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Chapter 11: Lipids

Voet & Voet: Pages 380-394

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Lipids

Lipids are distinguished by their high solubility in non polar solvents and low solubility in H_2O

- **Diverse group of compounds** including Fats, Oils, Waxes, some vitamins and hormones and most non-protein components of membranes

Lipids are (another) amphipathic molecules that can be:

(A) Major components of biological membranes

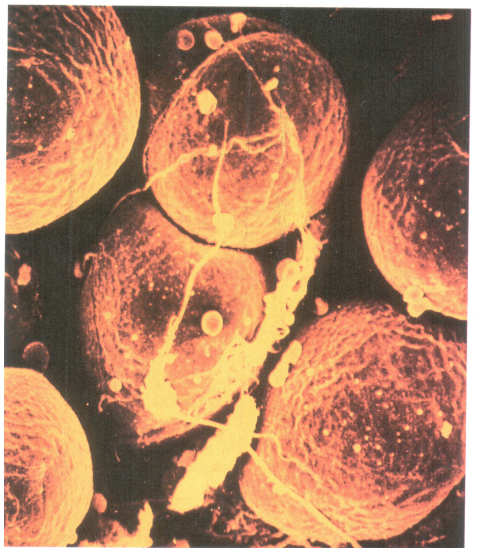
- membranes define the basic unit of life (cell) and subcellular compartments (eucaryotes)
- includes **cholesterol**

(B) Major form of stored energy in biological systems

- lipids are largely reduced compounds; complete oxidation of lipids generates lots of energy (ie. more than from sugars)

(C) Hormones

- signal transduction (communication) between cells



Adipocytes:

Fat storage cells

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Overview of Biological Lipids

Fatty acids: principal building blocks of complex lipids

Waxes: esters of fatty acids (heat sensitive)

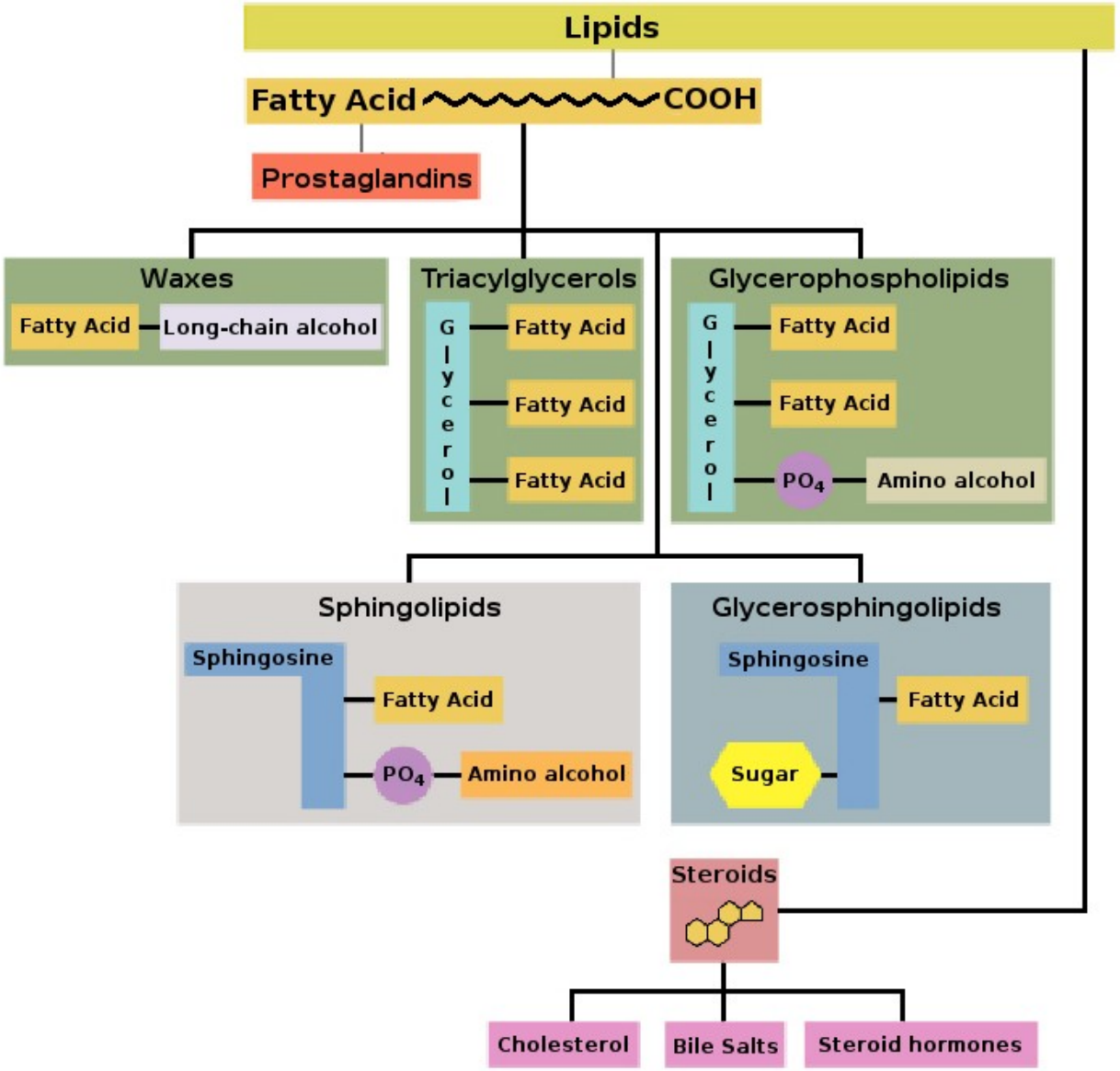
Triacylglycerols: membrane precursors, energy storage

