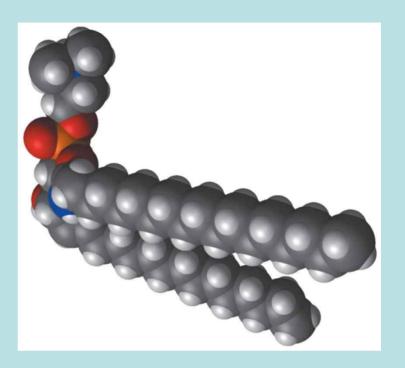
Chapter 10

Lipids





Lipids — Fats or Oils: stored forms of energy — Phospholipids, Sterols: major structural elements of biological membrane

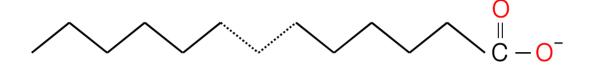
Other lipids: roles as enzyme cofactor, electron carrier, hydrophobic anchor, hormones, intracellular messengers



Storage lipids
Structural lipids in membranes
Lipids as signals, cofactors, and pigments

Storage lipids (derivatives of fatty acids)

Fatty acids: carboxylic acids with hydrocarbon chains (C_4 to C_{36})



Saturated fatty acids Unsaturated fatty acids

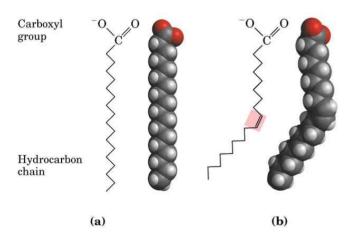
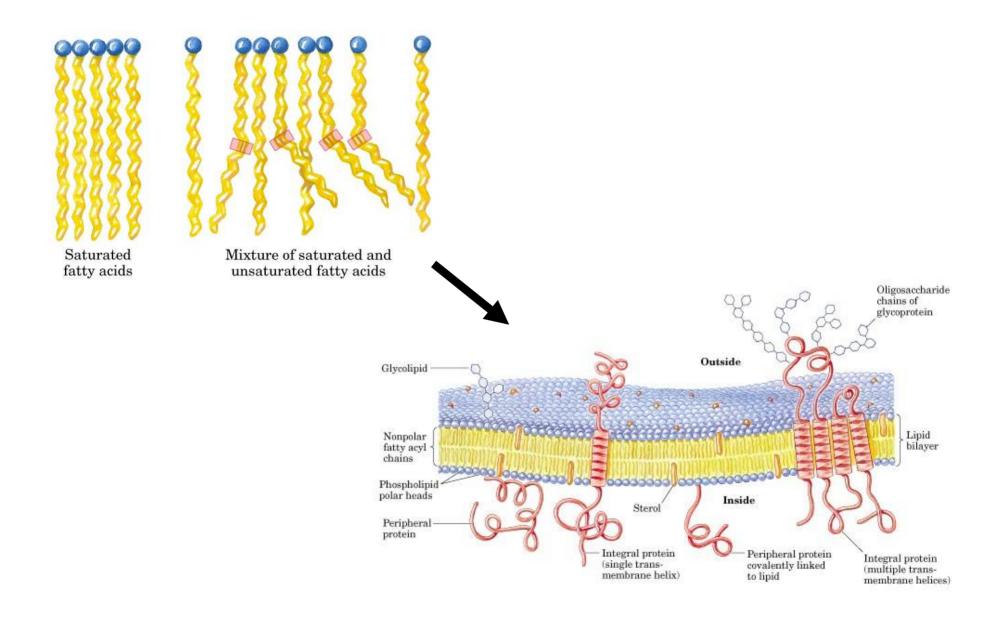


