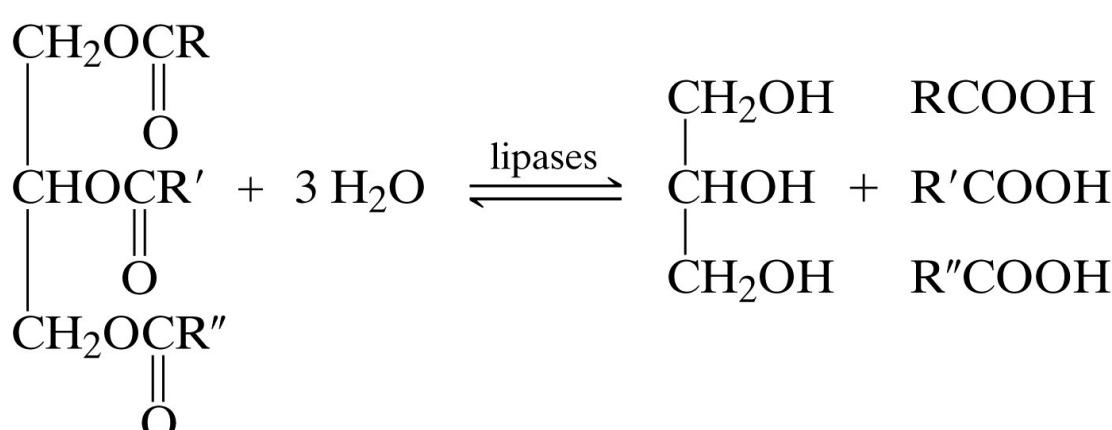


LIPIDS II:

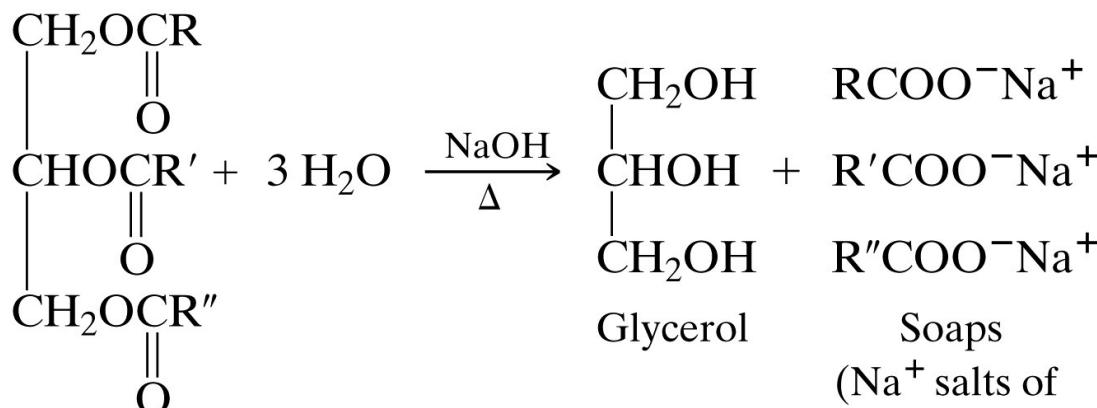
## 1. TRIACYLGLYCEROLS:

- How are they broken down?
    - Hydrolyzed into 3 fatty acids and 1 glycerol
    - Physiologically in body:
      - Enzyme called a **LIPASE** present in adipocytes and intestines



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- **Saponification**
    - Treat with base ( $\text{NaOH}$ ) and heat to produce soaps (salts of FAs) and glycerol
    - Used to (and still do!) boil animal fat with lye ( $\text{NaOH}$ ) to make soap!

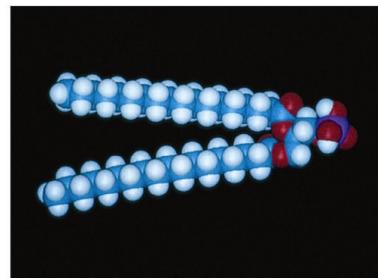
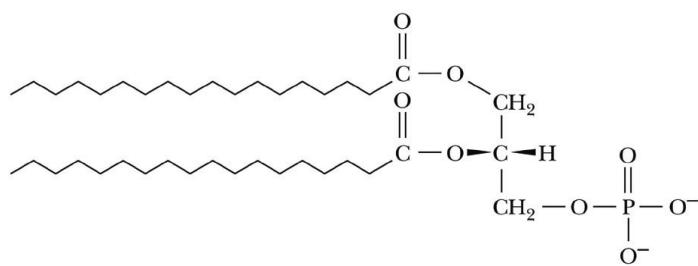


## Triacylglycerols

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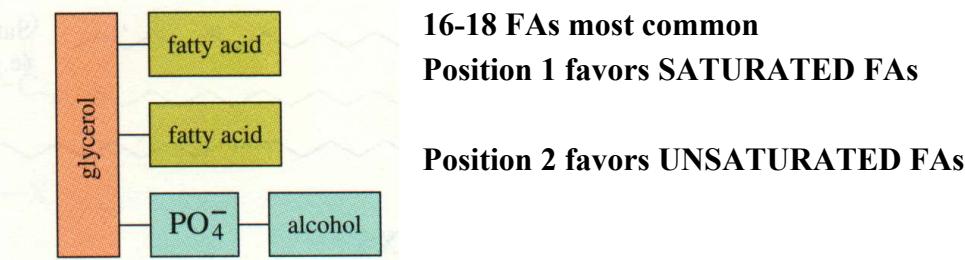
## 2. PHOSPHOACYLGLYCEROLS (Phospholipids; Phosphoglycerides)

- Very similar in structure to triacylglycerols except one of the alcohols of glycerol is esterified by **phosphoric acid** instead of a fatty acid = **phosphatidic acid (PA)**