Glycerophospholipids: membrane components

Sphingolipids: brain lipids, membrane components

Steroids: cholesterol, bile salts, steroid hormones

Terpenes: like turpentine



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Fatty Acids
Building blocks of lipids

Composed of a carboxylic acid "head group" and a long hydrocarbon "tail"

- **tail generally contains an even number of carbon atoms**

Hydrocarbon tail can be saturated or unsaturated

- **unsaturated hydrocarbon tails contain one or more double bonds**

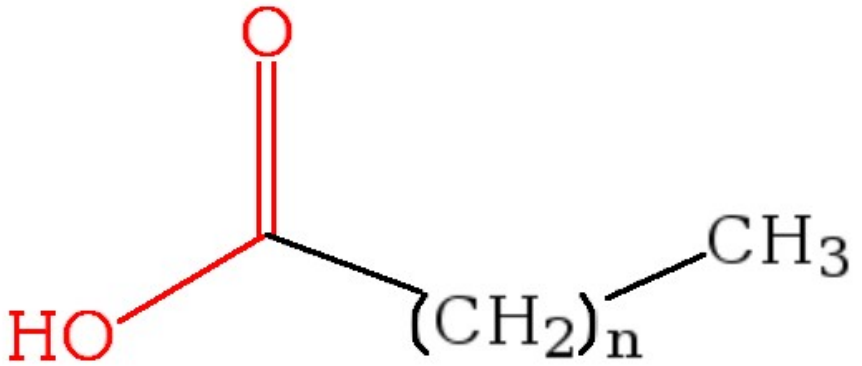
Both common and systematic nomenclatures are widely used

- ***eg.* stearic acid or octadecanoic acid ($1CH_3$, 16 CH_2 + 1 CO_2H)**

General structure of fatty acid

Carboxylic acid "head group" shown in red

Hydrocarbon "tail" shown in black



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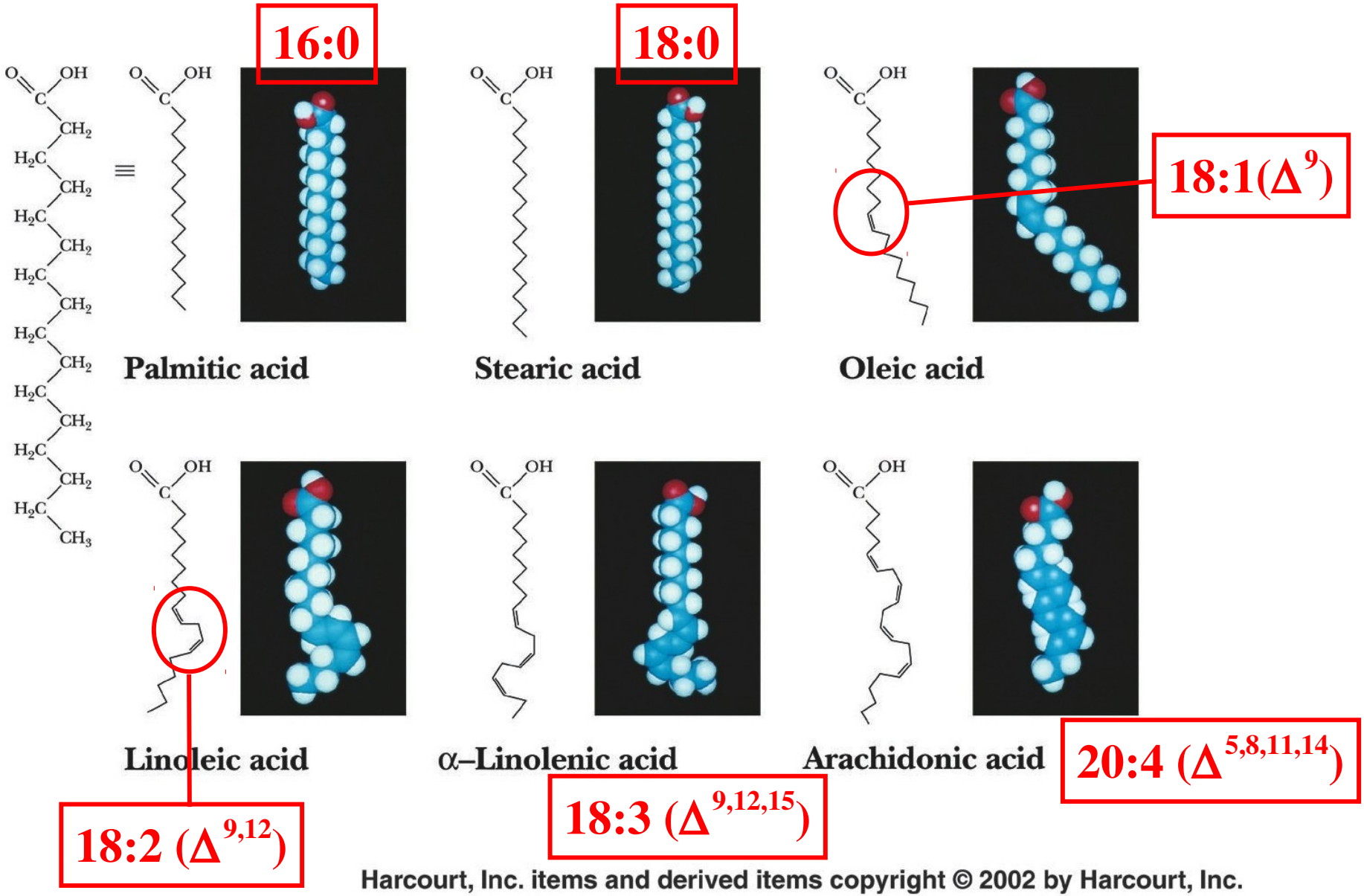
Typical Saturated and Unsaturated Fatty Acids



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(Some) Important Fatty Acids

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		
16:1(Δ^9)	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	*cis*-9-Hexadecenoic acid	Palmitoleic acid	1–0.5		
18:1(Δ^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	α-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		

Essential: can not be synthesized by humans

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Nutrition and Fatty Acids

Essential fatty acids: linoleic and α-linolenic fatty acids; must get these from plants

"Good fats": high in polyunsaturated fats.

