

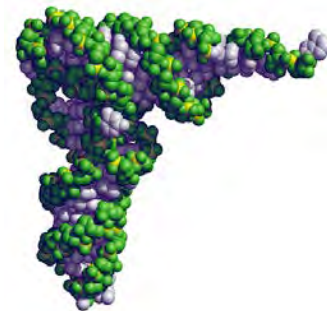
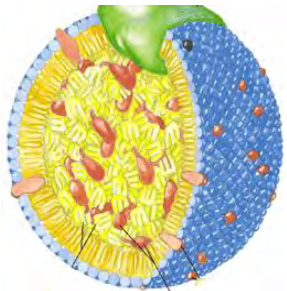


BIOCHEMISTRY REVIEW

Overview of Biomolecules

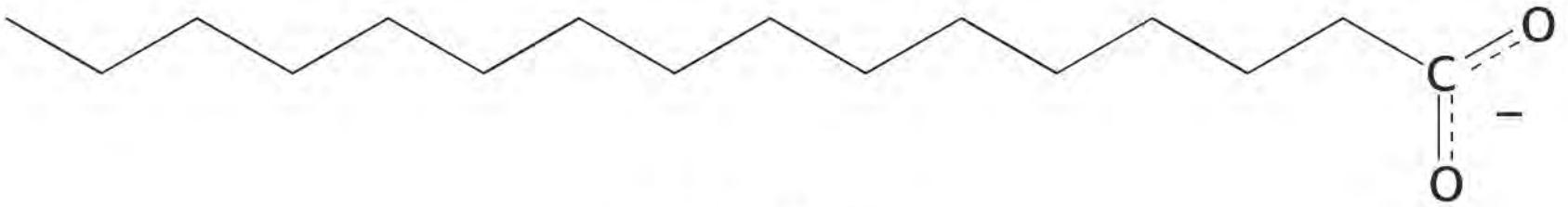
Chapter 8

Lipids

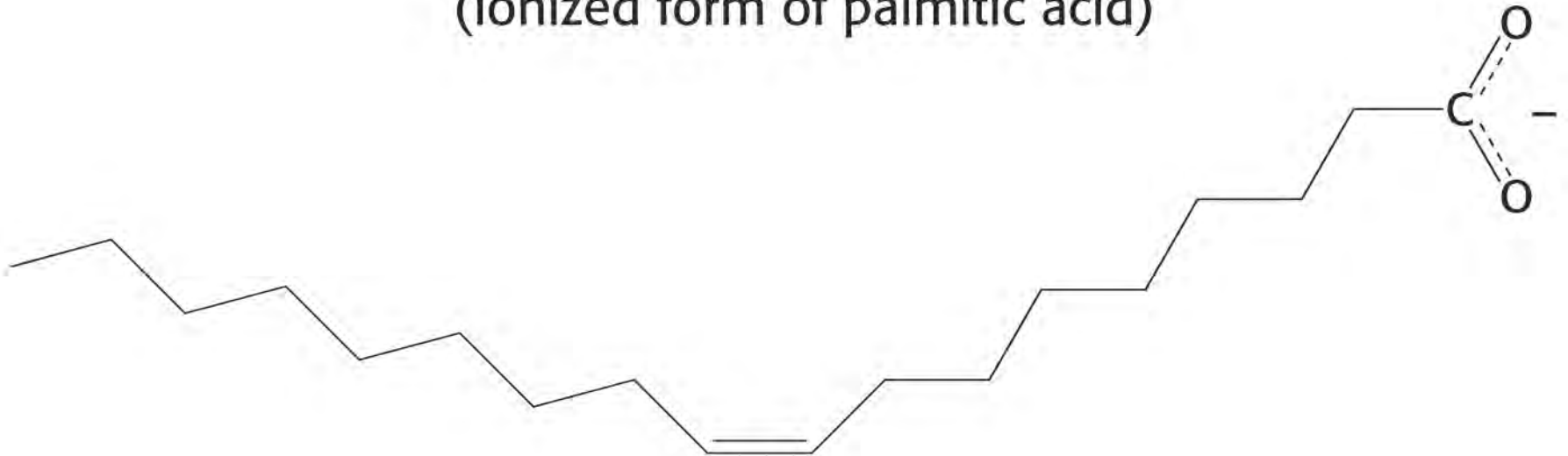


FATTY ACIDS

- **4-36 CARBONS**
- **ONE CARBOXYLIC ACID GROUP**
- **EVEN NUMBER OF CARBONS (USUALLY)**
- **LINEAR (USUALLY)**
- **SATURATED OR UNSATURATED**
- **CIS DOUBLE BONDS (USUALLY)**
- **UNCONJUGATED DOUBLE BONDS (USUALLY)**
(- CH = CH - CH₂ - CH = CH -)



Palmitate
(ionized form of palmitic acid)



Oleate
(ionized form of oleic acid)

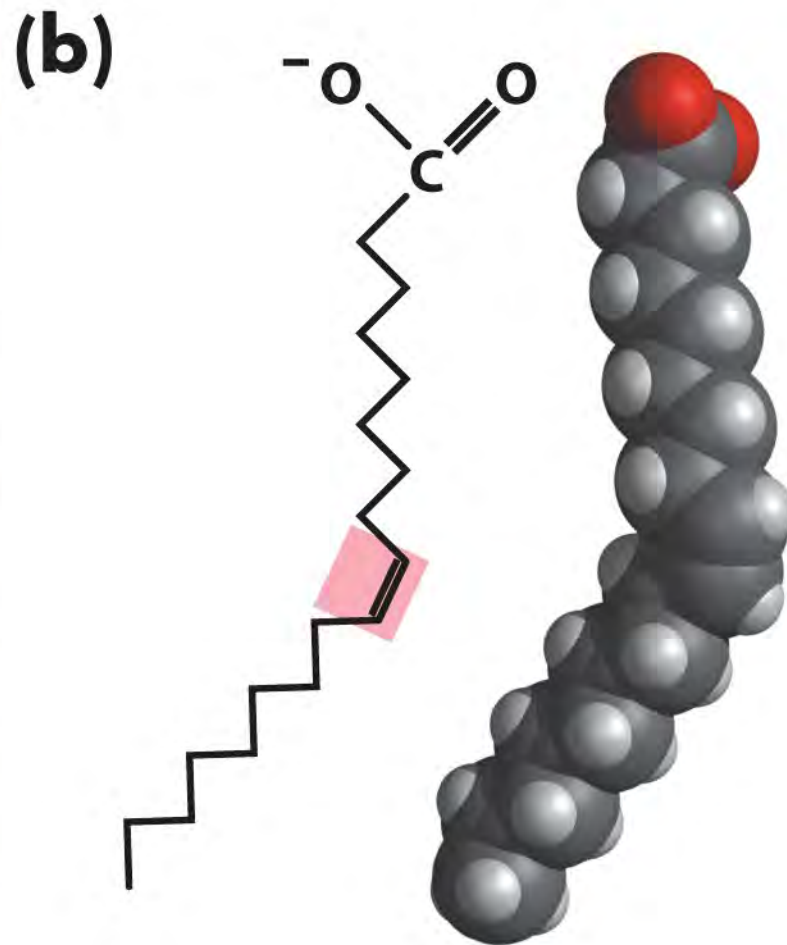
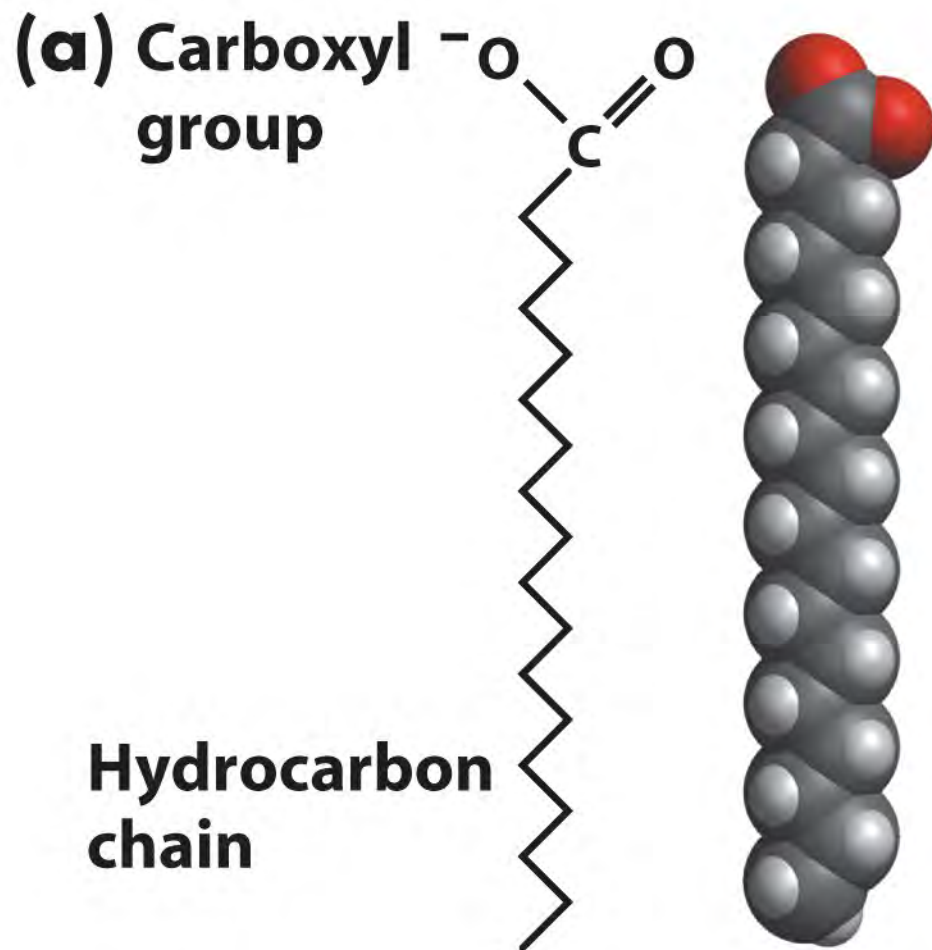


TABLE 12.1 Some naturally occurring fatty acids in animals

Number of carbons	Number of double bonds	Common name	Systematic name	Formula
12	0	Laurate	<i>n</i> -Dodecanoate	$\text{CH}_3(\text{CH}_2)_{10}\text{COO}^-$
14	0	Myristate	<i>n</i> -Tetradecanoate	$\text{CH}_3(\text{CH}_2)_{12}\text{COO}^-$
16	0	Palmitate	<i>n</i> -Hexadecanoate	$\text{CH}_3(\text{CH}_2)_{14}\text{COO}^-$
18	0	Stearate	<i>n</i> -Octadecanoate	$\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-$
20	0	Arachidate	<i>n</i> -Eicosanoate	$\text{CH}_3(\text{CH}_2)_{18}\text{COO}^-$
22	0	Behenate	<i>n</i> -Docosanoate	$\text{CH}_3(\text{CH}_2)_{20}\text{COO}^-$
24	0	Lignocerate	<i>n</i> -Tetracosanoate	$\text{CH}_3(\text{CH}_2)_{22}\text{COO}^-$
16	1	Palmitoleate	<i>cis</i> - Δ^9 -Hexadecenoate	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO}^-$
18	1	Oleate	<i>cis</i> - Δ^9 -Octadecenoate	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO}^-$
18	2	Linoleate	<i>cis, cis</i> - Δ^9, Δ^{12} - Octadecadienoate	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_2(\text{CH}_2)_6\text{COO}^-$
18	3	Linolenate	<i>all-cis</i> - $\Delta^9, \Delta^{12}, \Delta^{15}$ - Octadecatrienoate	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_6\text{COO}^-$
20	4	Arachidonate	<i>all-cis</i> - $\Delta^5, \Delta^8, \Delta^{11}, \Delta^{14}$ - Eicosatetraenoate	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_4(\text{CH}_2)_2\text{COO}^-$



Are You Getting It??



Which is the most likely structure for a common fatty acid?

- a) $\text{CH}_3(\text{CH}_2)_{15}\text{COOH}$
- b) $\text{HOOC}(\text{CH}_2)_{14}\text{COOH}$
- c) $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_{13}\text{COOH}$
- d) $\text{CH}_3(\text{CH}_2)_9\text{CH}=\text{CH}(\text{CH}_2)_3\text{COOH}$
- e) $\text{CH}_3(\text{CH}_2)_6\text{CH}=\text{CH}-\text{CH}=\text{CH}(\text{CH}_2)_4\text{COOH}$



Are You Getting It??



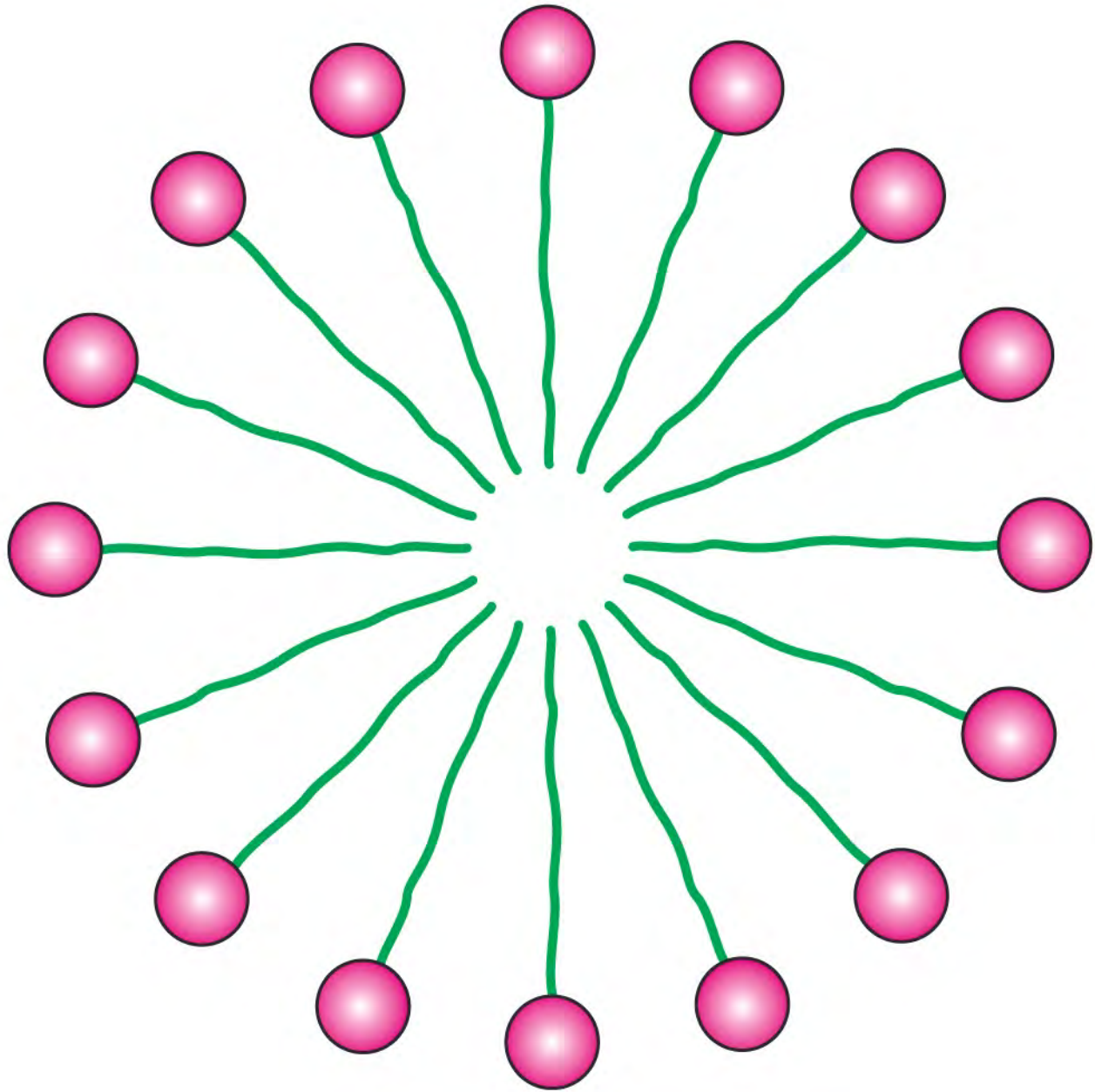
Answer

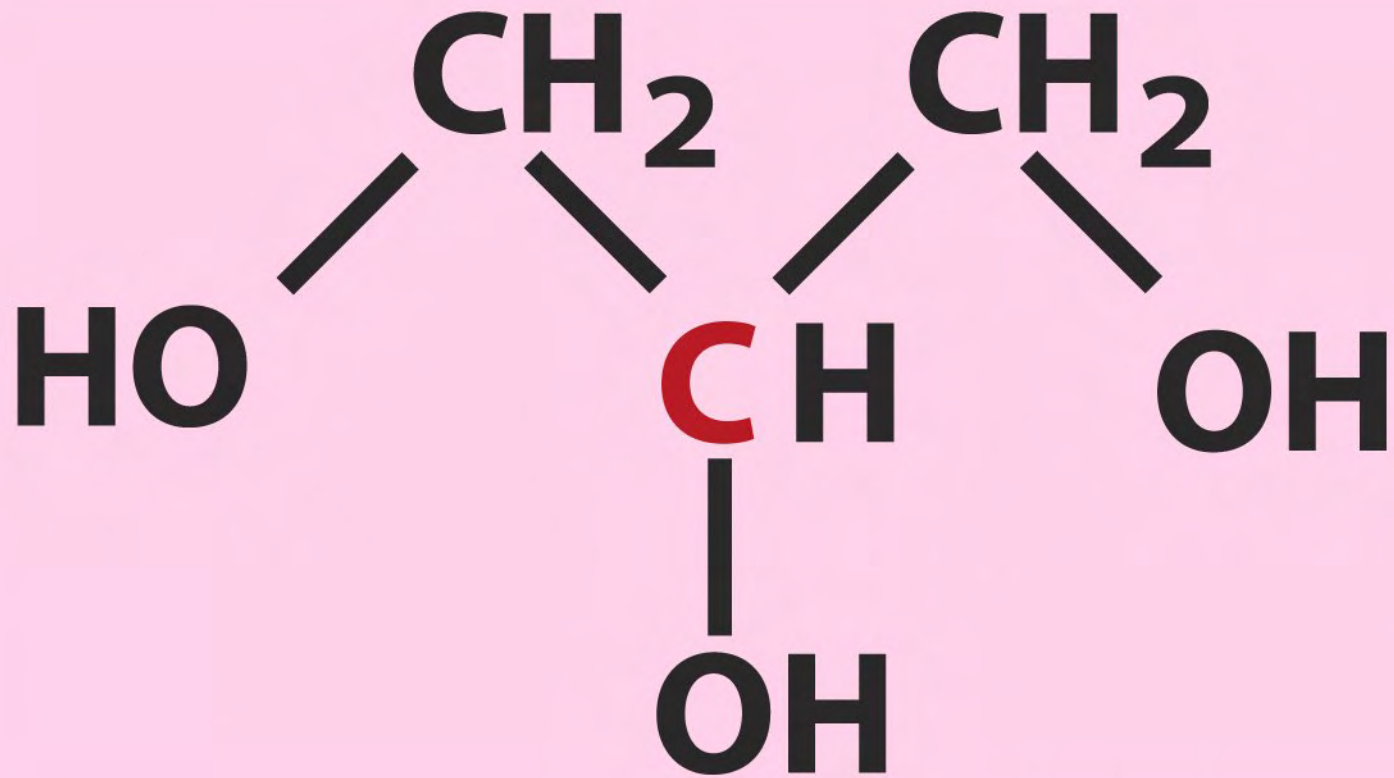
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- e) $\text{CH}_3(\text{CH}_2)_6\text{CH}=\text{CH}-\text{CH}=\text{CH}(\text{CH}_2)_4\text{COOH}$