- The phosphoric acid group is then esterified by a **second alcohol** to form the **phosphoacylglycerol**

Glycerophospholipids

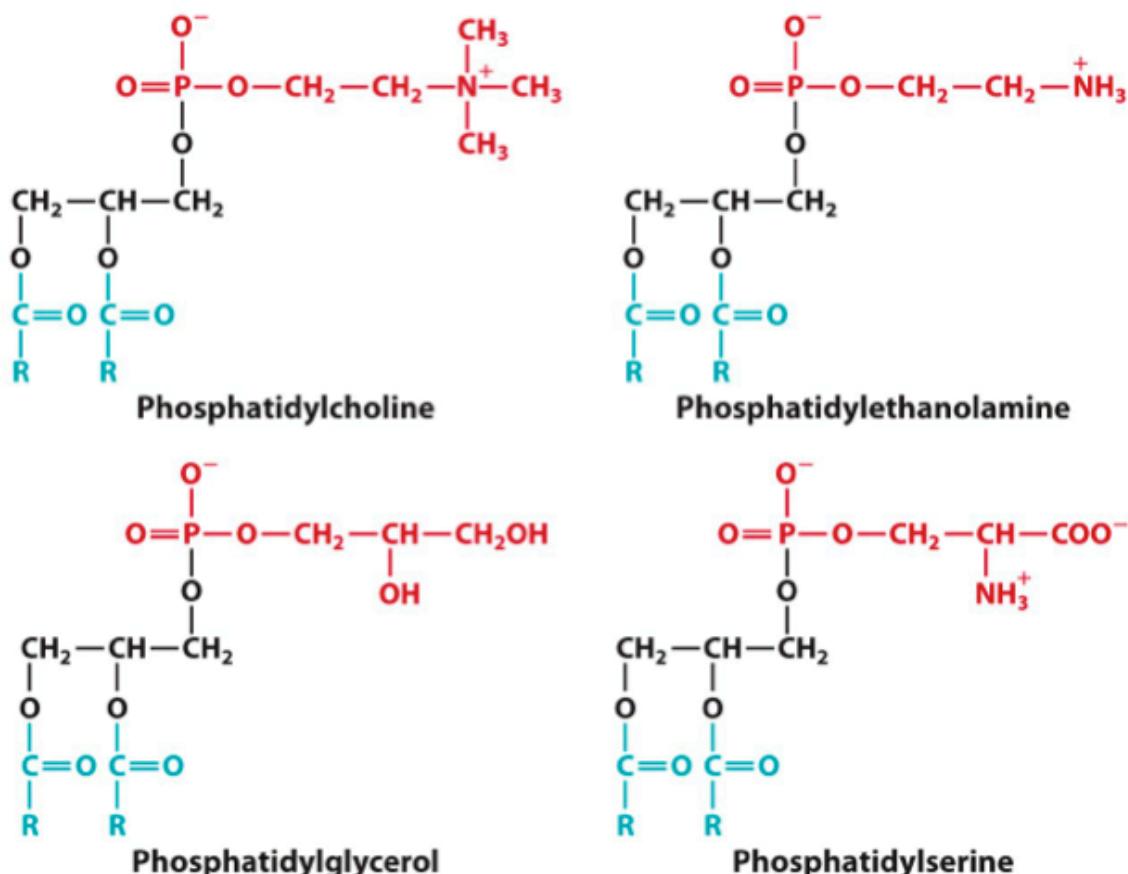


These alcohols give very different properties to the phospholipids due to different structures

Name of X	Structure of X	Name of Glycerophospholipids	Glycerophospholipid (general structure)
(a) Hydrogen	—H	Phosphatidic acid	
(b) Ethanolamine	—CH <sub>2</sub> —CH <sub>2</sub> —NH <sub>3</sub> <sup>+</sup>	Phosphatidylethanolamine	
(c) Choline	—CH <sub>2</sub> —CH <sub>2</sub> —N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	Phosphatidylcholine	
(d) Serine	—CH <sub>2</sub> —CH(NH <sub>3</sub> <sup>+</sup> )(COO <sup>-</sup> )	Phosphatidylserine	
(e) Inositol		Phosphatidylinositol	

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Figure 8-7 part 1 Concepts in Biochemistry, 3/e  
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- Phospholipids are MUCH MORE **amphiphilic** than triacylglycerols due to CHARGED groups at neutral pH
  - o Has both hydrophilic and hydrophobic regions
- Therefore we can say that phospholipids have:

- o One **POLAR HEAD**
- o **TWO NON-POLAR TAILS**

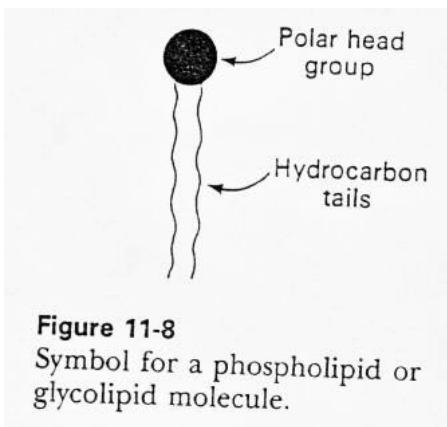
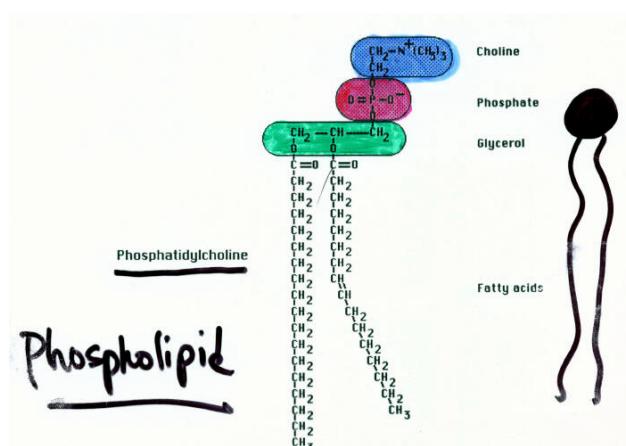


Figure 11-8

Symbol for a phospholipid or glycolipid molecule.