Typical foods include vegetable oils, like olive, canola, sunflower, etc.

"Bad fats": high in saturated fats.

Classic offenders stearic (beef); palm & coconut oils (found in candy)

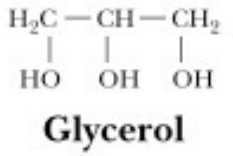
"Really bad fats": *trans* fatty acids; result from partial hydrogenation of vegetable oils.

Margarine has trans fatty acids.

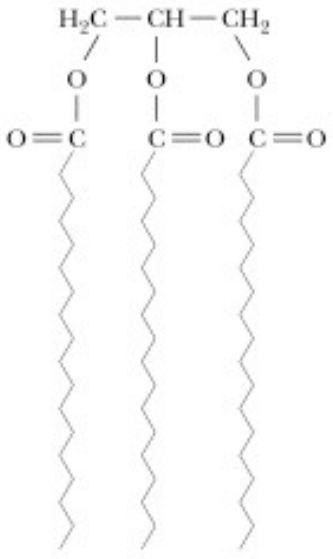
- difficult to metabolize; lead to increased cholesterol levels in the blood

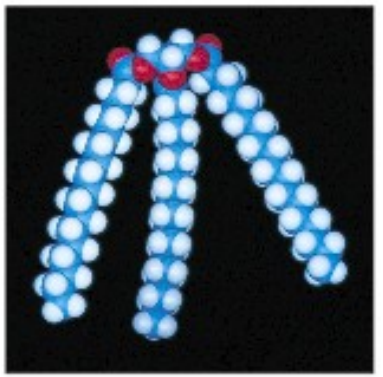
Triacylglycerols (triglycerides)
Energy Storage Lipids

- 1 Fatty Acid + Glycerol = monoacylglycerol
- 2 Fatty Acids + Glycerol = diacylglycerol
- 3 Fatty Acids + Glycerol = triacylglycerol

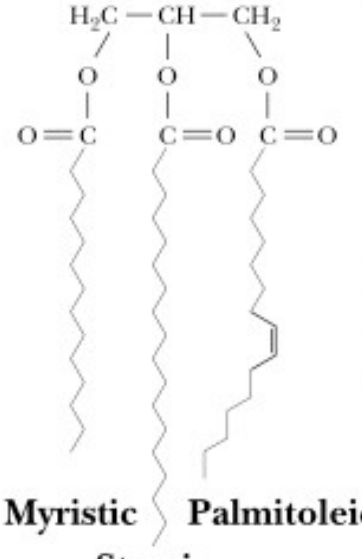


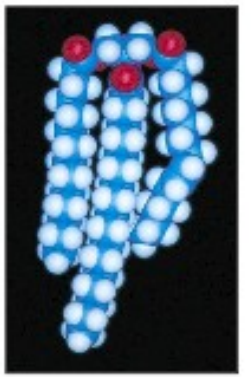
Glycerol





Tristearin
(a simple triacylglycerol)





A mixed triacylglycerol

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Triacylglycerols

Energy Storage Lipids

- **Most abundant form of fatty acids**
- **<u>Not</u> a part of biological membranes - Major energy reserve in animal**
  - Energy yield from burning: ~37 kJ/gram, as compared to ~16 kJ/gram for carbohydrates (*eg. sugars)*.

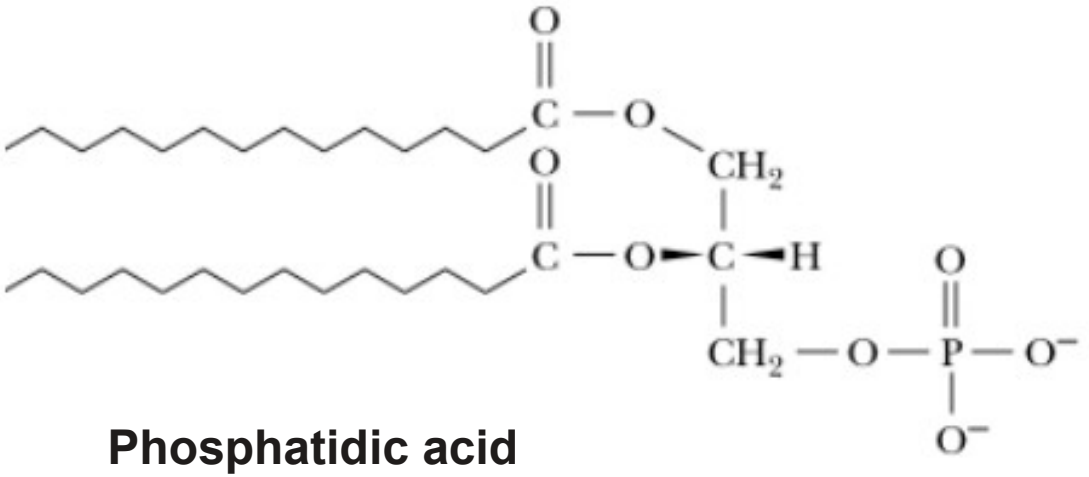
Stored Metabolic 'fuel' in a 70 kg male

Energy Constituent	~kJ/gram	Mass (g)	Energy (kJ)
Fat (adipose tissue)	37	15,000	555,000
Protein (muscle)	17	6,000	102,000
Glycogen (muscle)	16	120	1,920
Glycogen (liver)	16	70	1,120
Glucose (extracellular fluid)	16	20	320
Total			660,360