FATTY ACID SALT (SOAP)

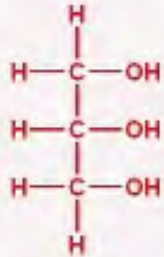






Glycerol

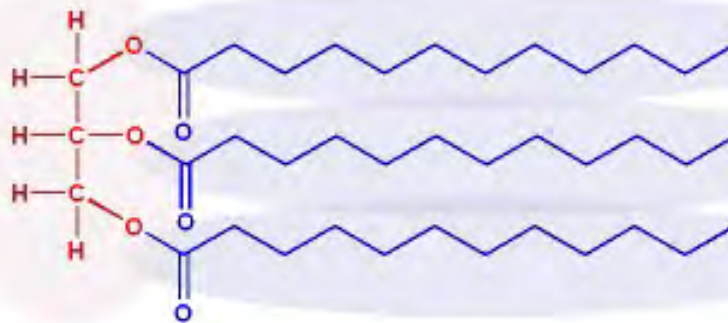
Glycerol

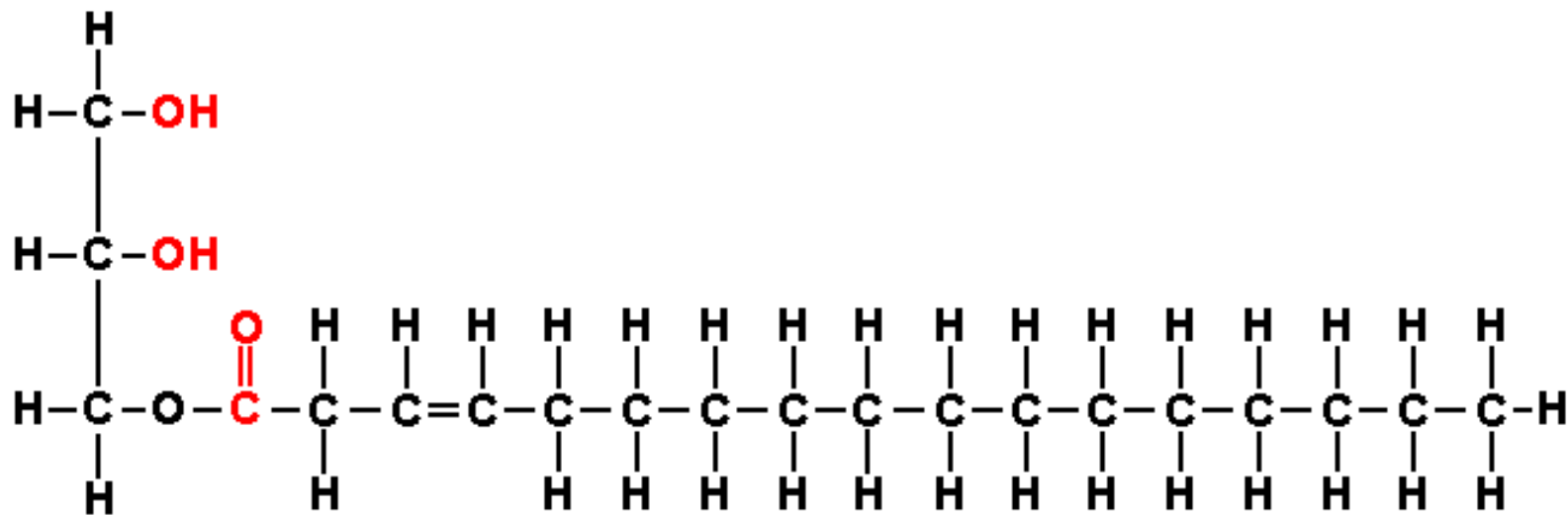


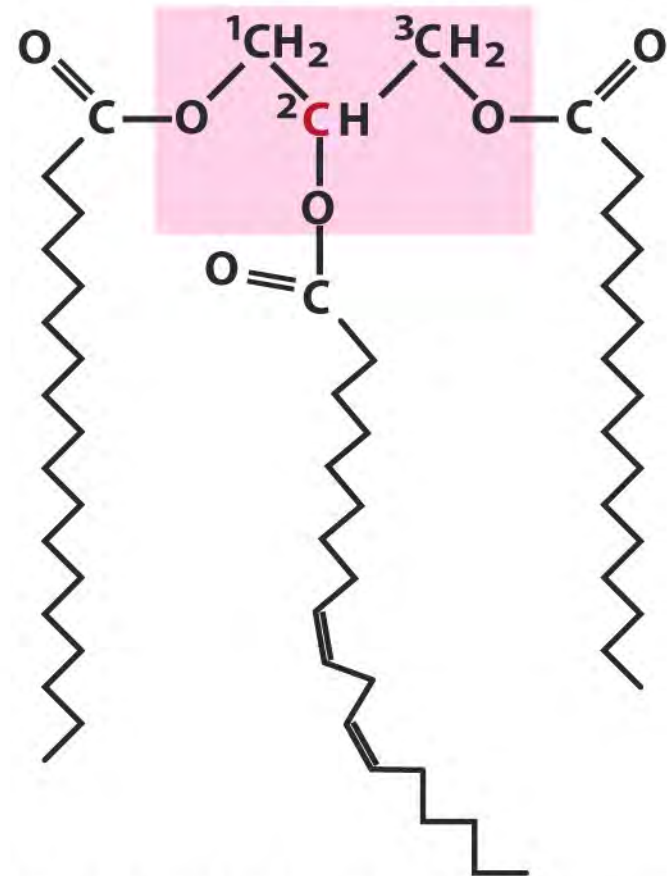
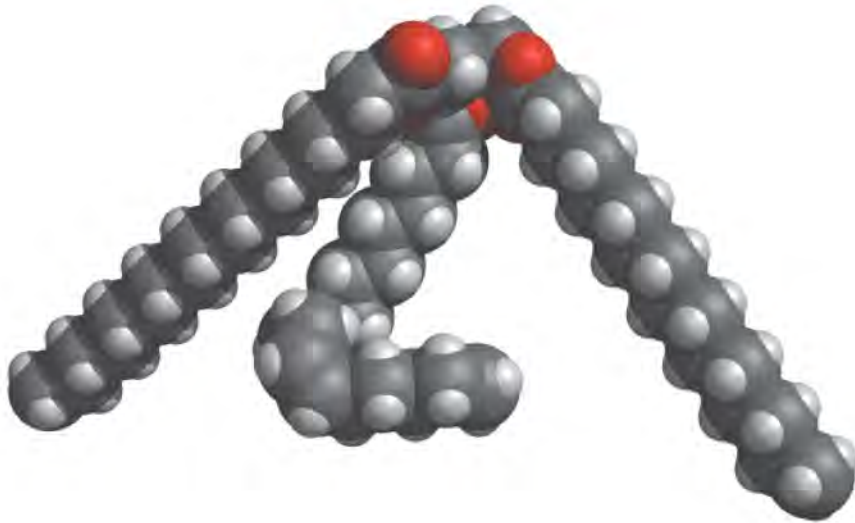
A "free" Fatty Acid



Triglyceride

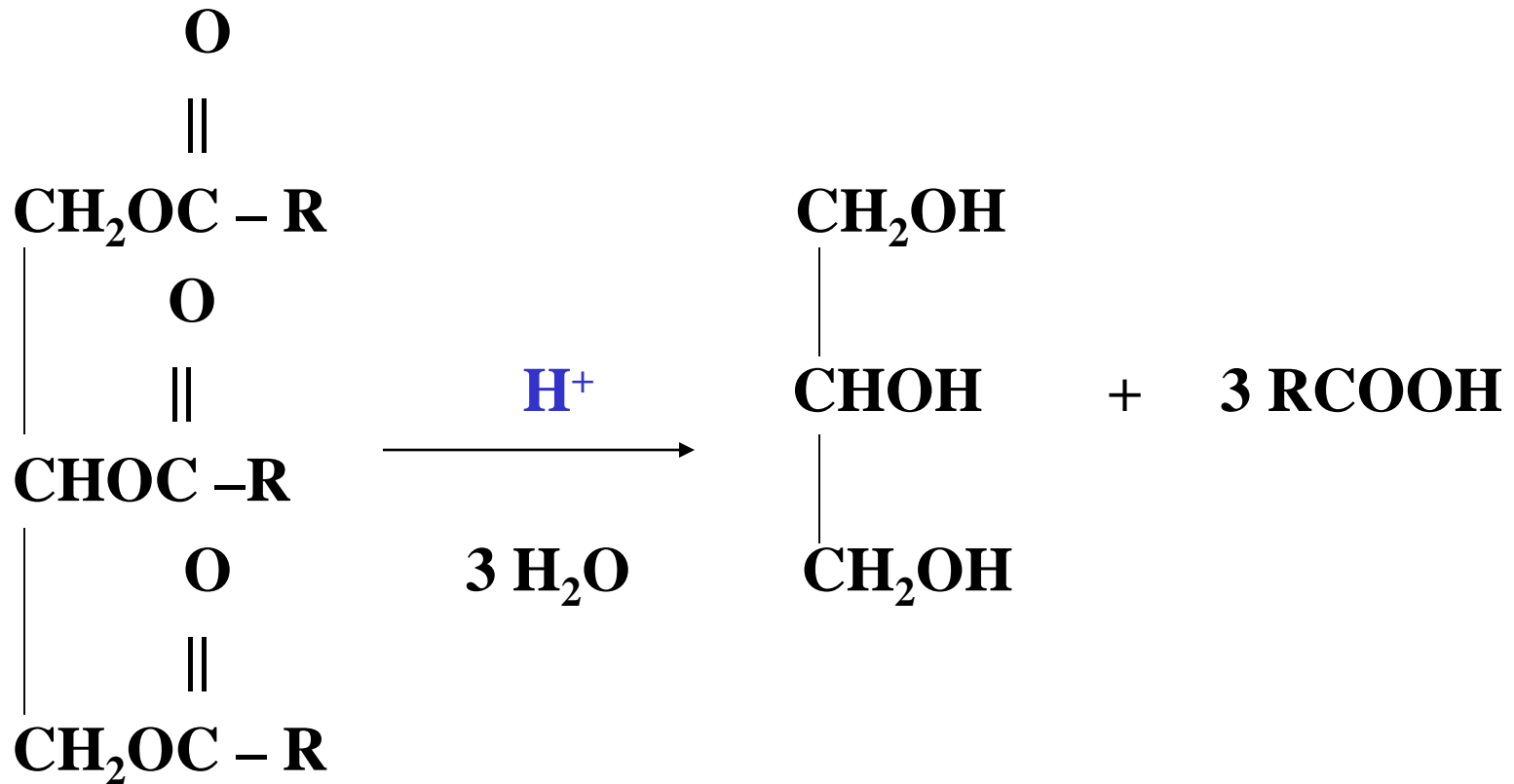






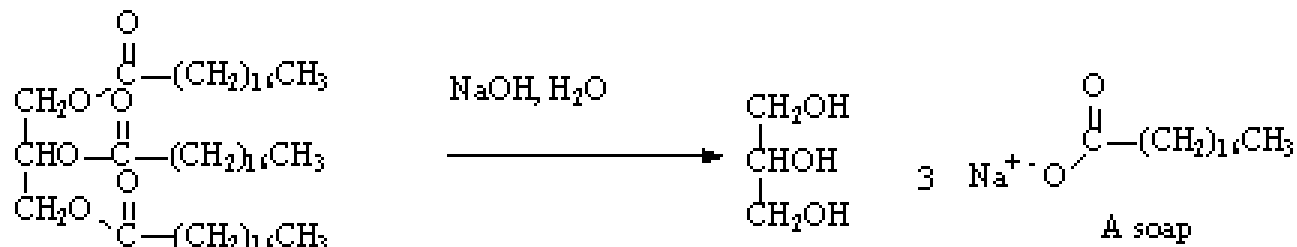
**1-Stearoyl, 2-linoleoyl, 3-palmitoyl glycerol,
a mixed triacylglycerol**

ACID HYDROLYSIS OF A TRIGLYCERIDE



Saponification

- Base catalyzed hydrolysis is called “saponification”



A fat (if solid)
An oil (if liquid)

A soap



Are You Getting It??



**Which properties are characteristic of triglycerides?
(multiple answers)**

- a) They contain one glycerol molecule.
- b) They contain three -COOH groups.
- c) They contain three ester bonds.
- d) They can be saponified in acid.
- e) They can be hydrolyzed in base.
- f) They are amphipathic.



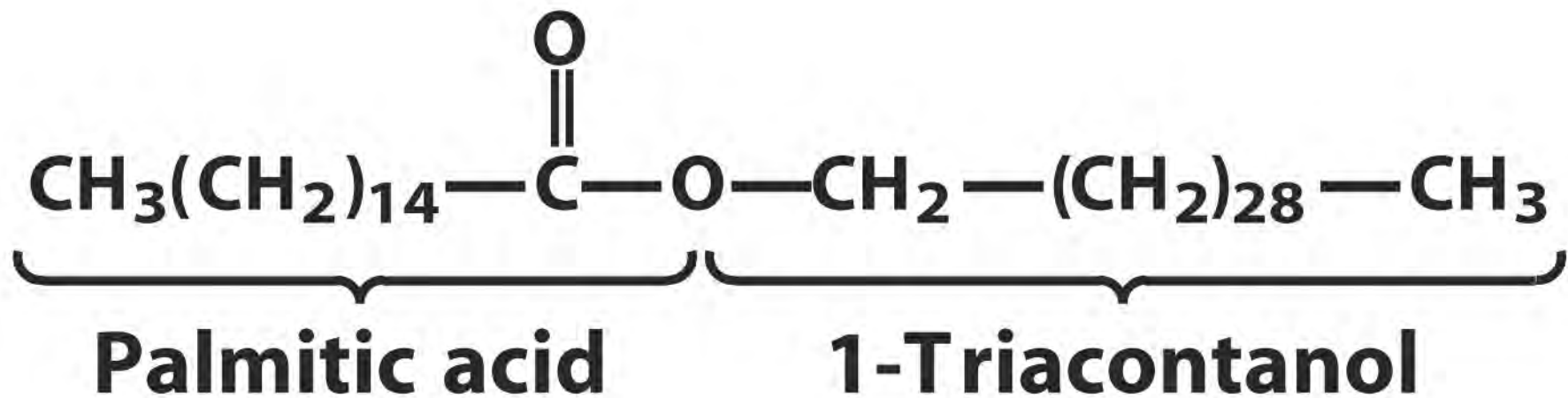
Are You Getting It??

