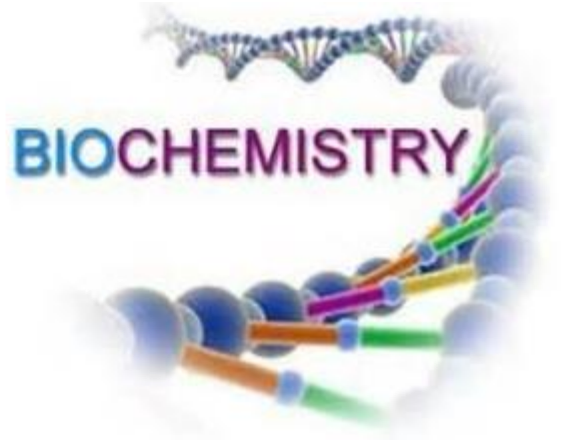
LEHNINGER PRINCIPLES OF BIOCHEMISTRY Sixth Edition

# CHAPTER 10

# Lipids

Xianming Deng

10.1 Storage Lipids
10.2 Structural Lipids in Membranes
10.3 Lipids as Signals, Cofactors, and Pigments
10.4 Working with Lipids



# Basic concepts of lipids

- **Lipids are biological molecules that are insoluble in water but soluble in nonpolar solvents.**

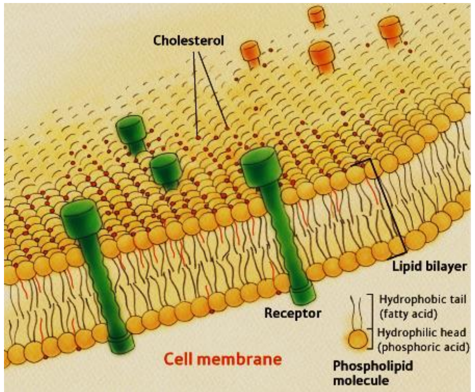
**Lipids are the waxy, greasy, or oily compounds found in plants and animals**

– wax coating that protects plants

– used as energy storage

– structural components (cell membranes)

– insulation against cold




## ➢ Classification of Lipids

Biological lipids are a **chemically diverse** group of compounds, the common and defining feature of which is their insolubility in water.

### ■ Lipids are divided into (chemistry aspect):

✓ Saponifiable lipids — contain esters, which can undergo saponification (hydrolysis under basic conditions) (waxes, triglycerides, phospho-glycerides, sphingolipids)

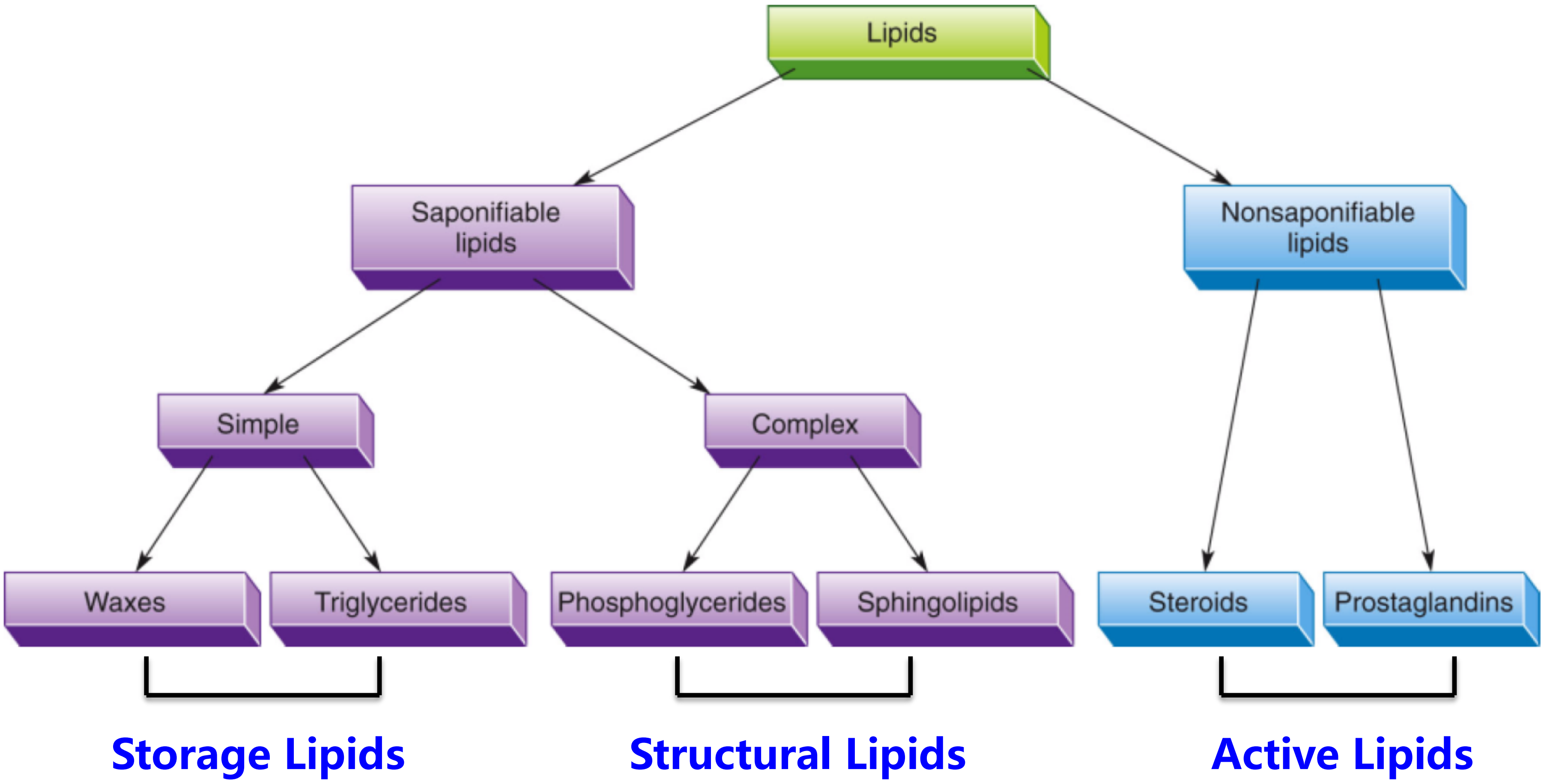
Saponifiable lipids can also be divided into groups:

a) Simple lipids — contain two types of components (a fatty acid and an alcohol)
b) Complex lipids — contain more than two components (fatty acids, an alcohol, and other components)

✓ Nonsaponifiable lipids — do not contain ester groups, and cannot be saponified (steroids, prostaglandins)

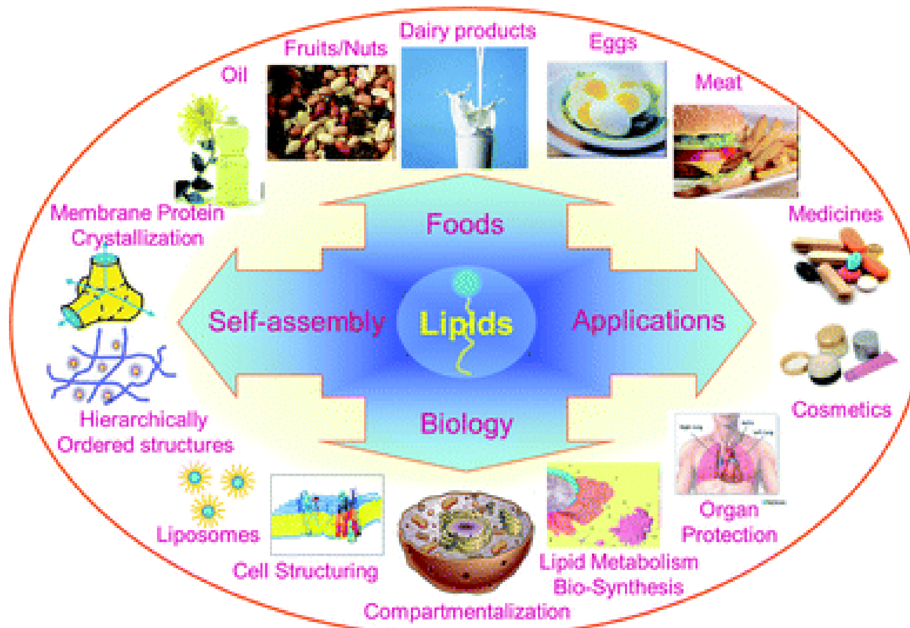
- **Lipids are divided into (Biology functional aspects):**
  - **Storage lipids**
    **Triacylglycerols, Waxes**
  - **Structural lipids** in membranes
    **Glycerophospholipids, Sphingolipids, Glycosphingolipids**…
  - **Active lipids** (Lipids act as signals, cofactors, and pigments)
    **Phosphatidylinositols, Sphingosine derivatives, Steroid hormones, Vitamins A, D, E, K**

## Classification of Lipids



## ➢ Biological functions of lipids

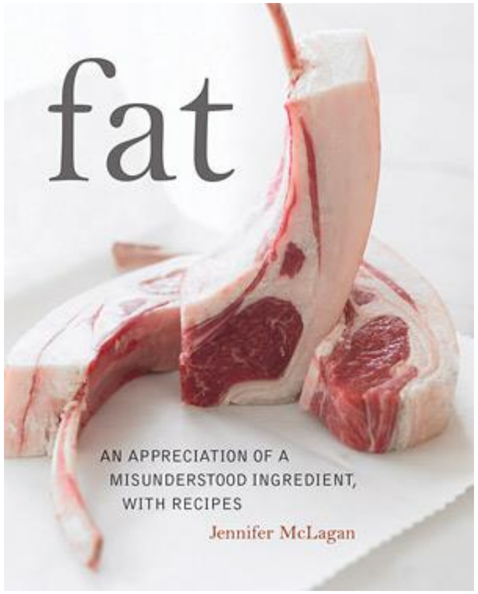
- ✓ Fats and oils are the principal stored forms of energy in many organisms;
- ✓ Phospholipids and sterols are major structural elements of biological membranes;
- ✓ Co-enzymes, vitamins, electron carriers, light-absorbing pigments, emulsifying agents, hormones, and intracellular;
- ✓ Protein modifiers;

# 10.1 Storage Lipids

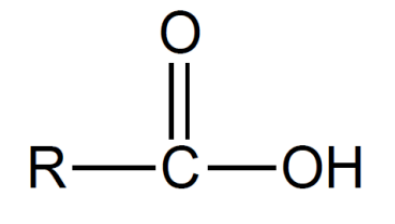
**Fatty acid** derivatives are used almost universally as stored forms of energy in living organisms, such as fats and oils.

**Triacylglycerols** and **waxes** are two major types of fatty acid-containing compounds.

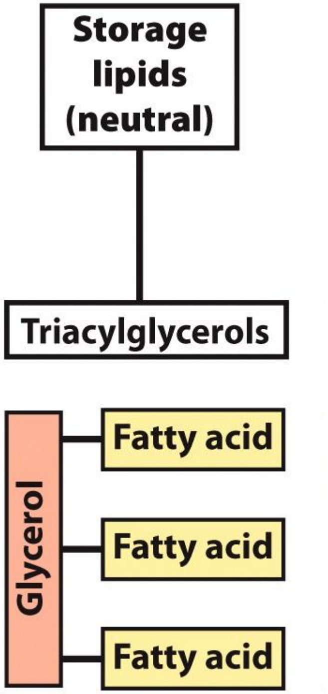



## ➢ Fatty acids

- **Fatty acids** are carboxylic acids with hydrocarbon chains (usually unbranched) ranging from **4** to **36** carbons long (C4 to C36). A few contain three-carbon rings, hydroxyl groups, or methyl-group branches.
- The most commonly occurring fatty acids have **even numbers** of carbon atoms in an unbranched chain of 12 to 24 carbons.
- The carbon chains may be **saturated** (all single bonds) or **unsaturated** (containing double bonds). Other than the carboxyl group and the double bonds, there are usually no other functional groups.



a carboxylic acid



# ■ Nomenclature of fatty acids

- **Saturated fatty acids**

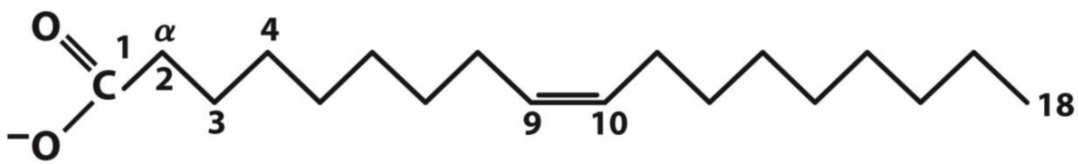
$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$$

- **Carbon skeleton:**
  **12:0**, simplified nomenclature for unbranched fatty acids specifies the chain length and number of double bonds, separated by a colon; for example, the 12-carbon saturated lauric acid is abbreviated 12:0.