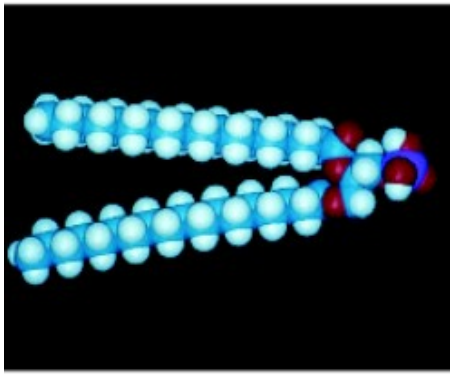
Glycerophospholipids
Membrane Lipids

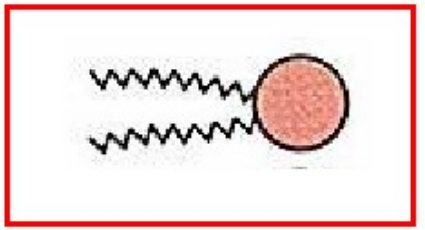
1,2-diacylglycerol (the fatty acids) with a phosphate group at position 3

- **Essential components of cell membranes and other cellular structures**
- **The parent molecule is phosphatidic acid**
- **You can have additional compounds esterified to the phosphate group**



Phosphatidic acid





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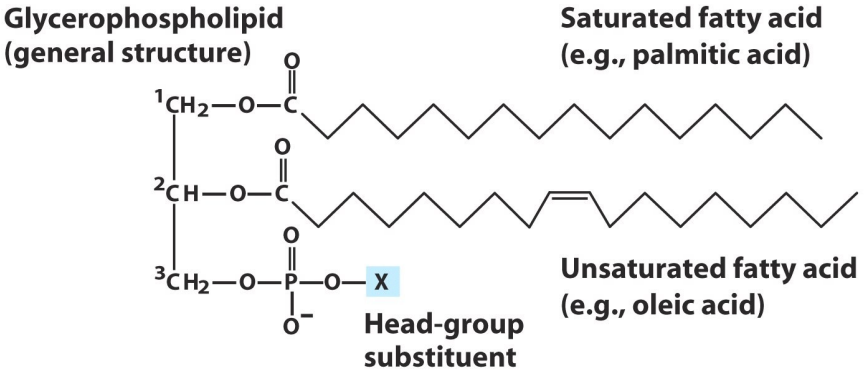
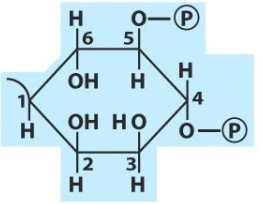
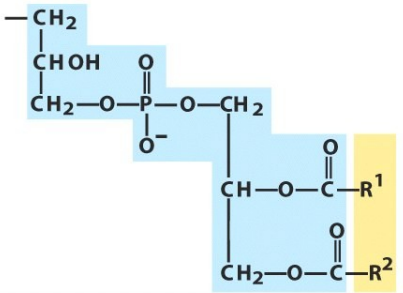
Glycerophospholipids (examples)

- **Phosphatidylcholine** (lecithin) and **phosphatidylethanolamine**: common membrane constituents

- **Cardiolipan**= diphosphatidylglycerol (note two phosphatidyl and extra glycerol)



Name of glycerophospholipid	Name of X	Formula of X	Net charge (at pH 7)
Phosphatidic acid	—	—H	−1
Phosphatidylethanolamine	Ethanolamine	$-CH_2-CH_2-\overset{+}{N}H_3$	0
Phosphatidylcholine	Choline	$-CH_2-CH_2-\overset{+}{N}(CH_3)_3$	0
Phosphatidylserine	Serine	$-CH_2-\underset{COO^-}{CH}-\overset{+}{N}H_3$	−1
Phosphatidylglycerol	Glycerol	$-CH_2-\underset{OH}{CH}-CH_2-OH$	−1
Phosphatidylinositol 4,5-bisphosphate	*myo*-Inositol 4,5-bisphosphate		−4
Cardiolipin	Phosphatidyl-glycerol		−2

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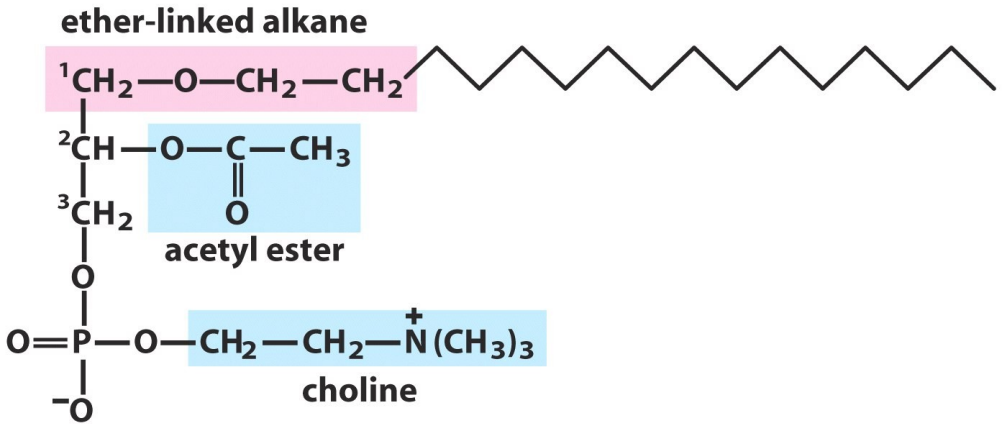
Other Glycerophospholipids