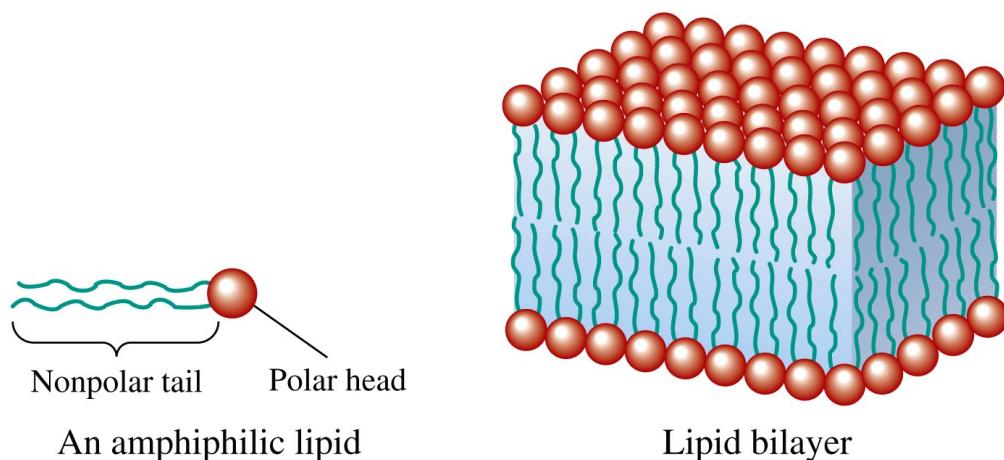
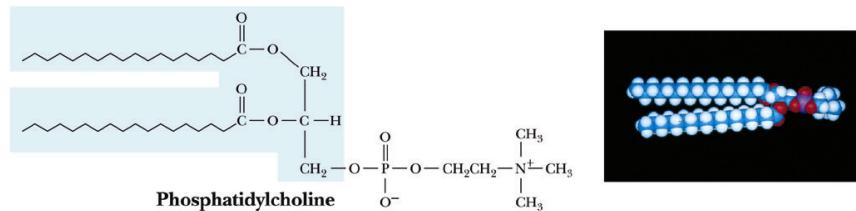
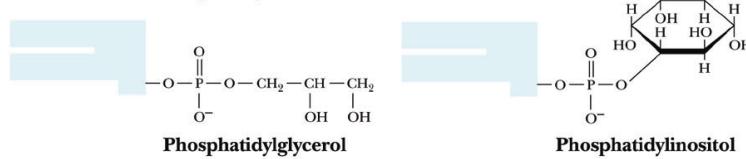
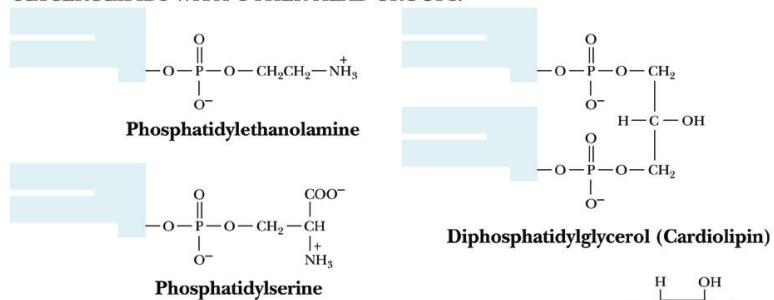


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#### GLYCEROLIPIDS WITH OTHER HEAD GROUPS:



- Phospholipids can be degraded to their component parts by a family of enzymes called **PHOSPHOLIPASES**

- **EXAMPLE: SNAKE VENOM**

- Venoms of poisonous snakes



Western diamondback rattlesnake. (Tom Bean/CORBIS)

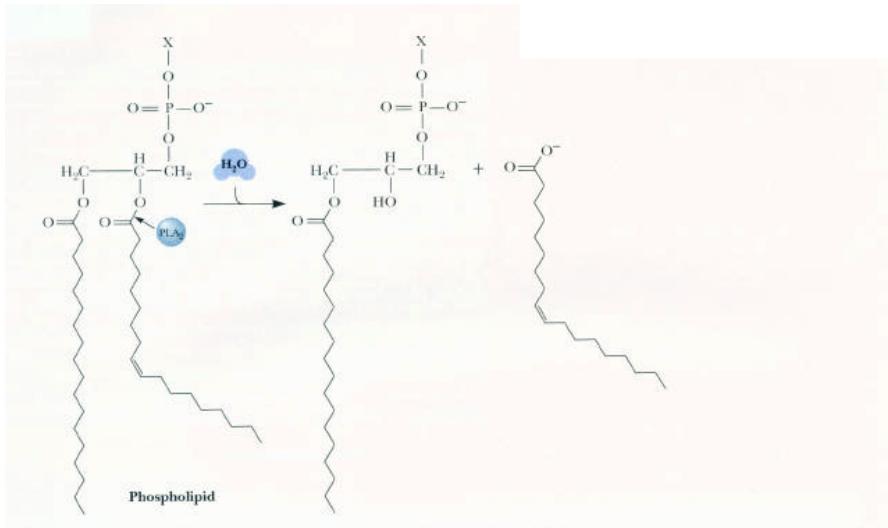


contain (among other things) phospholipases which cause the breakdown of the phospholipids