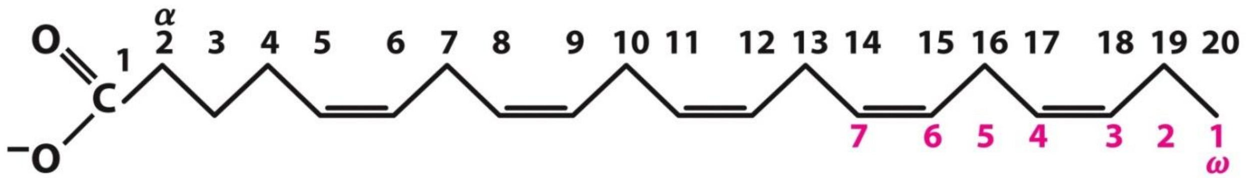
- **Systematic name:**
  ***n*-Dodecanoic acid**, *n*- indicates “normal” unbranched structure
  dodecanoic indicates 12 carbon atoms

- **Common name:**
  **Lauric acid (月桂酸)**

- **Unsaturated fatty acids**



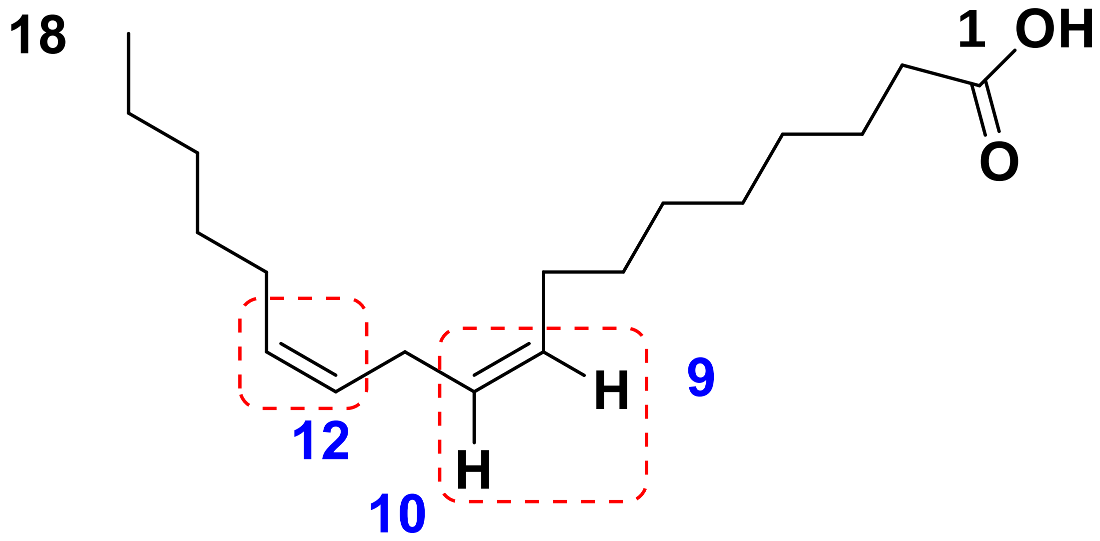

**(a) 18:1($\Delta^9$) *cis*-9-Octadecenoic acid**




**(b) 20:5($\Delta^{5,8,11,14,17}$) Eicosapentaenoic acid (EPA), an omega-3 fatty acid**

- ✓ specify the chain length and number of double bonds, separated by a colon (:).
- ✓ The position of any double bond(s) is indicated by Δ followed by a superscript number indicating the lower-numbered carbon in the double bond.

- **The double bonds are usually in *cis* configurations**



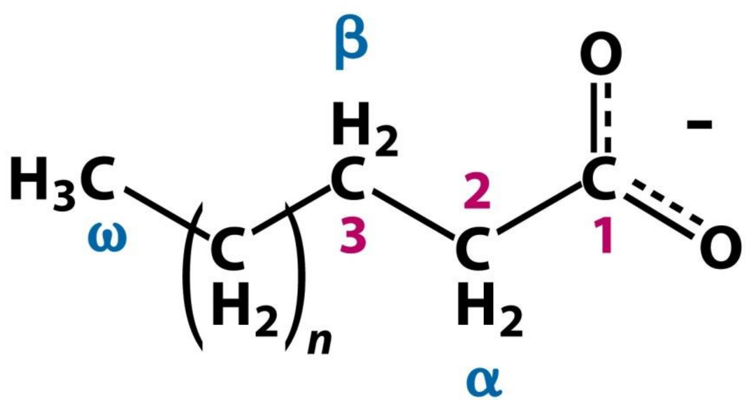

***Cis-***

The double bonds of polyunsaturated fatty acids are almost **never conjugated** (alternating single and double bonds, as in -CH=CH-CH=CH-), but are separated by a methylene group (-CH=CH-$CH_2$-CH=CH-).

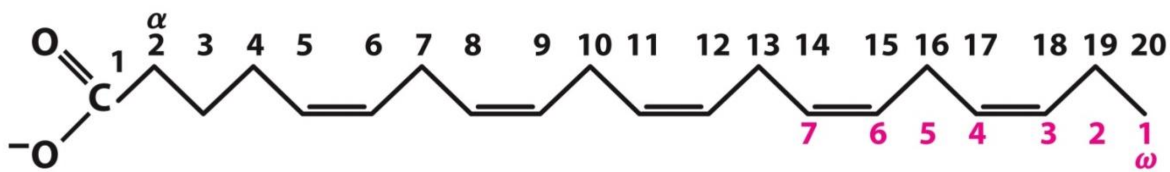
- **Omega end (ω) of fatty acid**

Assign the number 1 to the methyl carbon at the other end of the chain; this carbon is also designated ω (omega; the last letter in the Greek alphabet). The positions of the double bonds are indicated relative to the ω carbon.

Omega end (ω)

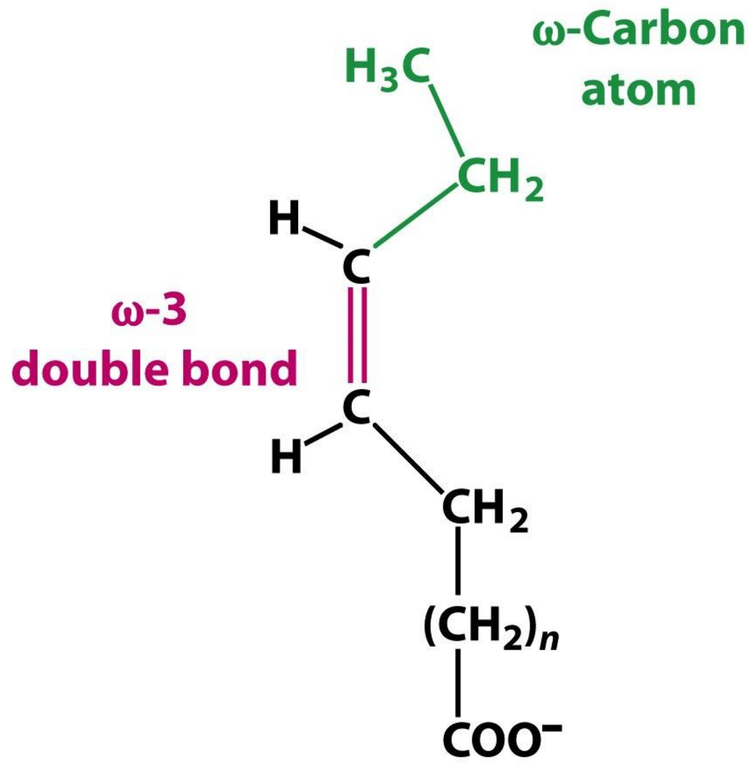



Carboxyl end (1)




**(b) 20:5($\Delta^{5,8,11,14,17}$) Eicosapentaenoic acid (EPA), an omega-3 fatty acid**

- **Omega-3 (ω-3) fatty acids**

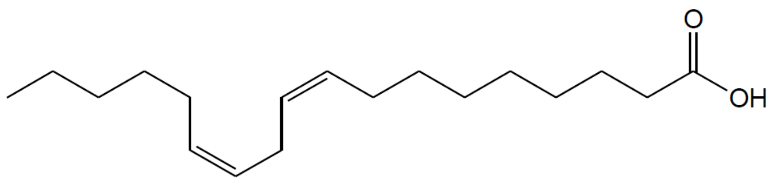



An ω-3 fatty acid


# ● Essential fatty acids

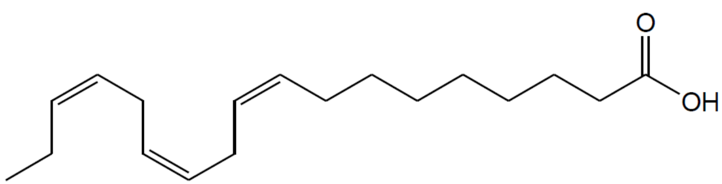
- ✓ Fatty acids that are not synthesized in mammals and yet are essential for normal growth and life, and are hence called essential fatty acids.

- ✓ Two fatty acids, **linoleic acid** and **linolenic acid**, both polyunsaturated fatty acids with 18-carbon chains, cannot be synthesized in the body and must be obtained from the diet. Both are found in plant and fish oils. In the body, they are used to produce hormonelike substances that regulate blood pressure, blood clotting, blood lipid levels, the immune response, and inflammatory reactions.




An omega-6 polyunsaturated fatty acid

Linoleic acid **亚油酸**




An omega-3 polyunsaturated fatty acid

Linolenic acid **亚麻酸**

- **Some natural fatty acids**

**TABLE 10–1 Some Naturally Occurring Fatty Acids: Structure, Properties, and Nomenclature**

| Carbon skeleton | Structure* | Systematic name† | Common name (derivation) | Melting point (°C) | Solubility at 30 °C (mg/g solvent) | |
|---|---|---|---|---|---|---|
| | | | | | Water | Benzene |
| 12:0 | $CH_3(CH_2)_{10}COOH$ | *n*-Dodecanoic acid | Lauric acid (Latin *laurus*, "laurel plant") | 44.2 | 0.063 | 2,600 |
| 14:0 | $CH_3(CH_2)_{12}COOH$ | *n*-Tetradecanoic acid | Myristic acid (Latin *Myristica*, nutmeg genus) | 53.9 | 0.024 | 874 |
| 16:0 | $CH_3(CH_2)_{14}COOH$ | *n*-Hexadecanoic acid | Palmitic acid (Latin *palma*, "palm tree") | 63.1 | 0.0083 | 348 |
| 18:0 | $CH_3(CH_2)_{16}COOH$ | *n*-Octadecanoic acid | Stearic acid (Greek *stear*, "hard fat") | 69.6 | 0.0034 | 124 |
| 20:0 | $CH_3(CH_2)_{18}COOH$ | *n*-Eicosanoic acid | Arachidic acid (Latin *Arachis*, legume genus) | 76.5 | | |
| 24:0 | $CH_3(CH_2)_{22}COOH$ | *n*-Tetracosanoic acid | Lignoceric acid (Latin *lignum*, "wood" + *cera*, "wax") | 86.0 | | |

Saturated

**TABLE 10–1** Some Naturally Occurring Fatty Acids: Structure, Properties, and Nomenclature

| Carbon skeleton | Structure* | Systematic name† | Common name (derivation) | Melting point (°C) | Solubility at 30 °C (mg/g solvent) | |
|---|---|---|---|---|---|---|
| | | | | | Water | Benzene |
| 16:1($\Delta^9$) | $CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$ | *cis*-9-Hexadecenoic acid | Palmitoleic acid | 1 to –0.5 | | |
| 18:1($\Delta^9$) | $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ | *cis*-9-Octadecenoic acid | Oleic acid (Latin *oleum*, "oil") | 13.4 | | |
| 18:2($\Delta^{9,12}$) | $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ | *cis*-,*cis*-9,12-Octadecadienoic acid | Linoleic acid (Greek *linon*, "flax") | 1–5 | | |
| 18:3($\Delta^{9,12,15}$) | $CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ | *cis*-,*cis*-,*cis*-9,12,15-Octadecatrienoic acid | $\alpha$-Linolenic acid | –11 | | |
| 20:4($\Delta^{5,8,11,14}$) | $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3COOH$ | *cis*-,*cis*-,*cis*-,*cis*-5,8,11,14-Icosatetraenoic acid | Arachidonic acid | –49.5 | | |

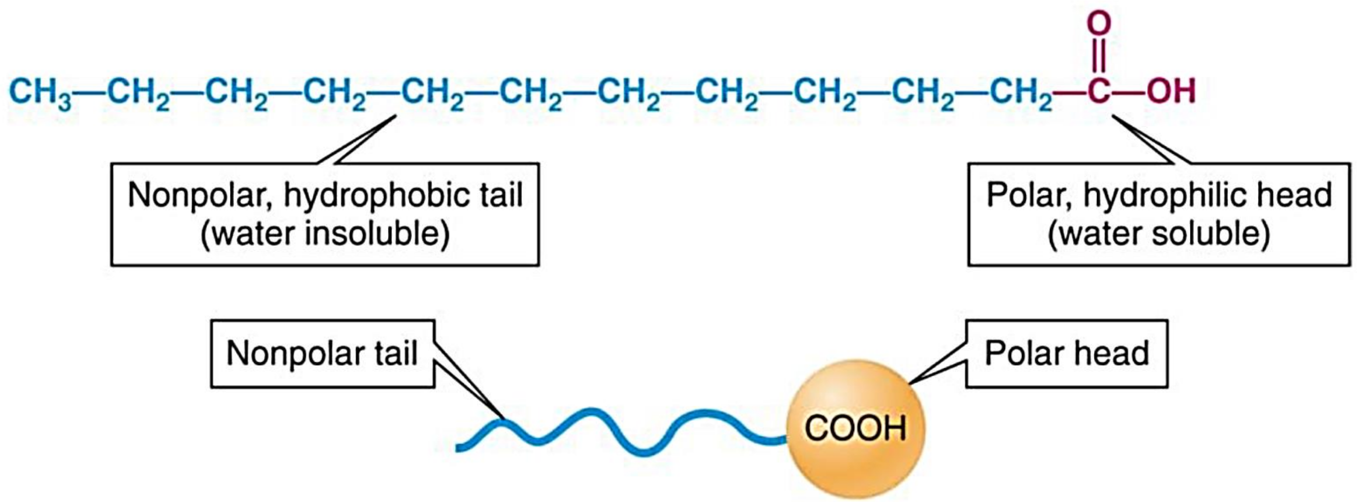
Mono-unsaturated (16:1, 18:1)

Poly-unsaturated (18:2, 18:3, 20:4)

The configuration of biological unsaturated fatty acids is almost always ***cis***.