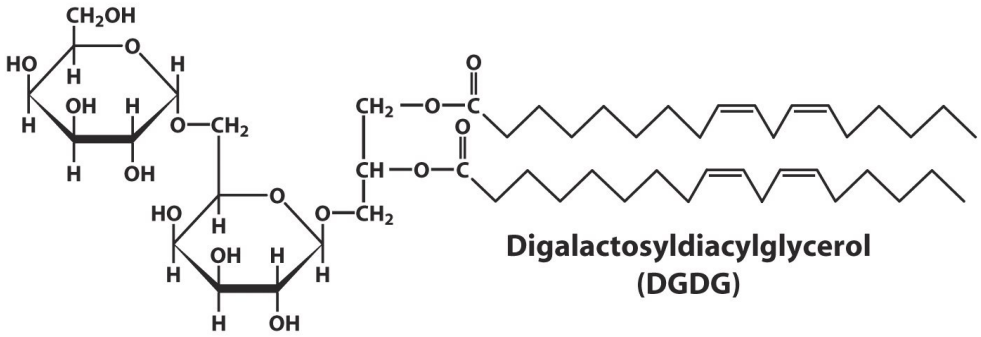
- **Ether glycerophospholipids** (e.g. platelet activating factor, an important lipid signaling molecule)



Platelet-activating factor

Galactolipids found in thylakoid membranes of chlorolasts.

70-80% of the total chloroplast membrane lipids.



Digalactosyldiacylglycerol (DGDG)

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Sphingolipids
Membrane Lipids (brain)

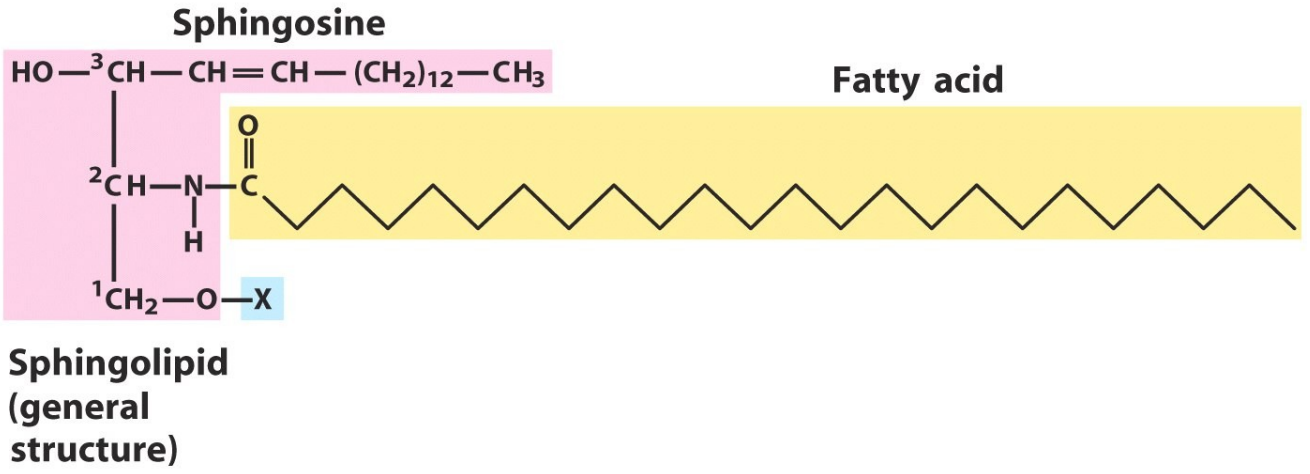
Sphingolipids are typically found in brain tissues (*eg.* brain lipids)

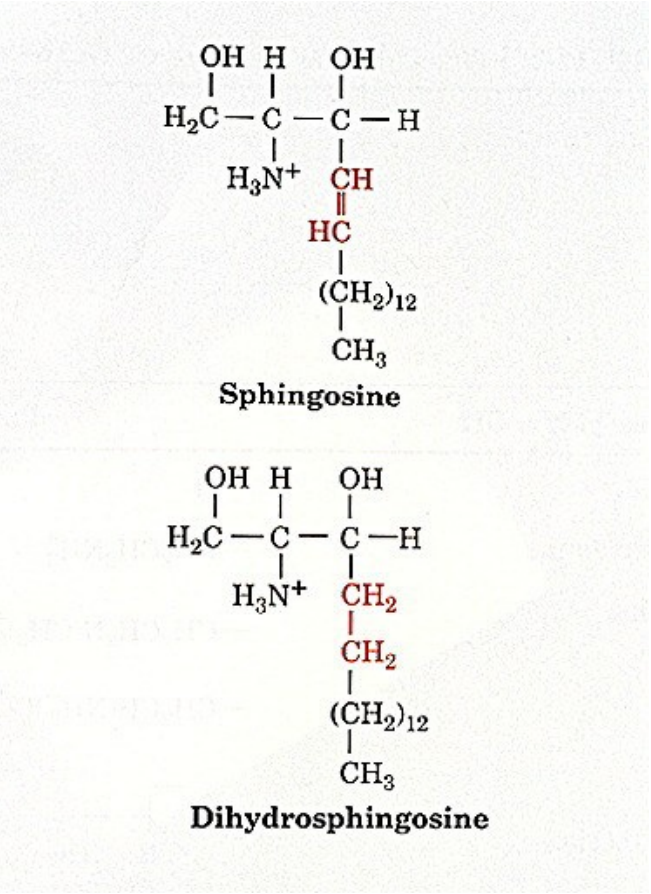
Based upon **sphingosine** (or dihydrosphingosine), an amino alcohol

