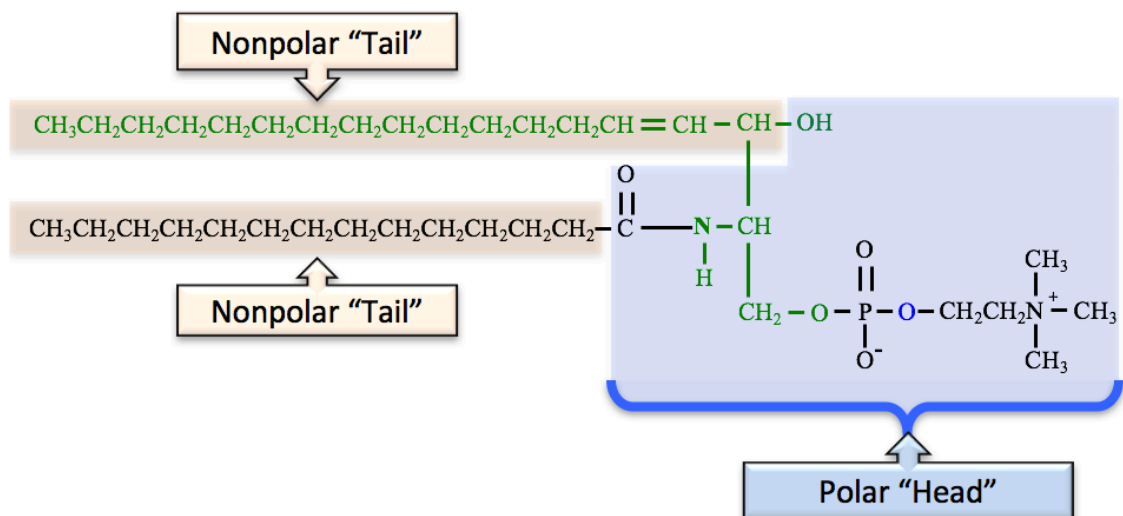
"X-group"	Sphingophospholipid Class
-H	Ceramide
$-\text{CH}_2\text{CH}_2\text{NH}_3^+$ or $-\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_2$	Sphingomyelin

Sphingomyelins have this name because they are the most abundant class of *phospholipid* found in myelin (although they are the most abundant *phospholipids* found in myelin, the most abundant *lipids* in myelin are *glycolipids*, which I will discuss soon). Myelin is a combination of lipids (85%) and proteins (~15%), assembled as a **bilayer** that wraps around nerve cell axons. The myelin sheath is an electrical insulator and its main function is to increase the speed at which nerve impulses are propagated along axons.



If the X-group of a sphingophospholipid is a hydrogen (instead of an organic group), then it is classified as a **ceramide**. *Ceramides* are found in cell membranes and in the myelin sheath of nerve cells.

A specific example of a sphingophospholipid (a sphingomyelin) is shown below.



If you are looking at a color image, the atoms from sphingosine are in green font. I arbitrarily chose to use *myristic acid* as the fatty acid residue; any fatty acid could have been used.

This particular sphingophospholipid is classified as a *sphingomyelin* since the X-group is  $\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3$ .

Sphingophospholipids are amphipathic; they have a *polar head* region and *nonpolar tails*.

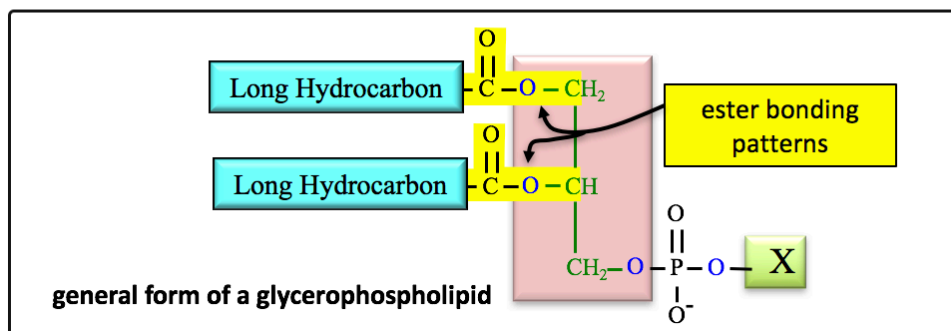
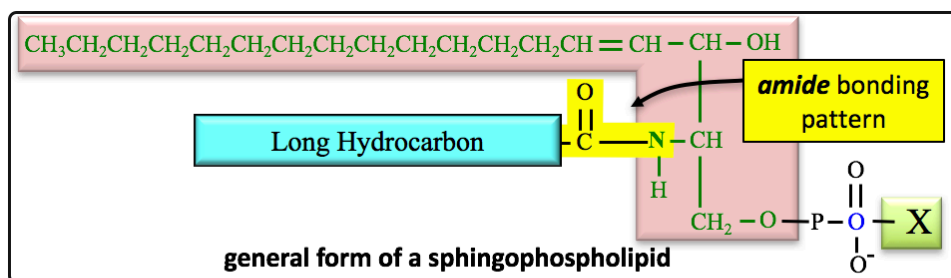
Note that most of the atoms from sphingosine are part of one of the lipid's nonpolar tails.

## Review of Phospholipid Structure: Glycerophospholipids vs. Sphingophospholipids

If you are given the structure of a **phospholipid**, you should be able to determine if it is a *glycerophospholipid* or a *sphingophospholipid*.

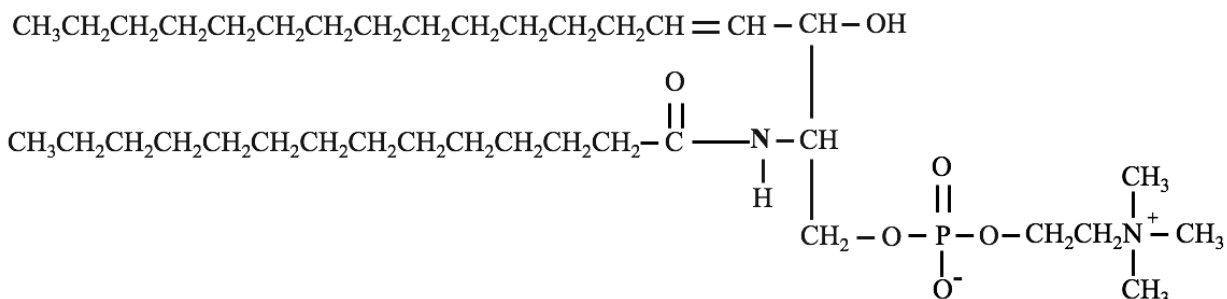
The key to doing so is to identify either a *glycerol backbone* (for glycerophospholipids) or a *sphingosine backbone* (for sphingophospholipids).

An easy way to do so is to look for the **nitrogen** in the **amide bond** between the fatty acid residue and the *sphingosine backbone*. This **amide bonding pattern** is **present in sphingophospholipids, but not in glycerophospholipids**.



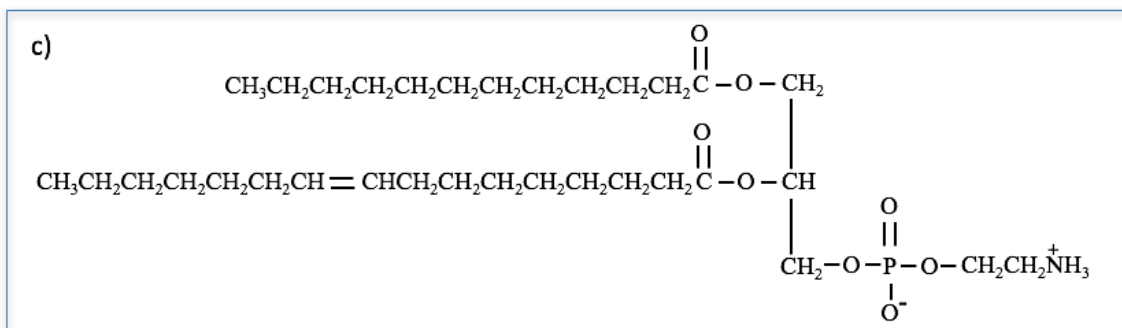
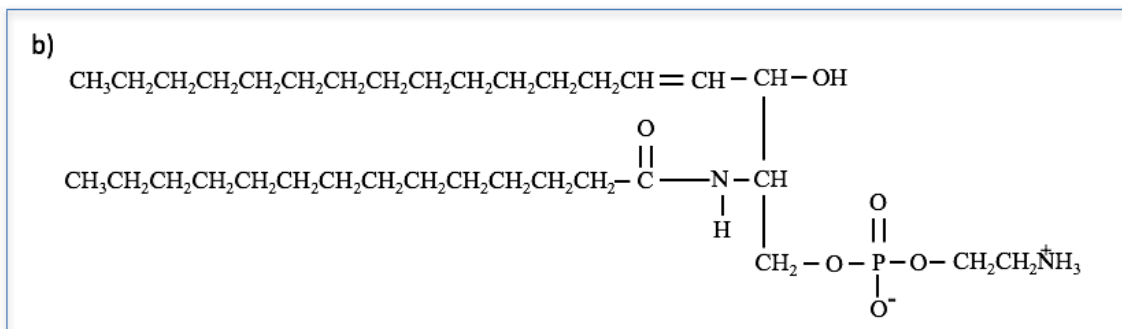
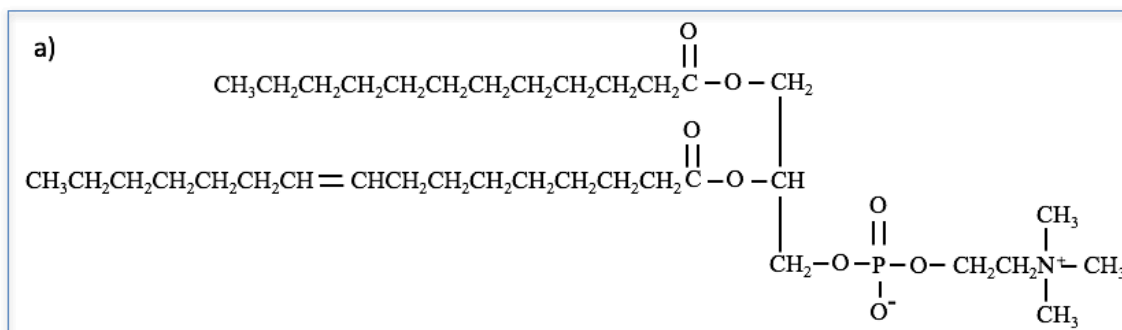
### Understanding Check

Identify (circle) the *nitrogen atom* that is contained in the amide bonding pattern in the sphingophospholipid shown here.



