

# LIPIDS

Lipids perform a variety of biological roles. Triacylglycerols are used for energy storage and metabolic fuel. Phospholipids, sphingolipids and cholesterol (a steroid) are structural components of cell membranes. Nonsaponifiable lipids perform a variety of regulatory functions (hormones, vitamins).

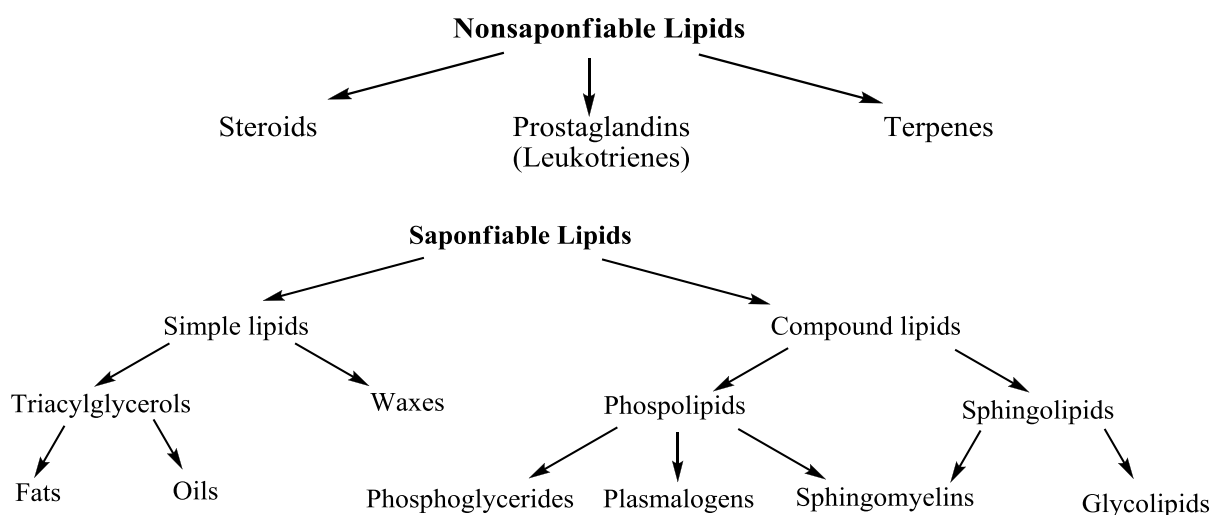
**Lipids** are organic compounds that are found in living organisms and that are soluble in non polar solvents.

## *Classification of lipids*

Lipids are divided into 2 groups: saponifiable and nonsaponifiable lipids.

**Saponifiable** lipids contain at least one ester group, which undergoes hydrolysis in the presence of an acid, a base, or an enzyme. Hydrolysis cleaves a saponifiable lipid into two or more smaller molecules.

**Nonsaponifiable** lipids do not undergo hydrolytic cleavage into smaller molecules.



**Simple lipids** are esters of fatty acids with various alcohols.

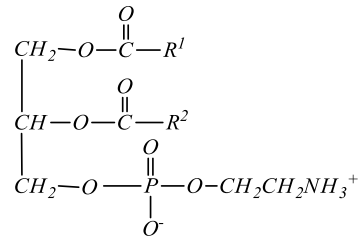
**Triacylglycerol** (triglycerids  $\begin{array}{c} CH_2 - O - COR \\ | \\ CH - O - COR \\ | \\ CH_2 - O - COR \end{array}$ ) are triesters of fatty acids with glycerol.

**Fats** are triglycerides in which saturated fatty acids components predominate; they are solids at room temperature.

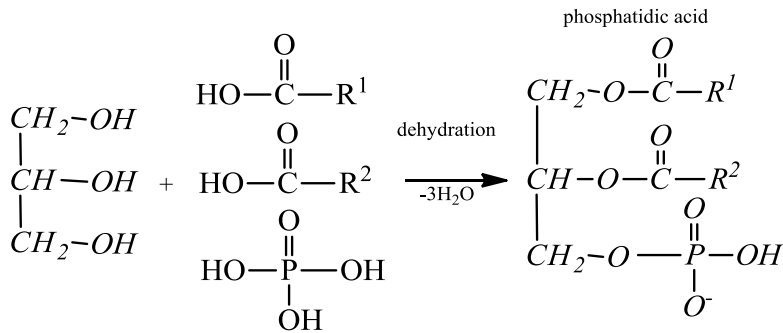
**Oils** are triglycerides in which unsaturated fatty acids components predominate; they are liquids at room temperature.