- Sphingosine is rare in plants and animals while sphingolipids are common

Simplest sphingolipids are **ceramides**

- Sphingosine + N-linked fatty acid = **ceramide**





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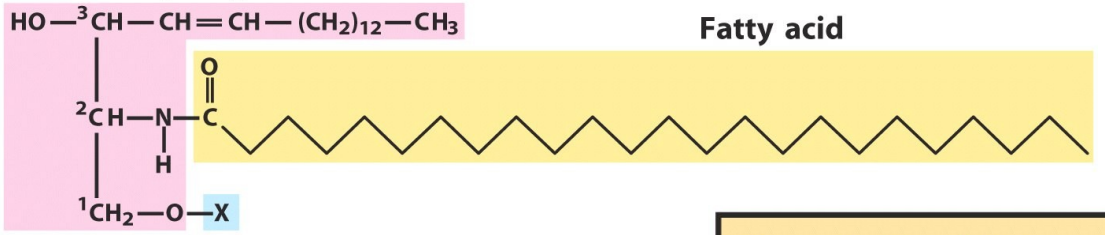
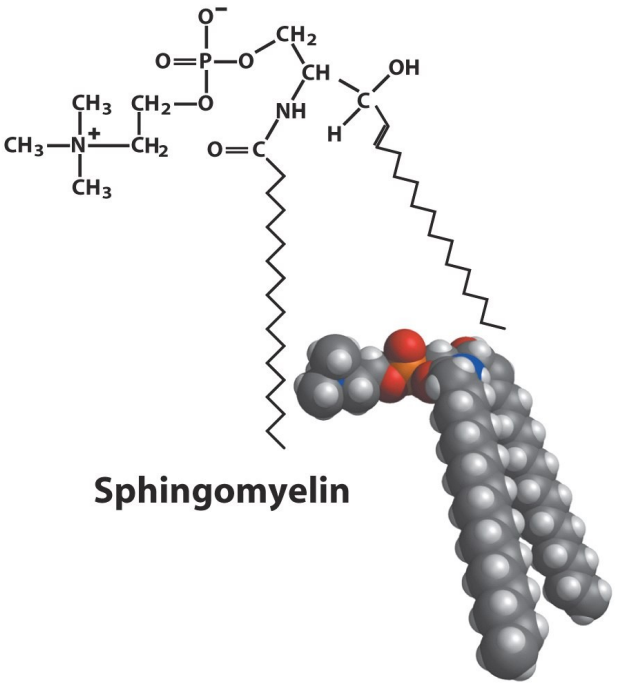
Sphingolipids (types)

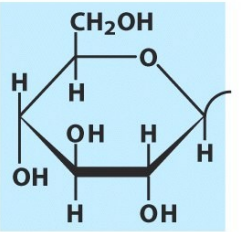
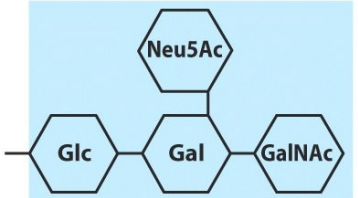
Sphingosine



Sphingolipid (general structure)



Sphingomyelin

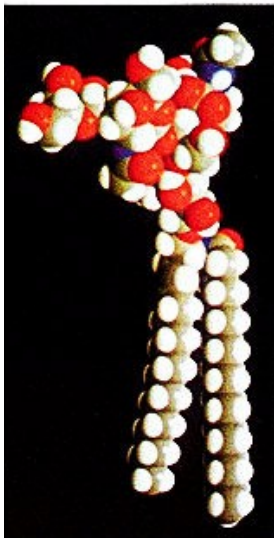
Name of sphingolipid	Name of X	Formula of X
Ceramide	—	— H
Sphingomyelin	Phosphocholine	— P(=O)(O⁻)—O—CH2—CH2—N+(CH3)3
Neutral glycolipids Glucosylcerebroside	Glucose	
Lactosylceramide (a globoside)	Di-, tri-, or tetrasaccharide	
Ganglioside GM2	Complex oligosaccharide	

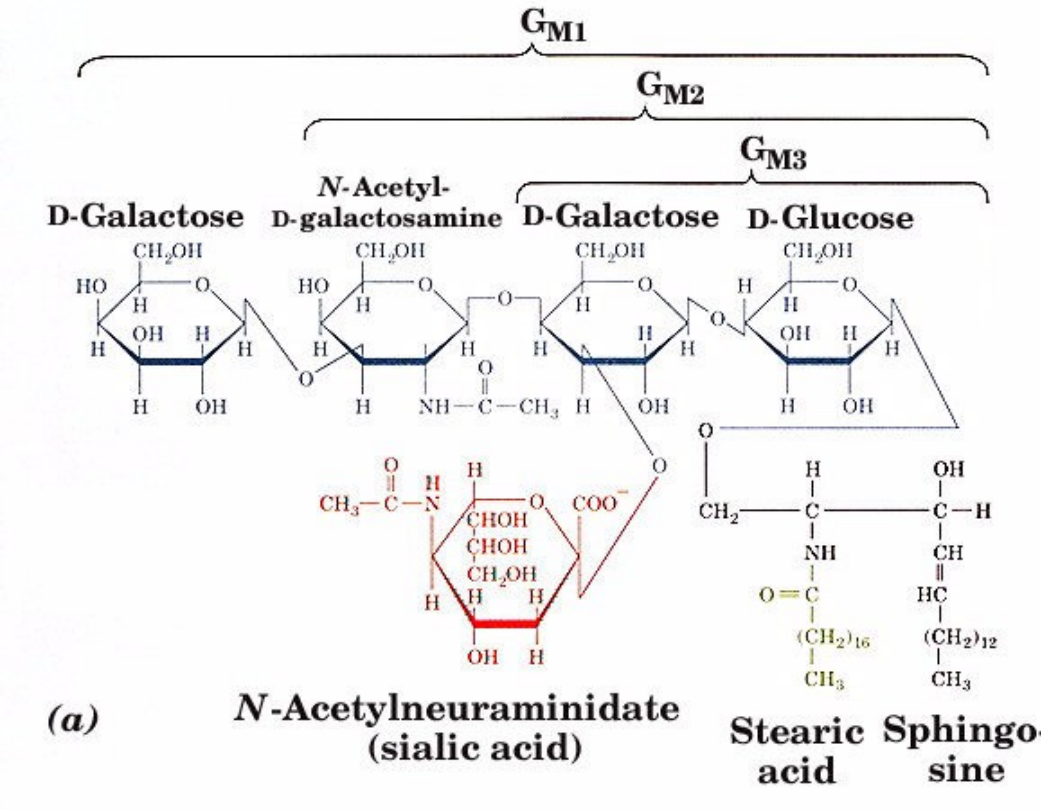
Gangliosides
Membrane Lipids (signalling)