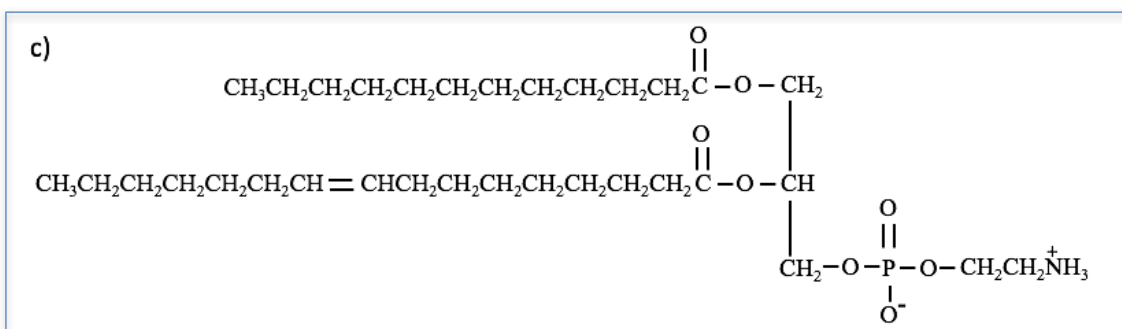
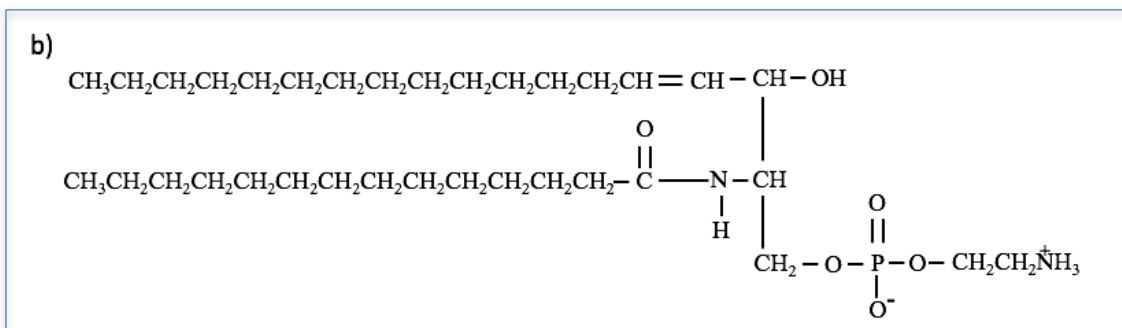
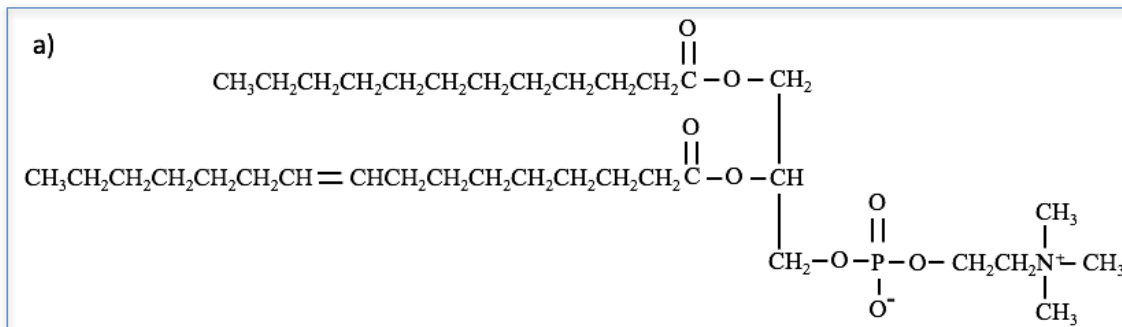
### Understanding Check

Categorize each of the following compounds as being either a *glycerophospholipid* or a *sphingophospholipid*.



### Understanding Check

Categorize each of the compounds shown here as being either a phosphatidylethanolamine, a phosphatidylcholine, a phosphatidylserine, a ceramide, or a sphingomyelin.



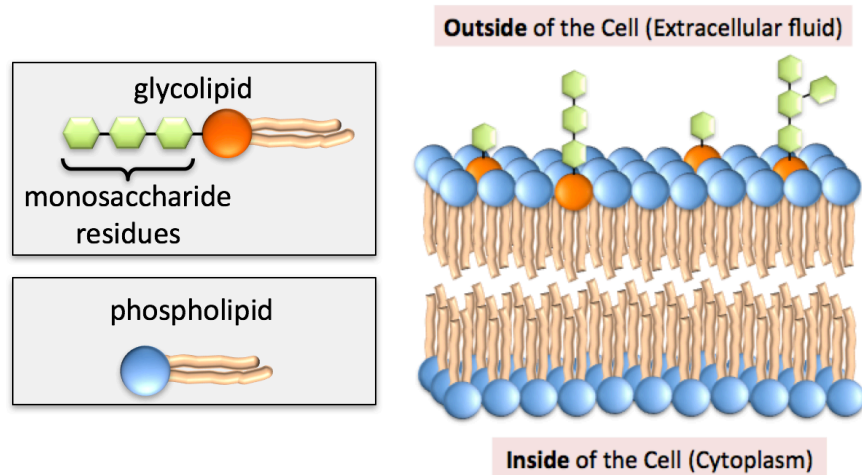
## Glycolipids

**Glycolipids** are *lipids* that contain one or more \_\_\_\_\_ **residues**.

- A *glycolipid* is easily distinguished from a *phospholipid* by the *presence* of a monosaccharide residue and the \_\_\_\_\_ of a phosphate residue.

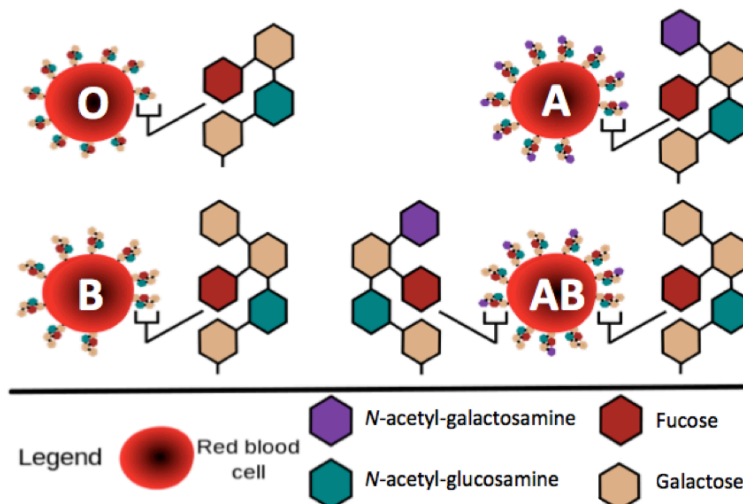
Glycolipids are found in the cell membranes of plants and animals.

- In all eukaryotic cells, the monosaccharide residues of the glycolipid extend from the outer surface of the cell membrane double layer into the aqueous region outside of the cell, as illustrated below.



The specific monosaccharide residues that protrude from the membrane serve in maintaining membrane stability, attaching cells to one another to form tissues, and as a “recognition site” for “cell signaling” chemicals. Cell signaling chemicals make it possible for the cells to respond to their environment in order to enable functions such as tissue homeostasis, immunity, and the development of the organism. When signaling systems are not operating correctly to process the communication between cells and their environments, diseases such as cancer, diabetes, and autoimmune disorders occur.

An example of glycolipid recognition sites are the monosaccharides that protrude from red blood cells and form the basis of ABO blood typing. The illustration below shows the various bonding patterns of glycolipid/monosaccharides used for ABO blood typing and their classification.

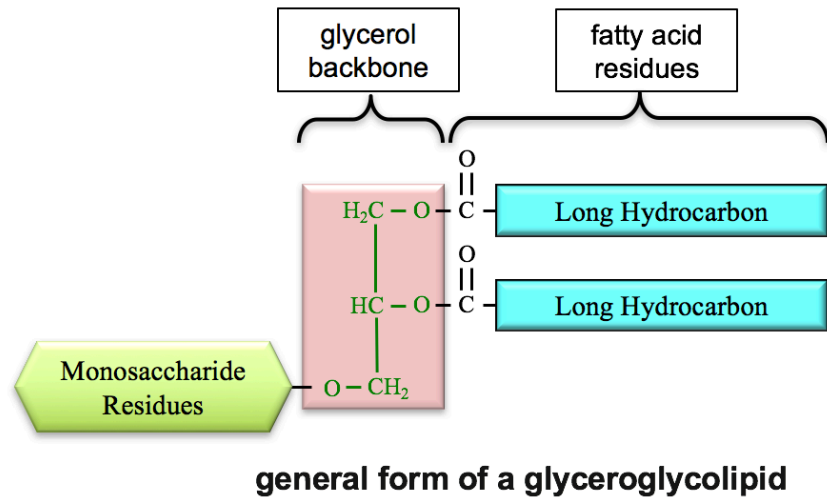


This image shows the glycolipid monosaccharides that define the four “ABO” blood types. Note that type AB red blood cells contain both type-A and type B glycolipids.