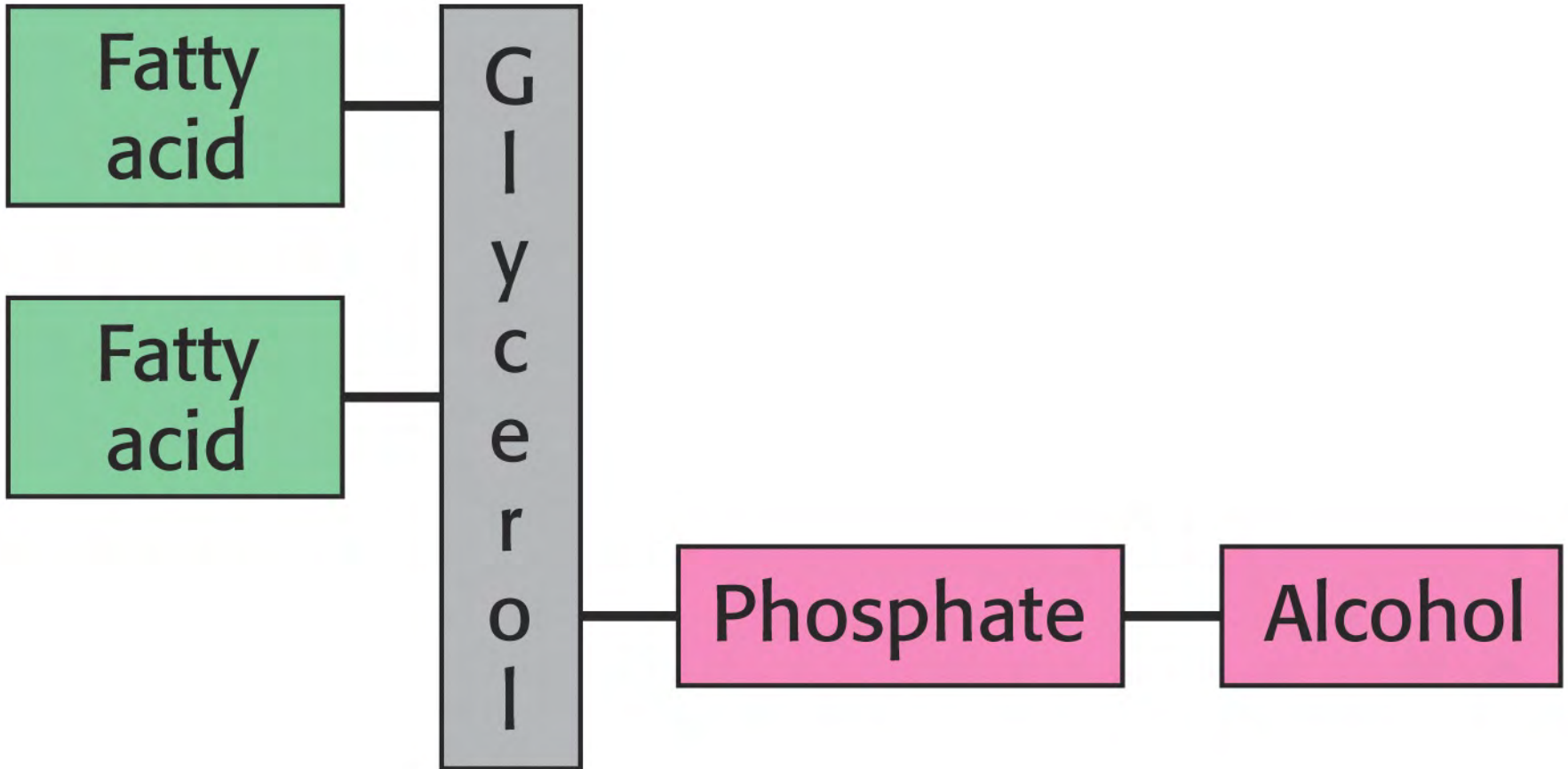


Answer

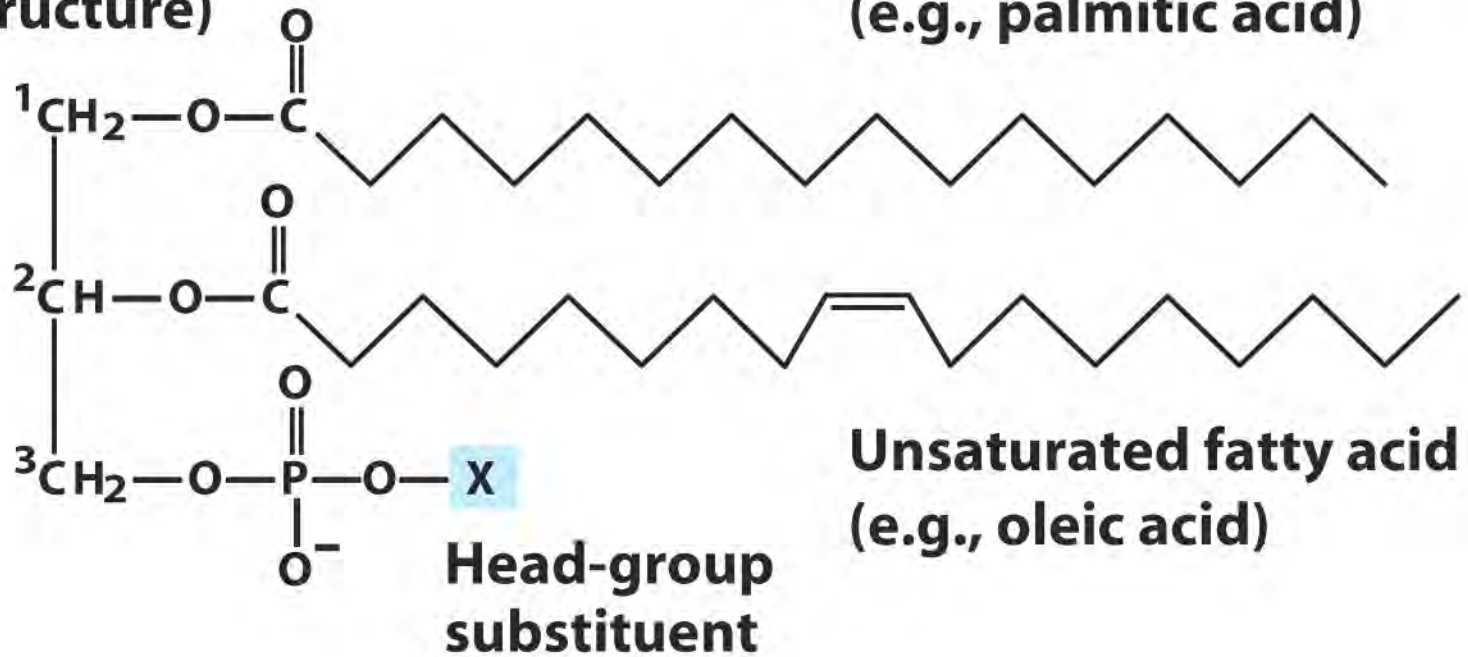
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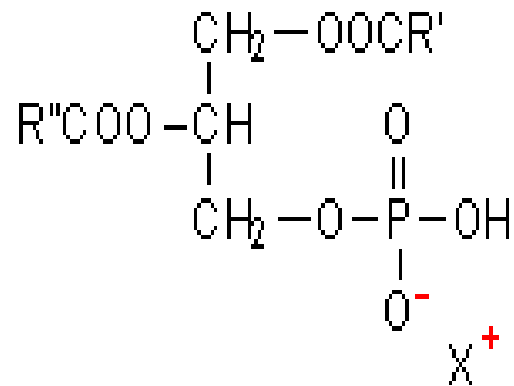


**Glycerophospholipid
(general structure)**

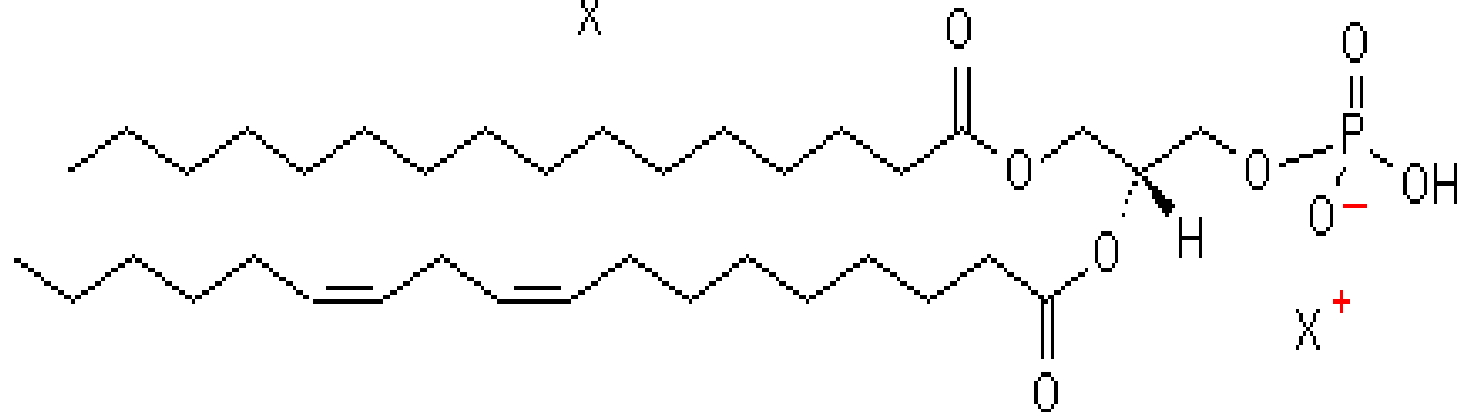


**Saturated fatty acid
(e.g., palmitic acid)**

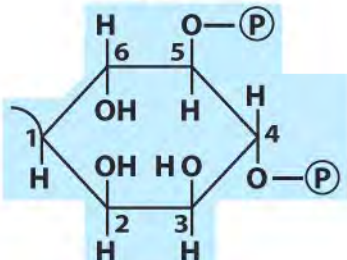
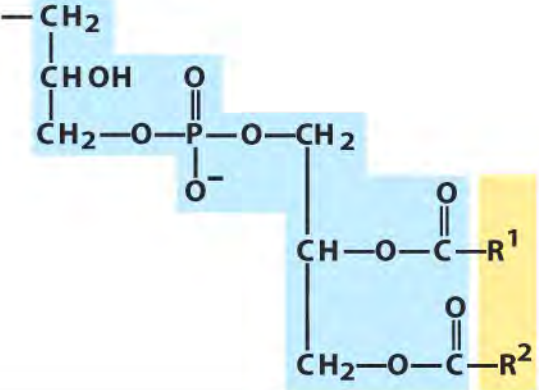
**Unsaturated fatty acid
(e.g., oleic acid)**

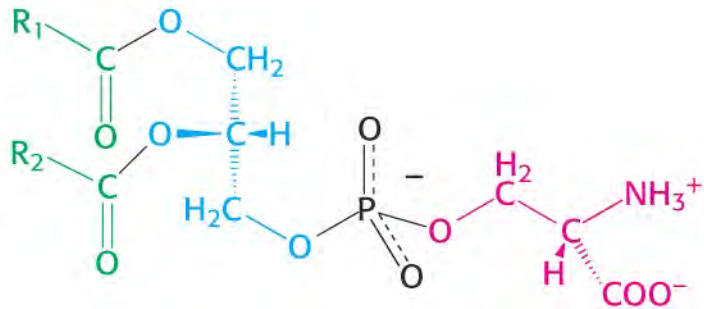


where, X = Na, K, H, Ca, etc.

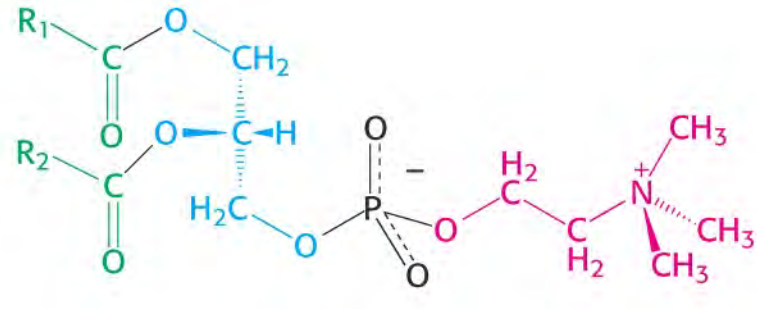


1-hexadecanoyl, 2-(9Z,12Z-octadecadienoyl)-sn-glycero-3-phosphate
(phosphatidic acid)

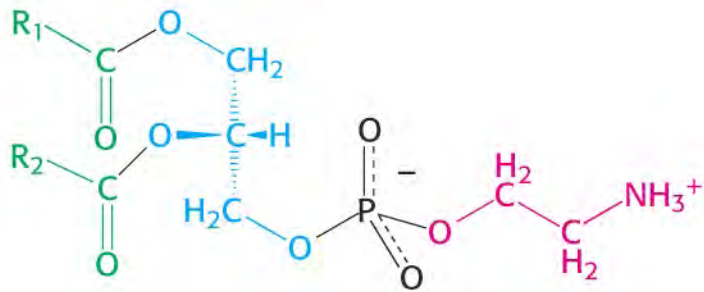
Name of glycerophospholipid	Name of X	Formula of X	Net charge (at pH 7)
Phosphatidic acid	—	— H	- 1
Phosphatidylethanolamine	Ethanolamine	— CH ₂ —CH ₂ —N ⁺ H ₃	0
Phosphatidylcholine	Choline	— CH ₂ —CH ₂ —N ⁺ (CH ₃) ₃	0
Phosphatidylserine	Serine	— CH ₂ —CH—N ⁺ H ₃ COO ⁻	- 1
Phosphatidylglycerol	Glycerol	— CH ₂ —CH—CH ₂ —OH OH	- 1
Phosphatidylinositol 4,5-bisphosphate	<i>myo</i> -Inositol 4,5-bisphosphate		- 4
Cardiolipin	Phosphatidyl-glycerol		- 2



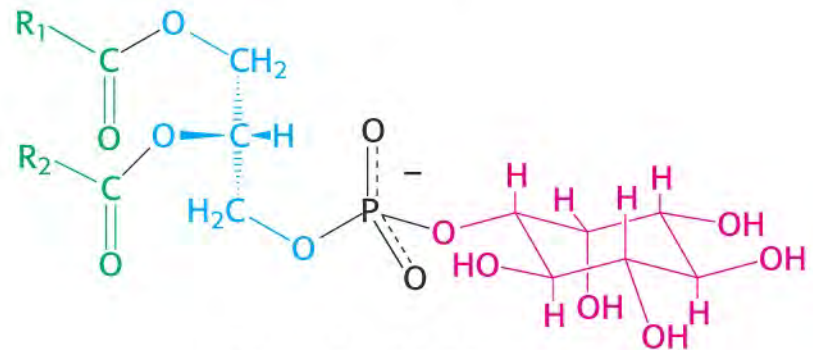
Phosphatidyl serine



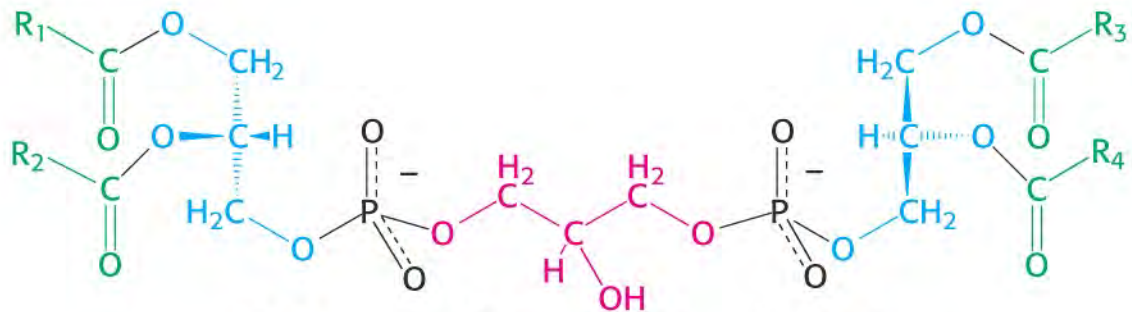
Phosphatidyl choline



Phosphatidyl ethanolamine



Phosphatidyl inositol



Diphosphatidyl glycerol (cardiolipin)



Are You Getting It??



Which properties are characteristic of glycerophospholipids? (*multiple answers*)

- a) They can contain two different fatty acids.
- b) They contain a polar group such as serine.
- c) They can be positively charged.
- d) They are saponifiable.
- e) They are amphipathic.



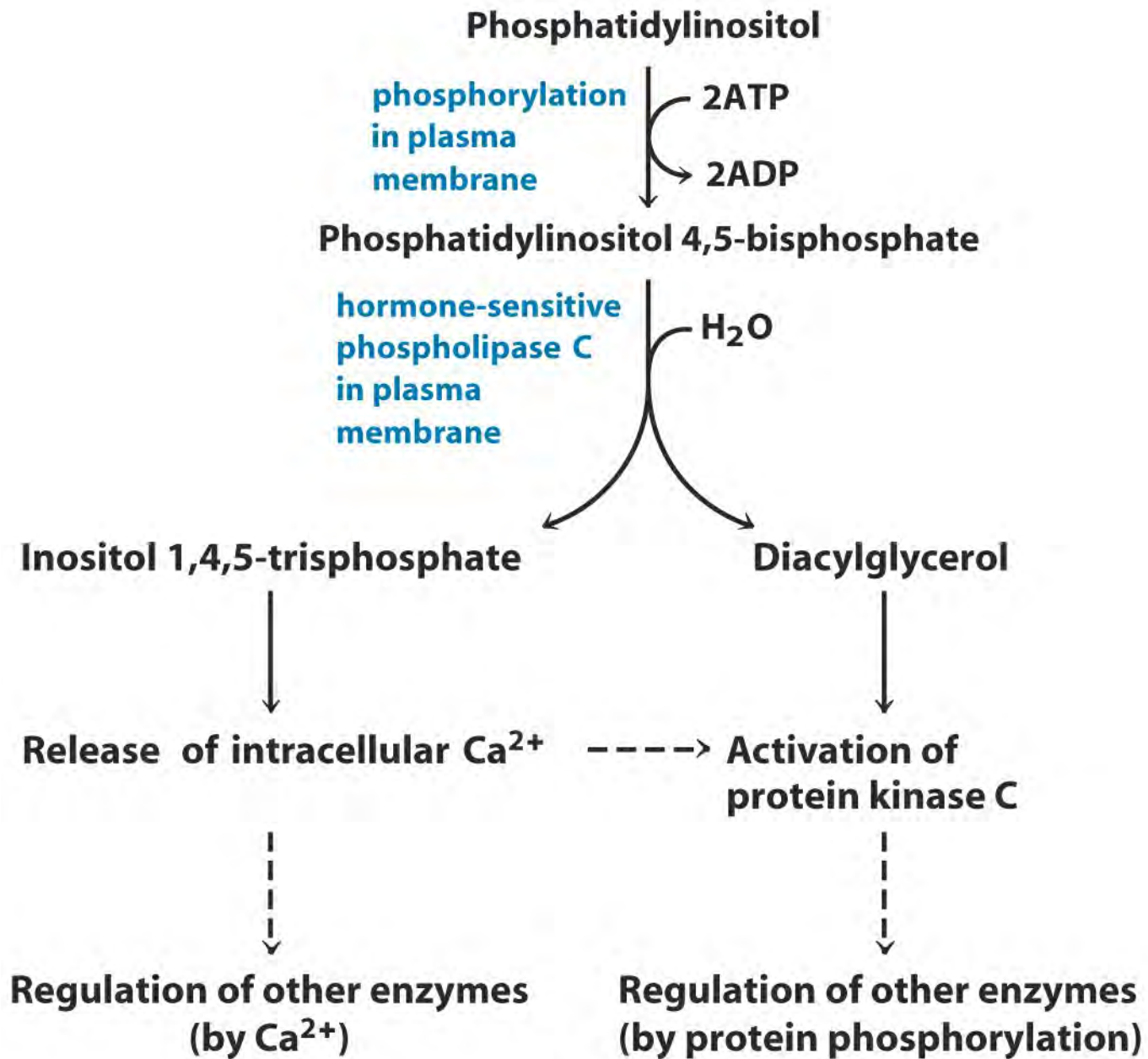
Are You Getting It??