Gangliosides are complex sphingolipids

- **Ceramide + 3 (or more) sugars including one sialic acid**

Limited abundance; key tissue specific signaling molecule





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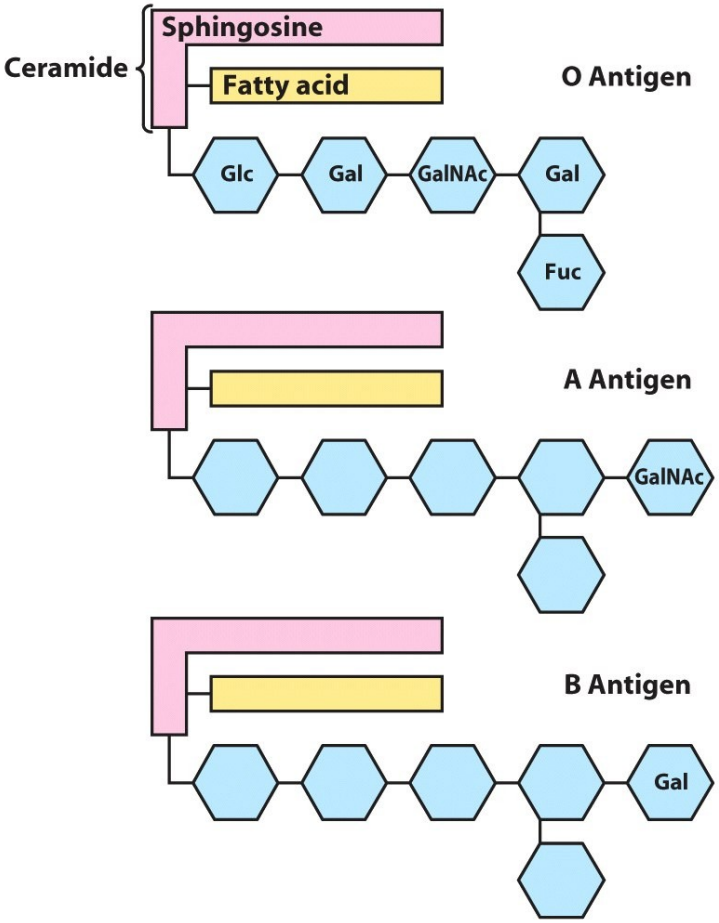
Gangliosides (example)

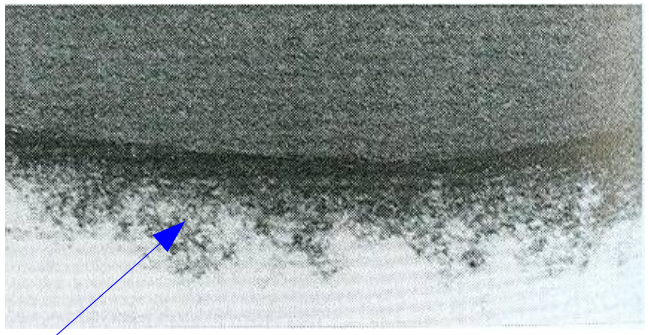
Gangliosides determine blood type

- O, A and B antigens that give rise to blood types are gangliosides

Polar "head groups" of these gangliosides differ



Electron Micrograph of Erythrocyte Outer Membrane



Gangliosides

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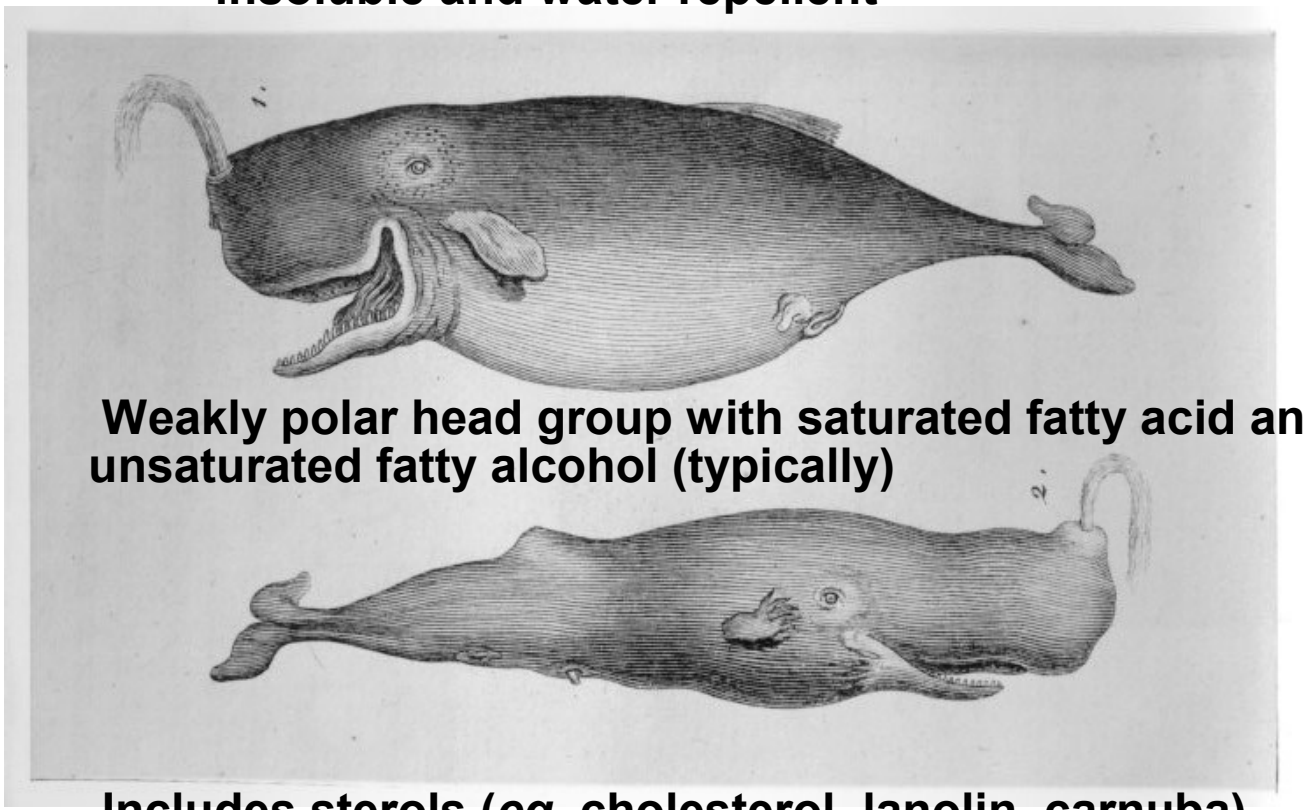
Waxes
Other Lipids