■ **Properties of Fatty Acids**

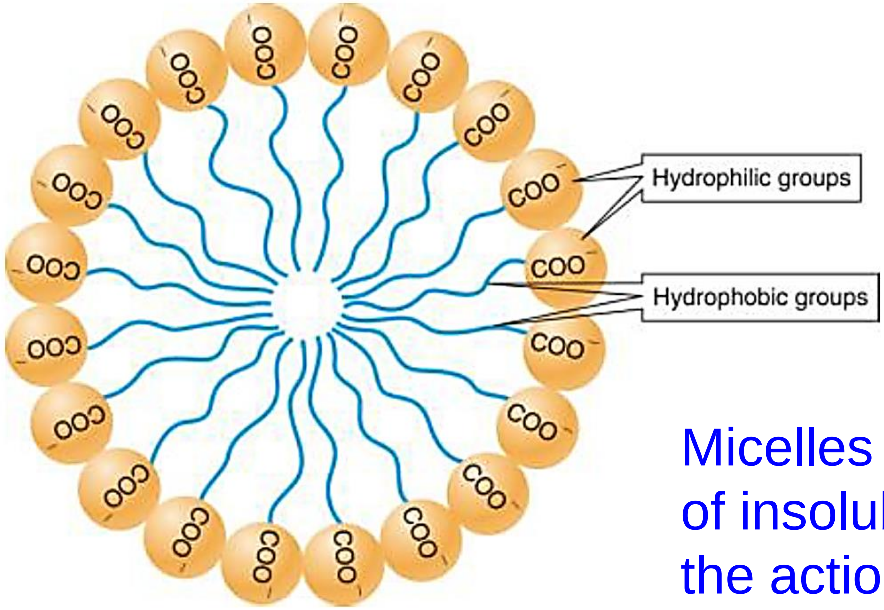
- The long, nonpolar hydrocarbon tails of fatty acids are responsible for most of the fatty or oily characteristics of lipids.
- The carboxyl (COOH) group is hydrophilic under basic conditions, such as physiological pH (7.4):




The longer the fatty acyl chain and the fewer the double bonds, the lower is the solubility in water.

- **Fatty acid micelles**

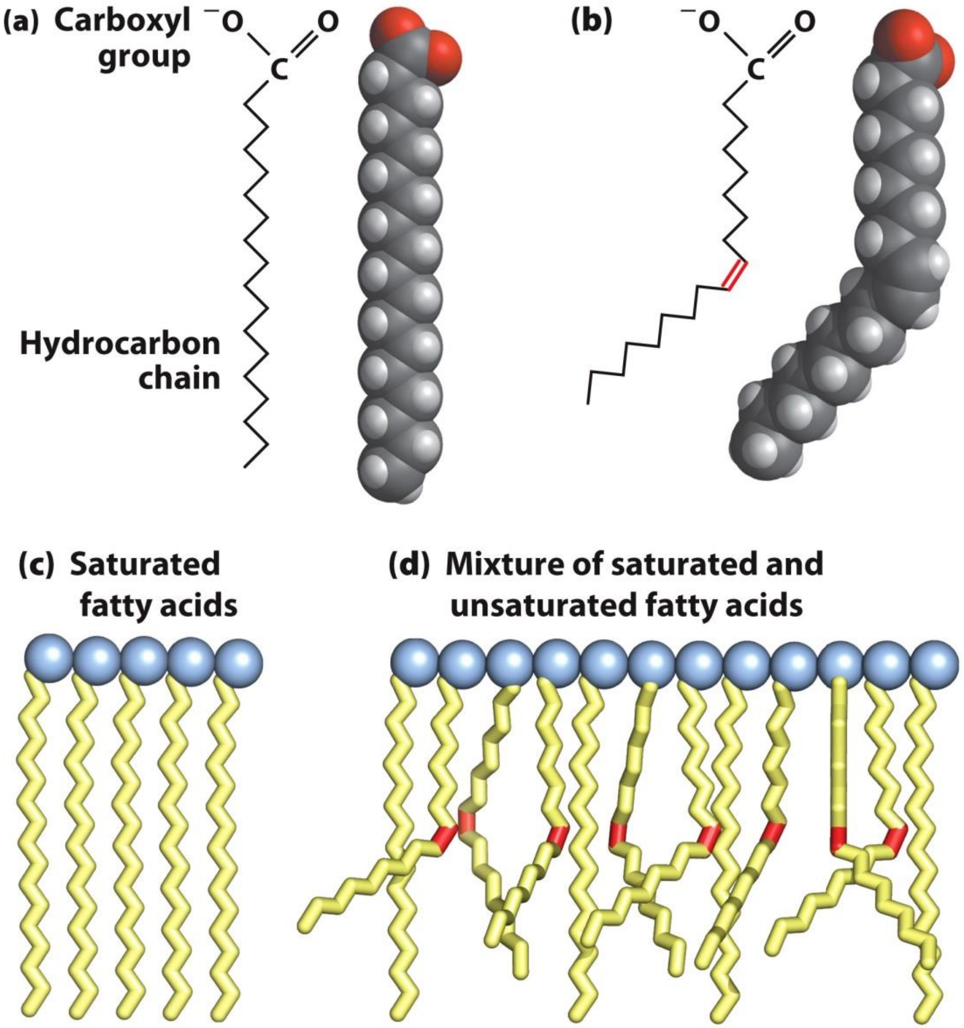
  In aqueous solutions, fatty acids associate with each other in spherical clusters called micelles, in which the hydrocarbon tails tangle each other up through dispersion forces, leaving a “shell” of polar carboxylate ions facing outwards, in contact with the water.




Micelles are important in the transport of insoluble lipids in the blood, and in the actions of soaps.

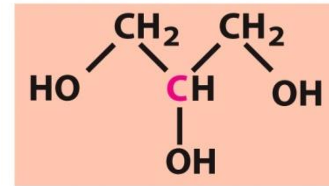
- Melting points are strongly influenced by the length and degree of unsaturation of the hydrocarbon chain.

- ✓ Shorter fatty acids usually have lower melting points than longer ones (stearic acid [18C] = 70ºC, palmitic acid [16C] = 63ºC).
- ✓ In unsaturated fatty acids, a *cis* double bond forces a kink in the hydrocarbon chain, preventing the molecules from packing together as tightly as saturated fatty acids do.
- ✓ The different degrees of packing of the fatty acid molecules cause difference in melting points.



## ➢ Triacylglycerols

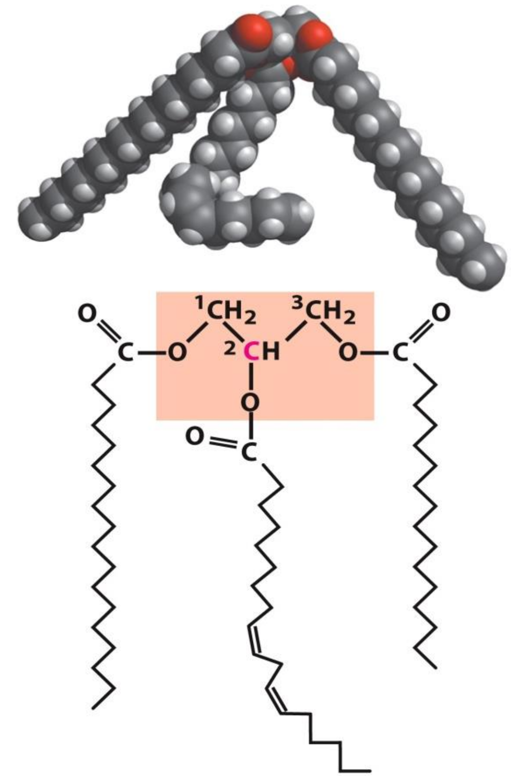
**Triacylglycerols** are fatty acid esters of glycerol, composed of three fatty acids each in ester linkage with a single glycerol. They are the simplest lipids constructed from fatty, also referred to as **triglycerides**, fats, or neutral fats.



Glycerol

**Simple triacylglycerols:** containing the same kind of fatty acid in all three positions, for example tripalmitin, tristearin, and triolein are simple triacylglycerols of 16:0, 18:0, and 18:1, respectively.

**Mixed triacylglycerols:** containing two or three different fatty acids. To name these compounds, the name and position of each fatty acid must be specified.

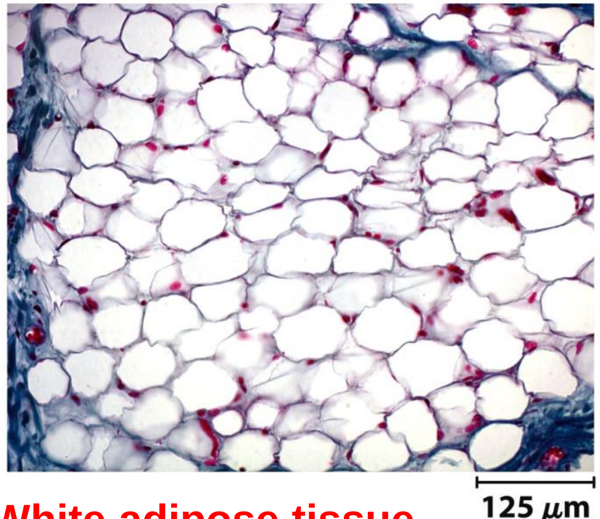


1-Stearoyl, 2-linoleoyl, 3-palmitoyl glycerol, a mixed triacylglycerol

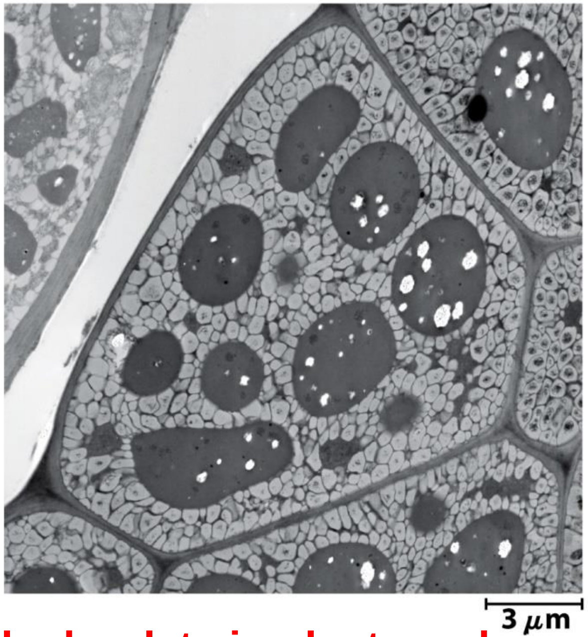
Because the polar hydroxyls of glycerol and the polar carboxylates of the fatty acids are bound in ester linkages, triacylglycerols are nonpolar, hydrophobic molecules, essentially insoluble in water.

## ■ Fats and oil

- The fatty acids in a triglyceride molecule are usually not all the same; in fact, most naturally occurring triacylglycerols are mixed.
- **Fats** are triglycerides that are solids at room temp.
  – usually derived from animals
  – mostly saturated fatty acids
- **Oils** are triglycerides that are liquids at room temp.
  – usually derived from plants or fish
  – mostly unsaturated fatty acids




**White adipose tissue**




**Oily droplets in plant seed**

## Triacylglycerols provide stored energy and insulation

- In most eukaryotic cells, triacylglycerols form a separate phase of microscopic, oily droplets in the aqueous cytosol, serving as depots of metabolic fuel.
- In some animals, triacylglycerols stored under the skin serve not only as energy stores but as insulation against low temperatures

## ■ Many foods contain triacylglycerols

Most natural fats, such as those in vegetable oils, dairy products, and animal fat, are complex mixtures of simple and mixed triacylglycerols.