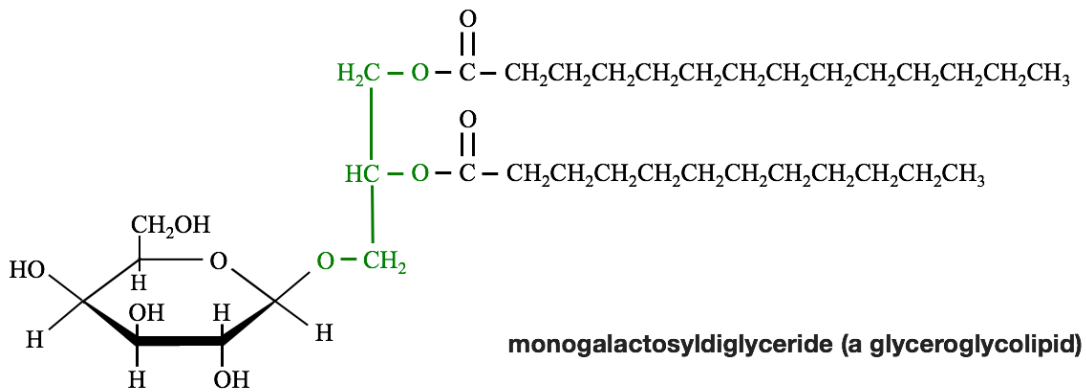
**Glycolipids** can be classified by their structures as **glyceroglycolipids** or **sphingoglycolipids**.

### 1) Glyceroglycolipids

Glycolipids with a *glycerol backbone* are called **glyceroglycolipids**.



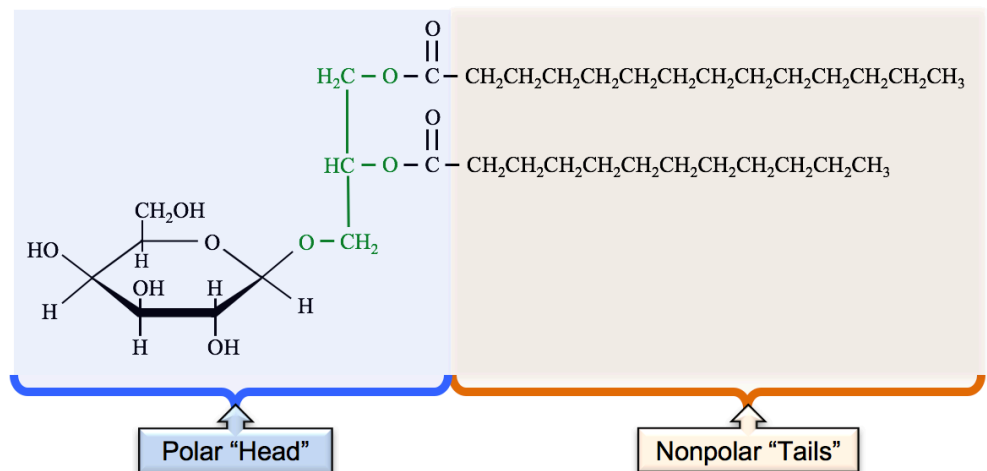
A specific example of a glyceroglycolipid is the monogalactosyldiglyceride (MGDG) shown below.



The monosaccharide residue in all monogalactosyldiglycerides is galactose. The fatty acid residues of monogalactosyldiglycerides vary; I arbitrarily chose the two fatty acid residues in the structure shown above. MGDG occurs in high quantity in the membranes that surround chloroplast organelles.

**All glycolipids** are *amphipathic*. They have a polar head region and nonpolar tails.

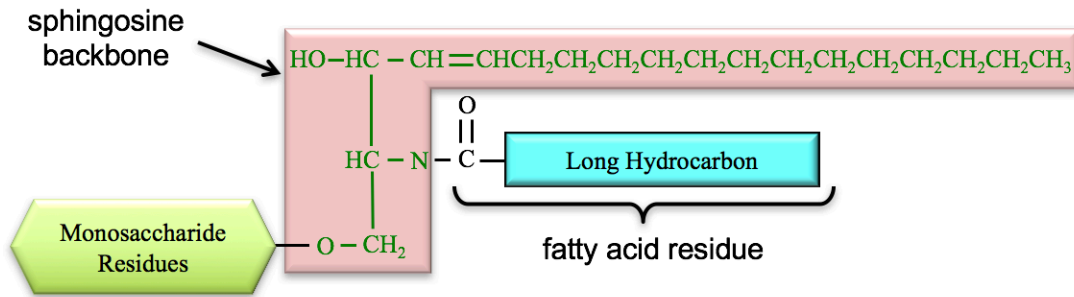
The multiple highly-polar **OH** groups from the monosaccharide make the polar head region quite hydrophilic.



## 2) Sphingoglycolipids

Glycolipids with a *sphingosine backbone* are called **sphingoglycolipids**.

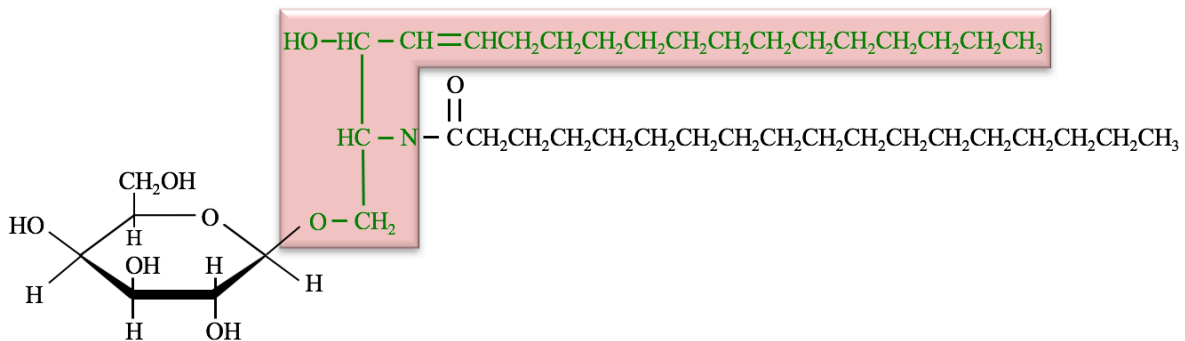
The general form of a sphingoglycolipid is shown below.



**general form of a sphingoglycolipid**

- Sphingoglycolipids are found predominantly in nerve and muscle cells.
- They are the major lipid component of the myelin sheath.

An example of a sphingoglycolipid is the glucosylceramide shown below:

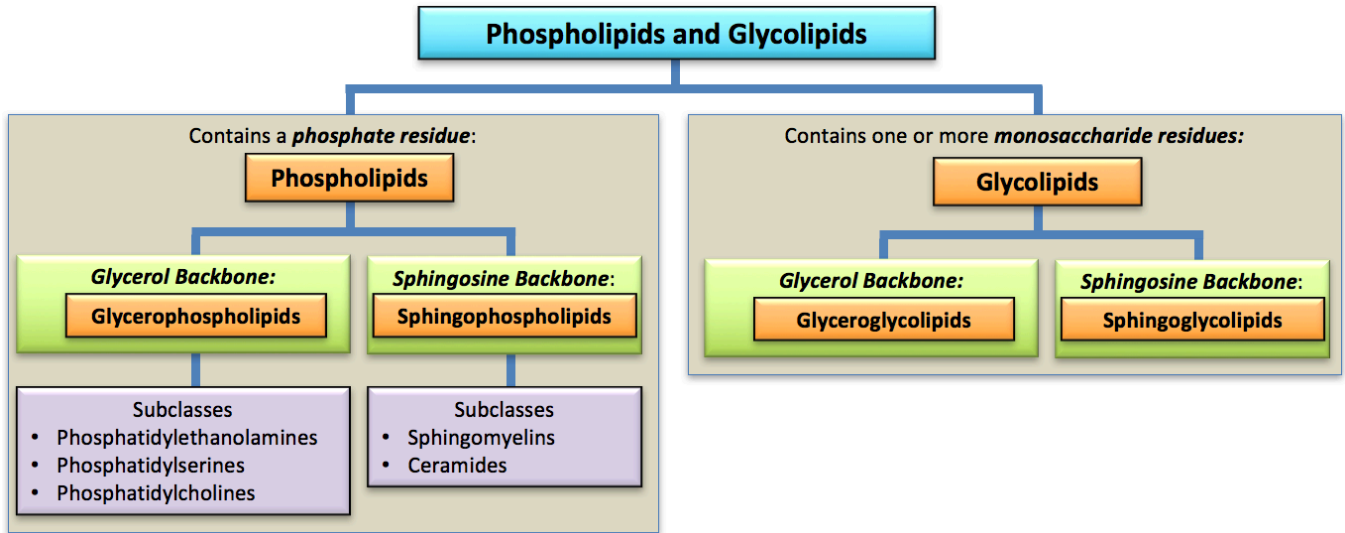


**a glucosylceramide (a sphingoglycolipid)**

The monosaccharide residue in all glucosylceramides is glucose. The fatty acid residue in glucosylceramides varies; I arbitrarily chose a stearic acid residue for the structure shown above.