TABLE 10-1 Some Naturally Occurring Fatty Acids: Structure, Properties, and Nomenclature						
Carbon			Common name	Melting	(mg/g	solvent)
skeleton	Structure*	Systematic name [†]	(derivation)	point (°C)	Water	Benzene
12:0	$\mathrm{CH_{3}(CH_{2})_{10}COOH}$	n-Dodecanoic acid	Lauric acid (Latin <i>laurus</i> , "laurel plant")	44.2	0.063	2,600
14:0	CH ₃ (CH ₂) ₁₂ COOH	n-Tetradecanoic acid	Myristic acid (Latin <i>Myristica</i> , 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	СН ₃ (СН ₂) ₁₆ СООН	n-Octadecanoic acid	Stearic acid (Greek stear, "hard fat")	69.6	0.0034	124
20:0	СН ₃ (СН ₂) ₁₈ СООН	n-Eicosanoic acid	Arachidic acid (Latin <i>Arachis</i> , legume genus)	76.5		
24:0	CH ₃ (CH ₂) ₂₂ COOH	n-Tetracosanoic acid	Lignoceric acid (Latin <i>lignum</i> , "wood" + cera, "wax")	86.0		
$16:1(\Delta^9)$	CH ₃ (CH ₂) ₅ CH=CH(CH ₂) ₇ COOH	cis-9-Hexadecenoic acid	Palmitoleic acid	1-0.5		
$18:1(\Delta^{9})$	$CH_3(CH_2)_7CH = CH(CH_2)_7COOH$	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	lpha-Linolenic acid	-11		
$20:4(\Delta^{5,8,11,14})$	$\mathrm{CH_3(CH_2)_4CH} = \mathrm{CHCH_2CH} =$ $\mathrm{CHCH_2CH} = \mathrm{CHCH_2CH} =$ $\mathrm{CH(CH_2)_3COOH}$	cis-,cis-,cis-5,8,11,14- lcosatetraenoic acid	Arachidonic acid	-49.5		

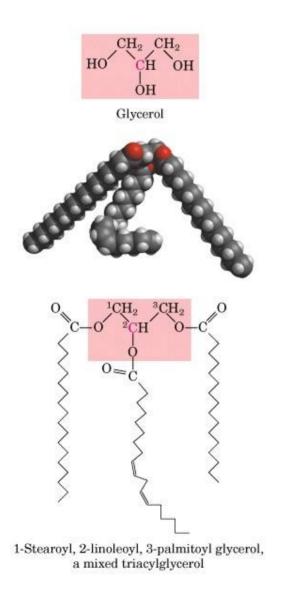
^{*}All acids are shown in their nonionized form. At pH 7, all free fatty acids have an ionized carboxylate. Note that numbering of carbon atoms begins at the carboxyl carbon.

The prefix *n*- indicates the "normal" unbranched structure. For instance, "dodecanoic" simply indicates 12 carbon atoms, which could be arranged in a variety of branched forms; "*n*-dodecanoic" specifies the linear, unbranched form. For unsaturated fatty acids, the configuration of each double bond is indicated; in biological fatty acids the configuration is almost always cis.

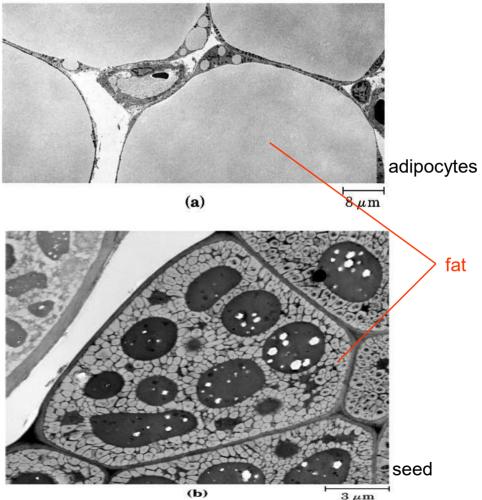
The packing of fatty acids into stable aggregates



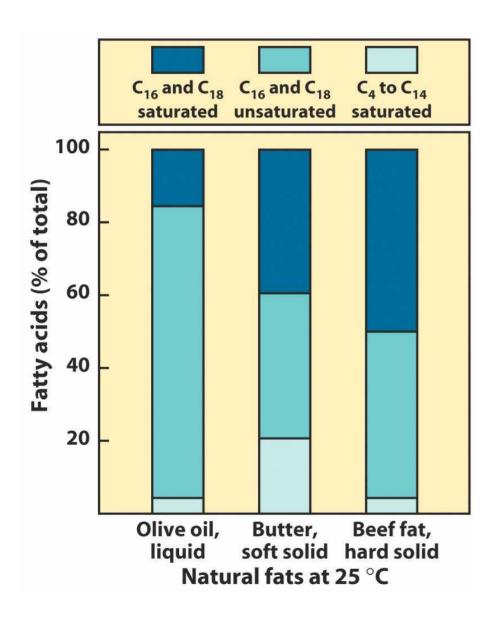
Triacylglycerols (triglycerides, fats)



provide stored energy and insulation (hydrolyzed by lipases)