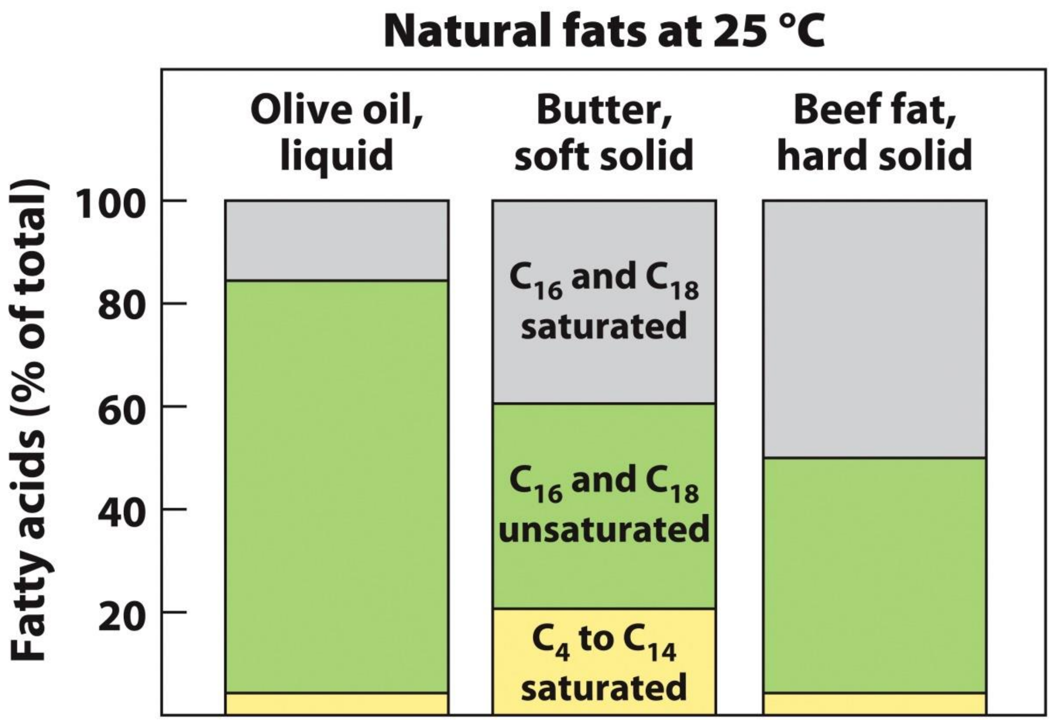
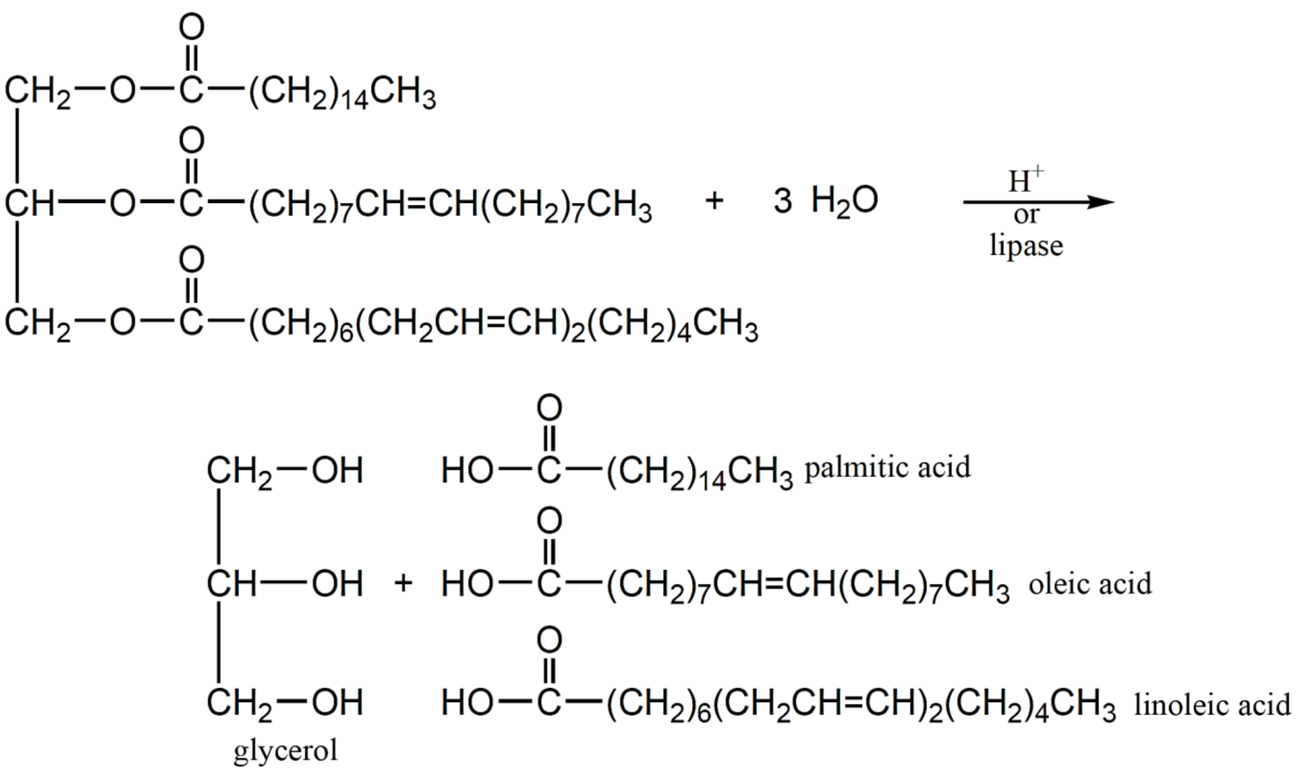



Figure 10-5
*Lehninger Principles of Biochemistry*, Sixth Edition

## Chemical properties of fats and oils

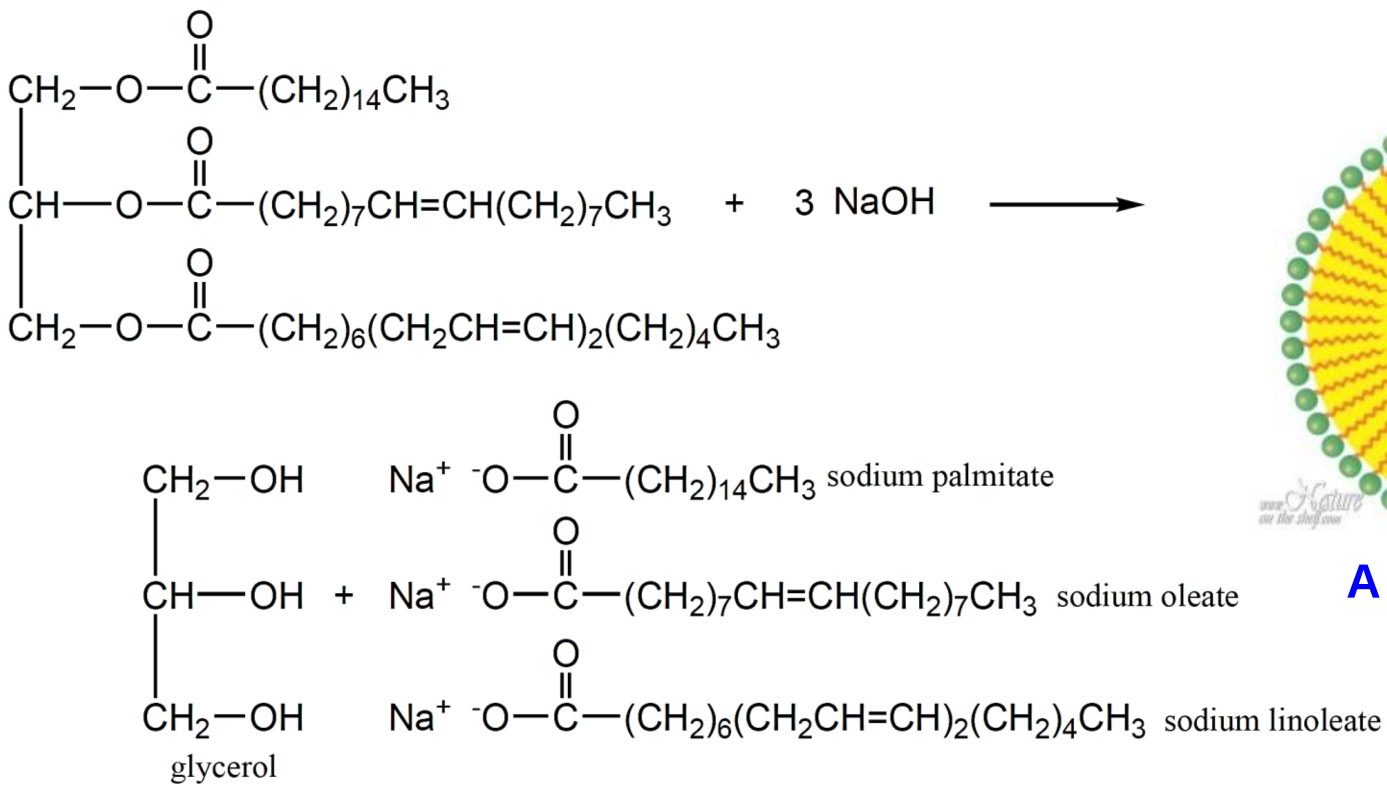
- **Hydrolysis of triglycerides**

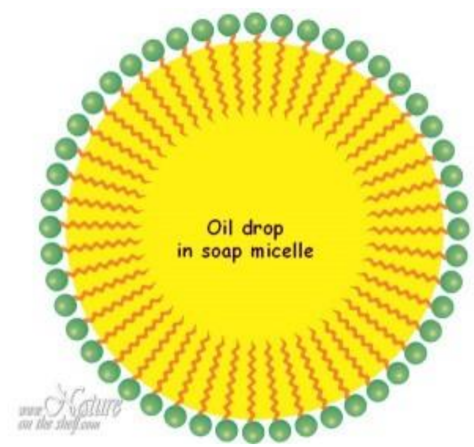
Triglycerides can be broken apart with water and an acid catalyst (hydrolysis), or by lipases, enzymes that catalyze the hydrolysis of triacylglycerols.



- **Saponification of Triglycerides**

  In saponification reactions, triglycerides react with strong bases (NaOH or KOH) to form the carboxylate salts of the fatty acids, called soaps.

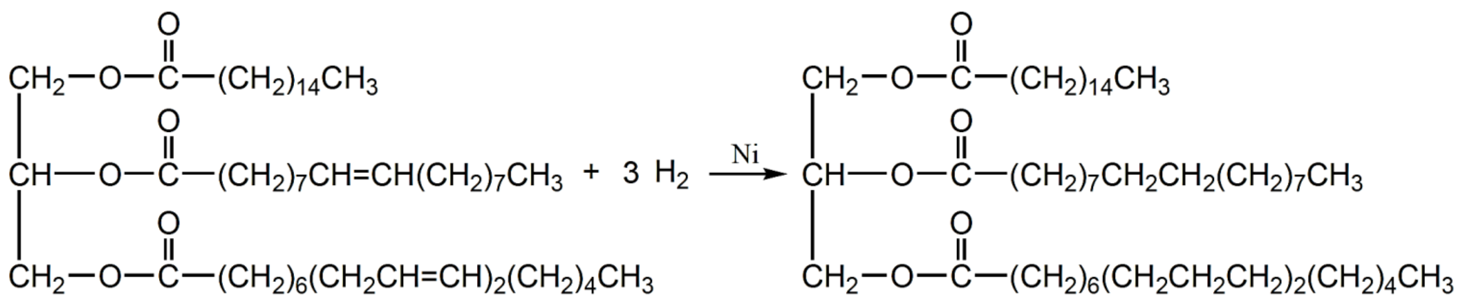



**A soap micelle**

- **Hydrogenation**

In hydrogenation reactions, **alkenes** are converted into **alkanes** with hydrogen gas ($H_2$) and a catalyst (Pt, Ni, or some other metal). This process is used to convert unsaturated vegetable oils, which are liquids at room temp., to saturated fats, which are solids at room temp.



## Side effect of partial hydrogenation

Partial hydrogenation has an undesirable effect: some ***cis*** double bonds are converted to ***trans*** double bonds.

**Many fast foods are deep-fried in partially hydrogenated vegetable oils and therefore contain high levels of trans fatty acids, leading to a higher incidence of cardiovascular disease ！**

**TABLE 10–2 Trans Fatty Acids in Some Typical Fast Foods and Snacks**

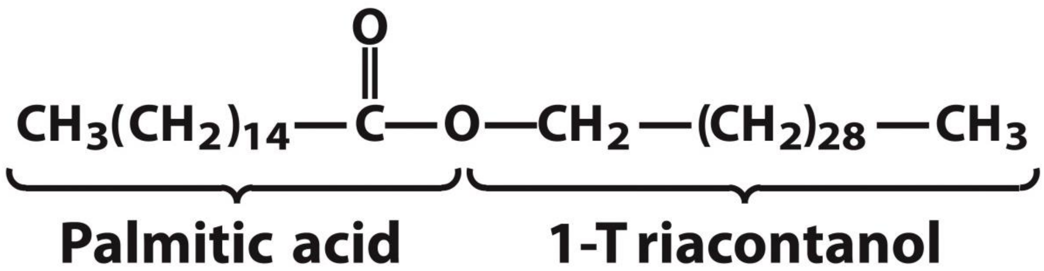
| | Trans fatty acid content | |
|---|---|---|
| | In a typical serving (g) | As % of total fatty acids |
| French fries | 4.7–6.1 | 28–36 |
| Breaded fish burger | 5.6 | 28 |
| Breaded chicken nuggets | 5.0 | 25 |
| Pizza | 1.1 | 9 |
| Corn tortilla chips | 1.6 | 22 |
| Doughnut | 2.7 | 25 |
| Muffin | 0.7 | 14 |
| Chocolate bar | 0.2 | 2 |

**Source:** Adapted from Table 1 in Mozaffarian, D., Katan, M.B., Ascherio, P.H., Stampfer, M.J., & Willet, W.C. (2006). Trans fatty acids and cardiovascular disease. *N. Engl. J. Med.* **354**, 1604–1605.

**Note:** All data for foods prepared with partially hydrogenated vegetable oil in the United States in 2002.

- **Waxes**

Biological waxes are esters of long-chain (C14 to C36) saturated and unsaturated fatty acids with long-chain (C16 to C30) alcohols.




The melting points of waxes (60 to 100°C) are generally higher than those of triacylglycerols.