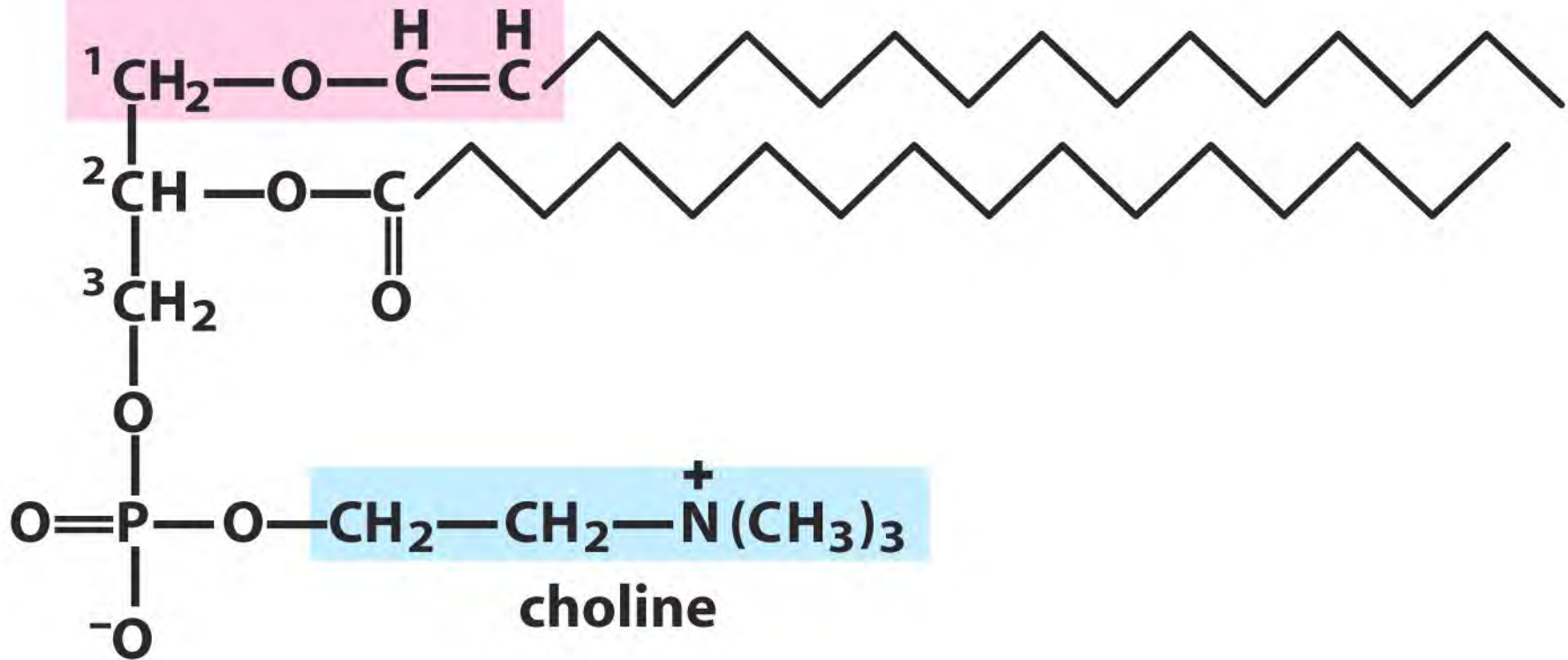
Answer

Which properties are characteristic of glycerophospholipids?

- a) They can contain two different fatty acids.***
- b) They contain a polar group such as serine.***
- c) They can be positively charged.**
- d) They are saponifiable.***
- e) They are amphipathic.***

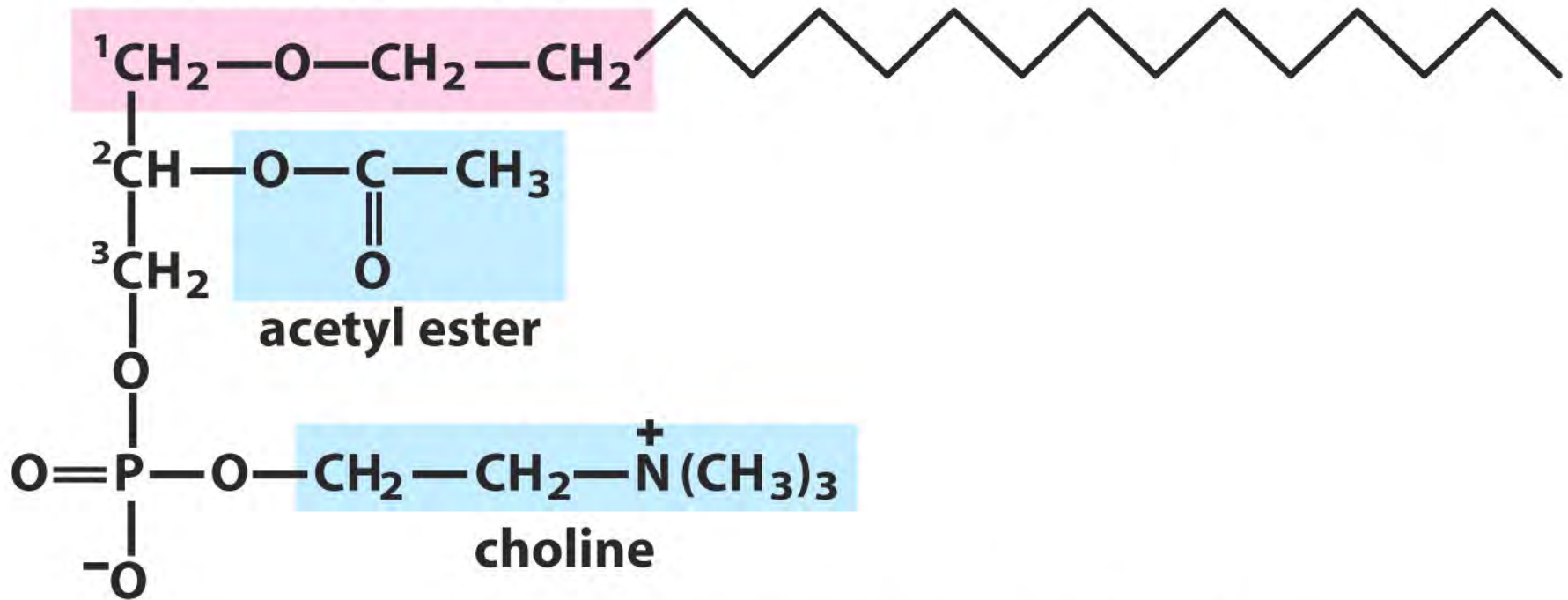


ether-linked alkene



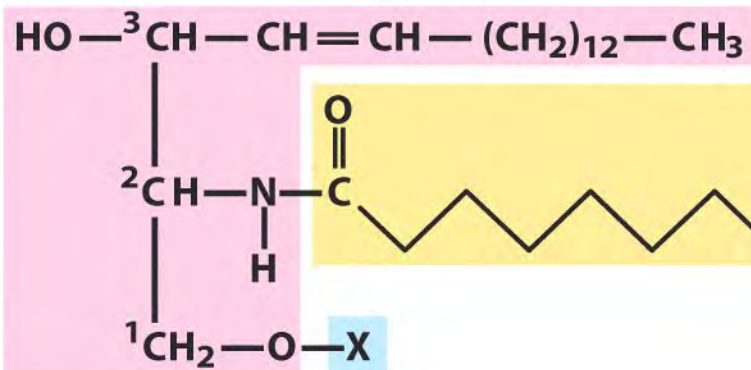
Plasmalogen

ether-linked alkane



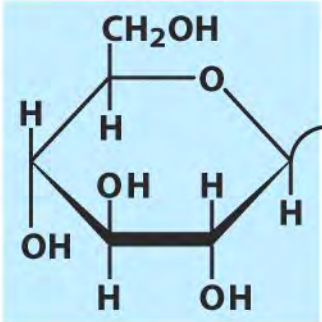
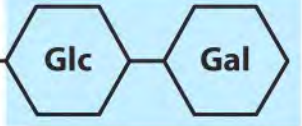
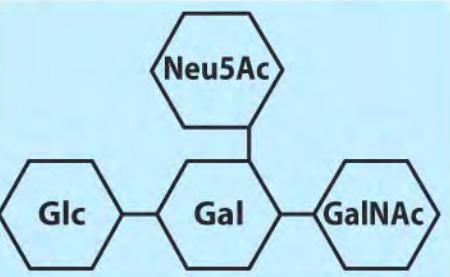
Platelet-activating factor

Sphingosine



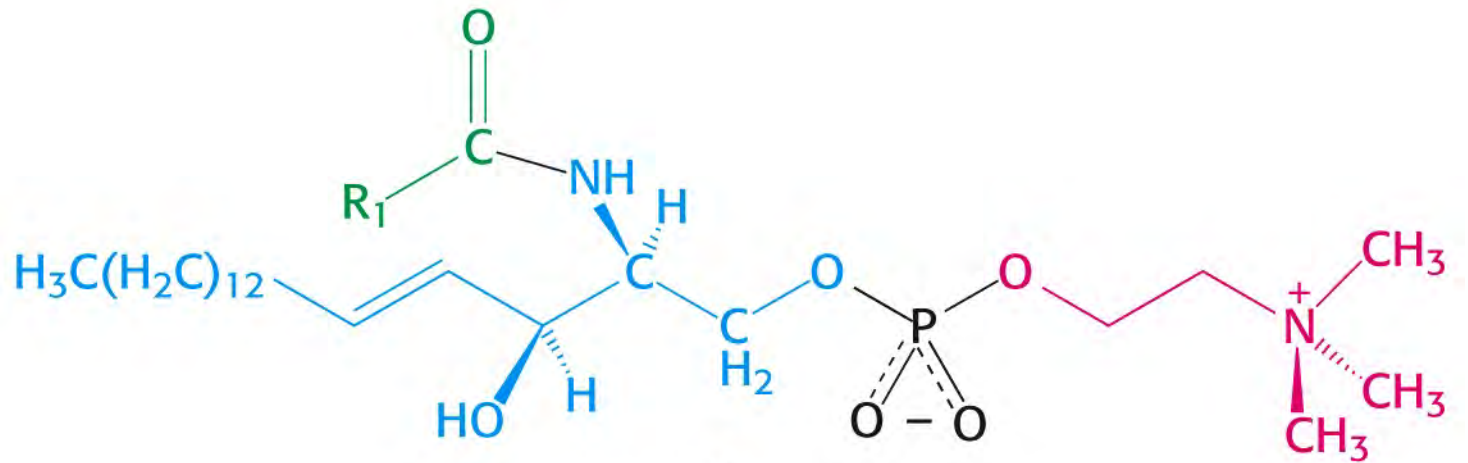
Fatty acid

**Sphingolipid
(general
structure)**

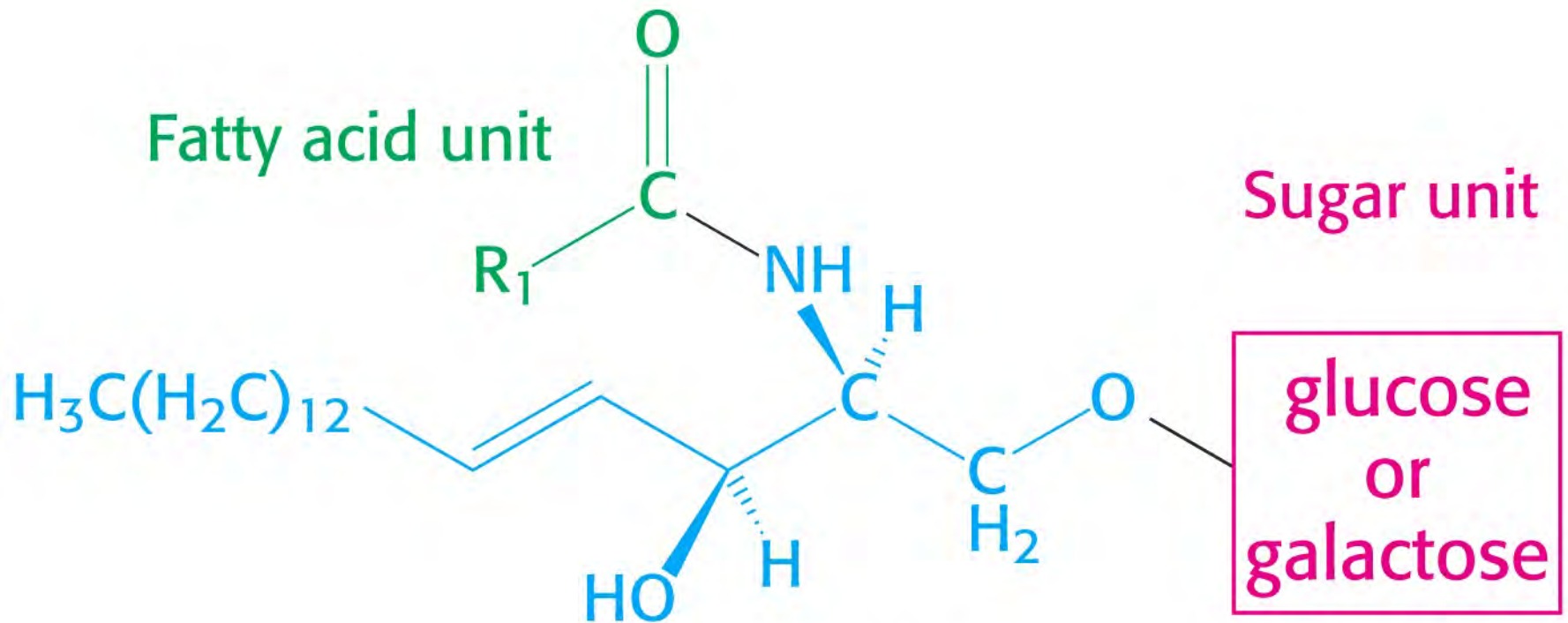
Name of sphingolipid	Name of X	Formula of X
Ceramide	—	— H
Sphingomyelin	Phosphocholine	$\begin{array}{c} \text{O} \\ \parallel \\ \text{— P — O — CH}_2\text{ — CH}_2\text{ — N}^+(\text{CH}_3)_3 \\ \\ \text{O}^- \end{array}$
Neutral glycolipids Glucosylcerebroside	Glucose	
Lactosylceramide (a globoside)	Di-, tri-, or tetrasaccharide	
Ganglioside GM2	Complex oligosaccharide	



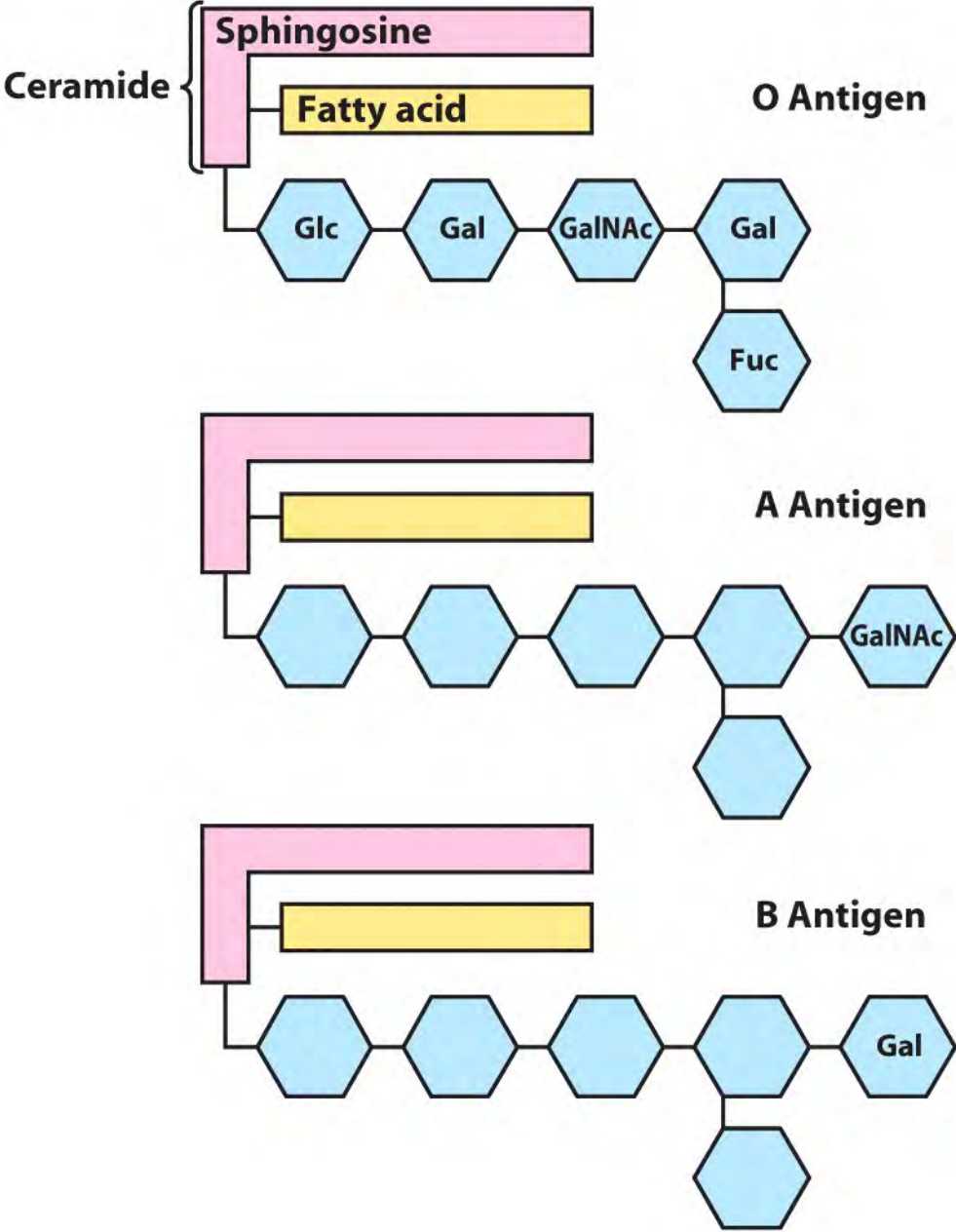
Sphingosine



Sphingomyelin



Cerebroside
(a glycolipid)





Are You Getting It??