**Compound lipids.** Esters of fatty acids containing groups, other than, and in addition, to an alcohol and fatty acids.

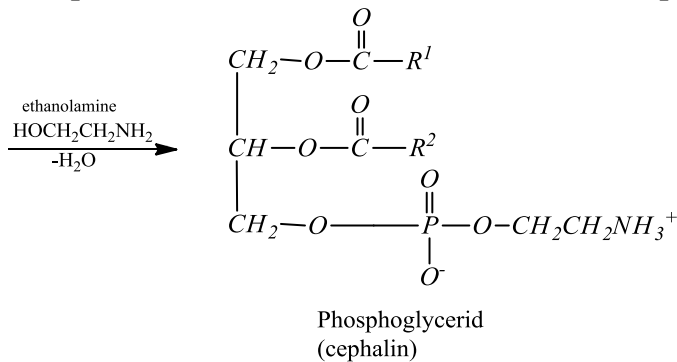
**Phospholipids.** They are derived from glycerol, fatty acids, phosphoric acid, and nitrogen – containing compound.



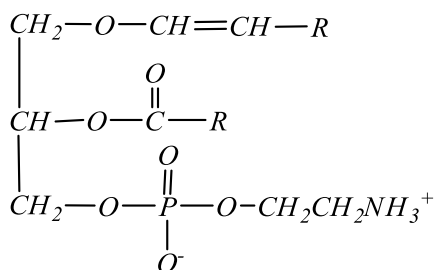
**Phosphoglycerides** are phospholipids based on glycerol. A phosphoglyceride forms by reaction of glycerol with two fatty acids and one phosphoric acid to form phosphatidic acid  $\Rightarrow$



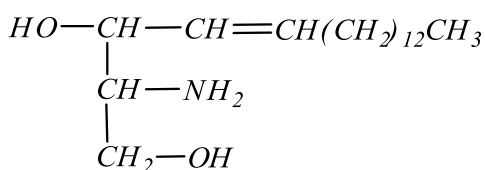
Phosphatidic acids react with amino alcohol to produce phosphoglycerid (cephalin)



**Plasmalogen** are similar to phosphoglycerides except that the fatty ester unit at C-1 is replaced by a fatty vinyl ether unit (-O-CH=CH-R)