Figure 10-6b
*Lehninger Principles of Biochemistry*, Sixth Edition

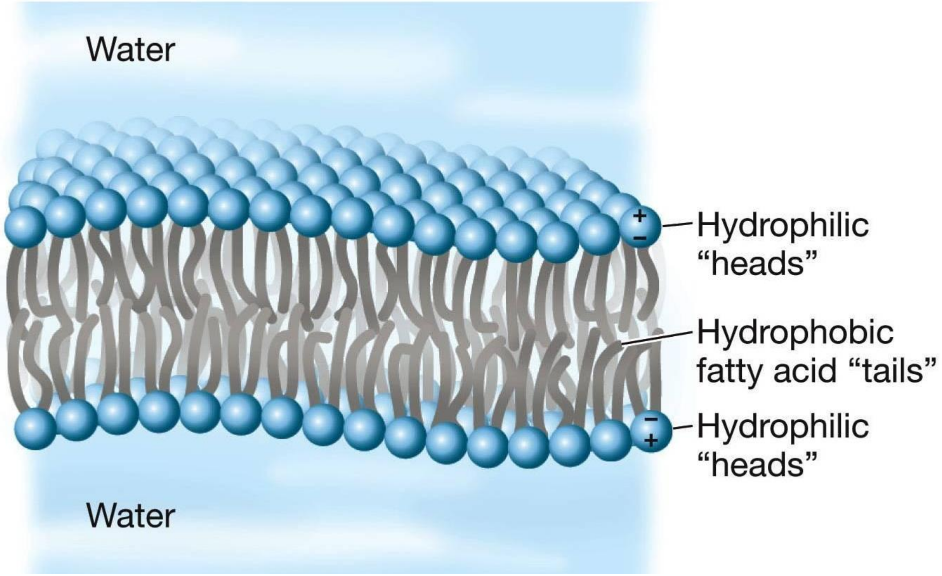
- **Waxes serve as energy stores and water repellents**
  - ✓ Waxes are the chief storage form of metabolic fuel in some organisms such as plankton (浮游生物).
  - ✓ Waxes are insoluble in water, and not as easily hydrolyzed as fats and oils. They often occur in nature as protective coatings on feathers, fur, skin, leaves, and fruits.
  - ✓ Sebum, secreted by the sebaceous glands of the skin, contains waxes that help to keep skin soft and prevent dehydration.
  - ✓ Waxes are used commercially to make cosmetics, candles, ointments, and protective polishes.

# 10.2 Structural Lipids in Membranes

The central architectural feature of biological membranes is a **double layer of lipids**, which acts as a barrier to the passage of polar molecules and ions.

**Membrane lipids are amphipathic:** one end of the molecule is hydrophobic, the other hydrophilic.

The hydrophobic interactions with each other and their hydrophilic interactions with water direct their packing into sheets called **membrane bilayers.**



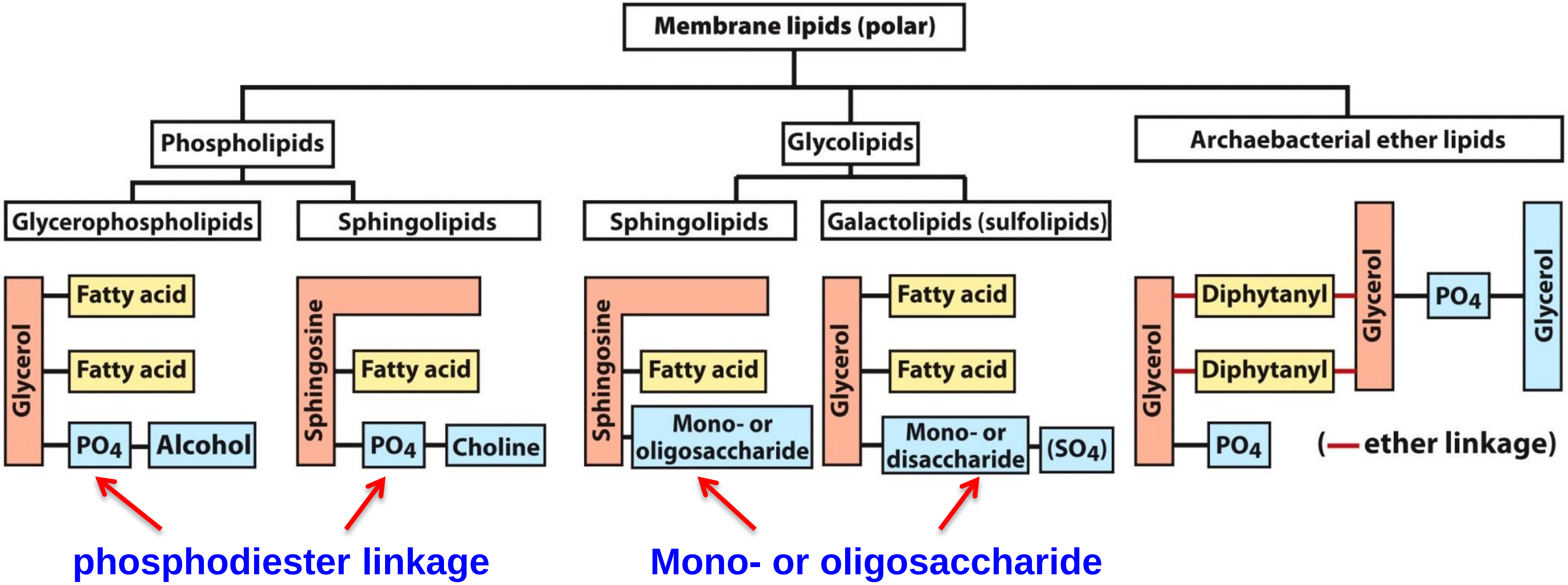

- ✓ **Polar head** are in contact with the aqueous environment
- ✓ **Nonpolar tails** are buried within the bilayer
- ✓ **The major force** driving the formation of lipid bilayers is hydrophobic interaction
- ✓ **The arrangement** of hydrocarbon tails in the interior can be rigid (if rich in saturated fatty acids) or fluid (if rich in unsaturated fatty acids)

## General types of membrane lipids

**Phospholipids**, a polar head group is joined to the hydrophobic moiety by a phosphodiester linkage;

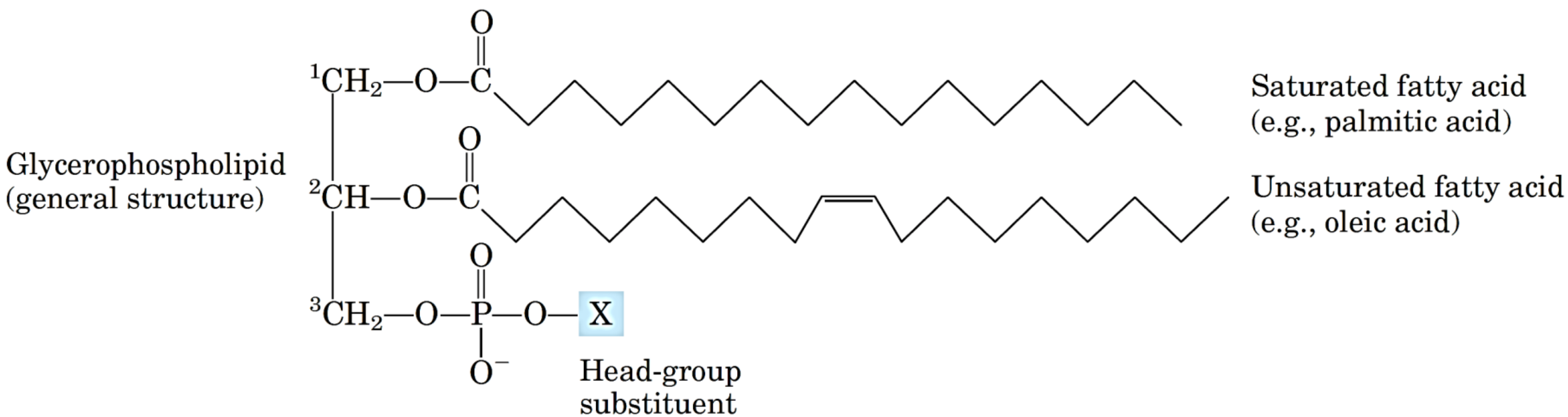
**Glycolipids**, lack phosphate but have a simple sugar or complex oligosaccharide at their polar ends;

**Archaeal tetraether lipids** (古生菌四醚脂) , two very long alkyl chains are ether-linked to glycerol at both ends.



## ➢ Glycerophospholipids

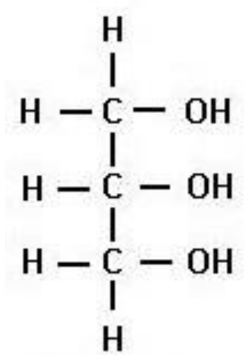
**Glycerophospholipids**, also called phosphoglycerides, are membrane lipids in which two fatty acids are attached in ester linkage to the first and second carbons of glycerol, and a highly polar or charged group is attached through a phosphodiester linkage to the third carbon.

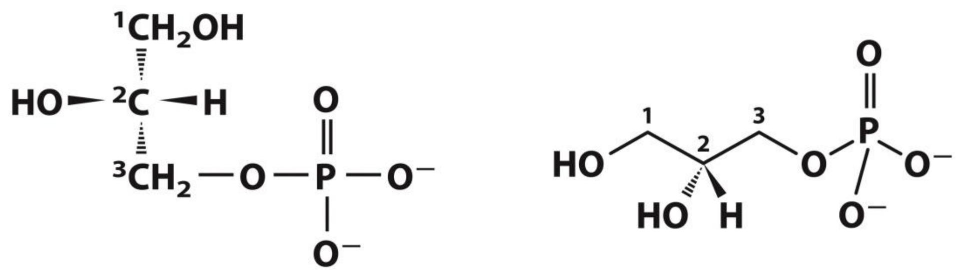



In general, glycerophospholipids contain a C16 or C18 saturated fatty acid at C-1 and a C18 or C20 unsaturated fatty acid at C-2, although the fatty acids in glycerophospholipids can be any of a wide variety.

- **L-Glycerol 3-phosphate, the backbone of phospholipids**

Glycerol itself is not chiral, however, glycerol is ***prochiral***—it can be converted to a chiral compound by adding a substituent such as phosphate to either of the —$CH_2OH$ groups.





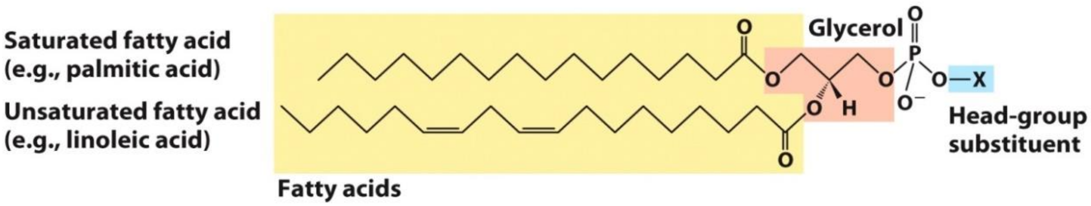
L-Glycerol 3-phosphate (*sn*-glycerol 3-phosphate)

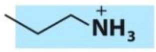
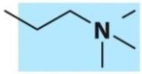
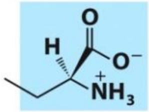
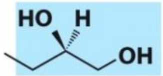
The stereoisomer of glycerol phosphate found in most lipids is correctly named either **L-glycerol 3-phosphate** or **D-glycerol 1-phosphate**.

Another way to specify stereoisomers is the ***sn*** (*s*tereospecific *n*umbering) system, in which C-1 is, by definition, the group of the prochiral compound that occupies the pro-S position. The common form of glycerol phosphate in phospholipids is, by this system, ***sn*-glycerol 3-phosphate** (in which C-2 has the R configuration).

In archaea, the glycerol in lipids has D-glycerol 3-phosphate.

- **Glycerophospholipids are named according to the polar alcohol in the head group**

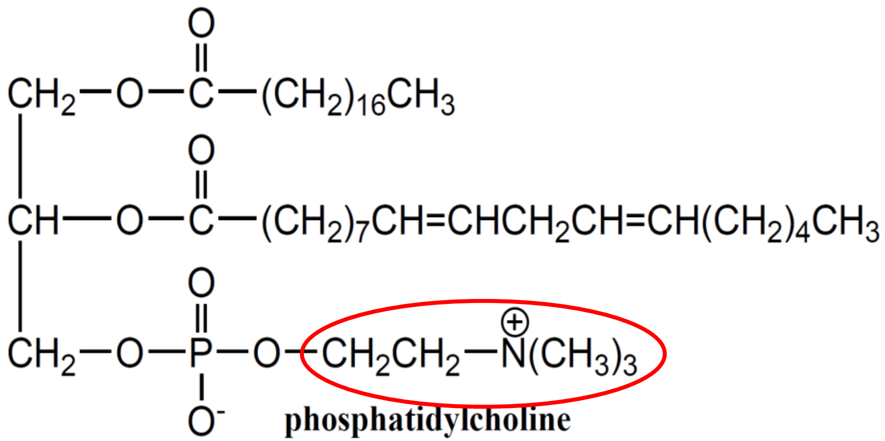



| Name of glycerophospholipid | Name of X—O | Formula of X | Net charge (at pH 7) |
|---|---|---|---|
| Phosphatidic acid | — | —H | −2 |
| Phosphatidylethanolamine | Ethanolamine |  | 0 |
| Phosphatidylcholine | Choline |  | 0 |
| Phosphatidylserine | Serine |  | −1 |
| Phosphatidylglycerol | Glycerol |  | −1 |

The head group is joined to glycerol through a phosphodiester bond, in which the phosphate group bears a negative charge at neutral pH. The polar alcohol may be negatively charged, neutral, or positively charged.