Which properties are characteristic of sphingolipids?
(multiple answers)

- a) All sphingolipids contain an amino alcohol.
- b) All sphingolipids contain phosphate.
- c) All sphingolipids contain a fatty acid.
- d) All sphingolipids contain a carbohydrate.
- e) All sphingolipids are amphipathic.
- f) All sphingolipids are saponifiable.



Are You Getting It??

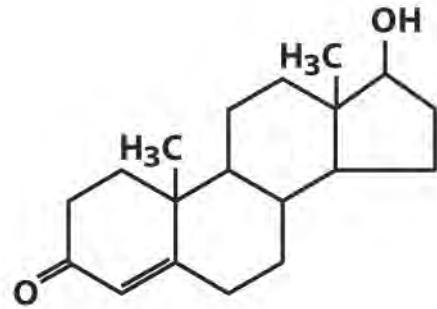


Answer

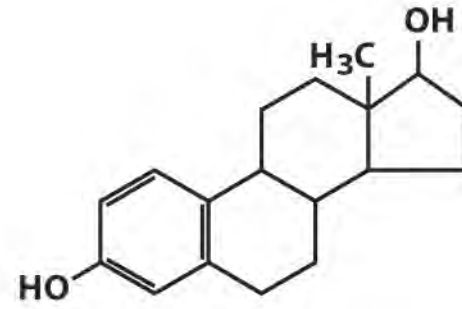
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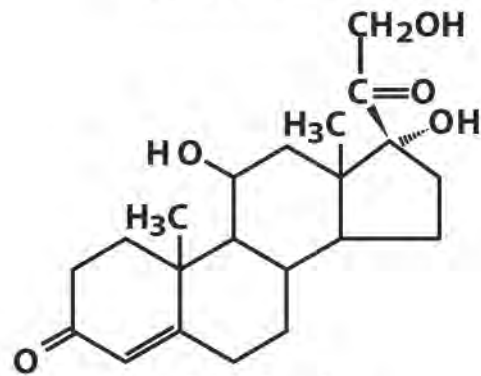




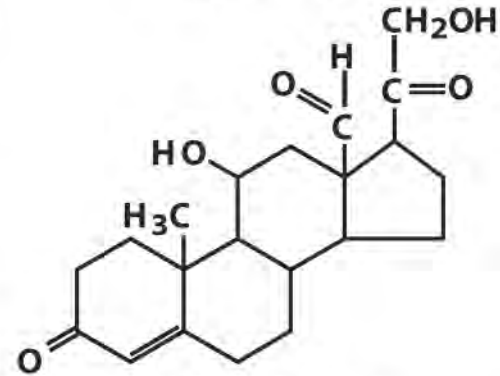
Testosterone



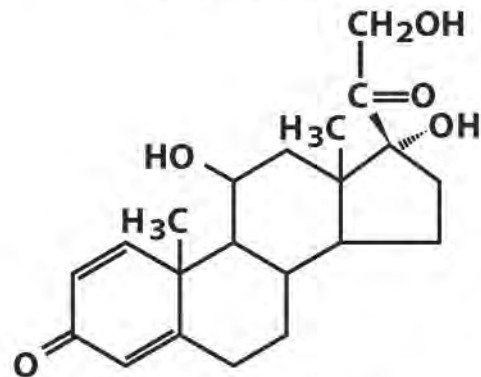
Estradiol



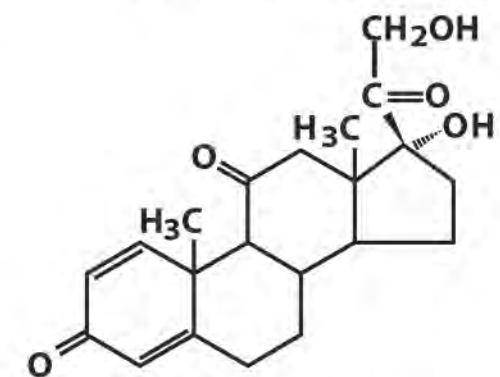
Cortisol



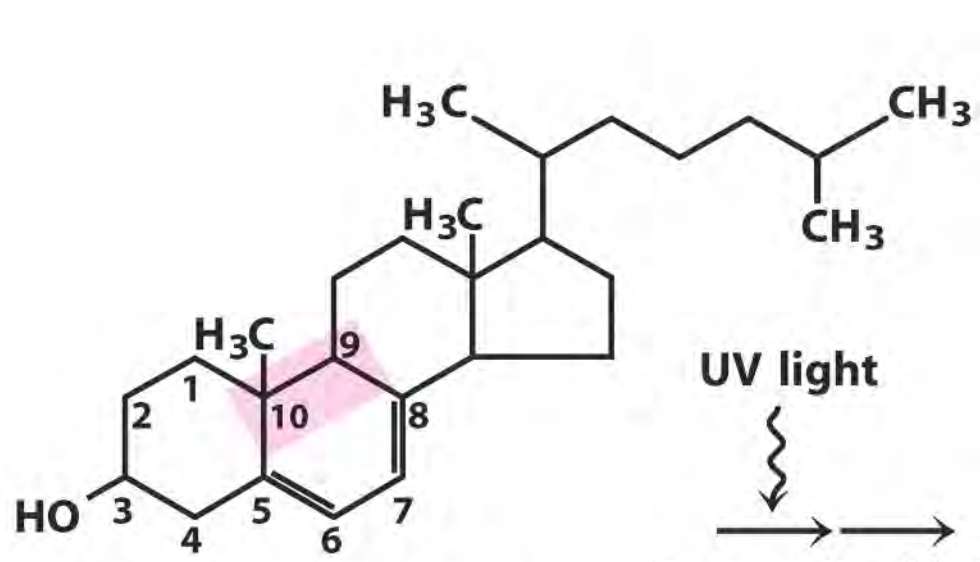
Aldosterone



Prednisolone



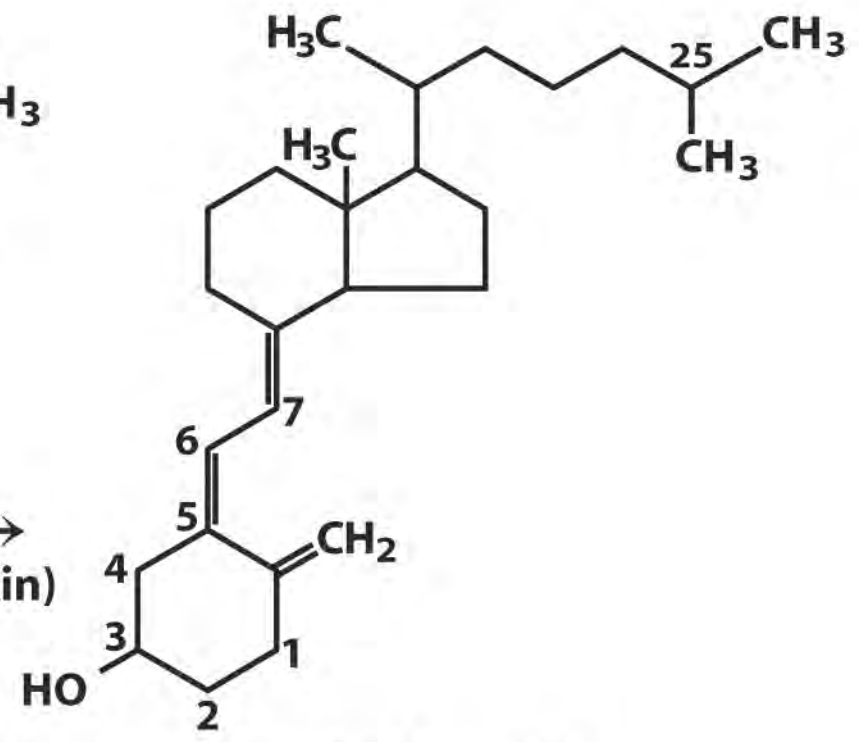
Prednisone



7-Dehydrocholesterol

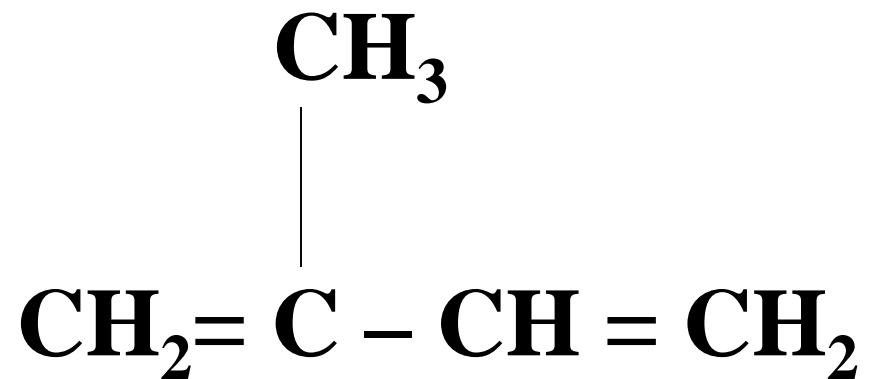
UV light

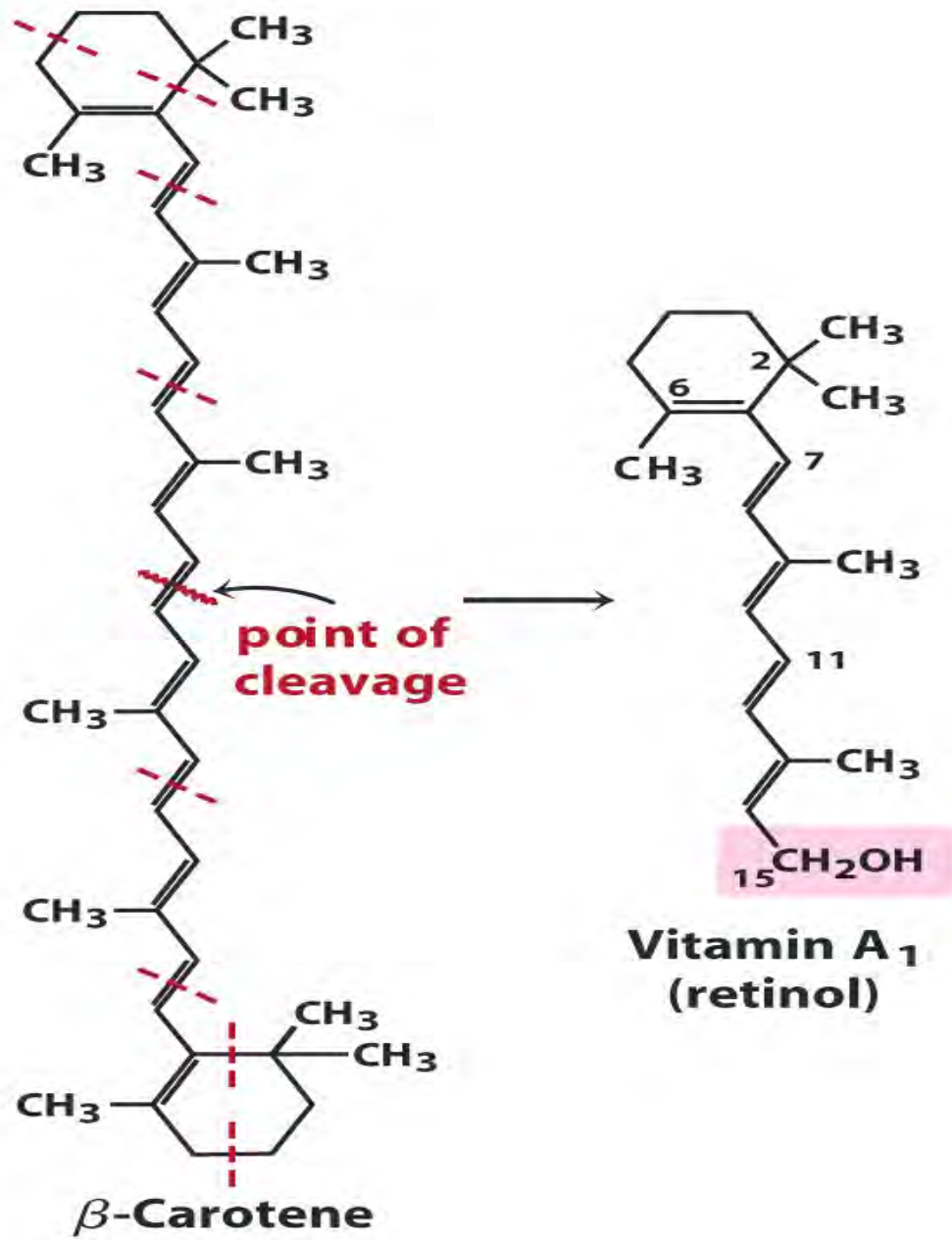
 2 steps (in skin)

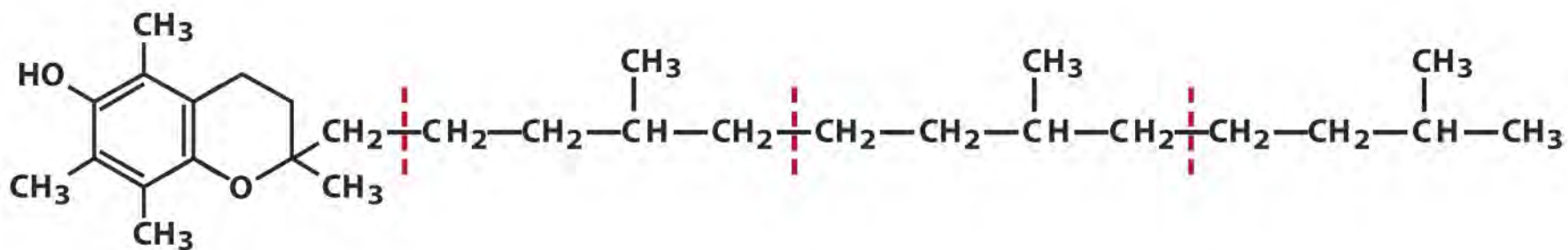


Cholecalciferol (vitamin D₃)

ISOPRENE

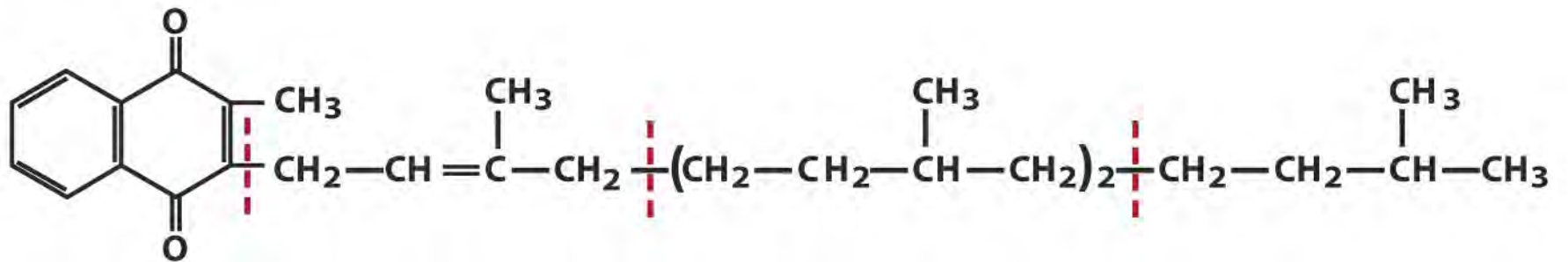






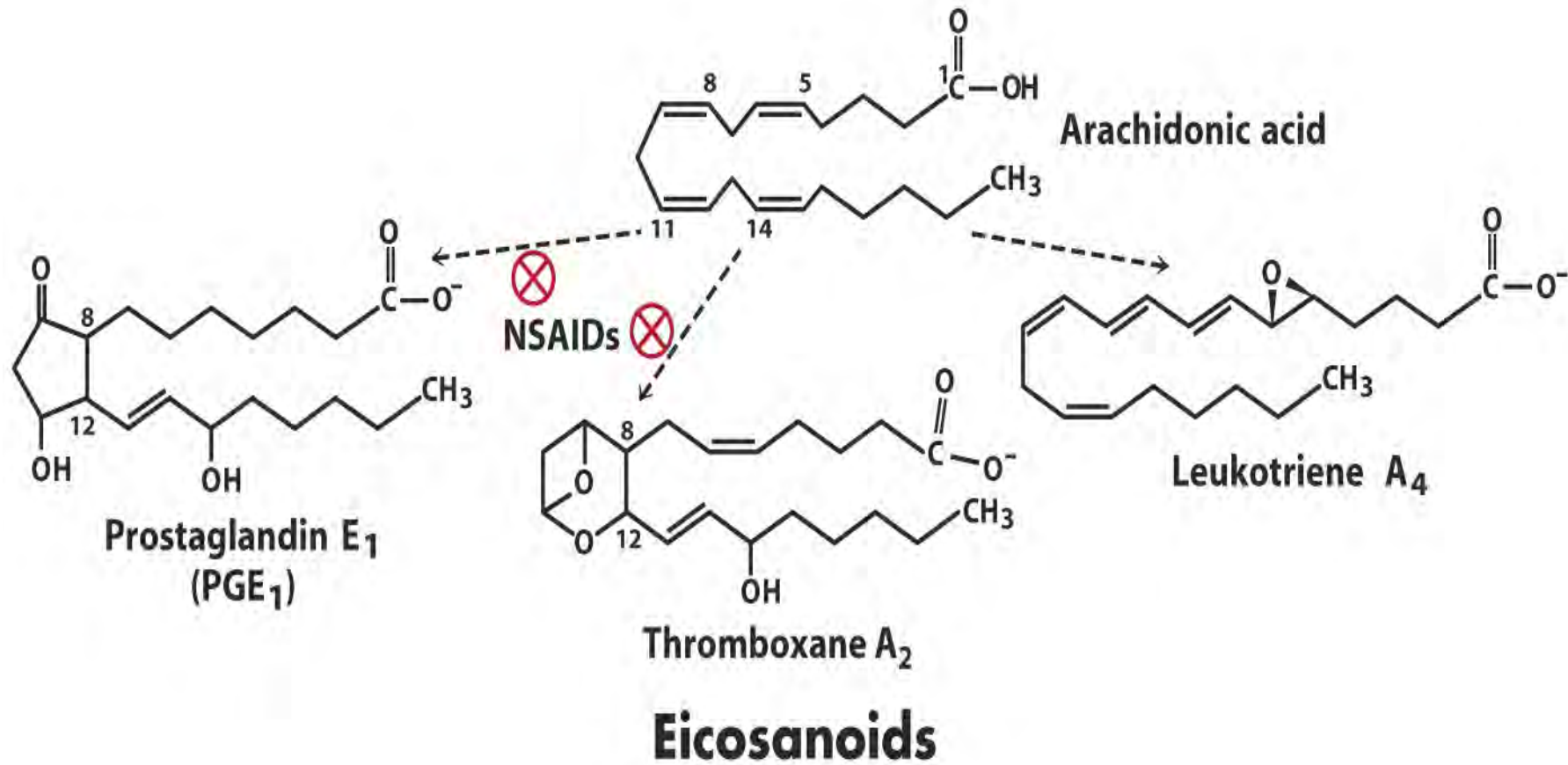
(a)

Vitamin E: an antioxidant



(b)

**Vitamin K₁: a blood-clotting
cofactor (phylloquinone)**





Are You Getting It??