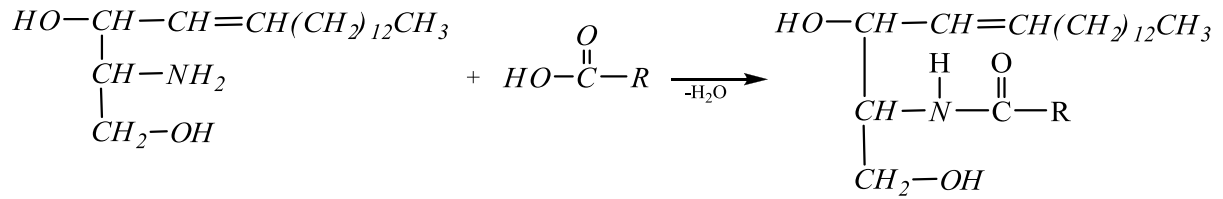


**Sphingolipids** are based on sphingosine instead of glycerol:

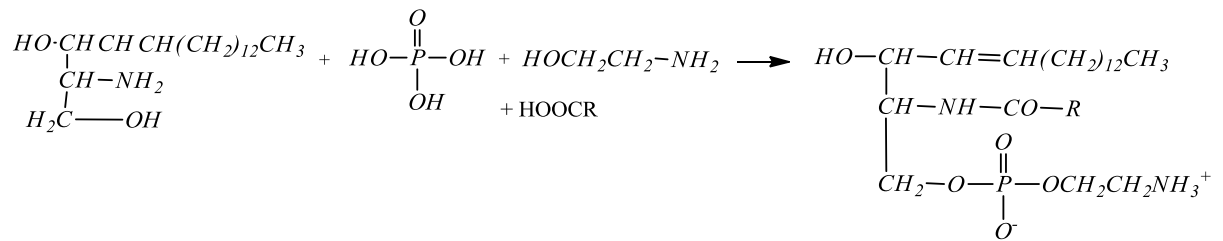


Other structural units are incorporated into sphingosine through reactions at the  $\text{NH}_2$  and  $\text{OH}$  groups to form **sphingomyelins** or **cerebrosides**. Both sphingomyelins and

cerebrosides incorporate a fatty acid unit by formation of an amide by reaction with the  $NH_2$  group.

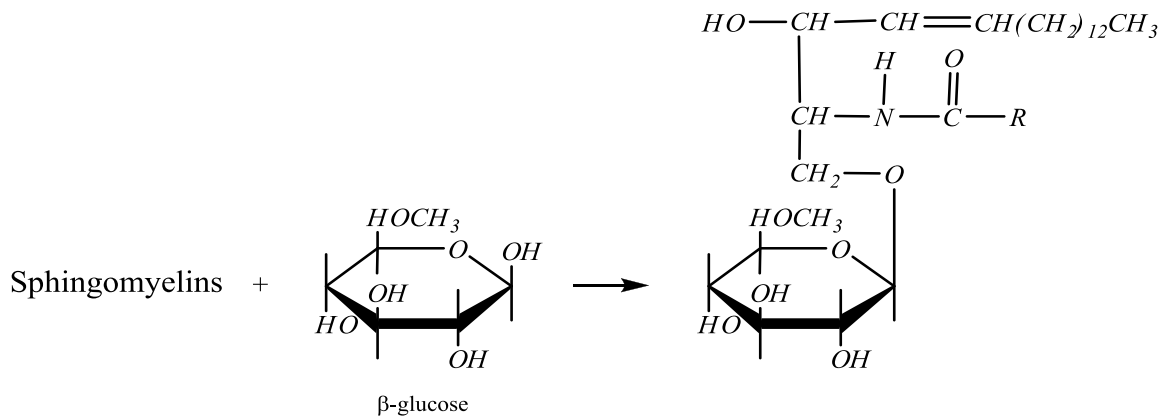


Sphingomyelins have a phosphate diester group with an amino alcohol incorporated as in phosphoglycerides and plasmalogens.



Sphingomyelins are categorized as phospholipids, as well as Sphingolipids, since they contain the phosphate diester group present in other phospholipids.

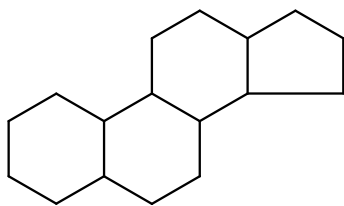
**Cerebrosides**, also referred to as **glycolipids**, contain a saccharide unit attaches by acetal formation at the  $OH$  of shingosine.



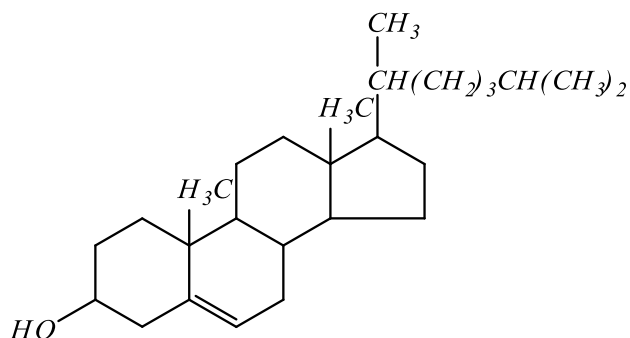
## NONSAPONIFIABLE LIPIDS

**Nonsaponifiable** lipids are not cleaved into smaller molecules by hydrolysis because of the absent of ester groups. Three classes of compounds comprise the nonsaponifiable lipids.