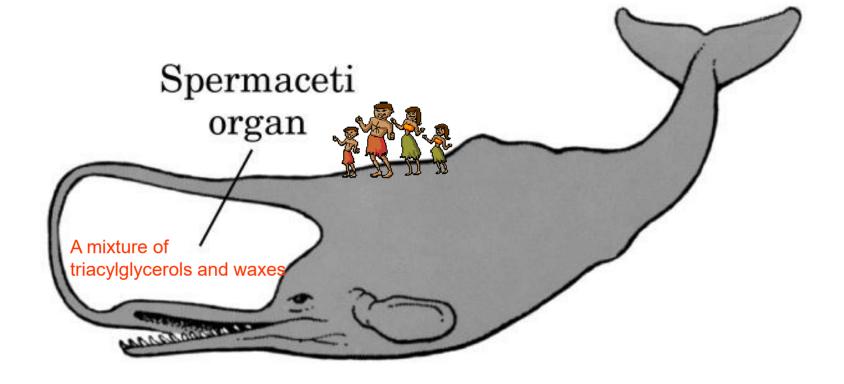
Many food contain triacylglycerol

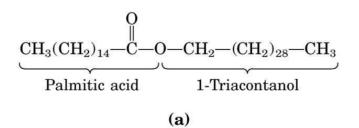


Using triacylglycerol as stored fuels:

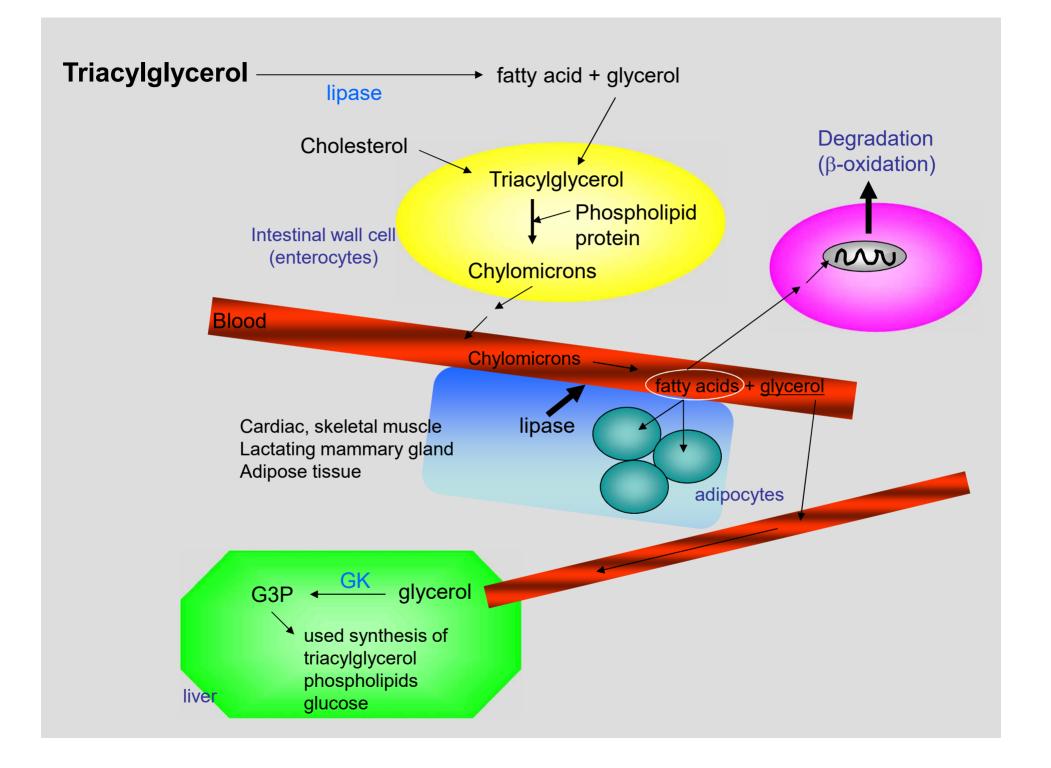
- (1) More reduced than those of sugars
- (2) Hydrophobic and unhydrated