- **Lecithin (卵磷脂 )**

Phosphoglycerides that contains the aminoalcohol choline are called **lecithins.** The fatty acids at the first and second positions are variable, so there are a number of different possible lecithins.




phosphatidylcholine

Because lecithins contain negatively charged oxygen atoms in the phosphate group and positively charged nitrogen atoms in the quaternary ammonium salt group, that end of the molecule is highly hydrophilic, while the rest of the molecule is hydrophobic.

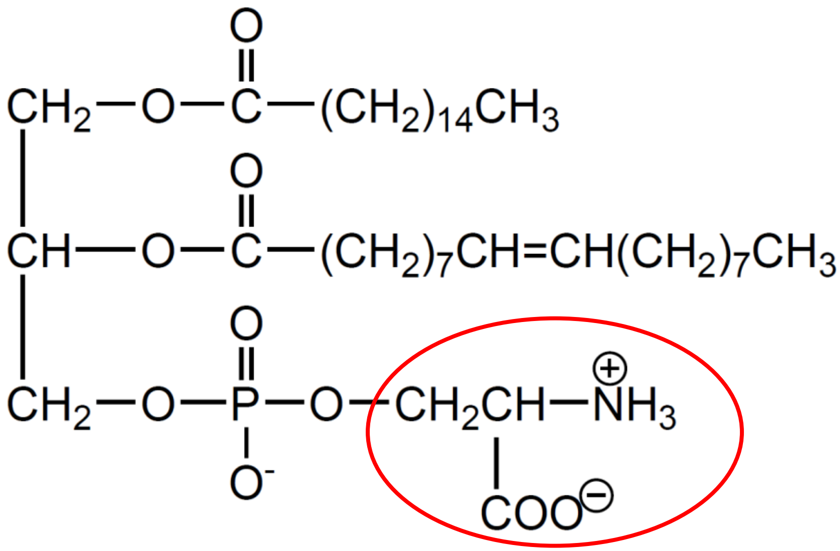
**Functions of lecithin:**

- forms an important structural component of cell membranes.
- forms micelles which play a role in the transport of lipids in the blood stream.

Commercially, lecithin extracted from soybeans is used as an emulsifying agent (乳化剂) in margarine and candies to provide a smooth texture.

- **Cephalins (脑磷脂 )**

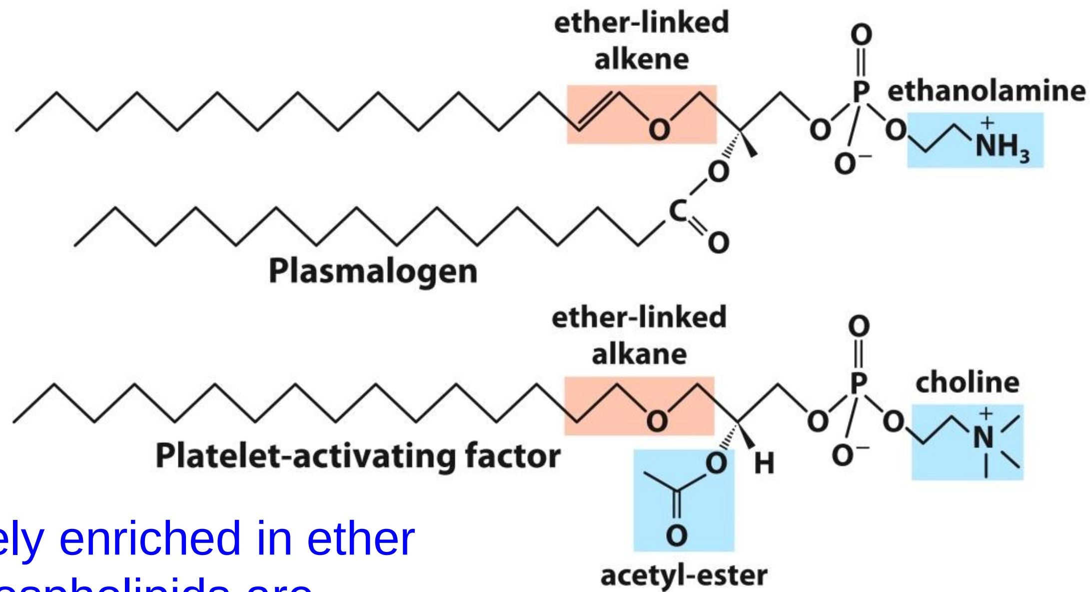
Phosphoglycerides that contains the amino alcohols ethanolamine or serine are called **cephalins.**




**Functions of cephalins:**
Cephalins are found in most cell membranes, and are particularly abundant in brain tissue. They are also found in blood platelets, and play a role in blood-clotting.

- **Some glycerophospholipids have ether-linked fatty acids**

**Ether lipids**, one of the two acyl chains is attached to glycerol in ether linkage. The ether-linked chain may be saturated, or may contain a double bond, as in **plasmalogens.**

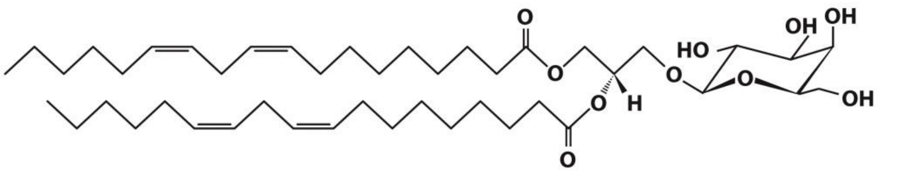



Vertebrate heart tissue is uniquely enriched in ether lipids; about half of the heart phospholipids are plasmalogens.

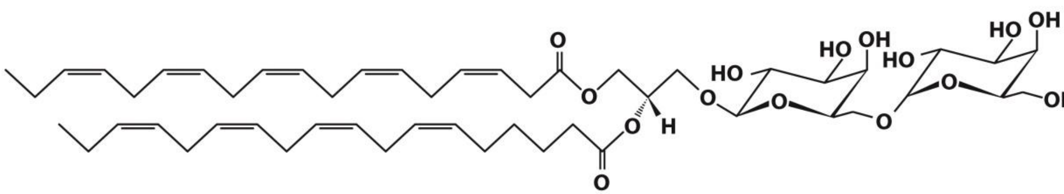
**Platelet-activating factor** is a potent molecular signal. It stimulates platelet aggregation and the release of serotonin (a vasoconstrictor) from platelets. It also plays an important role in inflammation and the allergic response.

## ➢ Galactolipids (半乳糖脂) and sulfolipids (硫脂)

- **Galactolipids**, in which one or two galactose residues are connected by a glycosidic linkage to C-3 of a 1,2-diacylglycerol

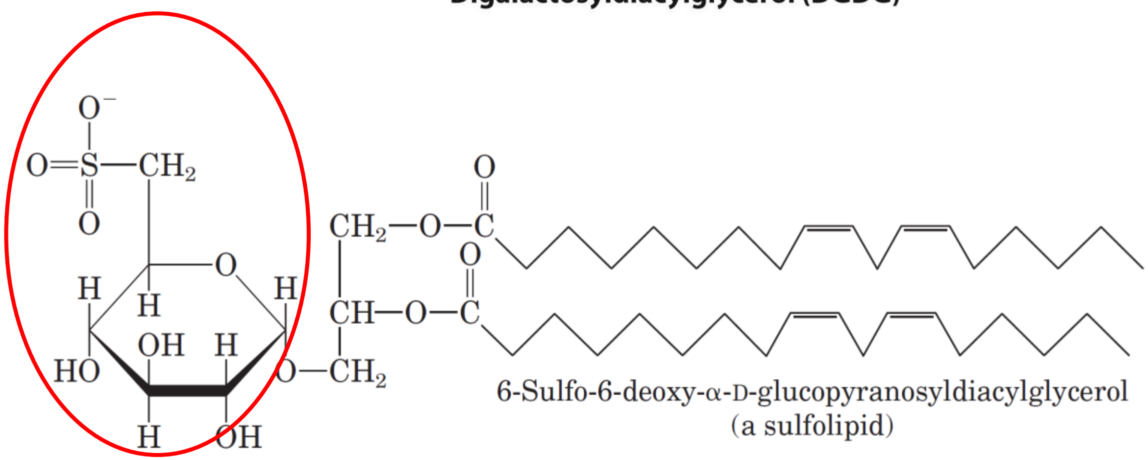


Monogalactosyldiacylglycerol (MGDG)



Digalactosyldiacylglycerol (DGDG)

- **Sulfolipids**, in which a sulfonated glucose residue is joined to a diacylglycerol in glycosidic linkage.



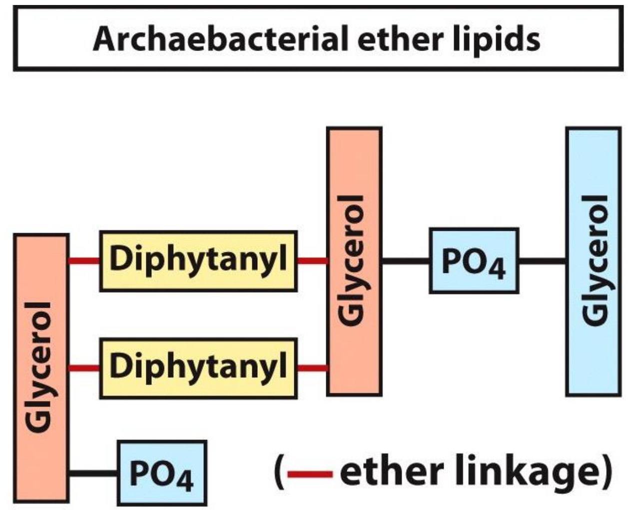
6-Sulfo-6-deoxy-α-D-glucopyranosyldiacylglycerol (a sulfolipid)

**Galactolipids and sulfolipids are predominant in plant cells.**

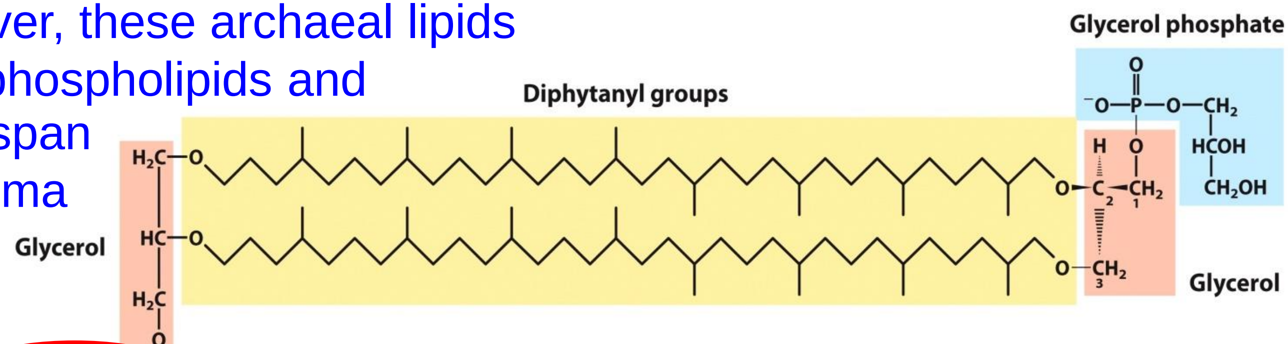
The sulfonate group bears a negative charge like that of the phosphate group in phospholipids.

## ➢ Archaeal tetraether lipids (古生菌四醚脂)

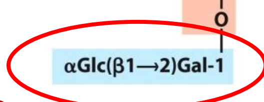
Some archaea that live in ecological niches with extreme conditions—high temperatures (boiling water), low pH, high ionic strength, for example—have membrane lipids containing long-chain (32 carbons) branched hydrocarbons ether-linked at each end to glycerol.




The ether linkages are much more stable to hydrolysis at low pH and high temperature than are the ester bonds found in the lipids of bacteria and eukaryotes. Moreover, these archaeal lipids are twice the length of phospholipids and sphingolipids, and can span the full width of the plasma membrane.



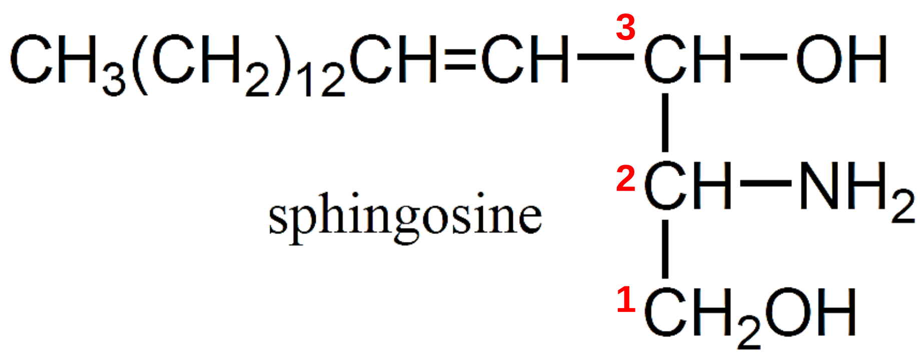

**phosphate or sugar residues**




The central carbon of glycerol is in the **R** configuration in archaea, in the **S** configuration in bacteria and eukaryotes.