**Steroids** contain a four-ring system of three 6-membered rings and one 5-membered ring:



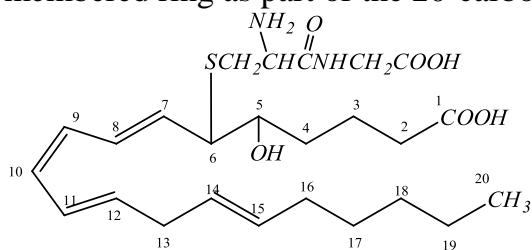
Steroid ring system



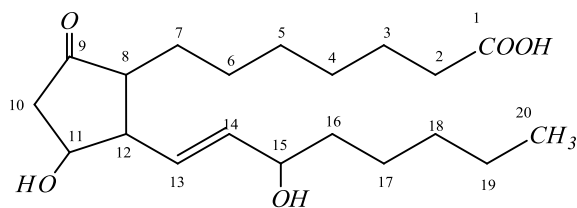
Cholesterol

Cholesterol, the most abundant steroid, is an important constituent of cell membranes and the starting material for biosynthesis of the steroids. This includes the sex hormones, such as progesterone, estradiol, testosterone, and androsterone, adrenocortical hormones such as aldosterone and cortisone, bile salts, and vitamin D.

**Leukotrienes** contain 20 carbons in a continuous chain with a  $COOH$  group at one end. Prostaglandins are similar to the leukotrienes except that there is a 5-membered ring as part of the 20-carbon chain.

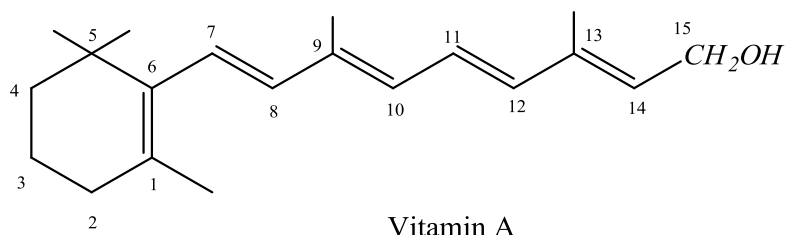
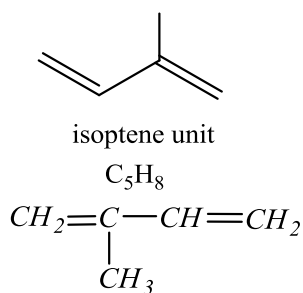


Leukotriene D



Prostaglandin E<sub>1</sub>

Terpenes contain multiples of five carbons since they are synthesized by linking together isoprene units. The isoprene unit is a branched C 5 unit. Vitamins A (trans-retinol), D, and E are terpenes. Other terpenes are intermediates in the biosynthesis of cholesterol.



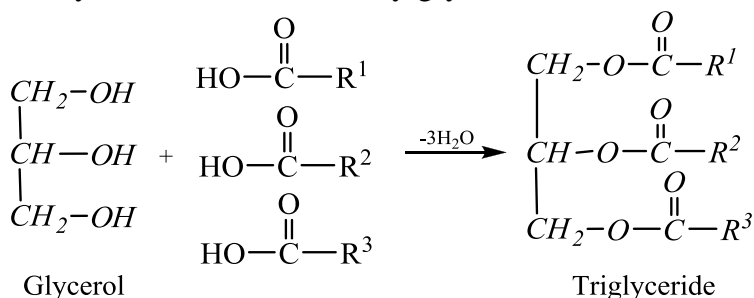
Vitamin A

## TRIACYLGLYCEROLS

### *Structure and Properties of triacylglycerols*

Animal fats such as butter, beef, pork, and poultry fats and vegetable oils such as corn, peanut, and olive oils are triacylglycerols or triglycerides.

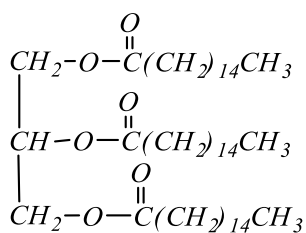
These are triesters of glycerol (IUPAC name: 1,2,3-propanetriol). Each of the three *OH* groups of glycerol forms an ester group by reaction with the *COOH* group of a fatty acid to form the triacylglycerol:



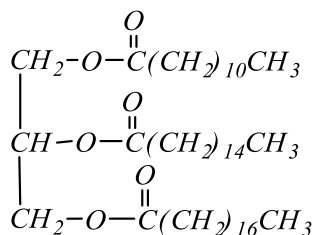
If all acid groups are the same, the triglyceride is called a **simple glycerid**, otherwise the triglyceride is a **mixed glyceride** (complex triacylglycerols).