Sperm whale

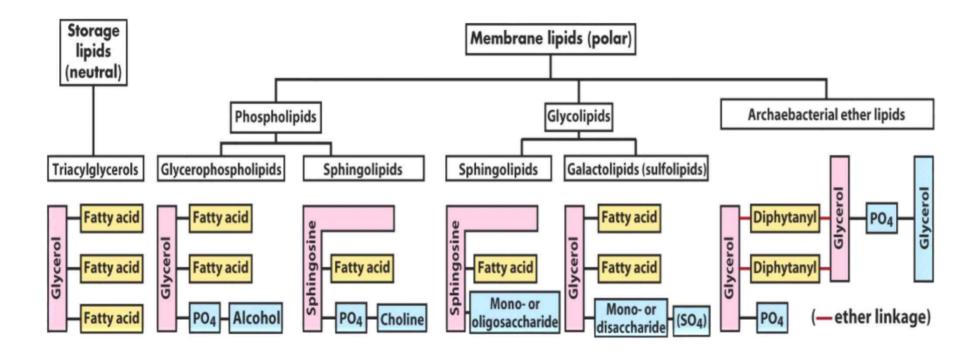






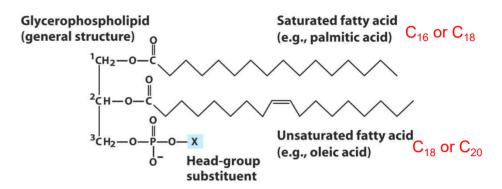


Structural lipids in membrane



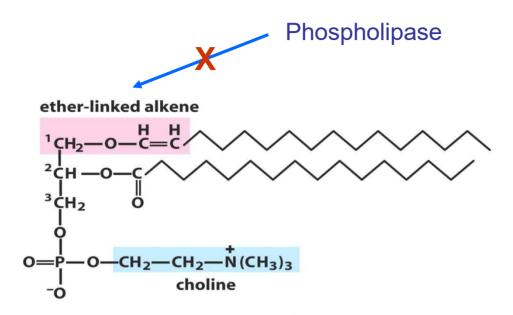
Glycerophospholipids (phosphoglycerides)

Glycerol 3-Phosphate

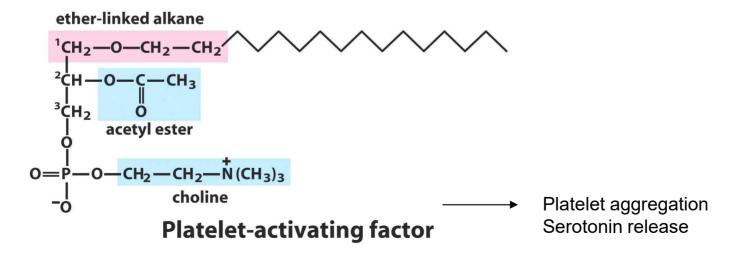


Name of glycerophospholipid	Name of X	Formula of X	Net charge (at pH 7)
Phosphatidic acid	_	— н	- 1
Phosphatidylethanolamine	Ethanolamine	— CH ₂ —CH ₂ —NH ₃	0
Phosphatidylcholine	Choline	$-CH_2-CH_2-N(CH_3)_3$	0
Phosphatidylserine	Serine	—сн ₂ —сн—йн₃ соо−	- 1
Phosphatidylglycerol	Glycerol	— СН ₂ —СН —СН ₂ —ОН ОН	- 1
Phosphatidylinositol 4,5-bisphosphate	<i>myo-</i> Inositol 4,5- bisphosphate	H O P OH H 4 H OH HO O P 11 OH HO O P	- 4
Cardiolipin	Phosphatidyl- glycerol	— СН ₂ СНОН О СН ₂ —О—Р—О—СН ₂ 0	- 2
		O- O O O O O O O O O O O O O O O O O O	