- Western Diamondback Rattlesnake and Indian Cobra contain **Phospholipase A2**
- **Phospholipase A2** catalyzes the hydrolysis of fatty acids at the C2 Position

### COBRA

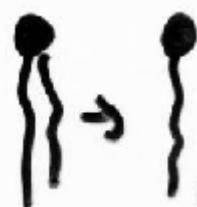
- Remaining compound called **lysolethicin**
  - “one-legged” phospholipids
  - Acts as a detergent
  - Dissolved membranes in red blood cells causing them to rupture

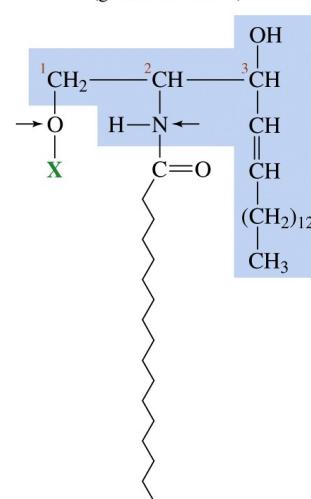


**Phospholipase A2  
cleaves at C2**

### LYSOLECITHIN:

Acts like a detergent that  
disrupts and dissolves membranes in red blood cells



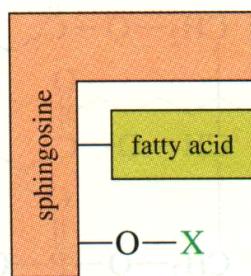
Sphingolipid  
(general structure)

### 3. SPHINGOLIPIDS

- Membrane lipids based on the core structure of SPHINGOSINE, a long chain amino alcohol
  - o Glycerol is replaced by sphingosine

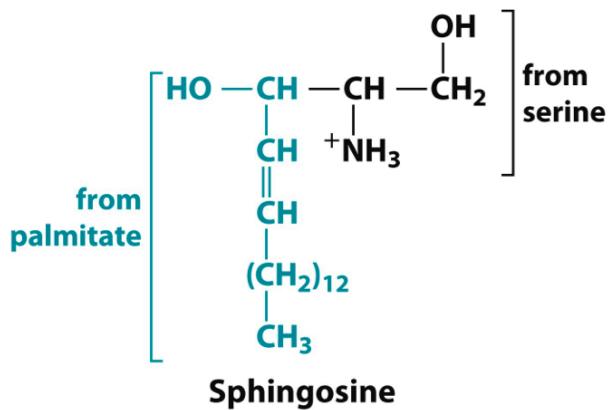
#### General Form:

Sphingolipids



1. Fatty acid linked to sphingosine at an **AMINO** group at position 2
2. 2<sup>nd</sup> esterification takes place at the **HYDROXYL** (-OH) on sphingosine

If X = H → Ceramide  
= Sugar → cerebroside  
= phosphocholine → sphingomyelin  
= complex oligosaccharide → ganglioside

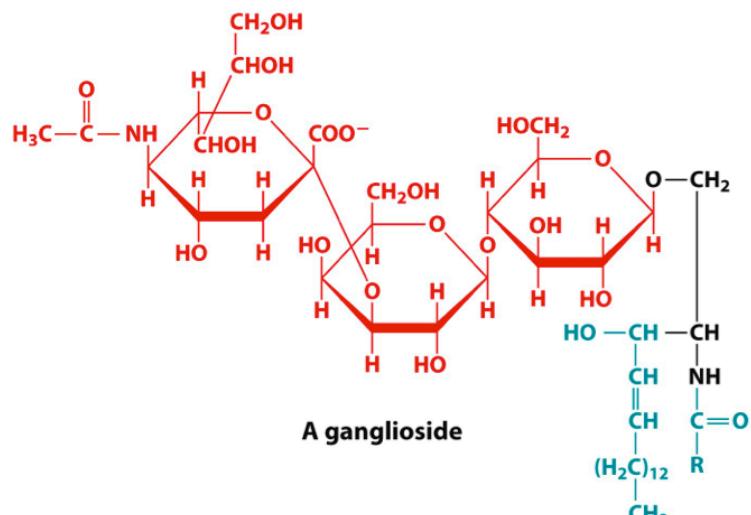
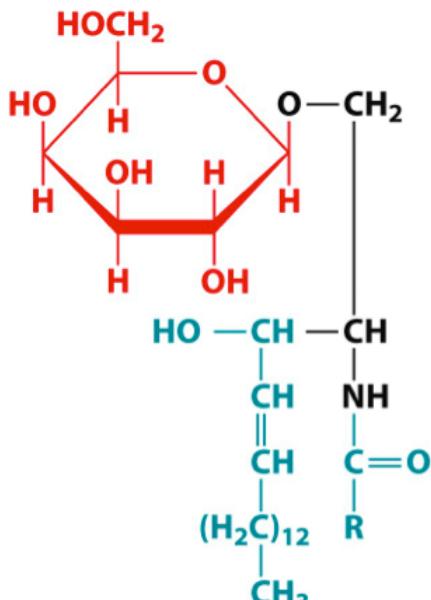
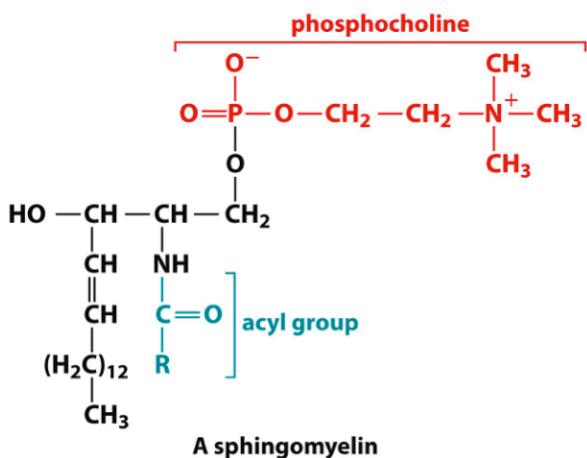