(**Simple** triacylglycerols are those in which  $R^1$ ,  $R^2$ , and  $R^3$  are the same, i.e., three molecules of the same fatty acids react with glycerol. Complex triacylglycerols are those in which  $R^1$ ,  $R^2$ ,  $R^3$  are different).

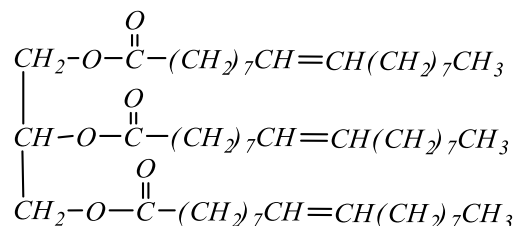
Naturally occurring triacylglycerols are complex triacylglycerols.



glyceryl tripalmitate  
tripalmitin  
(a simple glyceride; a fat)



glyceryl lauropalmitostearate  
(a mixed glyceride; a fat)



glyceryl trioleate, triolein  
(a simple glyceride; an oil)

Some common <i>fatty acids</i>				
Common Name	IUPAC name	Formula	Number of double bonds	Number of carbons
<b>Saturated fatty acids</b>				
Palmitic	Hexadecanoic acid	$\text{C}_{15}\text{H}_{31}\text{COOH}$ $(\text{CH}_3(\text{CH}_2)_{14}\text{COOH})$	0	16
Stearic	Octadecanoic acid	$\text{C}_{17}\text{H}_{35}\text{COOH}$ $(\text{CH}_3(\text{CH}_2)_{16}\text{COOH})$	0	18
<b>Unsaturated fatty acids</b>				
Palmitoleic	9-hexadecenoic	$\text{C}_{15}\text{H}_{29}\text{COOH}$ $(\text{CH}_3(\text{CH}_2)_5\text{CH=CH}(\text{CH}_2)_7\text{COOH})$	1	16
Oleic	9-octadecenoic acid	$\text{C}_{17}\text{H}_{33}\text{COOH}$ $(\text{CH}_3(\text{CH}_2)_7\text{CH=CH}(\text{CH}_2)_7\text{COOH})$	1	18
Linoleic	9,12-octadecadienoic	$\text{C}_{17}\text{H}_{31}\text{COOH}$ $(\text{CH}_3(\text{CH}_2)_4(\text{CH=CHCH}_2)_2(\text{CH}_2)_6\text{COOH})$	2	18
Linolenic	9,12,15-octadecatrienoic	$\text{C}_{17}\text{H}_{29}\text{COOH}$ $(\text{CH}_3\text{CH}_2(\text{CH=CHCH}_2)_3(\text{CH}_2)_6\text{COOH})$	3	18

Fatty acids (long – chain monocarboxylic acids) are the carboxylic acids used as building blocks for saponifiable lipids.

Fatty acids without double bonds are referred to as saturated fatty acids. Fatty acids with double bonds are referred to as unsaturated fatty acids.

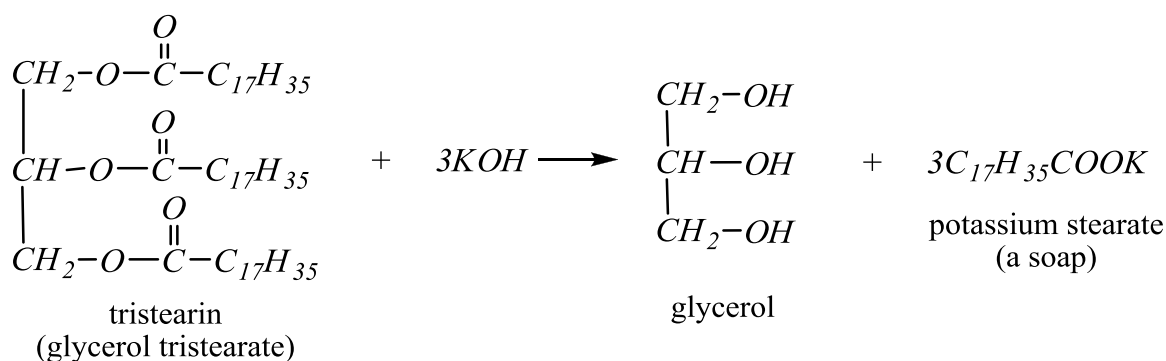
Linoleic and linolenic acids are essential fatty acids, i.e., they cannot be synthesized in the human body. All other fatty acids are nonessential fatty acids since they can be synthesized either from other fatty acids or from carbohydrates and proteins.