## ➢ Sphingolipids (神经鞘脂)

**Sphingolipids** are complex lipids that contain sphingosine (鞘胺醇) instead of glycerol.




sphingosine

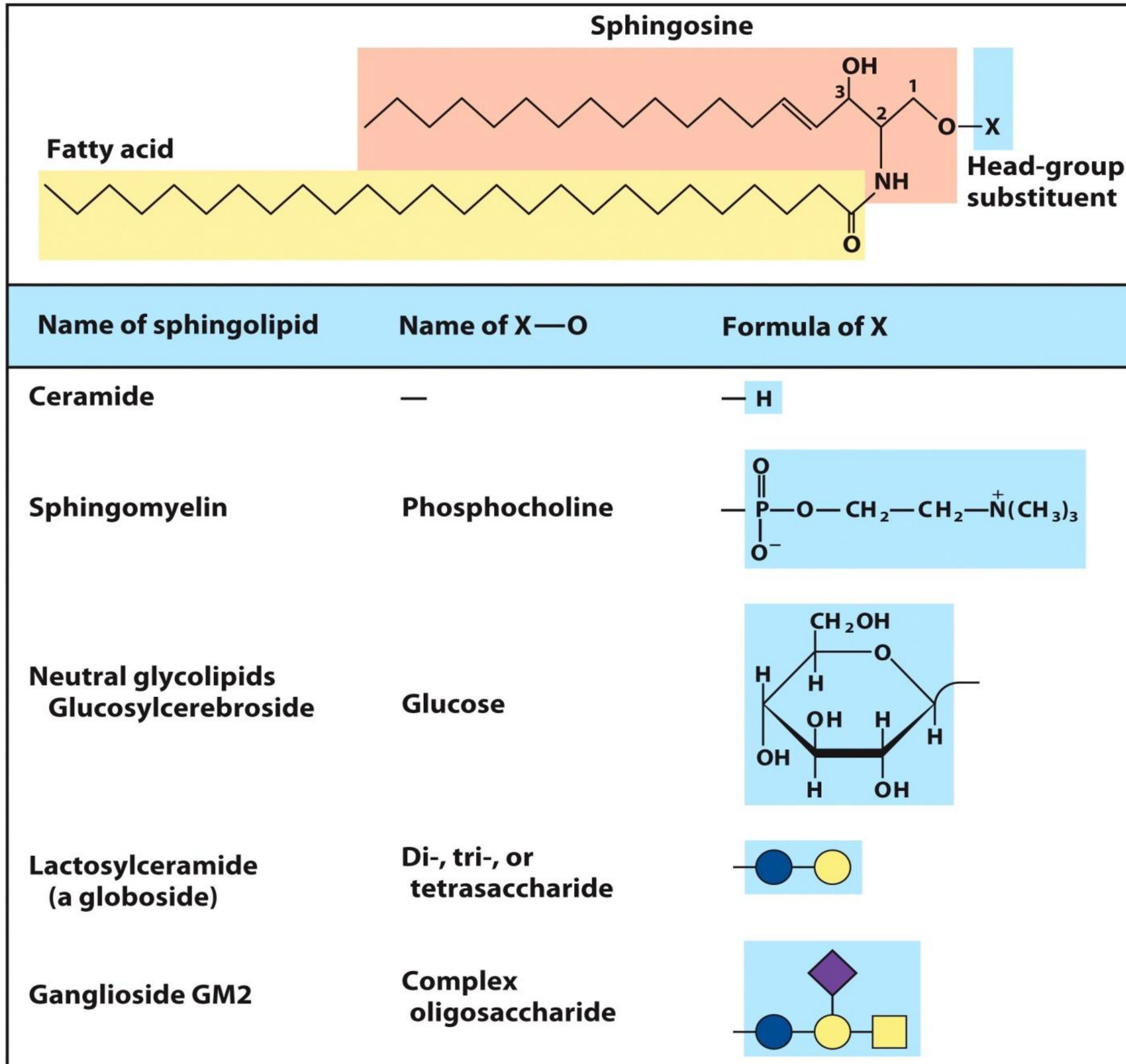
Carbons C-1, C-2, and C-3 of the sphingosine molecule are structurally analogous to the three carbons of glycerol in glycerophospholipids. When a fatty acid is attached in amide linkage to the $-NH_2$ on C-2, the resulting compound is a **ceramide** (神经酰胺), which is structurally similar to a diacylglycerol. Ceramide is the structural parent of all sphingolipids.

**Sphingolipids** are composed of

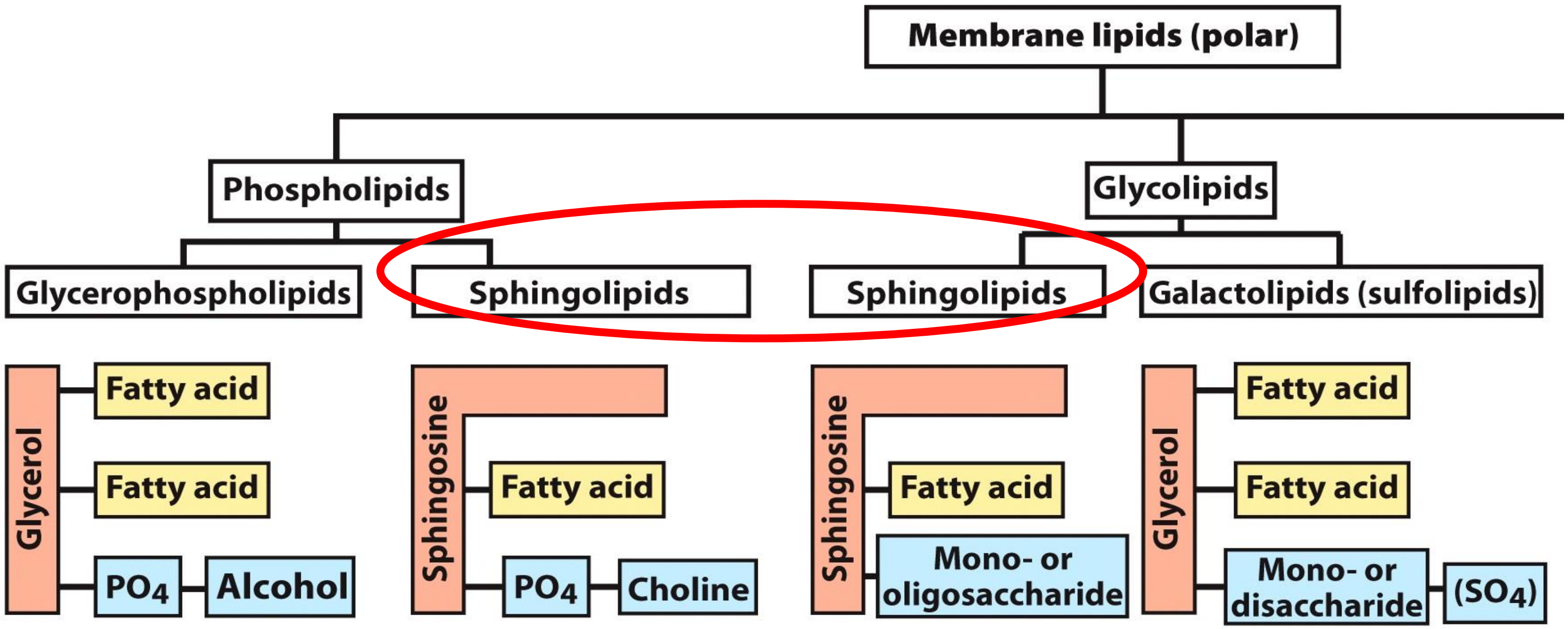
① one molecule of alcohol sphingosine or one of its derivatives,

② one molecule of a long-chain fatty acid,

③ and a polar head group that is joined by a phosphodiester or glycosidic linkage.



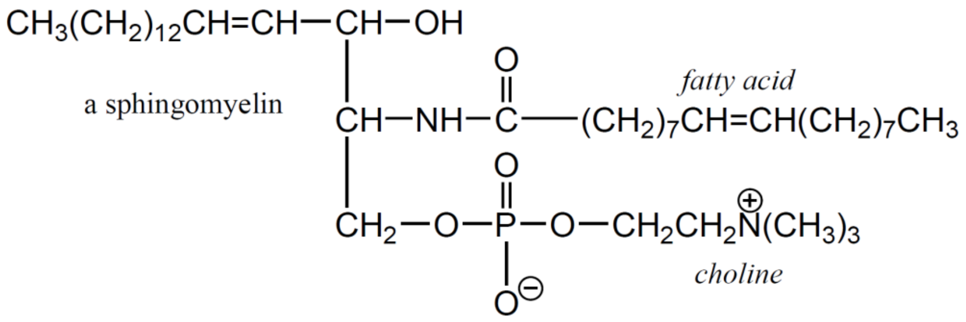
- **Three subclasses of sphingolipids: sphingomyelins**, **neutral (uncharged) glycolipids**, and **gangliosides** (all derivatives of ceramide but differing in their head groups).



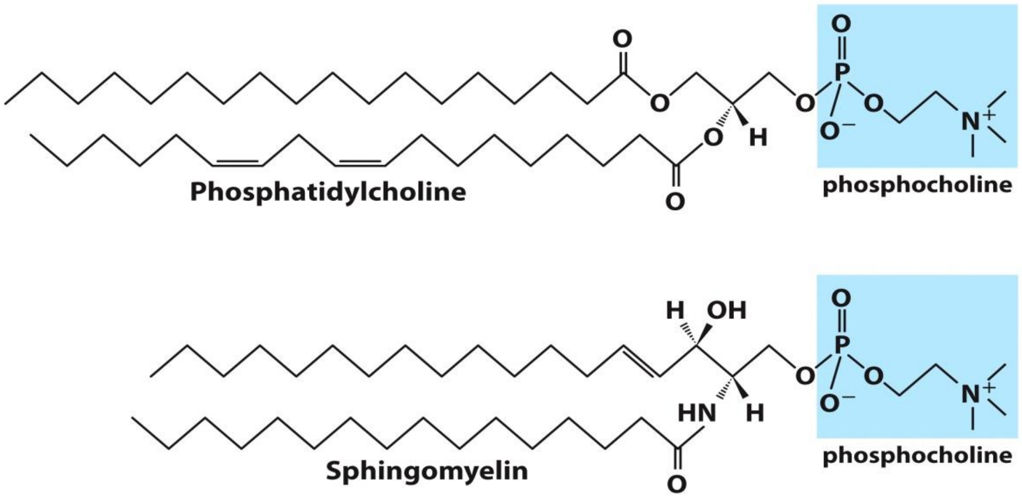

**Glycosphingolipids**, including neutral (uncharged) glycolipids and gangliosides, have head groups with one or more sugars connected directly to the —OH at C-1 of the ceramide moiety. They do not contain phosphate and occur largely in the outer face of plasma membranes.

## Sphingomyelins (神经鞘髓磷脂)

contain phosphocholine or phosphoethanolamine as their polar head group and are therefore classified as phospholipids.




Sphingomyelins resemble phosphatidylcholines in their general properties and three-dimensional structure, and in having no net charge on their head groups.



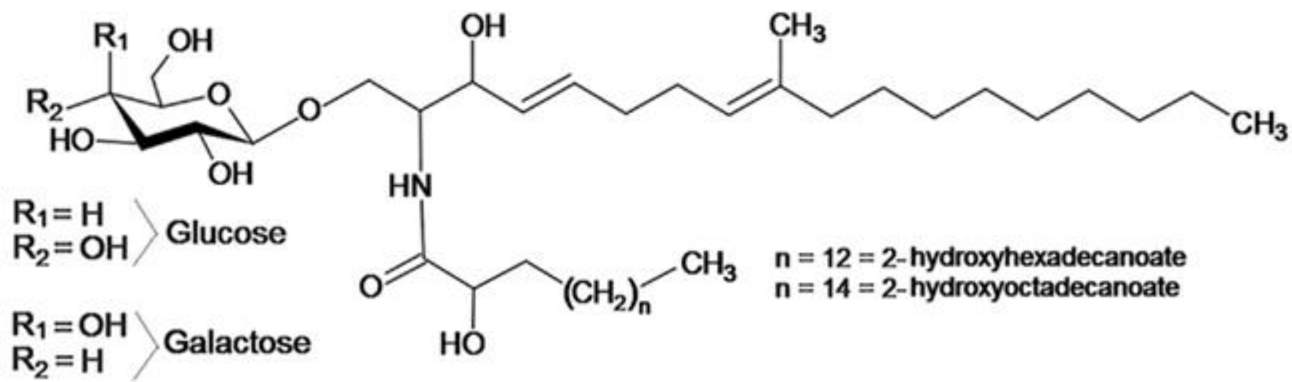

Sphingomyelins are present in the plasma membranes of animal cells and are especially prominent in myelin (髓鞘), a membranous sheath that surrounds and insulates the axons of some neurons—thus the name “sphingomyelins.”