Name of X	Structure of X	Name of Sphingolipid
(b) Hydrogen	—H	Ceramide
(c) Phosphocholine	$\text{—P}(\text{O}^-)(\text{O}^-)\text{O—CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3$	Sphingomyelin
(d) Glucose		Glucosylcerebroside
(e) Complex oligosaccharide		Ganglioside

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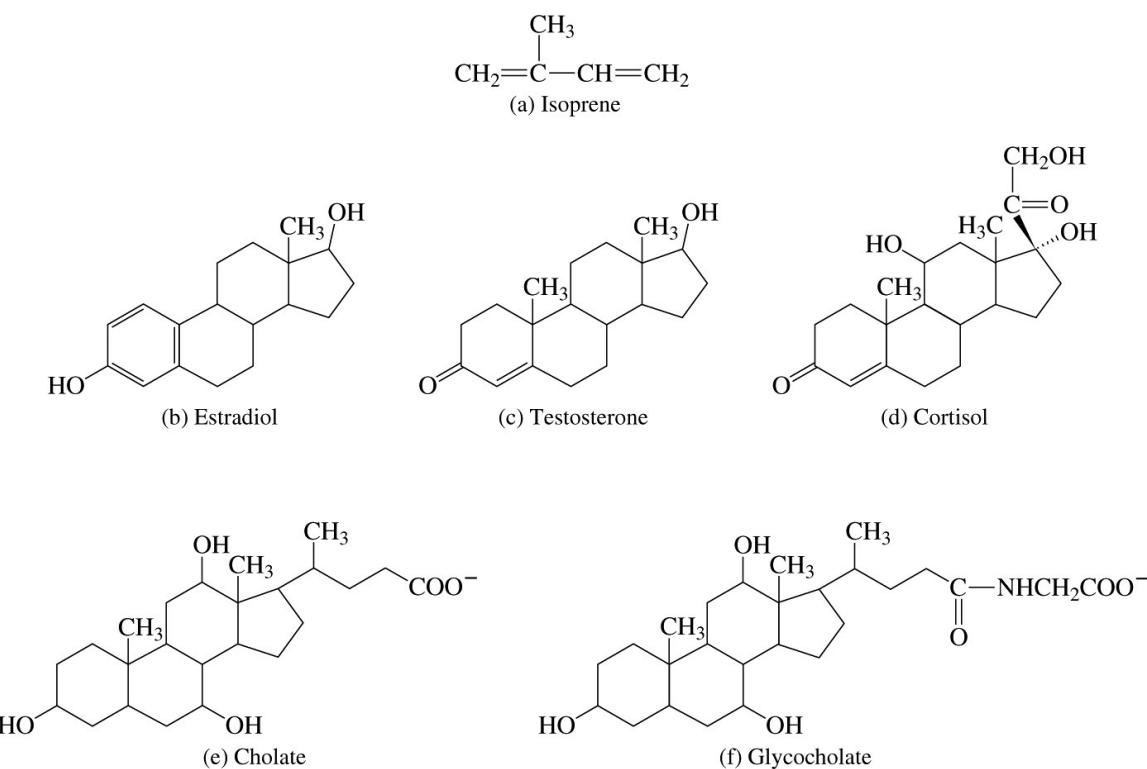
**Sphingolipids:**

- Much more amphiphilic than triacylglycerols
- **Sphingomyelin**
  - o Insulates nerve axons
  - o Major lipid of myelin sheaths
- **Cerebrosides and Gangliosides (glycolipids)**
  - o Abundant in brain and nervous system membranes
  - o Improper degradation results in many **metabolic diseases**
    - **Tay-Sachs Disease**
      - **Gangliosides** accumulate in nerve cells, brain, and spleen → Death!
    - **Gaucher Disease**
      - Accumulation of **glucocerebrosides**
        - o Enlarged liver and spleen
        - o Bone pain
        - o Anemia
      - Deficiency in the enzyme **glucocerebrosidase**



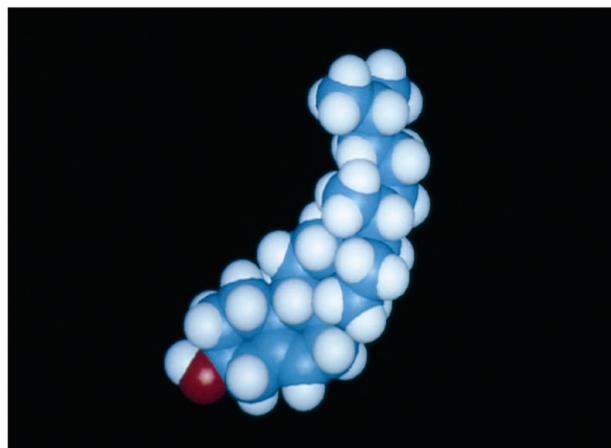
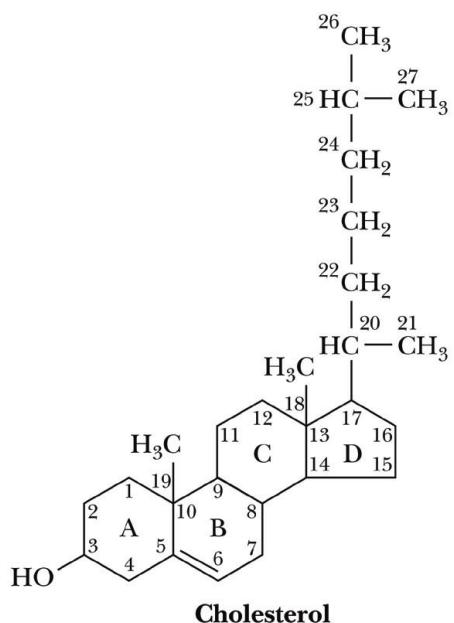
#### **4. NON-SAPONIFIABLE LIPIDS/STEROIDS**