Some phospholipids have ether-linked fatty acids



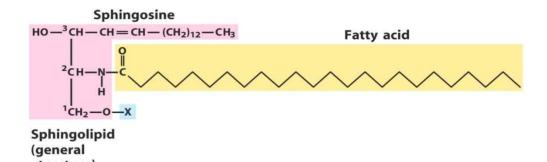
Plasmalogen (~ 50% of heart phospholipids in vertebrate)

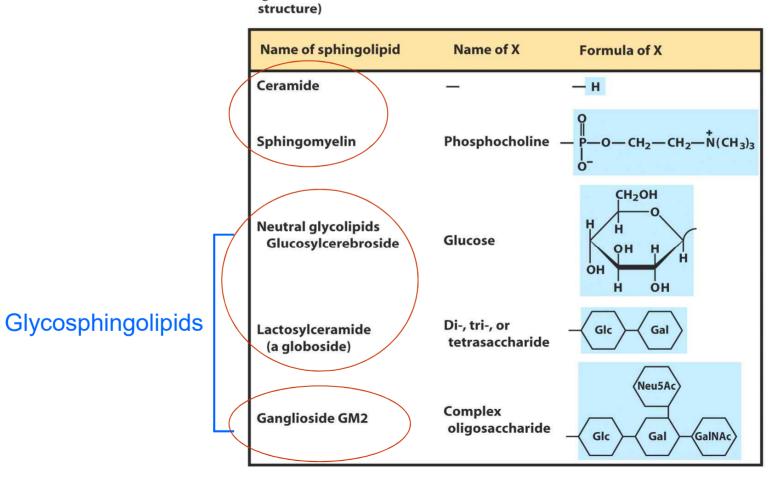


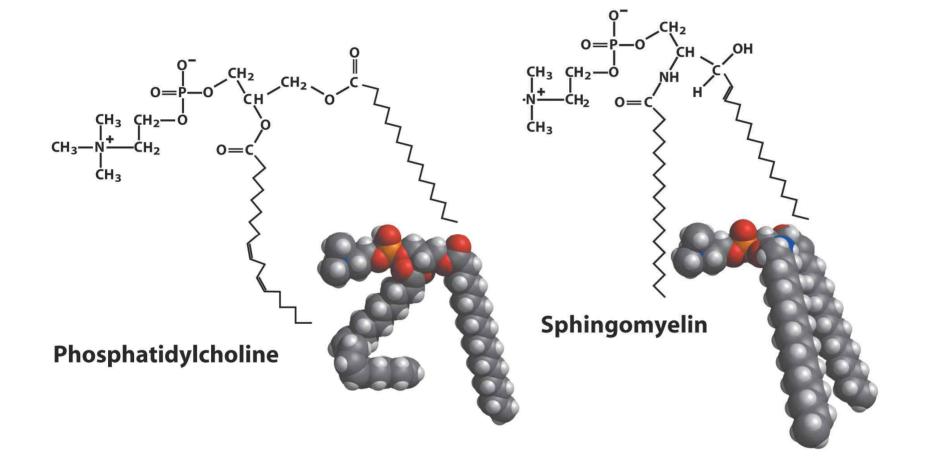
Galactolipids & Sulfolipids

predominate in plant cells localized in the thylakoid membranes of chloroplasts

Sphingolipids







Sphingolipids at cell surface are sites of biological recognition

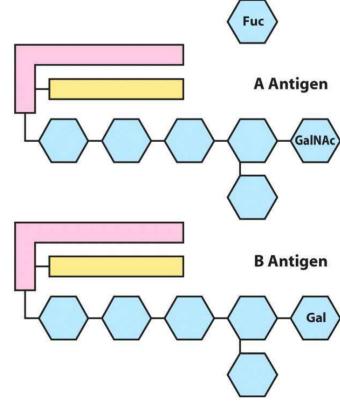
Ceramide Fatty acid O Antigen

Glc Gal GalNAc Gal

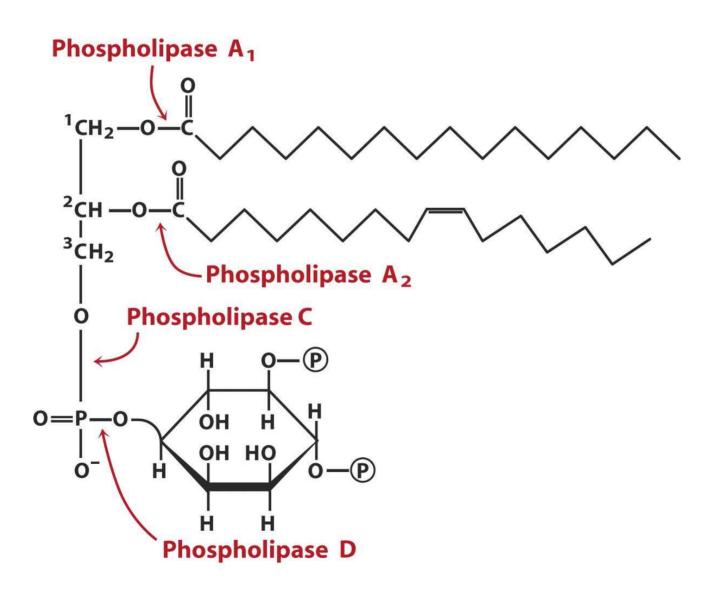
Fuc

Sphingosine

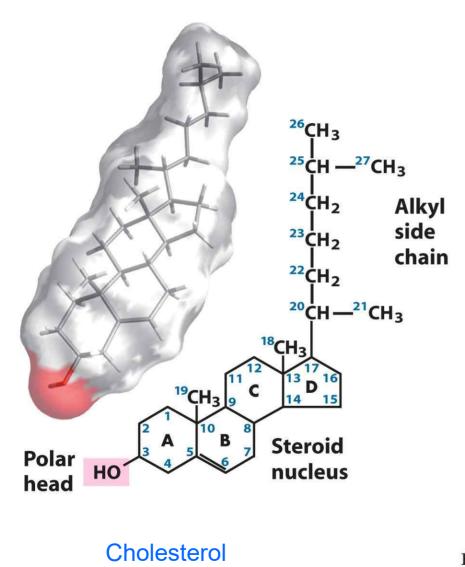
Glycosphingolipids as determinants of blood groups