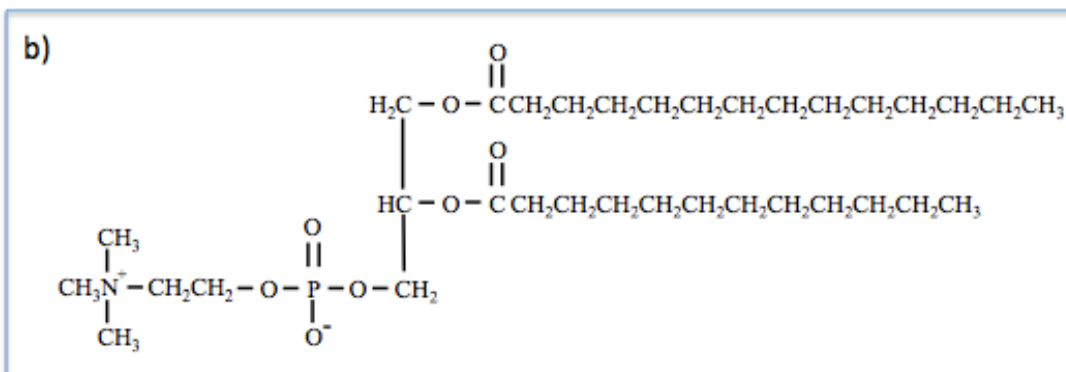
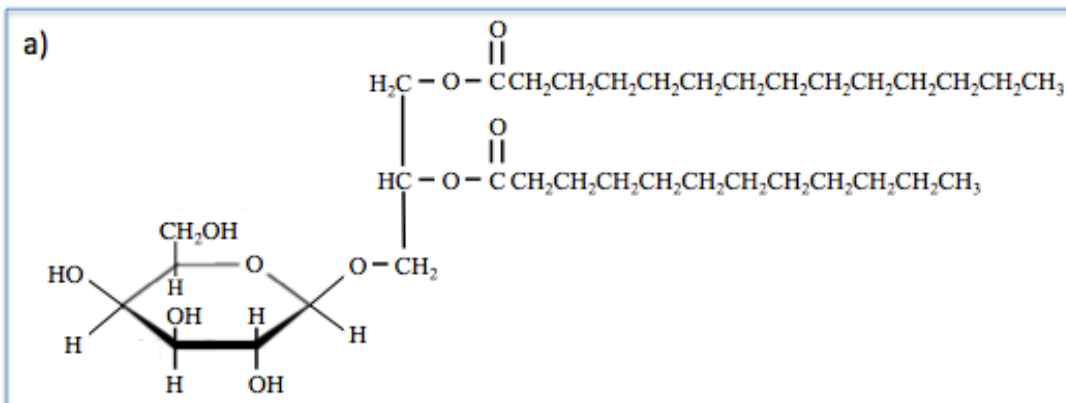
The accumulation of large quantities of sphingolipids in cells and organs results from certain genetic diseases called *lipidosis*. The body normally controls the amount of sphingolipids that accumulate by using enzymes that catalyze reactions that break down sphingolipids. Genetic disorders result in a deficiency of an enzyme responsible for the breakdown of a sphingolipid. Gaucher's disease is caused by a deficiency in the enzyme that breaks down glucosylceramide. Krabbe disease is caused from a deficiency in the enzyme responsible for catalyzing the breakdown of galactosylceramine (a sphingolipid in which the monosaccharide residue is galactose). Tay-Sachs disease is a genetic disorder that causes a deficiency of the enzyme responsible for the breakdown of GM2-ganglioside (a sphingolipid in which the monosaccharide residues are a particular oligosaccharide). The other sphingolipidosis diseases are Fabry disease, Sandhoff disease, and metachromatic leukodystrophy. Some of these diseases can be treated by a very costly enzyme replacement therapy, however most sphingolipidosis cases result in death before five years of age.

## Review of Phospholipid and Glycolipid Classification



### Understanding Check

Categorize each of the following compounds as being either a **phospholipid** or a **glycolipid**.



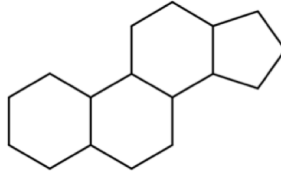


# Steroids

**Steroids** are lipids that contain a particular \_\_\_\_\_, \_\_\_\_\_ structure.

- *Fused rings* are rings that *share* atoms.

The fused four-ring structure, which is common to all steroids, contains three six-member rings and one five-member ring, that are fused to each other in the pattern shown below.



the fused, four-ring structure common to steroids

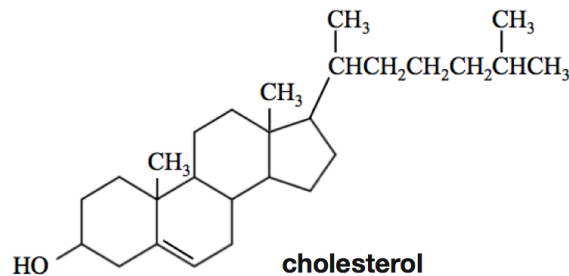
Outside of the health and scientific communities, the term “steroid” is often only associated with the performance enhancing drugs (*steroid hormones*) that are used by *some* athletes/bodybuilders. Those *steroid hormones* are just one type of steroid.

The *three types of steroids* are:

1. **cholesterol**
2. **steroid hormones**
3. **bile salts**

## Cholesterol

Cholesterol is the name of the particular molecule shown below.

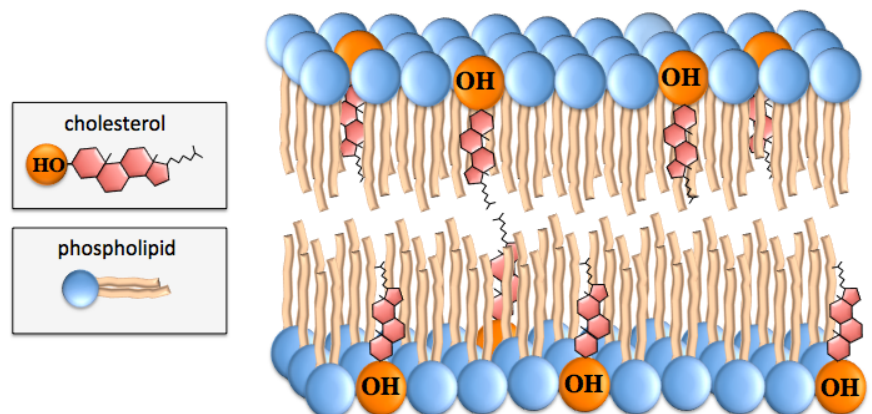


Cholesterol’s primary biological roles are as a \_\_\_\_\_ **component** of animal biological membranes and as a starting material for the biosynthesis of \_\_\_\_\_ steroids (steroid hormones and bile salts).

Cholesterol is not found in significant quantities in plants. Animals can make cholesterol from other compounds; therefore, cholesterol is present in your body even if you don’t ingest it.

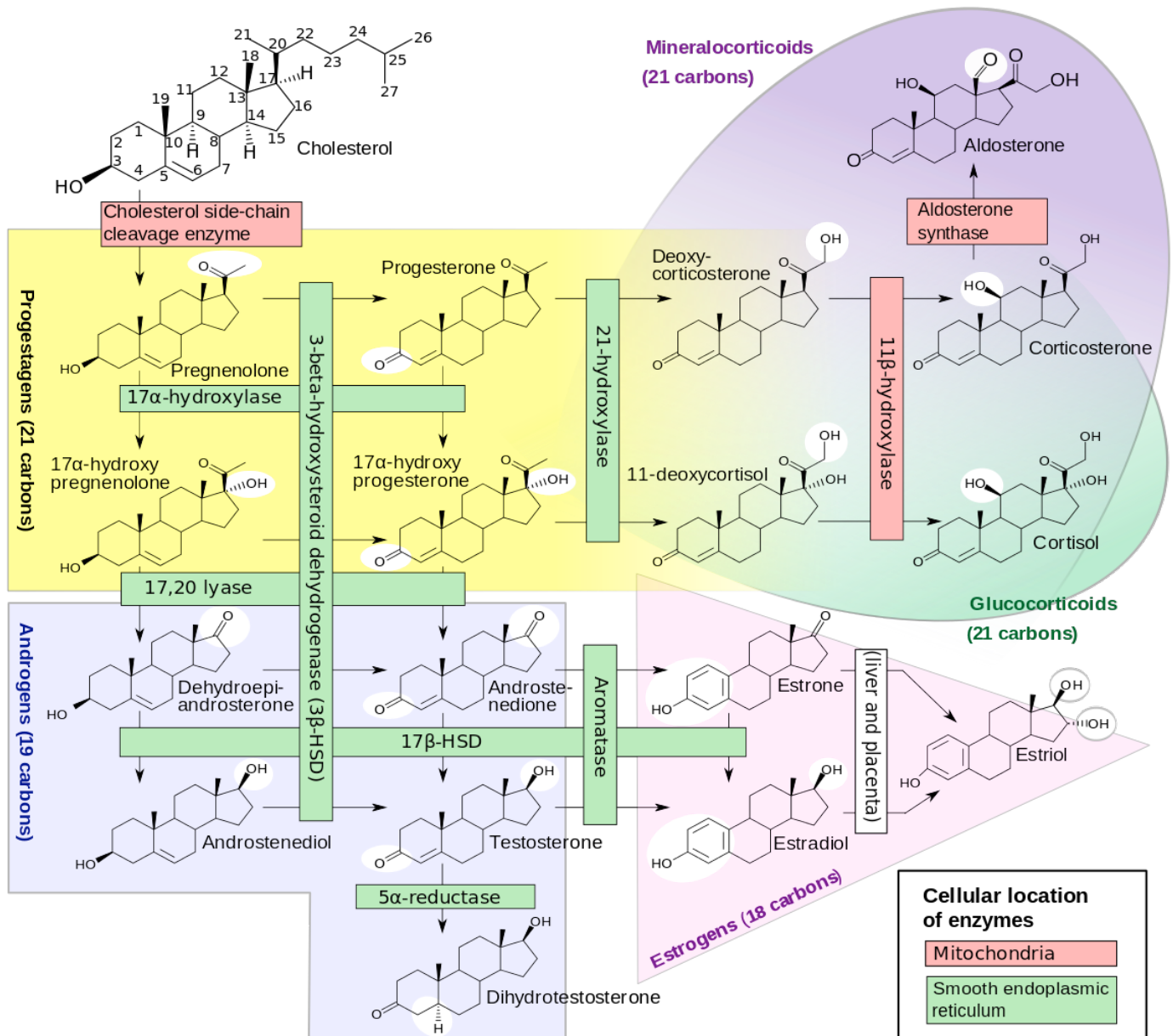
Cholesterol maintains the structural integrity and rigidity of biological membrane double layers by embedding its hydrophobic fused-ring structure within the nonpolar tails of the double layer.