Waxes are esters of a fatty acid and a fatty alcohol

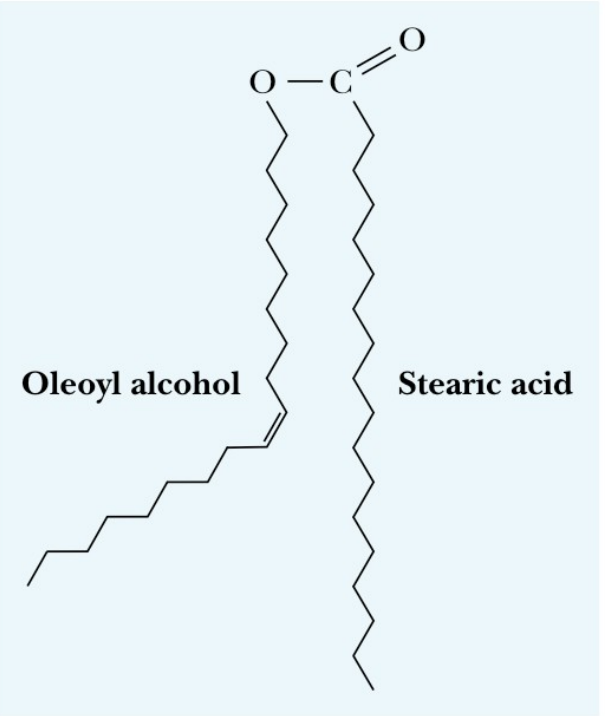
- insoluble and water repellent



Weakly polar head group with saturated fatty acid and unsaturated fatty alcohol (typically)

Includes sterols (*eg.* cholesterol, lanolin, carnuba)

Garrett/Grisham, Biochemistry with a Human Focus
Figure 6.14



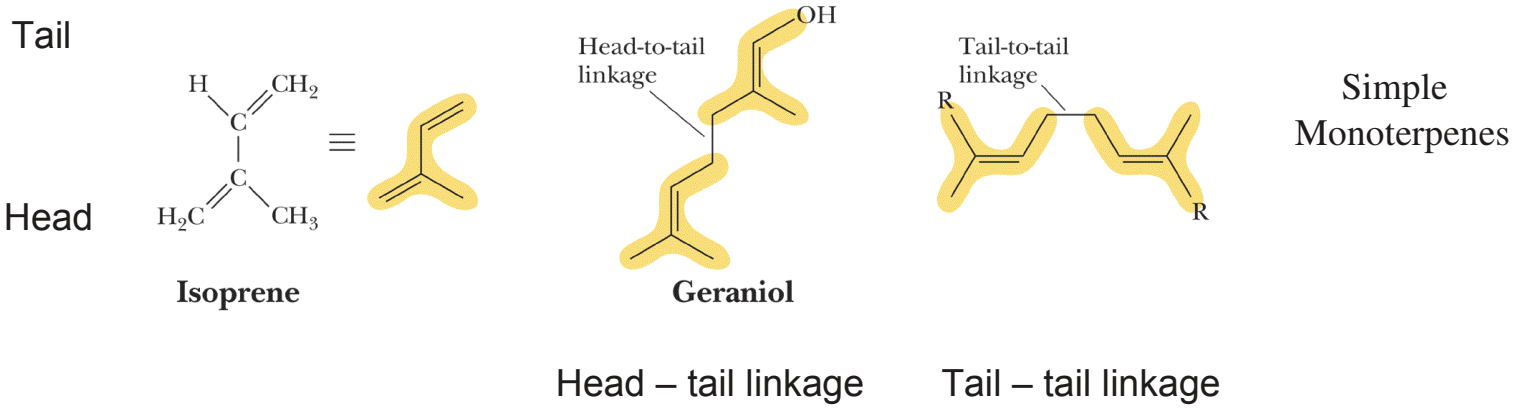
Terpenes
Other Lipids

Terpenes are abundant in plants

- **Built from 5 carbon isoprene units and do not contain fatty acids**
- **Monoterpenes contain 2 isoprene units, Diterpenes contain 4, *etc.***

Generally assembled by a 'head to tail' linkage of isoprene units

- **Diterpenes and larger terpenes arise from cyclization reactions**



Common terpenes have varied functions:

potent signalling molecules, pigments, chemical sensors, *etc*

intermediates in cholesterol and steroid biosynthesis