Which characteristics can be found in **steroids**, **terpenes**, or **eicosanoids**?

- a) They contain ring structures.
- b) They contain a carboxyl group.
- c) They contain isoprene.
- d) They are entirely hydrocarbon.
- e) They are formed from a fatty acid.
- f) They contain a hydroxyl group.



Are You Getting It??



Answer

Which characteristics can be found in **steroids**, **terpenes**, or **eicosanoids**?

- a) They contain ring structures. *all*
- b) They contain a carboxyl group. *eicosanoids*
- c) They contain isoprene. *terpenes, steroids*
- d) They are entirely hydrocarbon. *terpenes*
- e) They are formed from a fatty acid. *eicosanoids*
- f) They contain a hydroxyl group. *all*

**Membrane
bilayer**

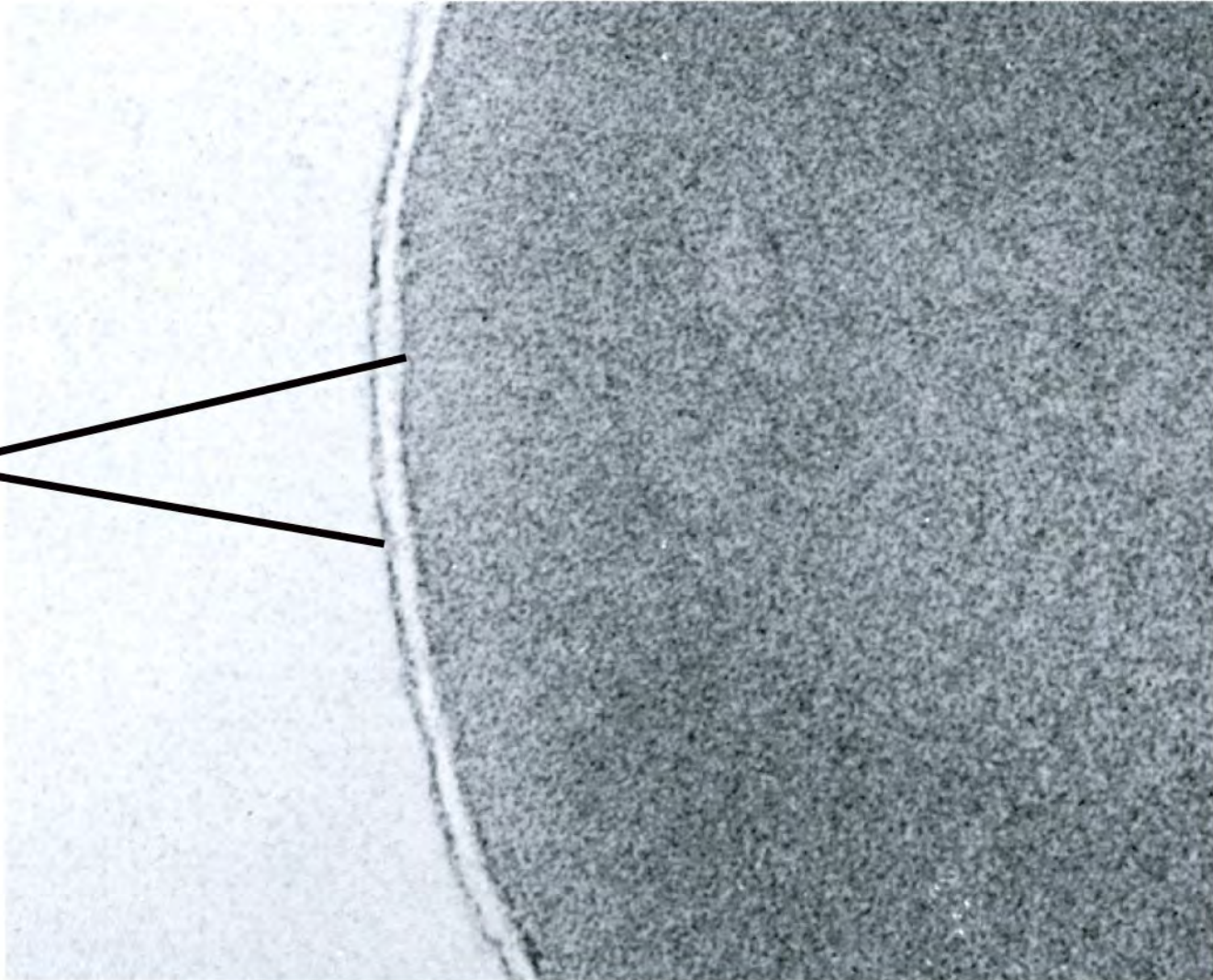
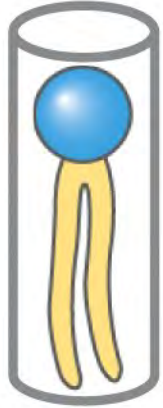


TABLE 11-1 Major Components of Plasma Membranes in Various Organisms*Components (% by weight)*

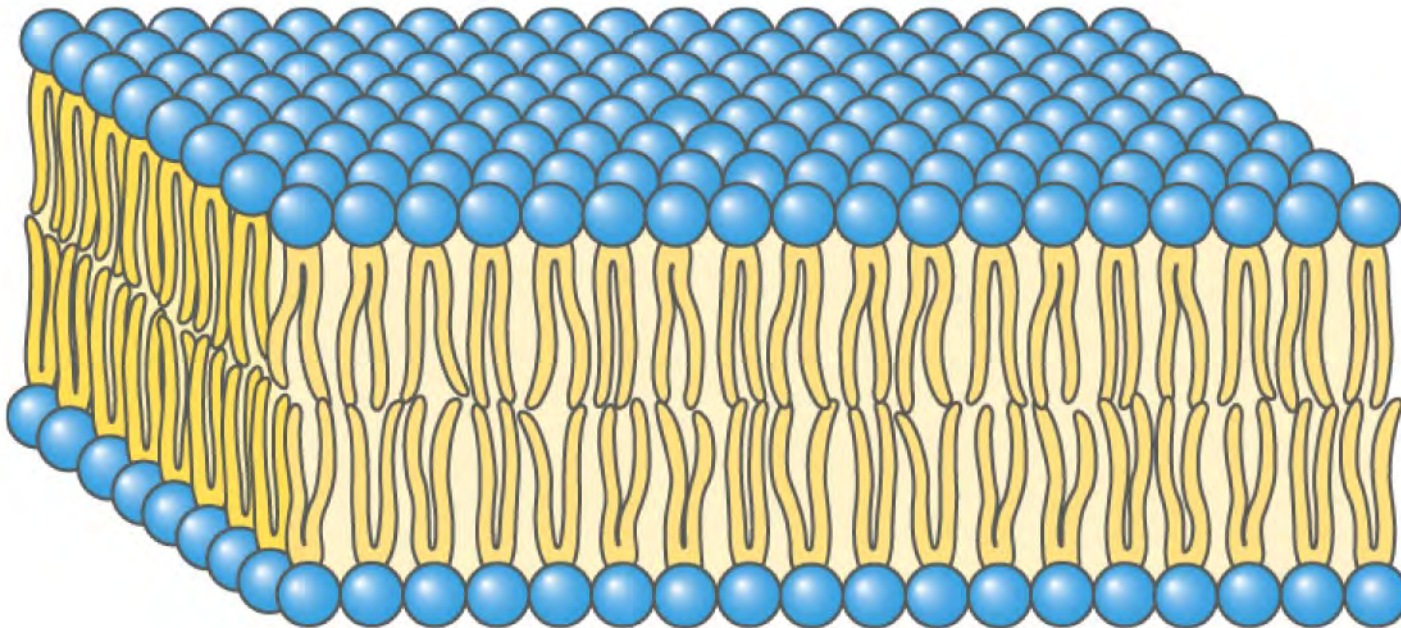
	<i>Protein</i>	<i>Phospholipid</i>	<i>Sterol</i>	<i>Sterol type</i>	<i>Other lipids</i>
Human myelin sheath	30	30	19	Cholesterol	Galactolipids, plasmalogens
Mouse liver	45	27	25	Cholesterol	—
Maize leaf	47	26	7	Sitosterol	Galactolipids
Yeast	52	7	4	Ergosterol	Triacylglycerols, steryl esters
<i>Paramecium</i> (ciliated protist)	56	40	4	Stigmasterol	—
<i>E. coli</i>	75	25	0	—	—

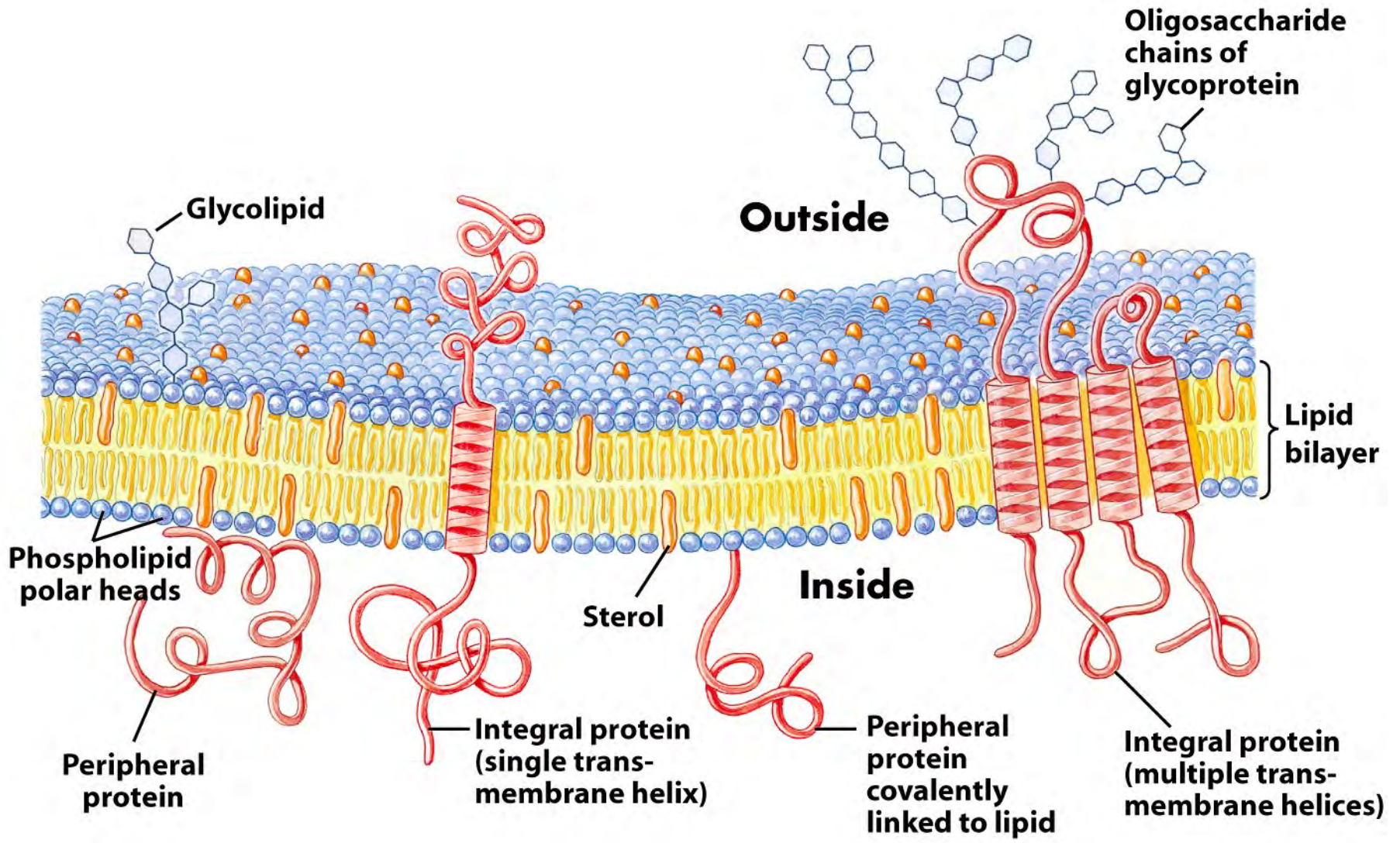
Note: Values do not add up to 100% in every case, because there are components other than protein, phospholipids, and sterol; plants, for example, have high levels of glycolipids.

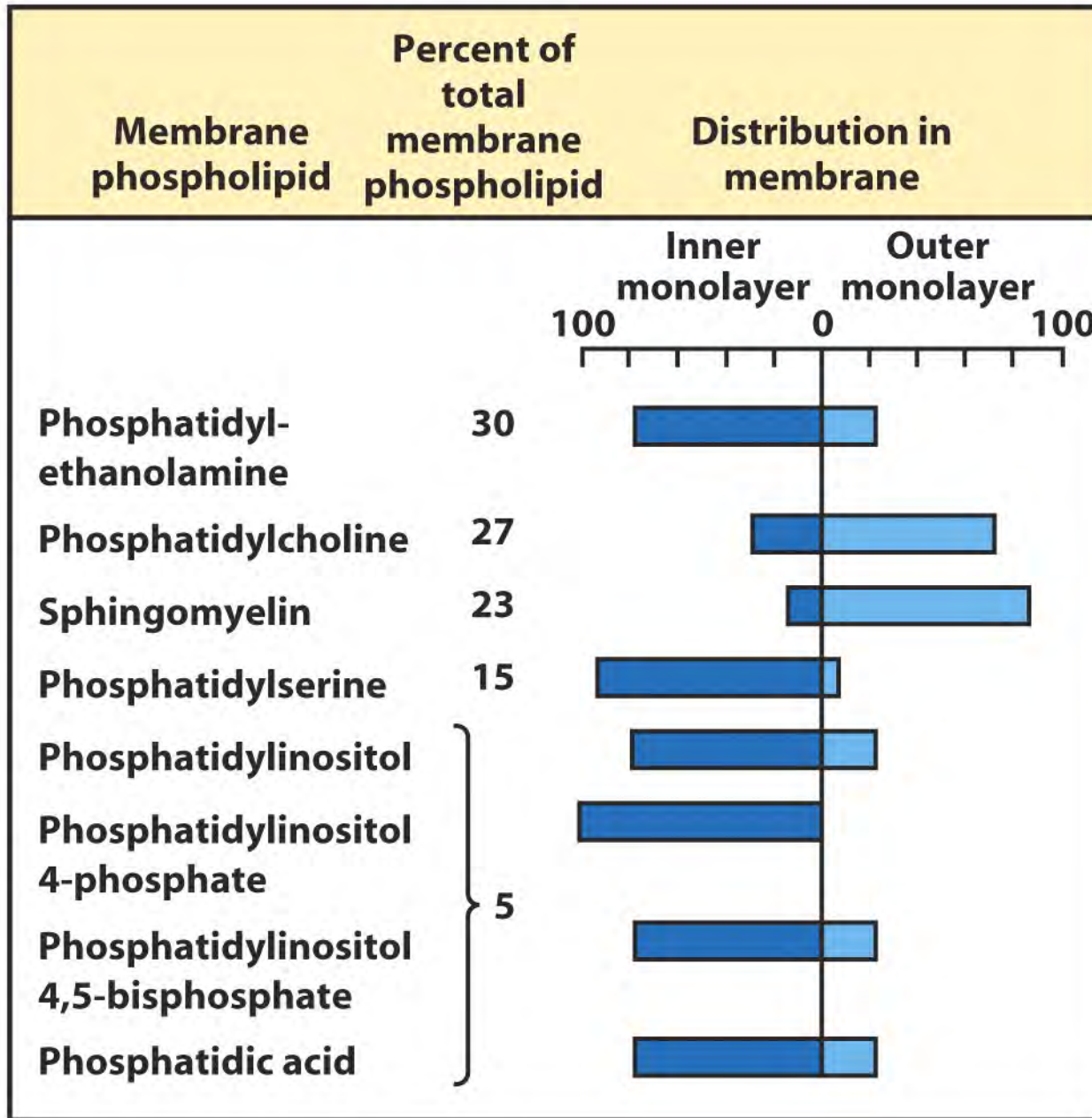
(b) Bilayer



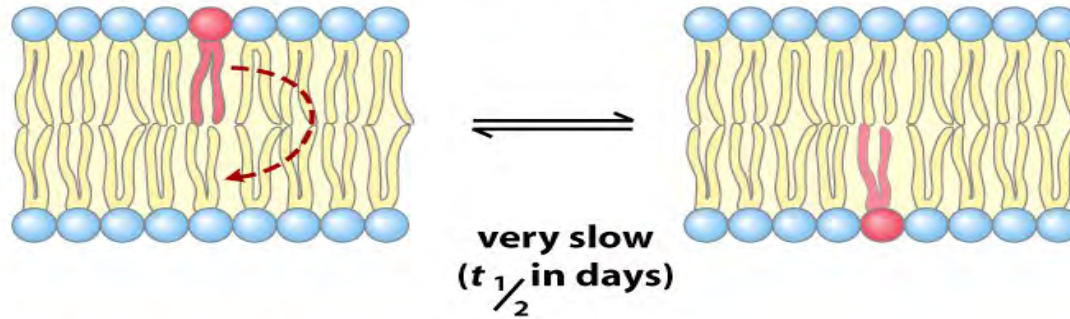
**Individual units are cylindrical
(cross section of head equals that
of side chain)**