- Based on a fused ring system – **RIGID** structure
  - No ester linkages
  - Includes **HORMONES** (testosterone, progesterone, estrogen)

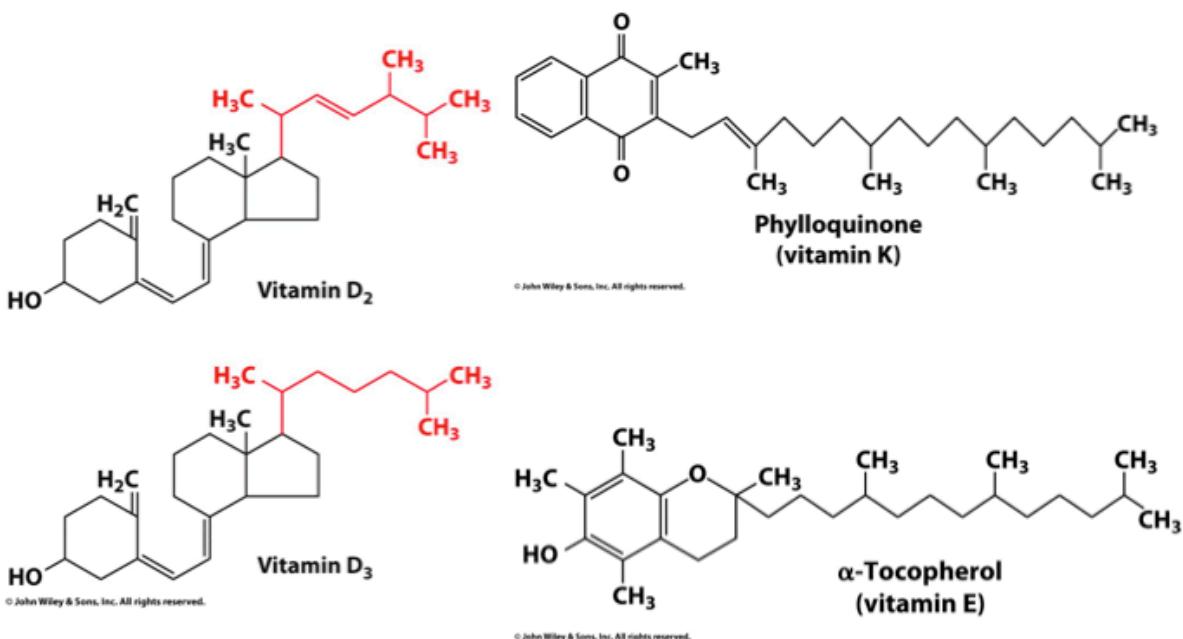


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- - Cholesterol**
      - Common membrane lipid
      - Almost exclusive to animal cells
      - Very hydrophobic but amphiphilic
        - Hydrophilic group is the –OH on ring A
      - Serves as the starting point for synthesis of steroid hormones



## LIPID VITAMINS



## BIOLOGICAL MEMBRANES

- Membranes surround all cells and organelles
- Membranes are based on LIPID BILAYERS (double layer of lipid)
  - o Made up of **phospholipids, glycosphingolipids, sphingolipids** and **cholesterol** (if animal)
  - o Non-polar components minimize exposure to water by forming a bilayer
  - o Polar head groups **face outward** and **H-bond with water**
  - o Lipid fatty acid chains **face inward** and interact via **hydrophobic interactions**

### LIPID BILAYERS

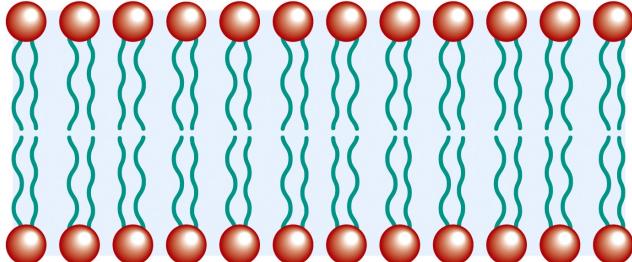


Figure 9-1a Concepts in Biochemistry, 3/e  
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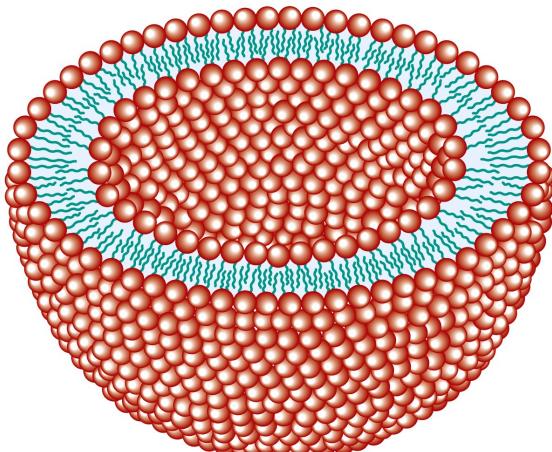
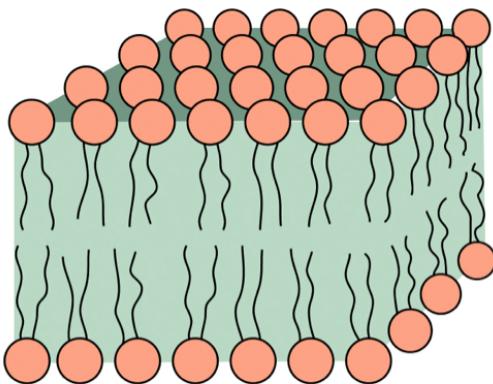