Phospholipids and Sphingolipids are degraded in lysosome



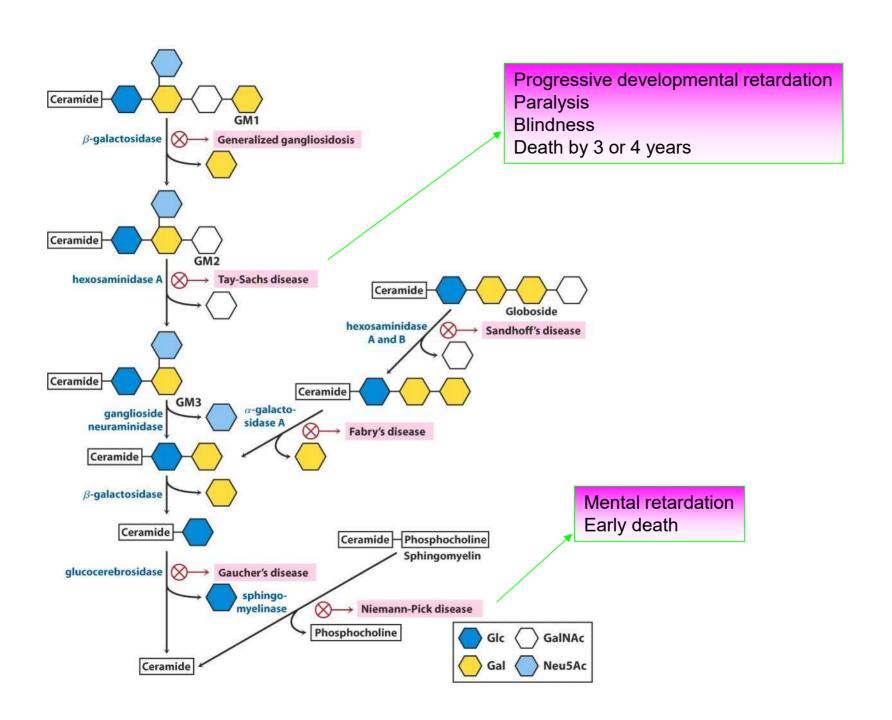
Sterols have four fused carbon rings



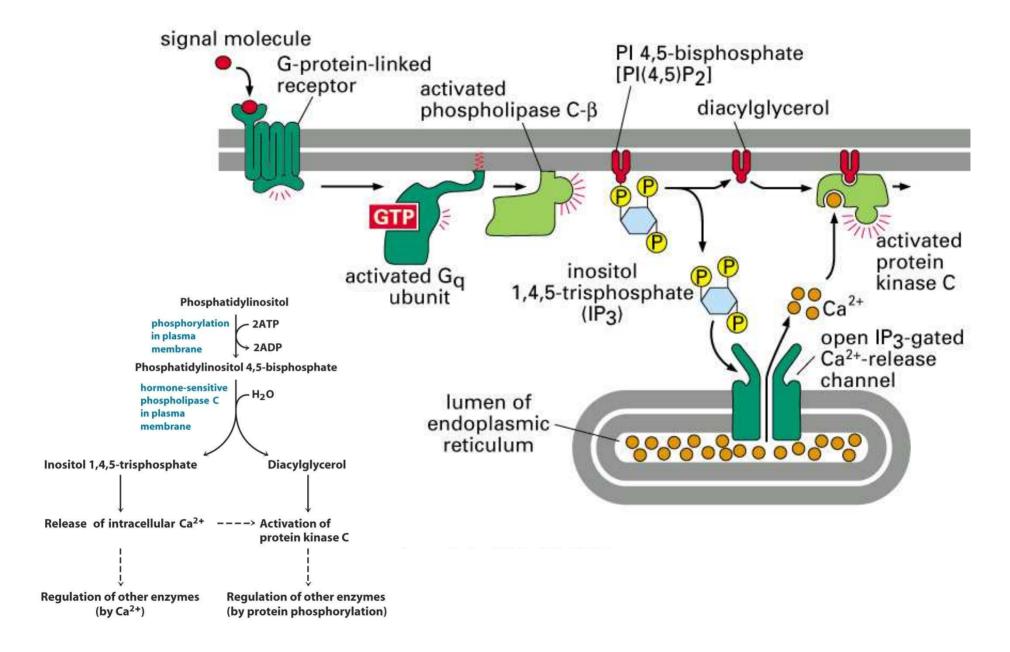
- Membrane components (memb. fluidity)