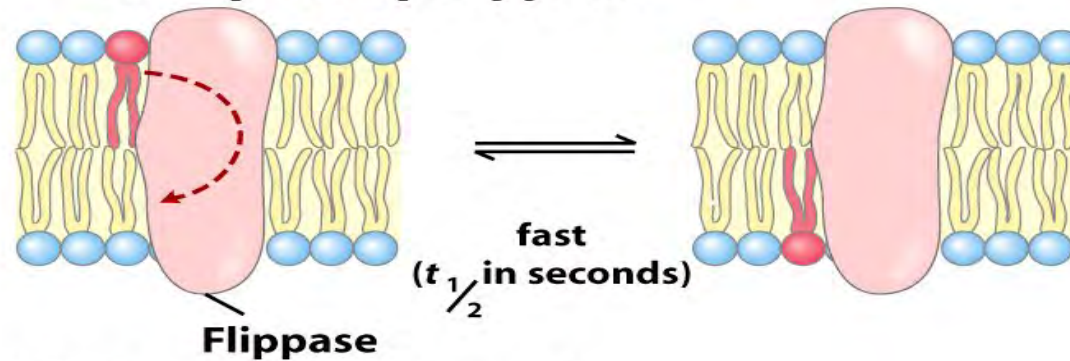




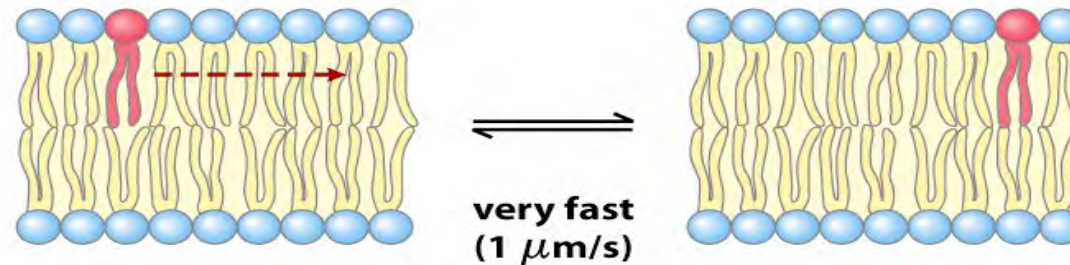
(a) Uncatalyzed transverse ("flip-flop") diffusion



(b) Transverse diffusion catalyzed by flippase

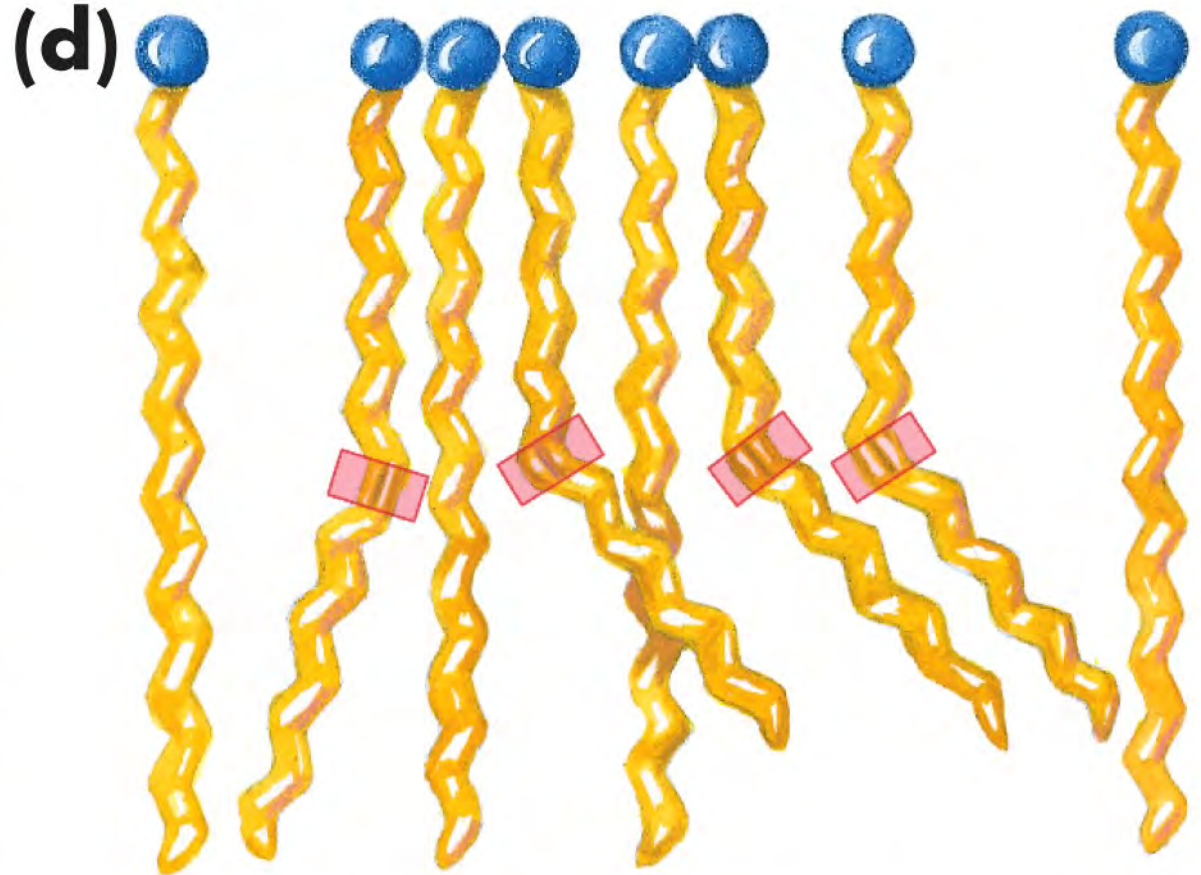


(c) Uncatalyzed lateral diffusion





**Saturated
fatty acids**



**Mixture of saturated and
unsaturated fatty acids**



Are You Getting It??



Which properties are characteristic of membrane lipids?
(multiple answers)

- a) The polar heads are on the membrane surfaces.
- b) Types of lipids include triglycerides and sterols.
- c) The two sides of the membrane are identical.
- d) A lipid molecule can diffuse laterally.
- e) A lipid molecule can flip from one side to the other.



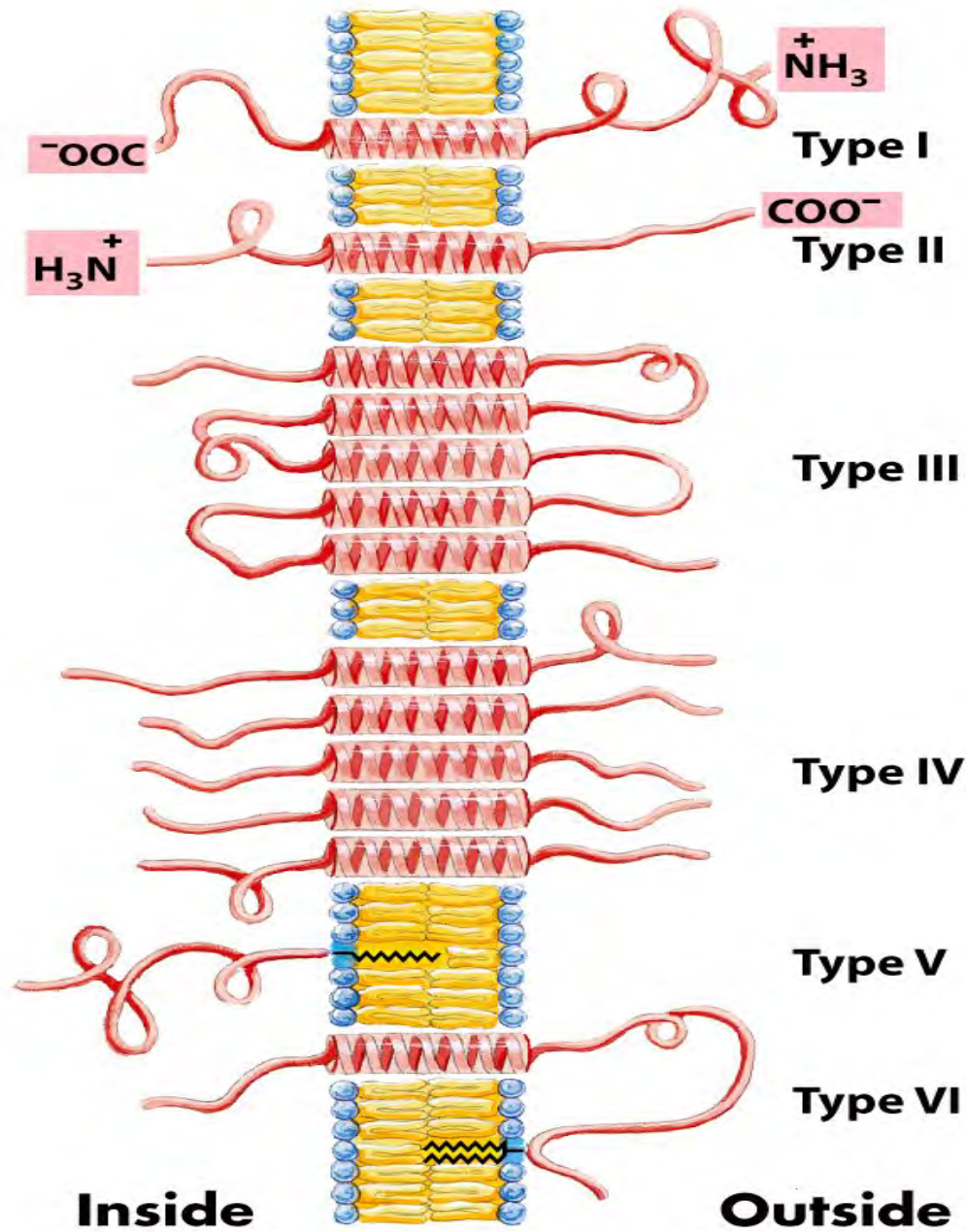
Are You Getting It??