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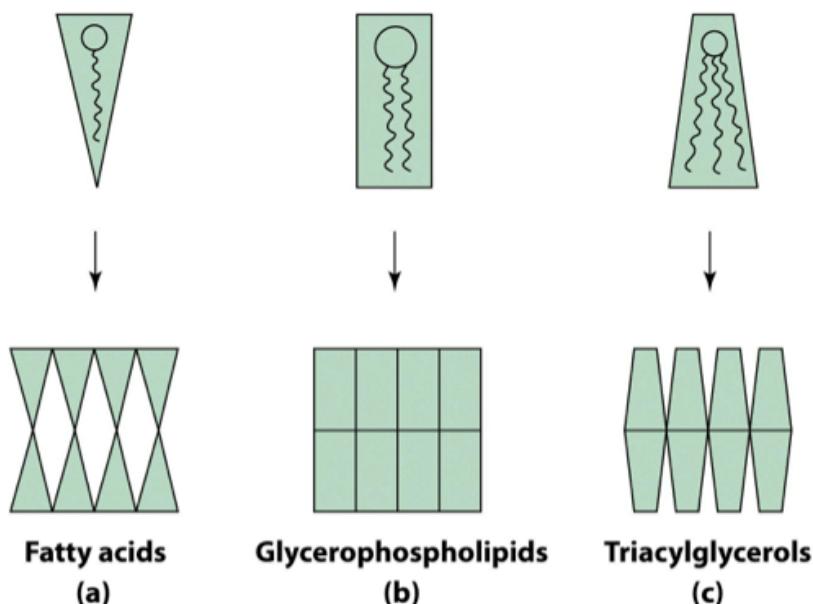


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Membranes are:

- **Fluid not static**
  - o Consistency of vegetable oil
  - o Nature of the **lipids (length, degree of saturation)** dictates **fluidity** and **melting temperature**
    - Saturated versus non-saturated – saturated higher melting temperature
    - Length of fatty acids – longer generally higher melting temperature
    - Saturated less fluid than unsaturated

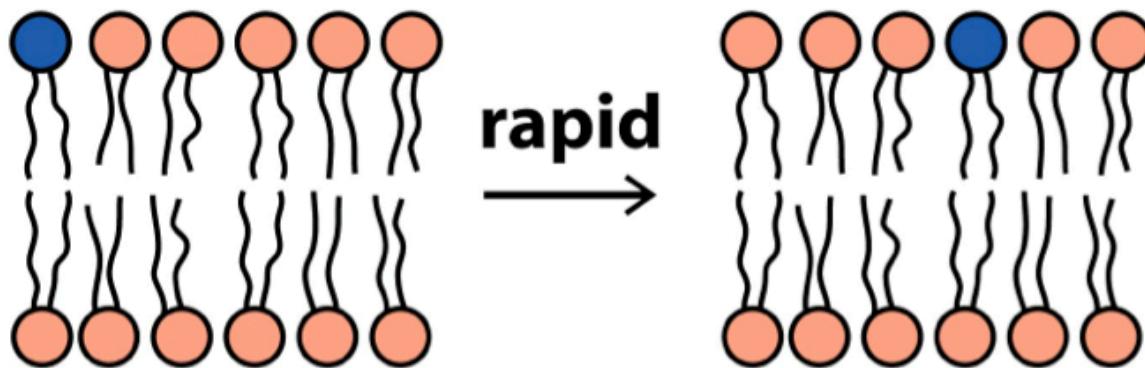
## Glycerophospholipids Form Bilayers Fatty Acids & TAGs Do Not



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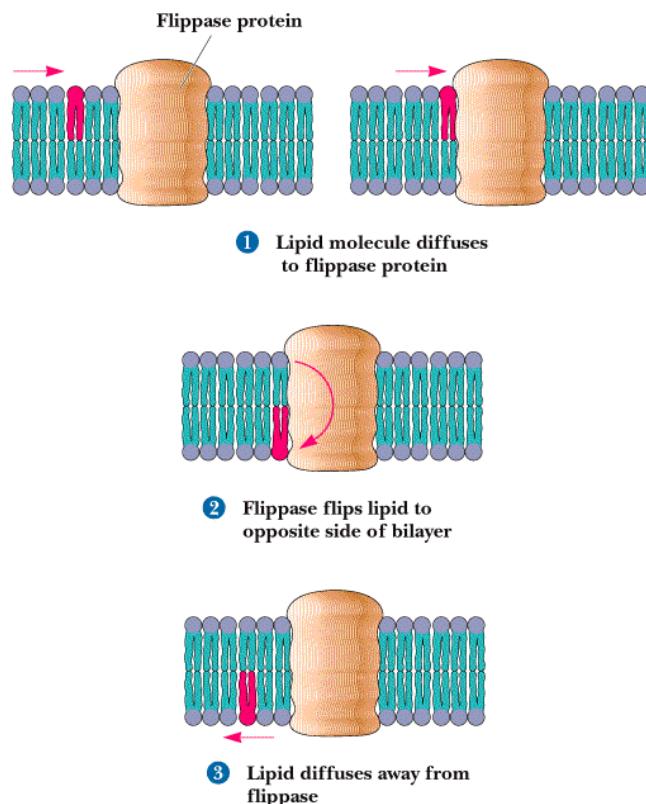
- Lipids are constantly moving **LATERALLY** (side to side)