Cholesterol imparts rigidity to membranes because of the *lack of free rotation* within its fused-ring structure.



Animals produce other essential steroids (steroid hormones and bile salts) using cholesterol as a \_\_\_\_\_ material.

- The production of steroids is called \_\_\_\_\_.
- **NOTE:** You **ARE NOT** required to memorize the steroidogenesis figure (below).



A diagram of the processes in which steroid hormones are produced from cholesterol is shown above. The enzymes that catalyze these reactions and their locations are indicated by the colored boxes drawn atop the reaction arrows. The white circles and ovals indicate the groups that were changed in the synthesis reactions. The cholesterol structure (upper left) has the *carbon positions* numbered. Wedges and dashes are used to indicate bonds that are oriented upward or downward, respectively, relative to the ring structure.  $\alpha$  and  $\beta$  designations have the same meaning as used for carbohydrates.

Source: Häggström M, Richfield D (2014). "Diagram of the pathways of human steroidogenesis". *Wikipedia Journal of Medicine* 1 (1). DOI:10.15347/wjm/2014.005. ISSN 20018762. Author: David Richfield and Mikael Häggström, CC-BY-SA, <http://creativecommons.org/licenses/by-sa/3.0/deed.en>

## Steroid Hormones

\_\_\_\_\_ are a class of *signaling compounds* that are produced by the glands of the endocrine or exocrine system, then released into the bloodstream (or sap in the case of plants).

Hormones vary in their chemical structure; those that are derived from cholesterol, as shown in the steroidogenesis diagram here, are called \_\_\_\_\_ *hormones*.

An example of a *steroid hormone* is a “male sex hormone” called **testosterone**. Testosterone and other male sex hormones (androgens) are responsible for the development of male characteristics such as larger muscle growth, thick facial hair, male sex organs, and sperm production. Although testosterone is classified as one of the male sex hormones, it is also present, at lower levels, in females. The structure of testosterone and other androgens are shown in the *steroidogenesis diagram* (see the previous page).

- Testosterone acts to decrease body fat and increase muscle mass. Synthetic derivatives of testosterone, called **anabolic steroids**, will enhance these effects. You have probably heard much in the news about the use of anabolic steroids by athletes. Many professional sports organizations ban their use, and periodically test athletes to enforce the policy. Anabolic steroids are currently used in medical practice to increase muscle growth and appetite, induce male puberty, and to treat chronic wasting conditions including cancer and AIDS. It is considered unwise to use anabolic steroids in order to enhance athletic performance and for recreational bodybuilding because of the detrimental side effects; this is especially true for high doses and/or long-term use. Such side effects for males include pattern baldness, breast development, a reduction in testicle size, low sperm count, and infertility. The side effects for females include abnormal menstrual function, breast atrophy, increased facial hair, voice-deepening, and baldness. Other possible adverse side effects - for both men and women - include liver disease, heart disease, and depression.

Other examples of steroid hormones are **estrogens** and **progestogens**, the “female sex hormones.” They are responsible for the development of female characteristics related to menstruation and reproductive cycles, such as broadening of the pelvis, fat deposited in breasts, and uterus size increase. An example of female sex hormone is *progesterone*, which is responsible for many of the biological functions associated with pregnancy. For example, it causes the mucous membrane of the uterus to prepare for the implantation of eggs. If pregnancy does not occur, then progesterone levels decrease and cause menstruation. The structure of *progesterone* and other *progestogens* are shown in *the steroidogenesis diagram*.

Although the adrenal gland is best-known for its production of *adrenaline* (a *nonsteroidal* hormone), it does produce several *steroid hormones*. Steroid hormones produced by the adrenal gland are called **adrenal corticosteroids**. Examples of *adrenal corticosteroids* are *cortisol* and *aldosterone*. One of the many roles of *cortisol* is to suppress immune responses. It is administered *as a therapeutic medication* under the name *hydrocortisone*. *Aldosterone* plays an important role in regulating blood pressure and the concentration of some electrolytes. The structure of *cortisol* and *aldosterone* are shown in the *steroidogenesis diagram*.

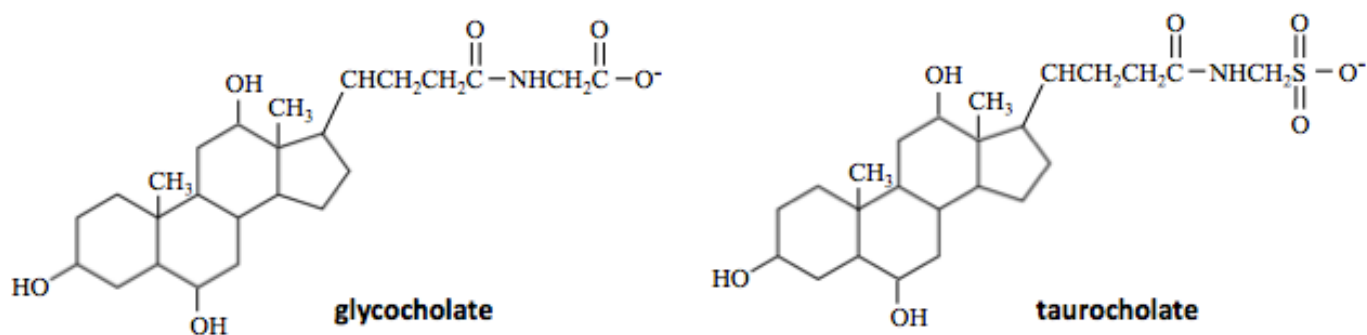
## Bile Salts

**Bile salts** are *amphipathic* compounds produced using \_\_\_\_\_ as a starting material.

They are produced in the liver and stored in the gallbladder.

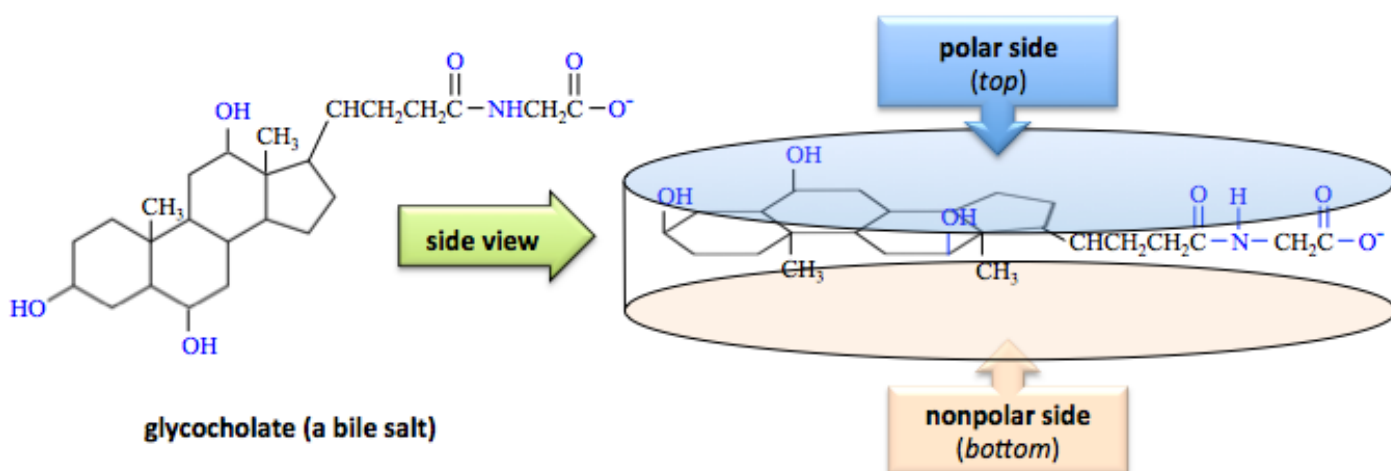
The biological role of bile salts is to \_\_\_\_\_ and \_\_\_\_\_ dietary triglycerides (fats and vegetable oils) and \_\_\_\_\_ in their metabolism.

The structures of two bile salts are shown below; note the four *fused-ring* structures, which are present in *all steroids*.



The amphipathic structure of a bile salt differs from the arrangement that you have seen for other amphipathic compounds. All of the amphipathic compounds that you have previously seen had polar “heads” connected to nonpolar “tails”. *This is not the case for bile salts.*

*Bile salts* can be modeled as oblong disks that have a **polar** \_\_\_\_\_ and a **nonpolar** \_\_\_\_\_, as illustrated below.