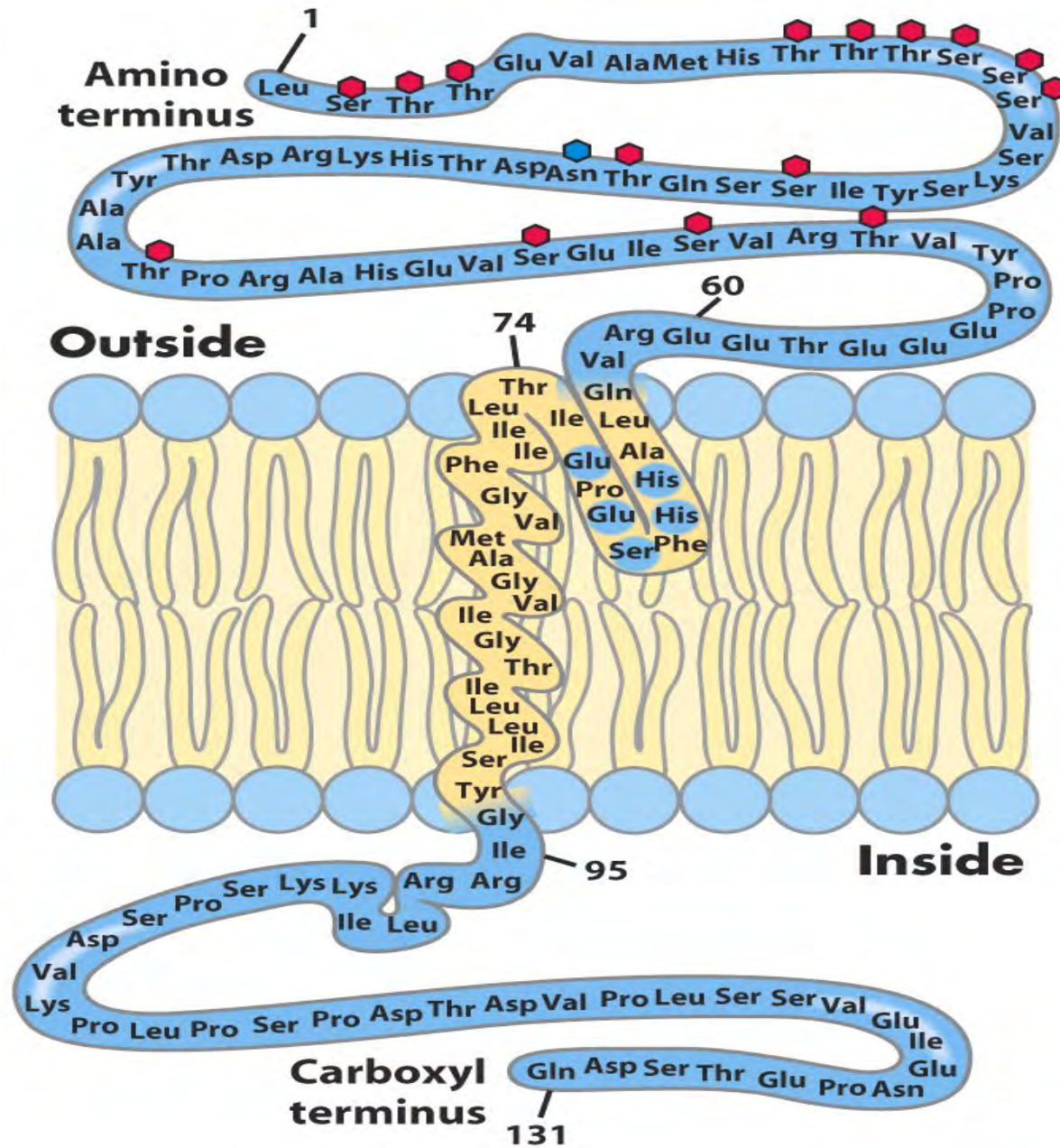


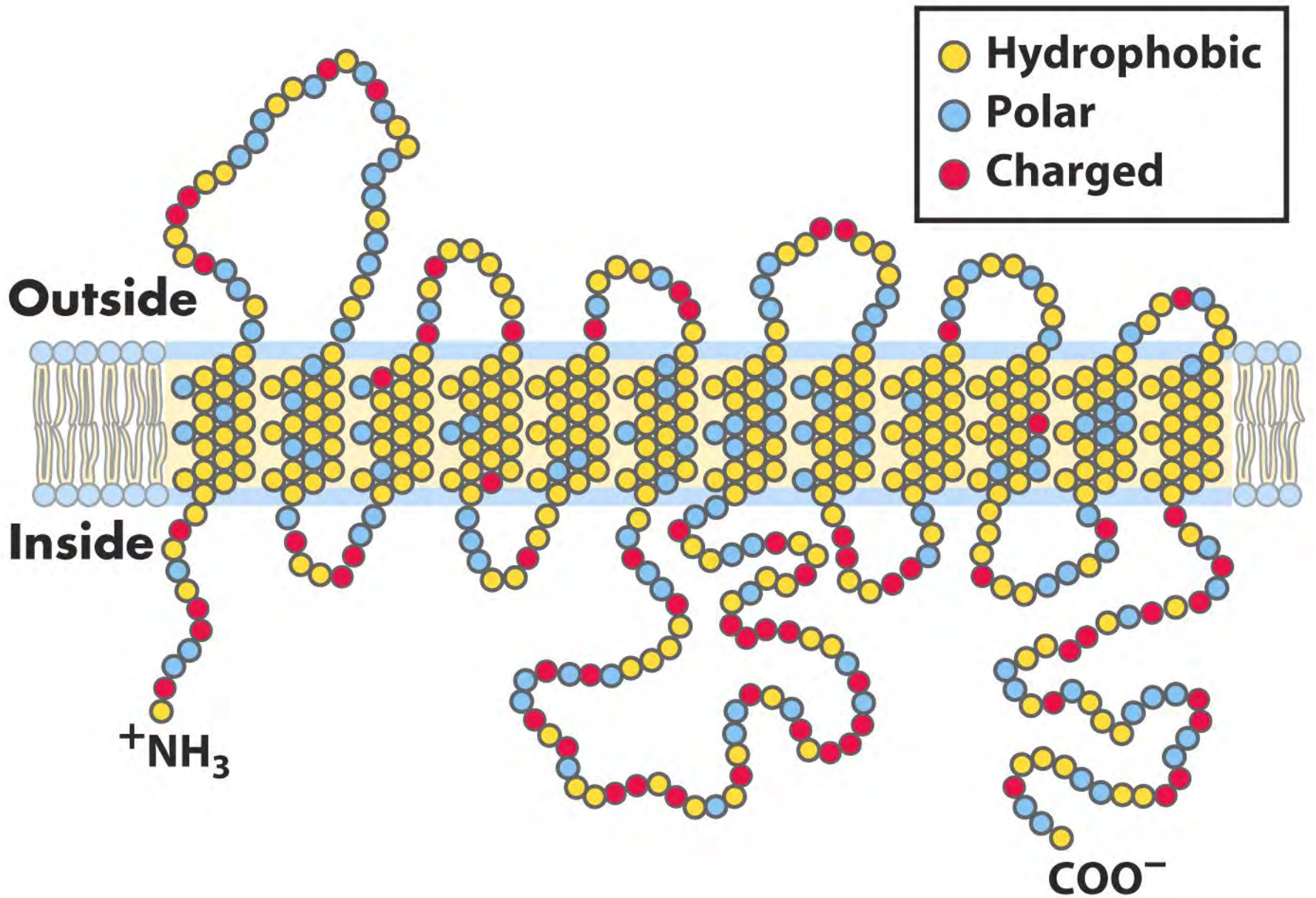
Answer

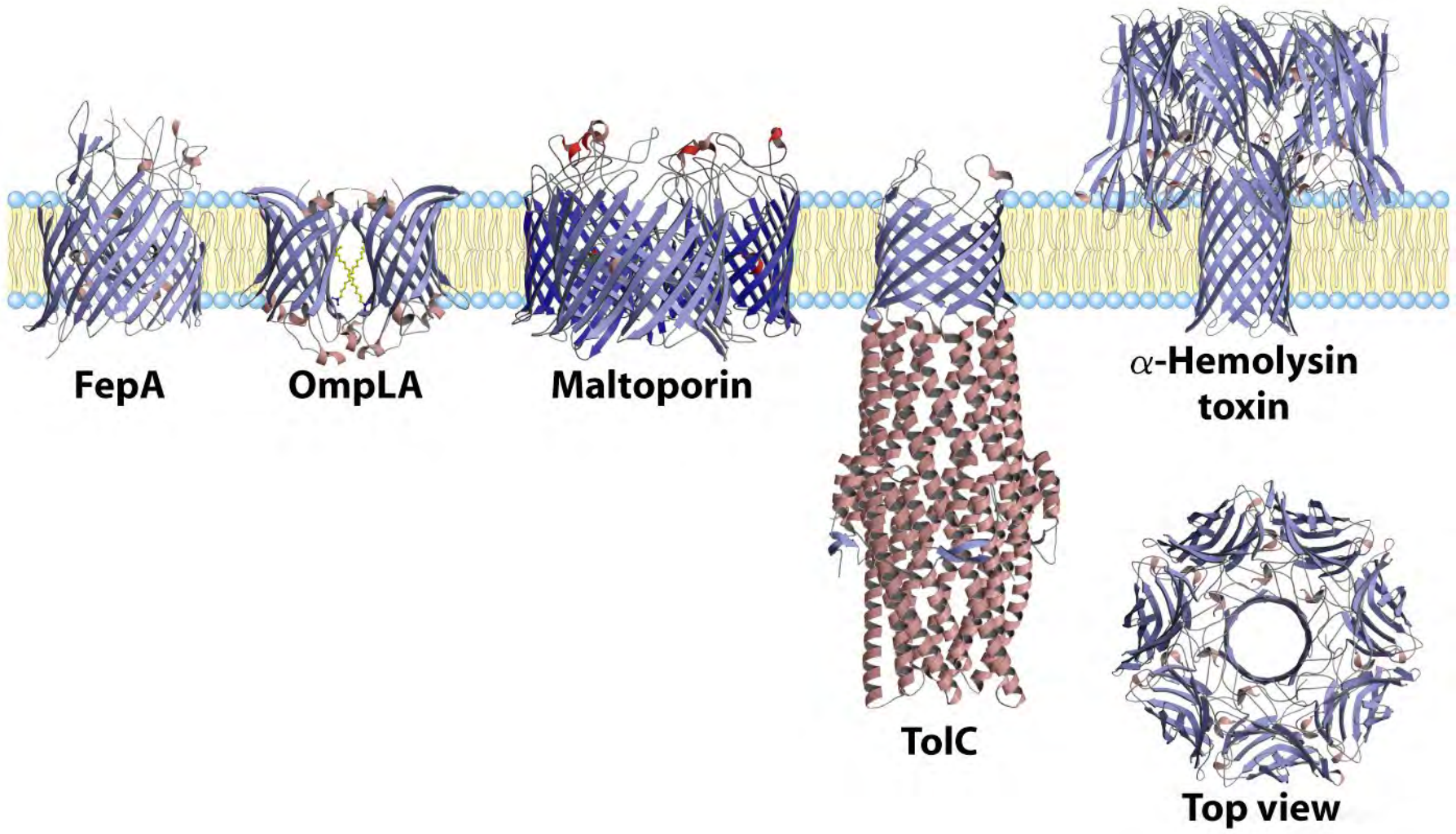
Which properties are characteristic of membrane lipids?

- a) *The polar heads are on the membrane surfaces.***
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- e) *A lipid molecule can flip from one side to the other.***



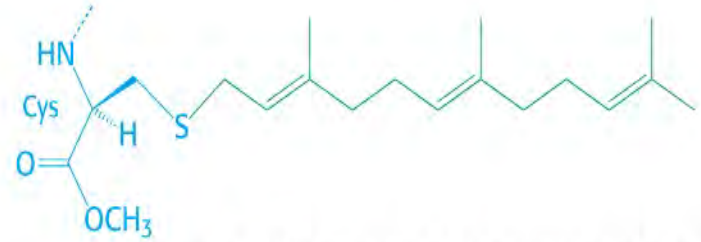




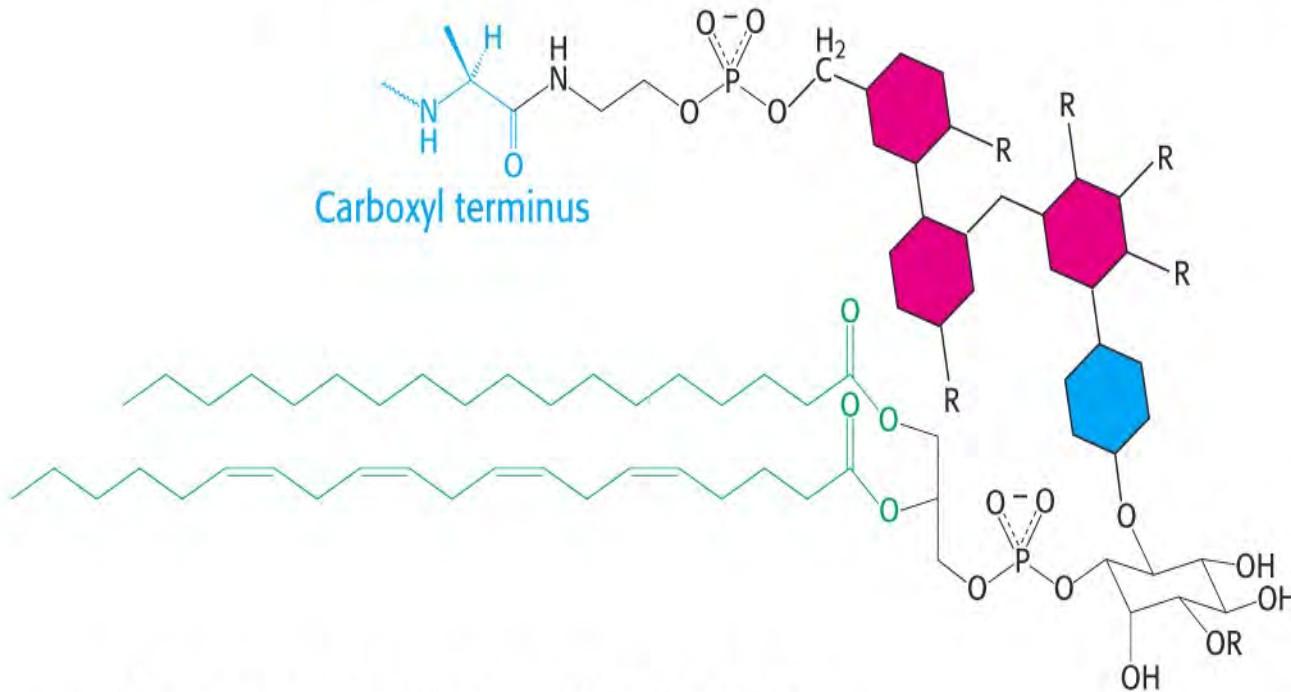




S-Palmitoylcysteine



C-terminal S-farnesylcysteine methyl ester



Glycosyl phosphatidyl inositol (GPI) anchor



Are You Getting It??



Which properties are characteristic of integral membrane proteins? *(multiple answers)*

- a) They contain a large number of hydrophobic R-groups.
- b) They are bound loosely to the membrane surface.
- c) They are covalently linked to fatty acids.
- d) They contain α -helices that cross the membrane.
- e) They are symmetrically oriented in the membrane.



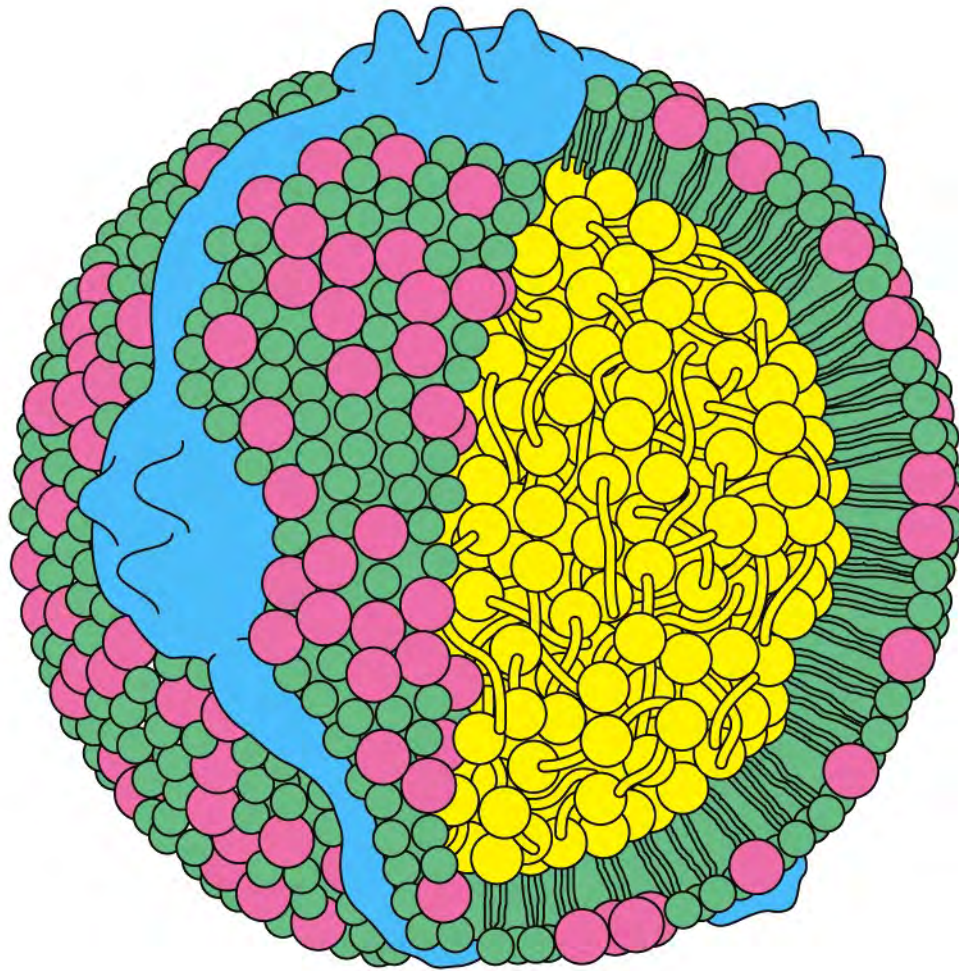
Are You Getting It??



Answer

Which properties are characteristic of integral membrane proteins?

- a) *They contain a large number of hydrophobic R-groups.***
- b) They are bound loosely to the membrane surface.**
- c) They are covalently linked to fatty acids.**
- d) *They contain α -helices that cross the membrane.***
- e) They are symmetrically oriented in the membrane.**



- Unesterified cholesterol
- Phospholipid
- Cholesteryl ester
- Apoprotein B-100

Table 12.2 Composition and Properties of Human Lipoprotein

Lipoprotein Class	Density (g/mL)	Diameter (nm)	Composition (% dry weight)			
			Protein	Cholesterol	Phospho-lipid	Triacyl-glycerol
HDL	1.063-1.21	5-15	33	30	29	8
LDL	1.019-1.063	18-28	25	50	21	4
IDL	1.006-1.019	25-50	18	29	22	31
VLDL	0.95-1.006	30-80	10	22	18	50
Chylomicrons	< 0.95	100-500	1-2	8	7	84

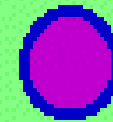
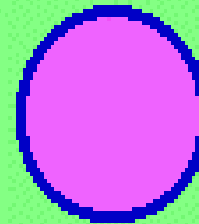
Adapted from Brown, M., and Goldstein, J., 1987. Chapter 315: The hyperlipoproteinemias and other disorders of lipid metabolism. In Braunwald, E., et al., eds., *Harrison's Principles of Internal Medicine*, 11th ed. New York: McGraw-Hill; and Vance, D., and Vance, J., eds., 1985. *Biochemistry of Lipids and Membranes*. Menlo Park, Calif.: Benjamin Cummings.

chylomicron

VLDL

LDL

HDL



Key to molecules:



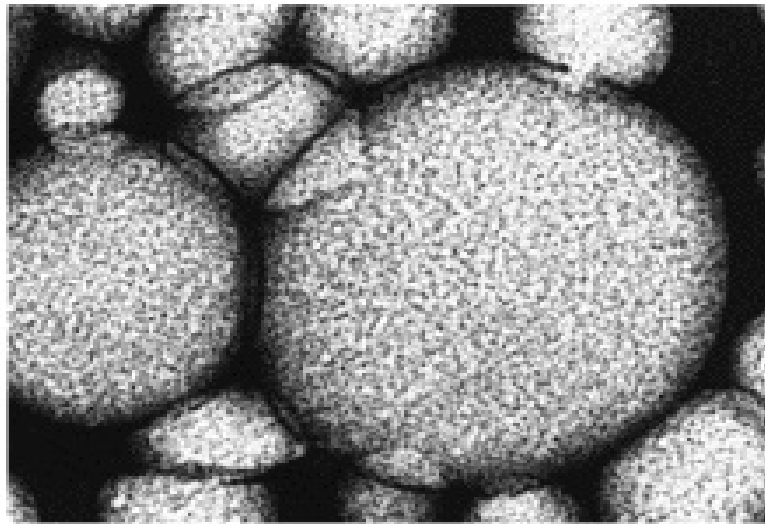
Protein

Lipid scale

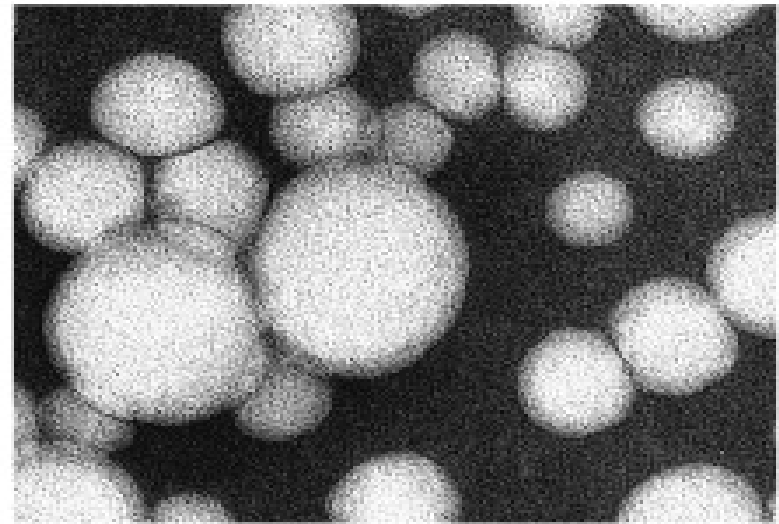


mainly
triglycerides

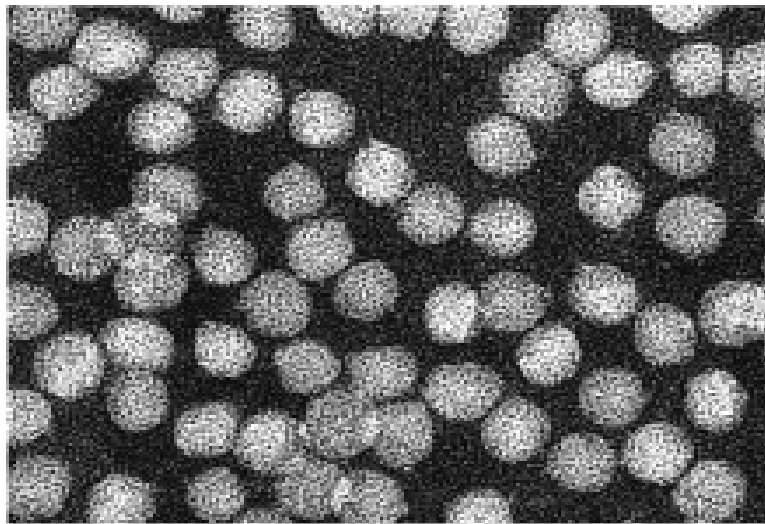
mainly
choles-
terol &
phospho-
lipids



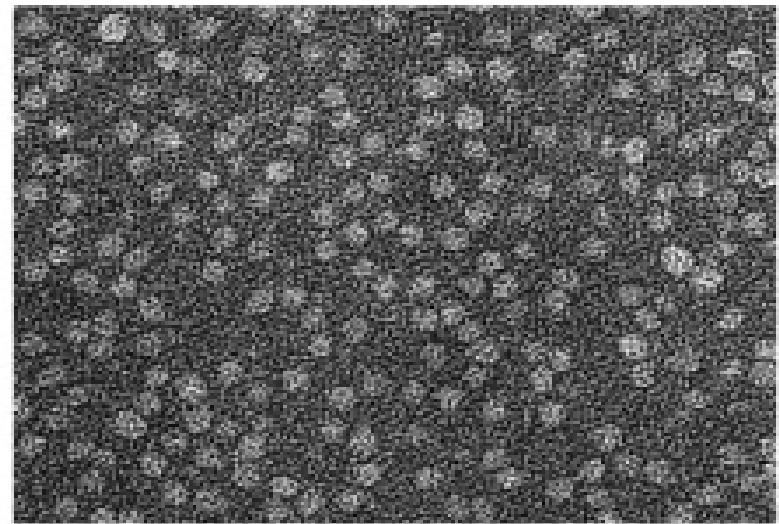
Chylomicrons (50–200 nm diameter)



VLDL (28-70 nm diameter)



LDL (20-25 nm diameter)



HDL (8-11 nm diameter)

(b)