### **Chemical reaction**

The chemical reaction of triacylglycerols are those expected of molecules containing ester and C=C functional groups.

The ester group undergoes hydrolysis while the C=C undergoes addition reactions. Hydrolysis of a triacylglycerol is the reverse of triacylglycerol formation. It yields glycerol and fatty acids. The reaction requires an acid or base in the laboratory.

Triacylglycerol can be hydrolyzed in alkaline solution to produce glycerol and the alkali metal salts of the fatty acids. These salts are commonly known as soaps, and the hydrolysis process is called saponification.



(A **soap** is a salt of a fatty acid.)

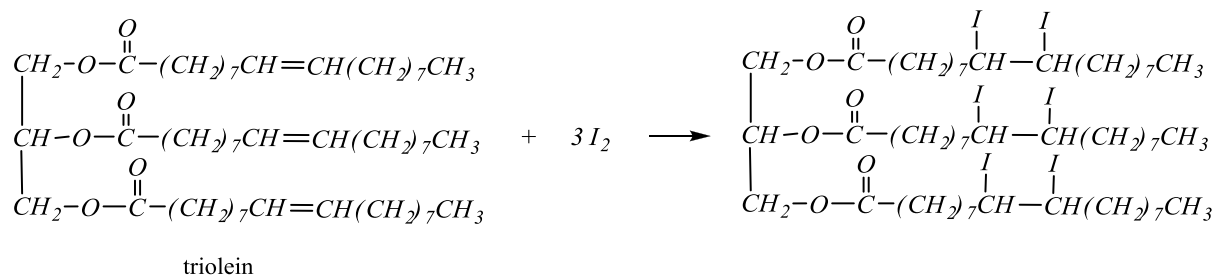
**Saponification** is the hydrolysis of a triglyceride by a strong base.)

Saponification reaction can be used in the laboratory to yield information about the structures of glycerides. The number of milligrams of *KOH* required to saponify 1.00 g of the glyceride is known as the saponification value.

Biological hydrolysis of a triacylglycerol occurs during digestion and requires the appropriate enzymes, referred to as **lipases**.

The C=C double bonds present in triacylglycerols undergo addition reactions with  $H_2$  and halogen ( $Cl_2$ ,  $Br_2$ ,  $I_2$ ). Hydrogen addition, referred to as **hydrogenation**, requires the presence of a metallic catalyst such as palladium or platinum. Hydrogenation of vegetable oils such as corn oil is used to produce margarine.

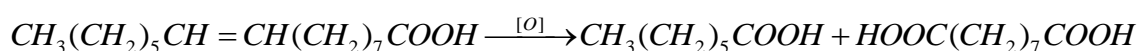
The **iodine number** of a triglyceride is the number of grams of  $I_2$  reacting with  $(1.00 \times 10^2 \text{ g})$  100g of the triglyceride. The iodine number indicates the degree of unsaturation in the fatty acid components.



Fats and oils become rancid on standing. Two reactions are involved in this process – hydrolysis and oxidation.

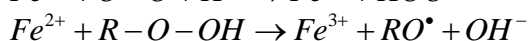
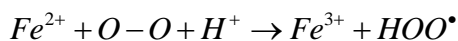
**Oxidation** cleaves the double bond, with each carbon of the double bond being converted to a *COOH* group.

Write the equation for oxidation of palmitoleic acid



Mechanism of oxidation (Radical substitution reaction)

### 1. Initiation



### 2. Propagation