## Neutral glycolipids

**Cerebrosides** (脑苷脂类) have a single sugar linked to ceramide; those with galactose are characteristically found in the plasma membranes of cells in neural tissue, and those with glucose in the plasma membranes of cells in nonneural tissues.

nonneural tissues

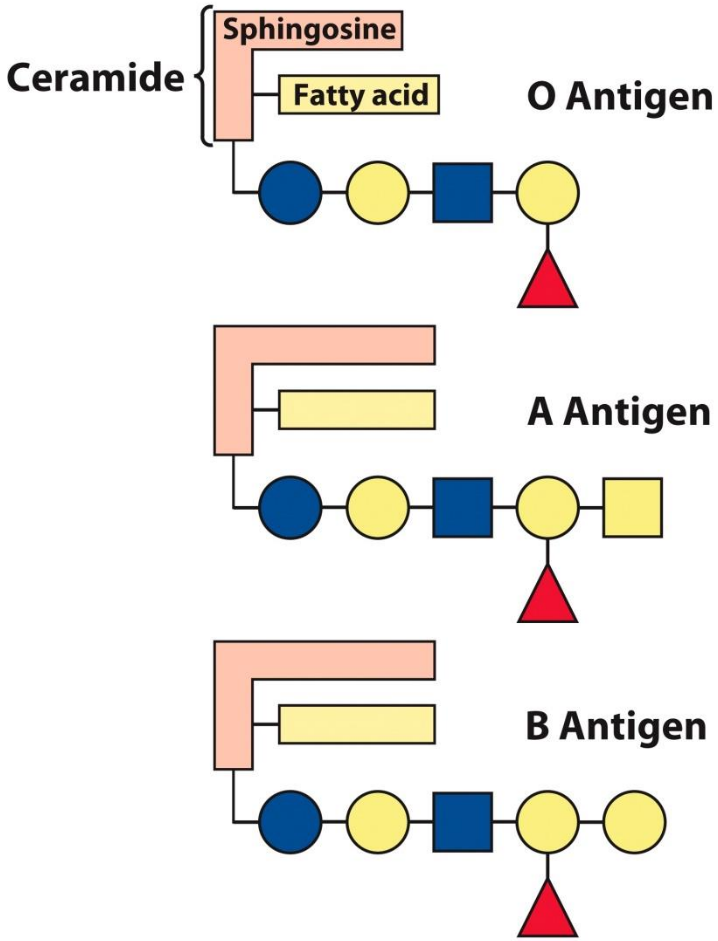
neural tissues




**Globosides** (红细胞糖苷脂) are glycosphingolipids with two or more sugars, usually D-glucose, D-galactose, or *N*-acetyl-D-galactosamine.

Cerebrosides and globosides are sometimes called **neutral glycolipids**, as they have no charge at pH 7.

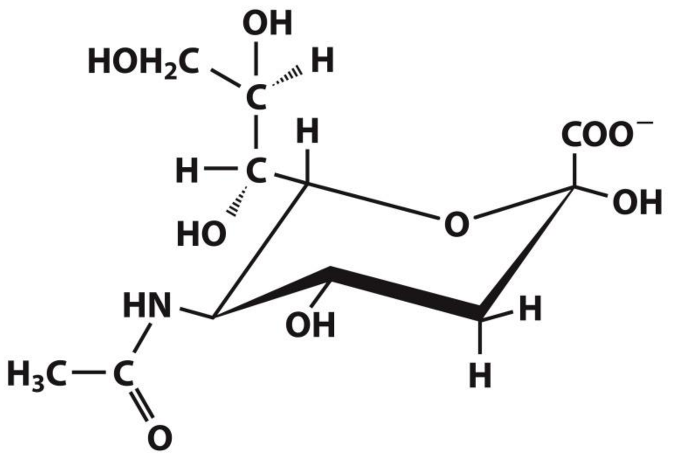
## Globosides determine the type of blood




| | |
|---|---|
| Fucose | Fuc |
| Galactose | Gal |
| Glucose | Glc |
| *N*-Acetylgalactosamine | GalNAc |
| *N*-Acetylglucosamine | GlcNAc |

## ■ **Gangliosides** (神经节苷脂)

is the most complex sphingolipids, have oligosaccharides as their polar head groups and one or more residues of *N*-acetylneuraminic acid (Neu5Ac), a sialic acid (唾液酸) (often simply called “sialic acid”), at the termini.




***N*-Acetylneuraminic acid (a sialic acid)**
**(Neu5Ac)**

Gangliosides with one sialic acid residue are in the **GM** (*M* for mono-) series, those with two are in the **GD** (*D* for di-) series, and so on (**GT**, three sialic acid residues; **GQ**, four).

Sialic acid gives gangliosides the negative charge at pH 7 that distinguishes them from globosides.

Gangliosides are concentrated in the outer surface of cells, functioning as **recognition sites** for extracellular molecules or surfaces of neighboring cells.

## ■ Phospholipids and sphingolipids are degraded in lysosomes

Most cells continually degrade and replace their membrane lipids.

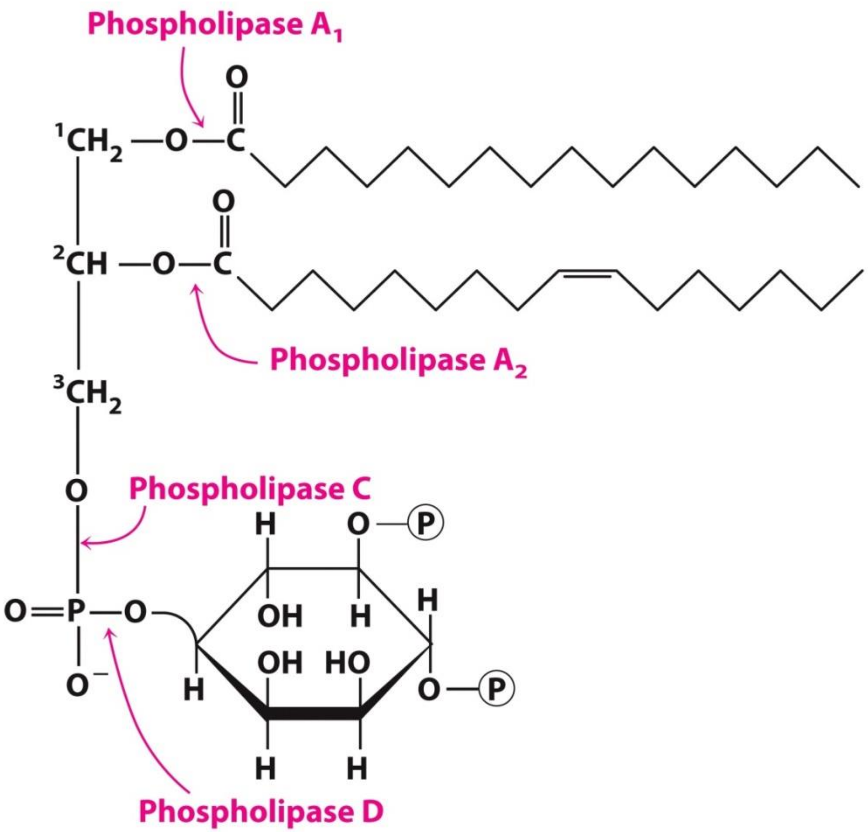
① Phospholipases of the A type remove one of the two fatty acids, producing a lysophospholipid.

② Lysophospholipases remove the remaining fatty acid.

Gangliosides are degraded by a set of lysosomal enzymes that catalyze the stepwise removal of sugar units, finally yielding a ceramide.

A genetic defect in any of these hydrolytic enzymes leads to the accumulation of gangliosides in the cell, with severe medical consequences.

**For each hydrolyzable bond in a glycerophospholipid, there is a specific hydrolytic enzyme in the lysosome.**




Phosphatidylinositol 4,5-bisphosphate

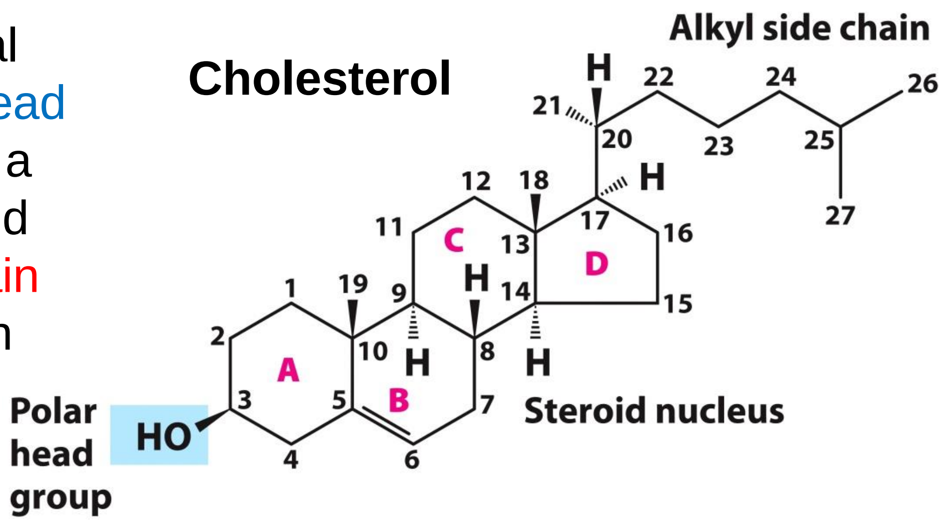
- **Sterols** (固醇类), compounds characterized by a rigid planar system of four fused hydrocarbon rings, three with six carbons and one with five. Sterols are structural lipids present in the membranes of most eukaryotic cells.

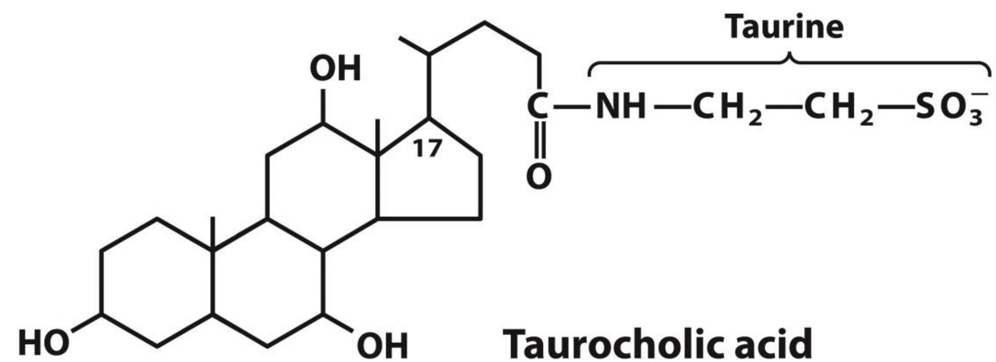
  - **Cholesterol**, the major sterol in animal tissues, is amphipathic, with a polar head group (the hydroxyl group at C-3) and a nonpolar hydrocarbon body (the steroid nucleus and the hydrocarbon side chain at C-17), about as long as a 16-carbon fatty acid in its extended form.

  - **Bile acids** are polar derivatives of cholesterol that act as detergents in the intestine, emulsifying dietary fats to make them more readily accessible to digestive lipases.

Bacteria cannot synthesize sterols.

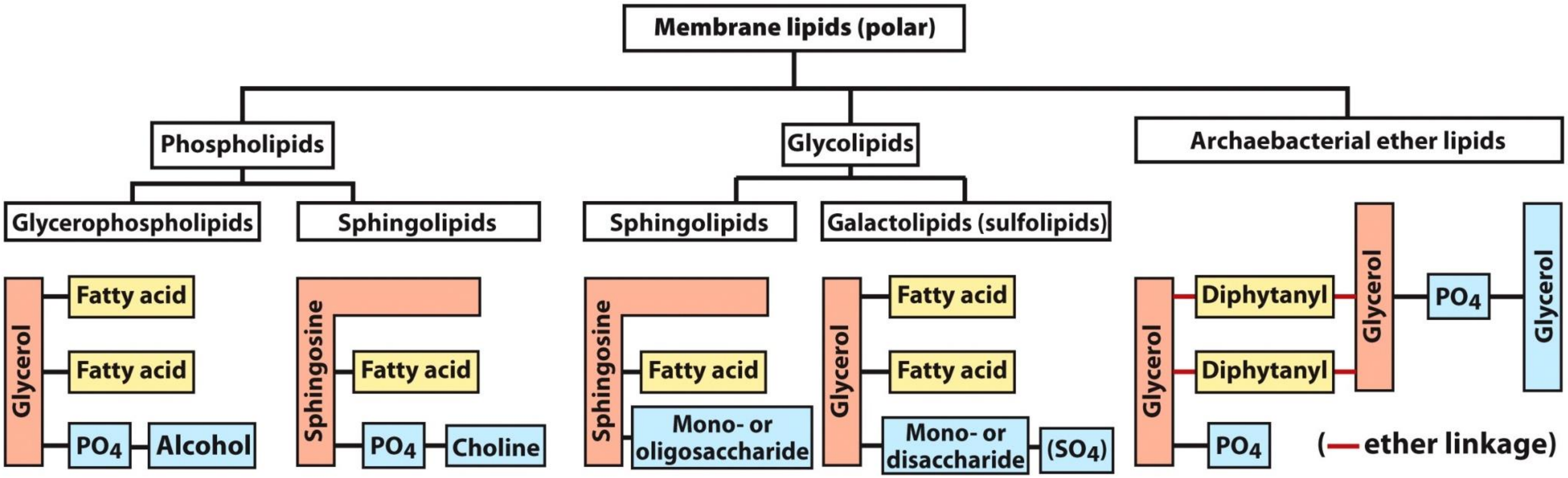
**Cholesterol**




**Taurocholic acid**
**(a bile acid)**

# Summary


Membrane lipids (polar)
Phospholipids
Glycolipids
Archaebacterial ether lipids
Glycerophospholipids
Sphingolipids
Sphingolipids
Galactolipids (sulfolipids)
Glycerol
Fatty acid
Fatty acid
PO4
Alcohol
Sphingosine
Fatty acid
PO4
Choline
Sphingosine
Fatty acid
Mono- or oligosaccharide
Glycerol
Fatty acid
Fatty acid
Mono- or disaccharide
(SO4)
Glycerol
Diphytanyl
Diphytanyl
Glycerol
PO4
Glycerol
PO4
(— ether linkage)

# Take home messages …

- ✓ **Basic Concepts of Lipids**
  Classification, biological function
- ✓ **Storage Lipids :**
  Fatty acids, Triacylglycerols
- ✓ **Structural Lipids in Membranes**
  Five general types of membrane lipids