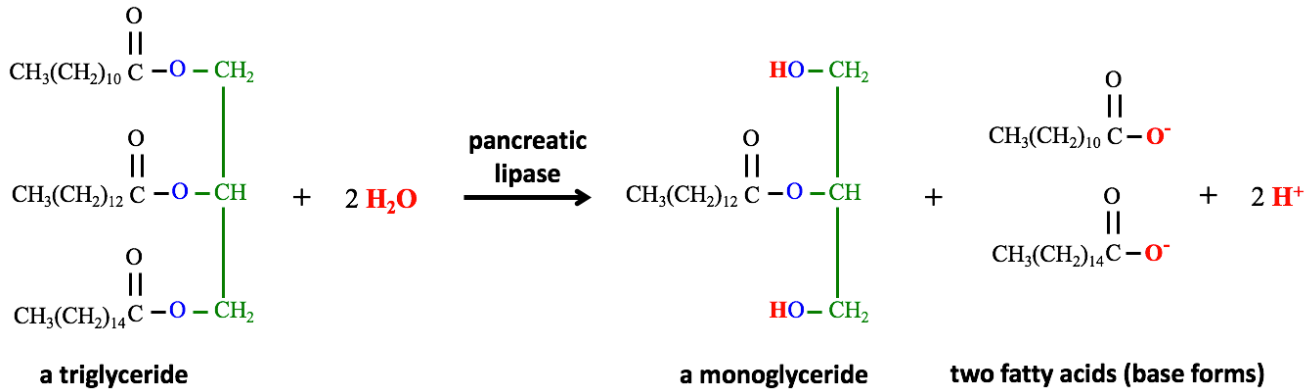


How do bile salts *emulsify* and *transport* dietary triglycerides and *assist* in their metabolism?

The triglycerides (fats and oils) that we eat are unable to pass through the intestine wall.

- In order for these nutrients to be used by the body, they must be broken down into smaller molecules, in a process called \_\_\_\_\_.

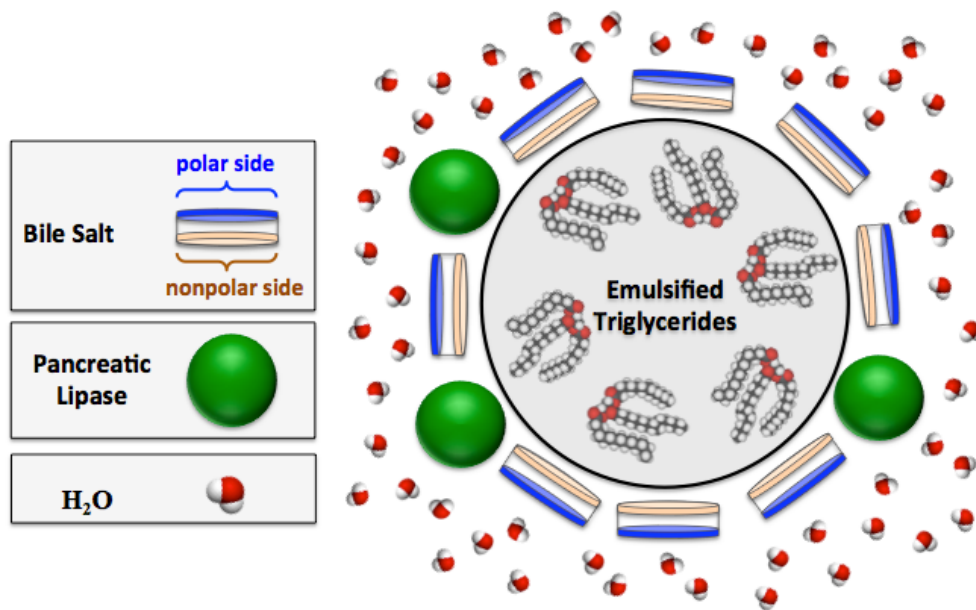
Digestion of fats and oils involves the *partial hydrolysis* of triglycerides to produce fatty acid salts and \_\_\_\_\_, as shown for a typical triglyceride in the chemical equation below.



The enzyme responsible for catalyzing this reaction is called *pancreatic lipase*.

Bile salts disassemble the large globules of dietary triglycerides and cholesterol within the intestine into small droplets emulsified in micelles.

Pancreatic lipase enzymes are incorporated into the bile salt micelle monolayer, as illustrated in the cross sectional view shown below.



The fatty acids and monoglycerides that are formed by the digestion of fats and oils can pass through the walls of the intestine and then can be used by the body.

After being absorbed into the intestine walls, the fatty acids and monoglycerides are re-assembled back into triglycerides.

The triglycerides are then emulsified and transported, along with cholesterol, in a colloid called a \_\_\_\_\_.

## Transport of Cholesterol and Triglycerides

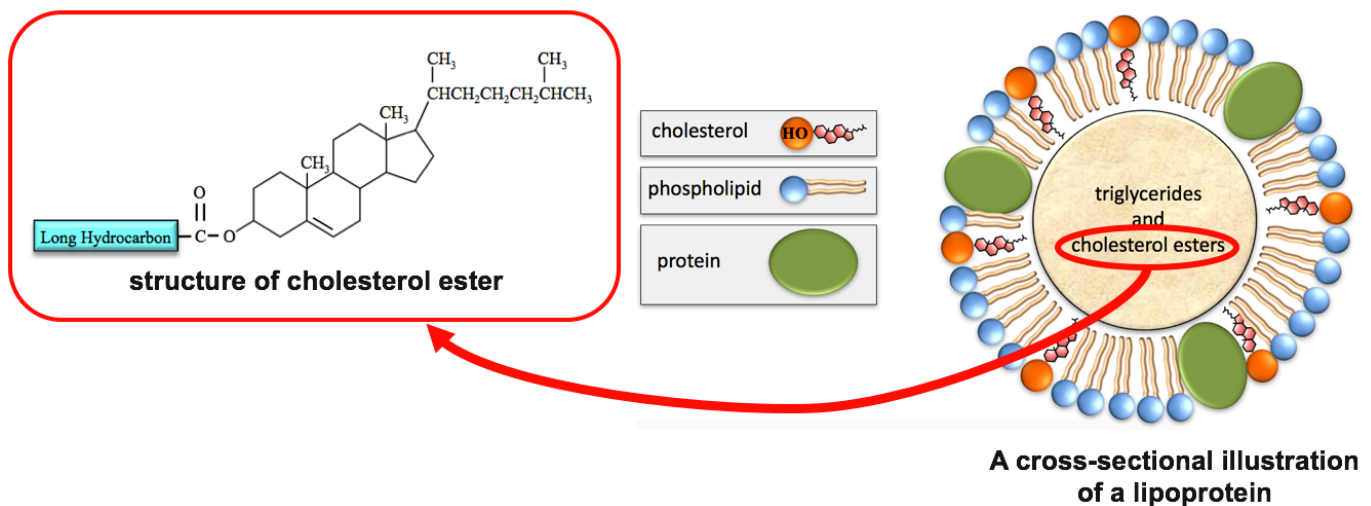
Since blood, lymph, and intercellular fluid are \_\_\_\_\_ *mixtures*, cholesterol and triglycerides must be \_\_\_\_\_ in order to be transported throughout the body.

- This is done by *lipoproteins*.

*Lipoproteins* are composed of a core that contains emulsified triglycerides and cholesterol, which is surrounded by a micelle monolayer made from proteins, phospholipids, and cholesterol.

Lipoproteins contain cholesterol in their micelle monolayers, **and** in their emulsified cores.

The cholesterol *in the emulsified core* of lipoproteins is in the form of *cholesterol esters*, formed by the esterification reaction of cholesterol with a fatty acid.



There are five classes of lipoproteins: *chylomicrons*, *very low-density lipoproteins* (VLDL), *intermediate-density lipoproteins* (IDL), *low-density lipoproteins* (LDL), and *high-density lipoproteins* (HDL).

These classifications are based on the \_\_\_\_\_ of the lipoprotein particles.

- Since protein is more dense than lipid, the greater the percentage of protein, the higher the density of the lipoprotein.

**Density Ranges and Percent (w/w) Compositions for Lipoprotein Classes**

Lipoprotein Classification	Density (g/cm <sup>3</sup> )	% Protein	% Cholesterol	% Phospholipids	% Triglycerides and Cholesterol Esters
chylomicrons	< 0.94	< 2	8	7	84
VLDL	< 1.006	10	22	18	50
IDL	1.006 - 1.019	18	29	22	31
LDL	1.019 - 1.063	25	50	21	8
HDL	1.063 - 1.21	33	30	29	4

The amounts of HDL and LDL in the blood have been correlated with the constriction (occlusion) of the coronary artery, which makes the heart work harder and can lead to myocardial infarction (heart attack). The thickening of the inner layer of the artery is caused by the accumulation of **plaque**, which is made from living white blood cells and remnants of dead cells, including **cholesterol** and **triglycerides**.

- A high LDL level is correlated with a greater risk of heart disease.
- A high HDL level is correlated with a lowered risk of heart disease.

For these reasons, it is recommended that adults have the lipid levels in their blood tested *at least* once every five years. The test is called a **lipoprotein panel**. Although the concentration of cholesterol is not directly measured in these tests, the terms “total cholesterol,” “bad cholesterol”, and “good cholesterol” are often used by practitioners when describing or discussing the results of lipid panels. Cholesterol is the name of a *particular molecule*, however, *in lipid panels*, the term “total cholesterol” is used for the concentration of HDL + LDL + 20% of the triglycerides. The term “bad cholesterol” is used for the concentration of LDL. The term “good cholesterol” is given to HDL since it transports cholesterol back to the liver (the liver can remove cholesterol from the body) and lowers the risk of heart disease.