- Steroid hormone
- Bile acids

$$\begin{array}{c} CH_3 \\ OH \\ CH_3 \\ C-NH-CH_2-CH_2-SO_3^- \\ O\\ OH \end{array}$$

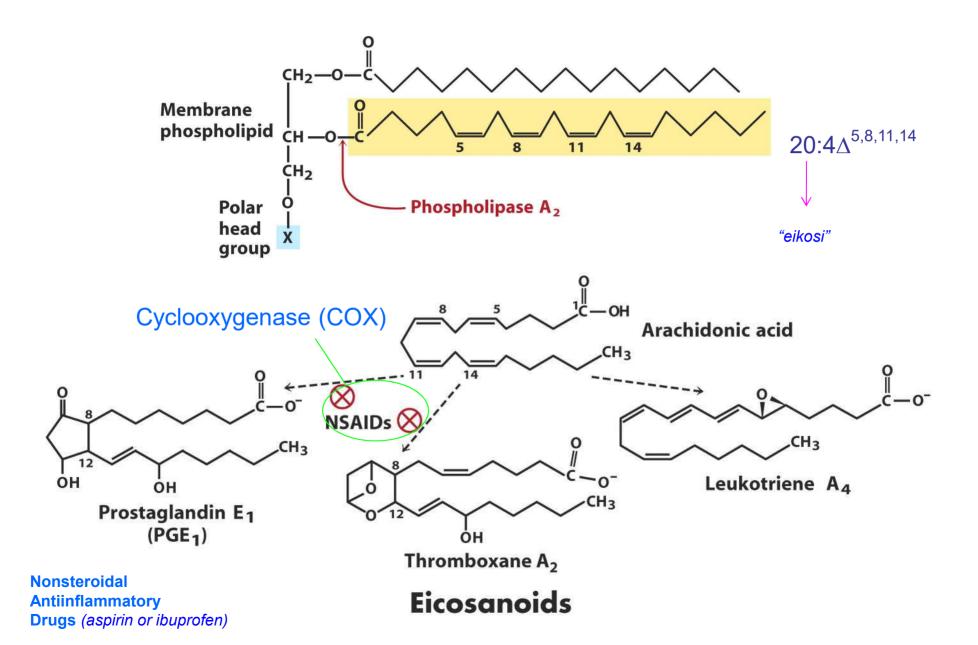
Taurocholic acid
(a bile acid)