## Lateral diffusion

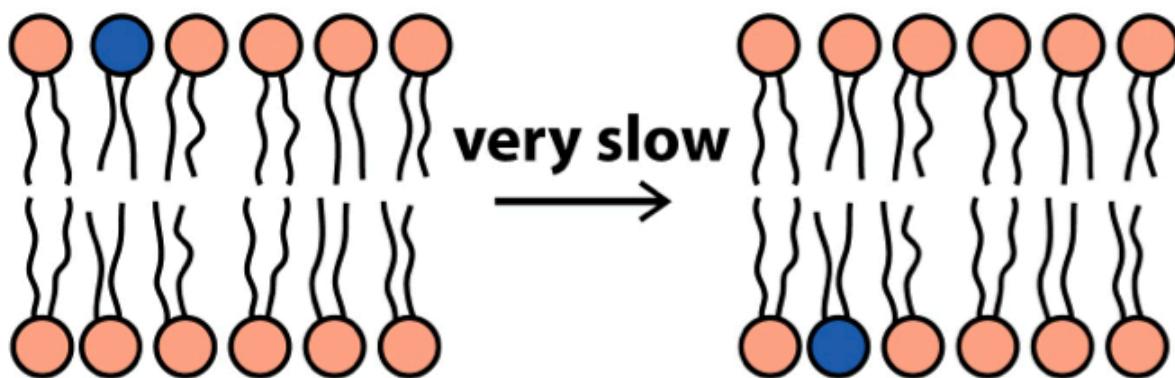


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- Rarely flip from one leaflet to the other
- When does, requires a lot of energy
- Use proteins called **FLIPPASES**

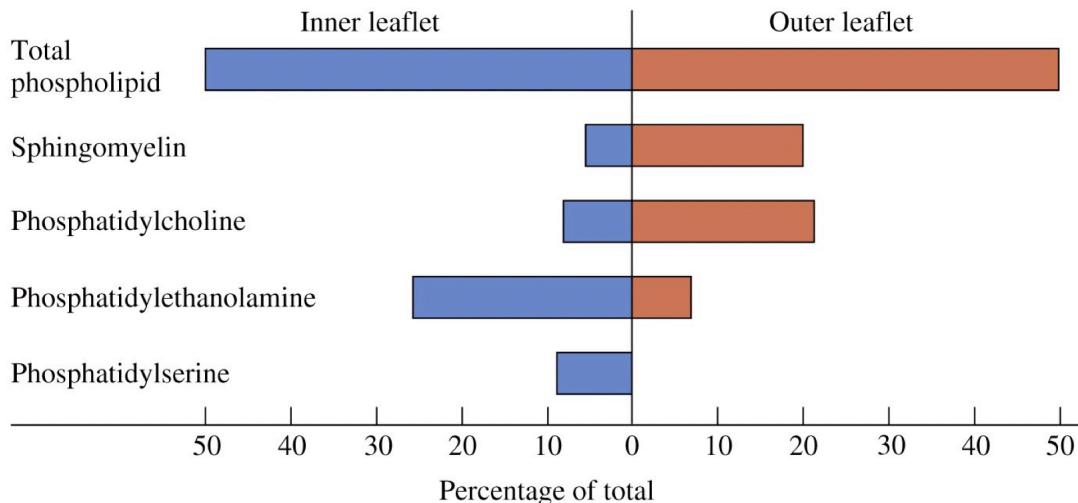


## Transverse diffusion (flip-flop)



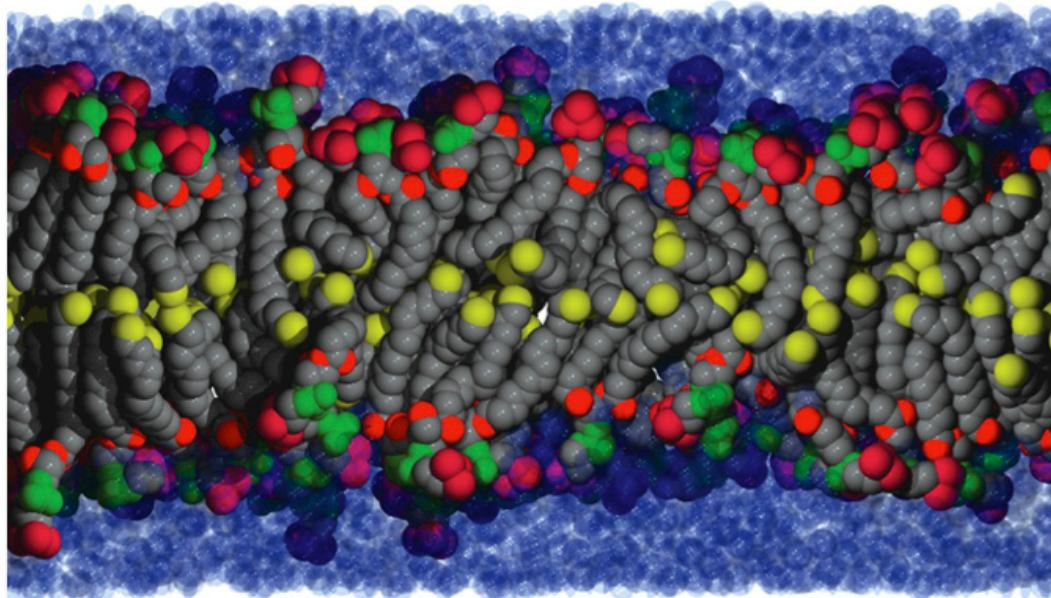
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- Because of this, lipid bilayers are **ASYMMETRIC**
- Some lipids on inner leaflet only
- Some lipids on outer leaflet only
- Distribution is NOT random



**Figure 9-2 Concepts in Biochemistry, 3/e**  
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## LIPID BILAYER



C = gray & yellow; O esters = red; Phosphate = green  
 · Choline head groups = magenta; Water = blue spheres

### LIPID MOVEMENT ANIMATIONS:

<http://www.d.umn.edu/~sdowning/Membranes/animationindx.html>