Substance	Desirable/Recommended Level	Borderline High Level	High Level
“Total Cholesterol” (HDL + LDL + 20% of the triglycerides)	below 200 mg/dL	200-239 mg/dL	240 mg/dL and above
Triglycerides	below 150 mg/dL	150-199 mg/dL	200 mg/dL and above
LDL “Bad Cholesterol”	below 100 mg/dL (ideal)* 100-129 mg/dL (near ideal)	130-159 mg/dL	160-189 mg/dL (high) 190 and above mg/dL (very high)
	<b>Considered <i>Protective</i> Against Heart Disease</b>	<b>Intermediate Values (the higher, the better)</b>	<b>A Major <i>Risk Factor</i> for Heart Disease</b>
HDL “Good Cholesterol”	60 mg/dL and above	40-59 mg/dL	less than 40 mg/dL

Lipid and lipoprotein concentrations are measured in milligrams (mg) of substance per deciliter (dL) of blood.  
 \*The LDL desirable values are lower than those shown in the table for persons at risk of heart attack.  
 Source: National Institutes of Health, *Medline Plus* (2012). Volume 7 Number 2 Page 6-7

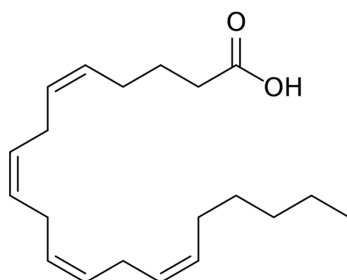
## Eicosanoids

The “*eicosa*” prefix in *eicosanoids* is from the Greek “*eicosa*,” which means twenty.

The lipids called **eicosanoids** are \_\_\_\_\_ *molecules* that contain \_\_\_\_\_ carbon atoms.

- They are derived from one of three, twenty-carbon polyunsaturated fatty acids (arachidonic acid, eicosapentaenoic acid, or dihomo-gamma-linolenic acid).

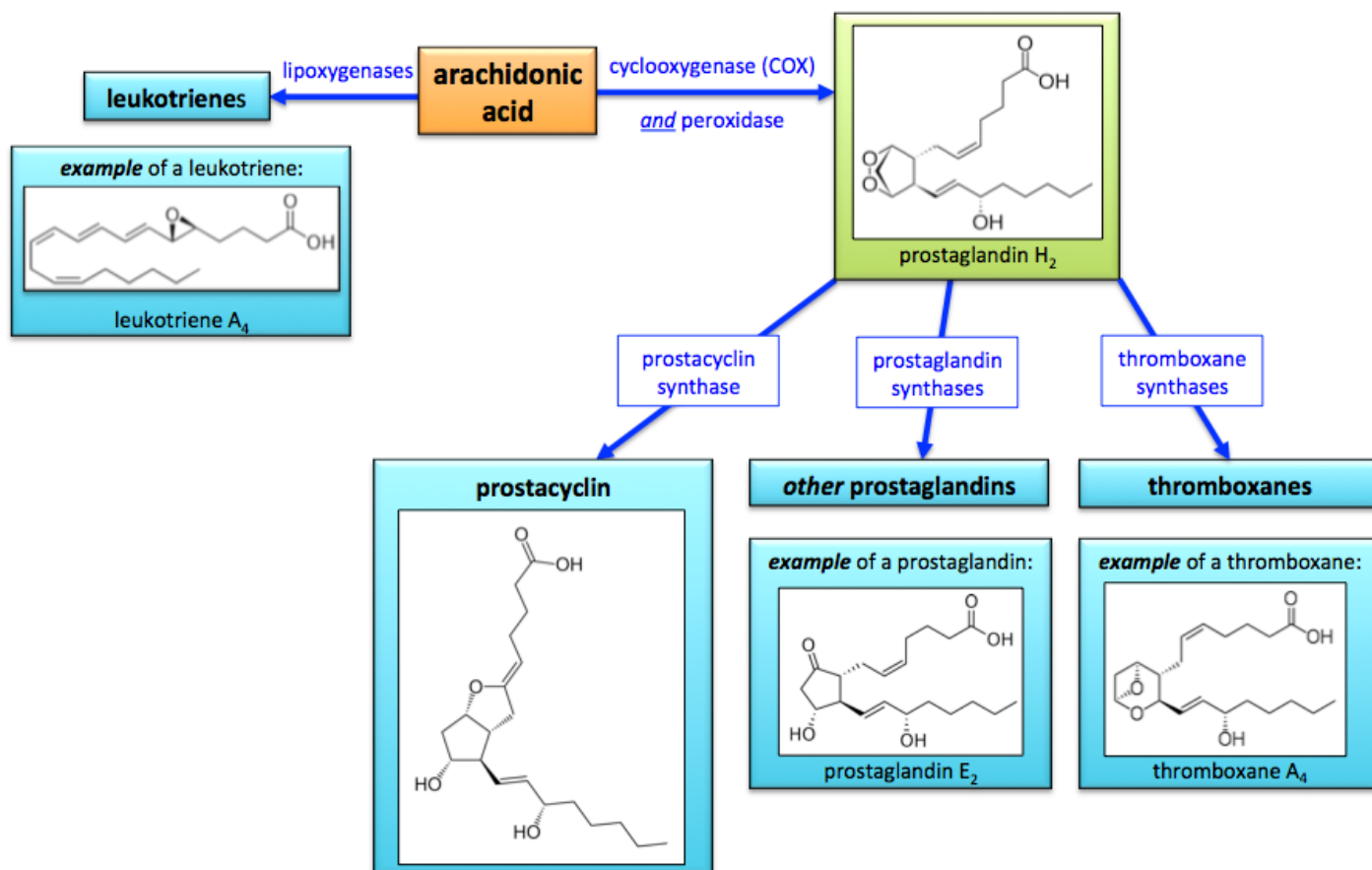
Arachidonic acid, shown below, is the major precursor of eicosanoids.



arachidonic acid

Arachidonic acid, eicosapentaenoic acid, or dihomo-gamma-linolenic acid undergo *reactions* that transform them into the various classes of *eicosanoids* - such as **prostaglandins**, **thromboxanes**, **leukotrienes**, and **prostacyclin**.

- For example, *arachidonic acid* can be converted to various eicosanoids as shown in the diagram below.



**NOTE:** You are **not** responsible for memorizing the enzymes for these reactions or the structures of the various eicosanoids.



## **Prostaglandins**

*Prostaglandins* have a wide range of biological effects, including causing pain, causing inflammation, causing fever, affecting blood pressure, inducing sleep, regulating blood flow to particular organs, controlling ion transport across membranes, and inducing labor.

## **Thromboxanes**

Thromboxane A<sub>2</sub> is the major biologically-active form of thromboxanes. It acts as vasodilator and is involved in the facilitation of blood clotting.

## **Leukotrienes**

Leukotrienes are involved in the regulation of immune responses and in induced muscle contractions in the lungs. The overproduction of a particular leukotriene (leukotriene D<sub>4</sub>, *not* shown in the diagram on the previous page) is a major cause of inflammation in asthma. Some anti-asthma drugs block the production of leukotrienes.

## **Prostacyclin**

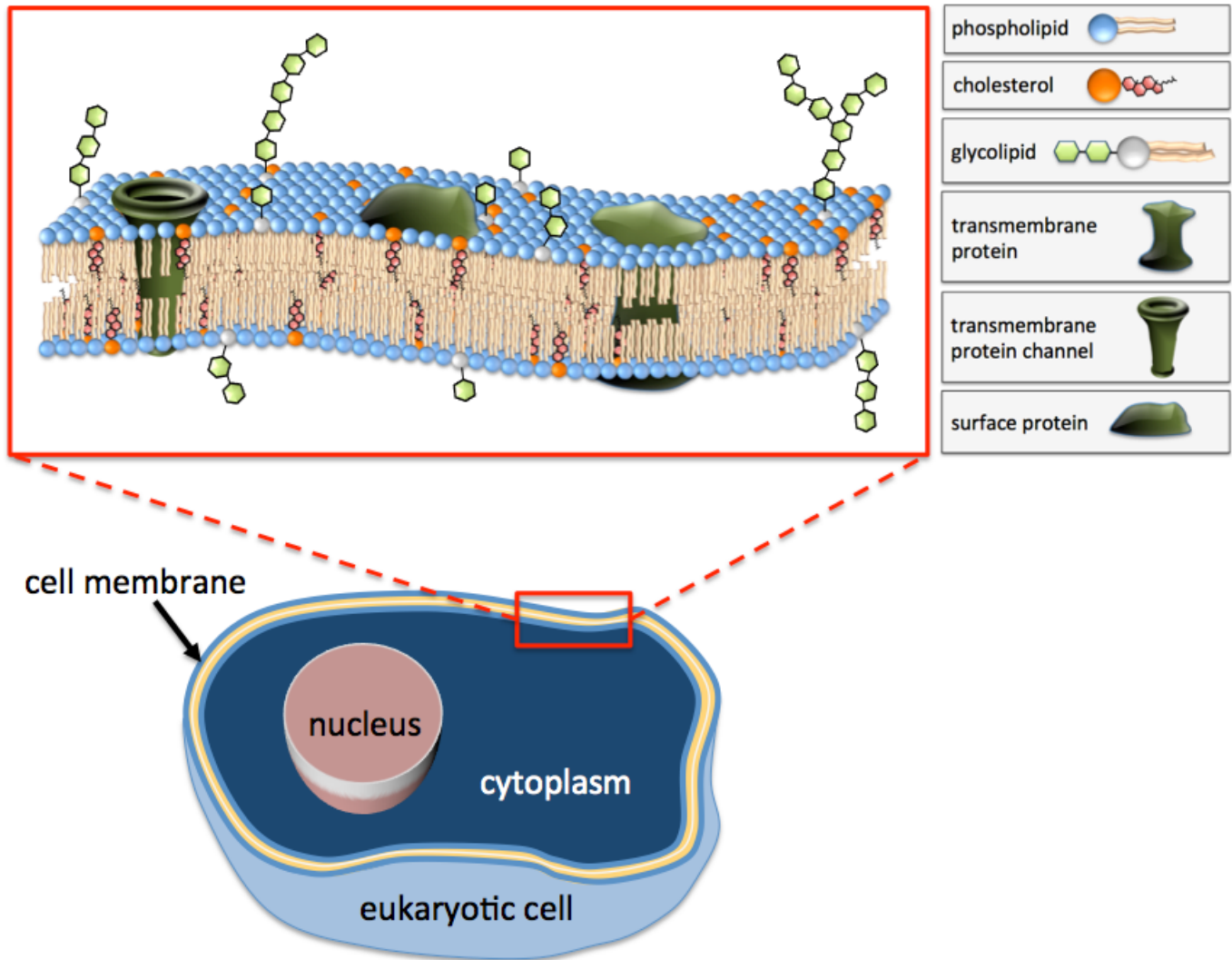
Prostacyclin is involved in vasodilatation, *inhibition* of blood clotting, regulation of the contraction of smooth muscle, and inflammation.