Lipids as signals, cofactors, and pigments



Eicosanoids carry messages to nearby cells



Phospholipid containing arachidonate phospholipase A2 > Lysophospholipid COO Arachidonate, $20:4(\Delta^{5,8,11,14})$ > 20₂ cyclooxgenase activity of COX aspirin, ibuprofen PGG₂ OOH peroxidase activity of COX COO PGH_2 OH Other Thromboxanes prostaglandins (a)

Cyclooxygenase (COX) (Prostaglandin H₂ synthase)

COX-1, COX-2

$$\begin{array}{c} \text{COO} \\ \text{Ser} \\ \text{OH} \\ + \\ \text{COX} \\ \text{Aspirin} \\ \text{(acetylsalicylate)} \\ \text{(acetylsalicylate)} \\ \end{array} \begin{array}{c} \text{Ser} \\ \text{O-C} \\ \text{CH}_3 \\ \text{Acetylated,} \\ \text{inactivated} \\ \text{COX} \\ \end{array}$$

Steroid hormones derived from cholesterol

Prednisolone

Testosterone

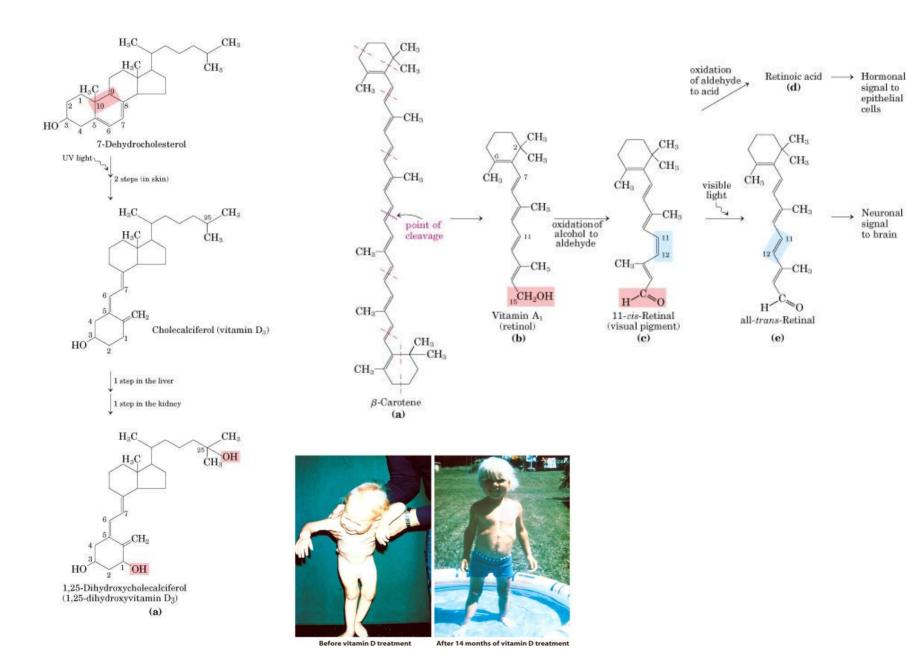
$$\begin{array}{c} CH_2OH \\ H_3C \\ C=O \\ COrtisol \\ \end{array}$$

$$\begin{array}{c} CH_2OH \\ H_3C \\ \end{array}$$

$$\begin{array}{c} CH_2OH \\ \end{array}$$

Prednisone

Vitamin A and D are hormone precursors



signal to

epithelial cells

Neuronal

signal

to brain

$$\begin{array}{c} \mathsf{CH_3} \\ \mathsf{HO} \\ \\ \mathsf{CH_2} \\$$

(a)
Vitamin E: an antioxidant

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