## **Nonsteroidal Anti-inflammatory Drugs (NSAIDs)**

NSAIDs such as aspirin, acetaminophen, and ibuprofen are taken to reduce pain, fever, and inflammation by blocking the action of the cyclooxygenase enzyme (COX) that catalyzes the conversion of arachidonic acid into prostaglandins and thromboxanes (see the eicosanoids formation diagram on the previous page).

## Biological Membranes

Biological membranes are semipermeable physical barriers. Biological lipid double layer membranes not only function as cell membranes, but also exist within cells in order to form specialized compartments. For example, intracellular lipid double layer membranes surround a cell's nucleus, chloroplasts, and mitochondria. The lipid double layers in biological membranes contain components other than phospholipids and glycolipids. These other components, which include cholesterol and various proteins, are distributed throughout the lipid double layer, as illustrated *below* for a eukaryotic cell membrane.



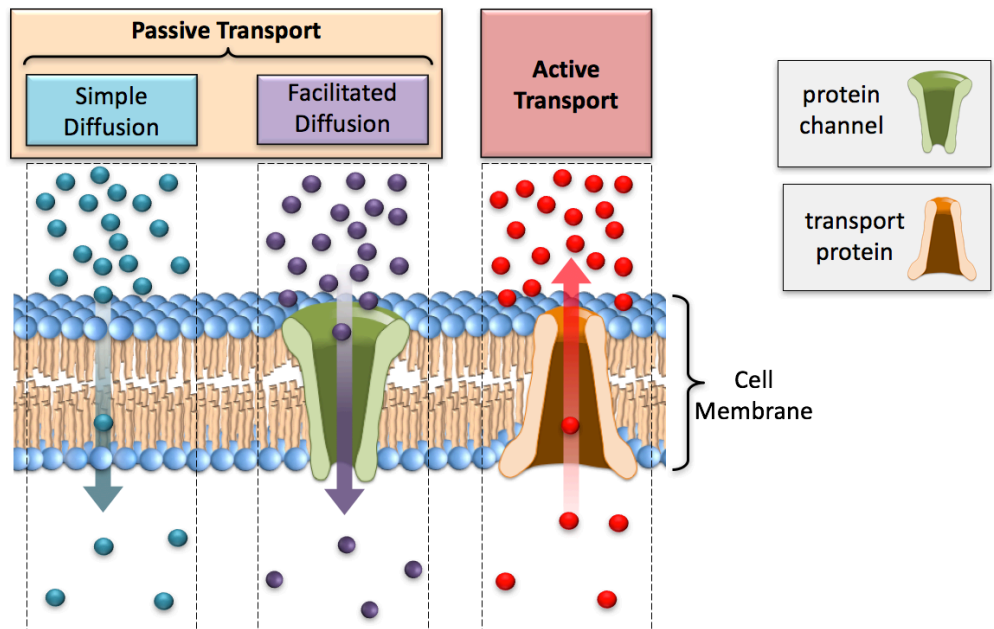
The forces holding the lipids and other components together in each of the two monolayer sheets are relatively weak. For this reason, membranes are flexible, and the membrane components are not locked in place; they are able to “slide” past each other. The flexibility of membranes *decreases* as the *chain lengths* and *degree of saturation* of the lipid nonpolar tails increase. This is the same trend as you saw for the melting points of fatty acids and triglycerides, because it results from increasing London forces. In animals, the amount of membrane-cholesterol also regulates flexibility.

## The Transport of Molecules and Ions Across Membranes

Certain compounds must be able to pass through cell membranes in order for cells to perform their biological functions.

The processes in which species are transported through membranes are classified as either

\_\_\_\_\_ *transport*  
or  
\_\_\_\_\_ *transport*.



Some *nonpolar* and *amphipathic* compounds can pass through a membrane because of their attraction to the phospholipids in the membrane by noncovalent interactions.

- Species that are able to move through membranes in this way are called *lipophilic compounds*.

The direction of the net transport of a *lipophilic* compound is determined by \_\_\_\_\_; there will be a net transport from the side of the membrane where its concentration is greater, to the side where its concentration is less.

- Recall, from chapter 7, that we described this type of transport as “with the concentration gradient.” The energetic driving force for diffusion is the potential energy of the diffusing species’ concentration gradient.

This diffusive movement of lipophilic compounds through a membrane is referred to as \_\_\_\_\_ **diffusion**.

Diffusion of small ions and polar molecules, which are *not* lipophilic, through membranes is facilitated by *protein channels* that pass through the cell membrane.

This diffusion of ions and polar molecules though protein channels is referred to as \_\_\_\_\_ **diffusion**.

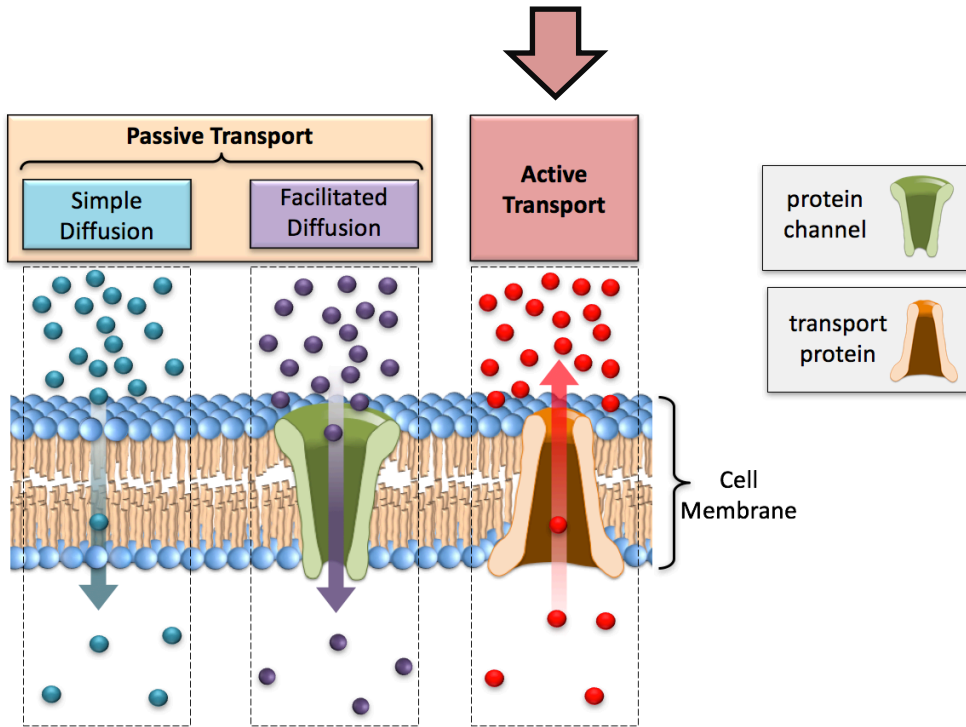
- In *facilitated diffusion*, as with *simple diffusion*, a molecule or ion is transported from the side of the membrane where its concentration is greater to the side where its concentration is less, or “with the concentration gradient,” and the energetic driving force is the potential energy of the diffusing species’ concentration gradient.

Both *simple diffusion* and *facilitated diffusion* are called **passive transport** because they do not require an energetic input from sources other than the concentration gradient of the transported species.

- The transport of water molecules through membranes is a passive transport process, and is best described by *osmosis* (you learned about osmosis in chapter 7). The protein channels in which water molecules pass are called *aquaporins*.

In order for molecules or ions to be transported in the direction “against the concentration gradient” - from the side of the membrane where their concentration is less to the side where their concentration is greater - \_\_\_\_\_ *must be supplied*.

This type of transport is referred to as \_\_\_\_\_ *transport*.



- Unlike the *passive transport* processes that are driven by the potential energy provided by the transported species' concentration gradient, in *active transport*, energy must be supplied by *some other source*.

In the *active transport* process, the ions or molecules cross the membrane with assistance from a \_\_\_\_\_ *protein*.

- An example of active transport is the transport of ions, amino acids, sugars, lipids, drugs, or other molecules “against their concentration gradient” through **ATP binding cassette transport proteins (ABC transporters)**. *ABC transporters* use chemical energy, supplied by **ATP**, to transport compounds through a membrane.

### Understanding Check

- a) Compare and contrast **simple diffusion** with **facilitated diffusion**.
  
  
  
  
  
  
  
  
  
  
- b) Describe the *difference* between **passive transport** and **active transport**.