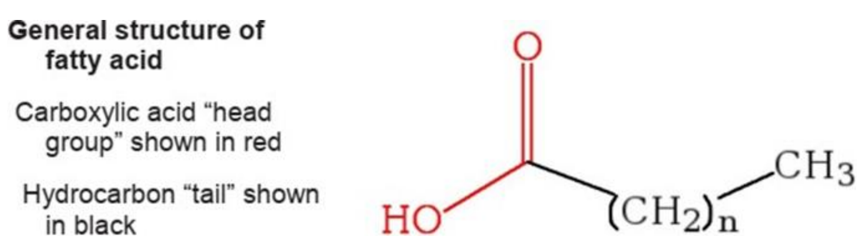
Lipids

Lipids are water-insoluble that are either hydrophobic (nonpolar) or amphipathic (polar and nonpolar regions).

Fatty acids

- The simplest with structural formula of R-COOH where R = hydrocarbon chain.
- They differ from each other by the length of the tail, degree of unsaturation, and position of double bonds.
- If there is no double bond, the fatty acid is saturated.
- If there is at least one double bond, the fatty acid is unsaturated.
- Monounsaturated fatty acids contain 1 double bond; polyunsaturated fatty acids having over than 2 double bonds.
- Physical properties differ between saturated and unsaturated fatty acids.
  Saturated = solid at RT; often animal source; e.g. Fat
  Unsaturated = liquid at RT; plant source; e.g. vegetable oil
- The length of the hydrocarbon tails influences the melting point.
- As the length of tails increases, melting points increases due to number of van der Waals interactions.
- Also affecting the melting point is the degree of unsaturation.
- As the degree of unsaturation increases, fatty acids become more fluid--> melting point decreases.
- Fatty acids are also an important sources of energy, 9 kcal/g vs. 4 kcal/g for carbohydrates and 5.5 for proteins.



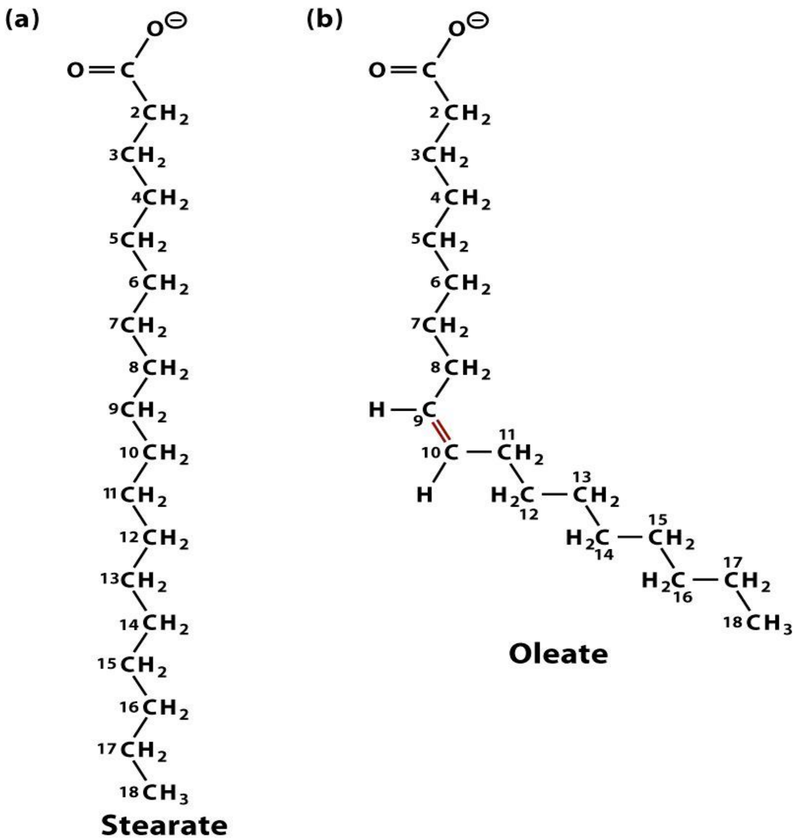


Figure 9-3 Principles of Biochemistry, 4/e

TABLE 9.1 Some common fatty acids (anionic forms)

Number of carbons	Number of double bonds	Common name	IUPAC name	Melting point, °C	Molecular formula
12	0	Laurate	Dodecanoate	44	$CH_3(CH_2)_{10}COO^{\ominus}$
14	0	Myristate	Tetradecanoate	52	$CH_3(CH_2)_{12}COO^{\ominus}$
16	0	Palmitate	Hexadecanoate	63	$CH_3(CH_2)_{14}COO^{\ominus}$
18	0	Stearate	Octadecanoate	70	$CH_3(CH_2)_{16}COO^{\ominus}$
20	0	Arachidate	Eicosanoate	75	$CH_3(CH_2)_{18}COO^{\ominus}$
22	0	Behenate	Docosanoate	81	$CH_3(CH_2)_{20}COO^{\ominus}$
24	0	Lignocerate	Tetracosanoate	84	$CH_3(CH_2)_{22}COO^{\ominus}$
16	1	Palmitoleate	*cis*-Δ^9-Hexadecenoate	−0.5	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COO^{\ominus}$
18	1	Oleate	*cis*-Δ^9-Octadecenoate	13	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COO^{\ominus}$
18	2	Linoleate	*cis, cis*-$\Delta^{9,12}$-Octadecadienoate	−9	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COO^{\ominus}$
18	3	Linolenate	all *cis*-$\Delta^{9,12,15}$-Octadecatrienoate	−17	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COO^{\ominus}$
20	4	Arachidonate	all *cis*-$\Delta^{5,8,11,14}$-Eicosatetraenoate	−49	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COO^{\ominus}$

Table 9-1 Principles of Biochemistry, 4/e

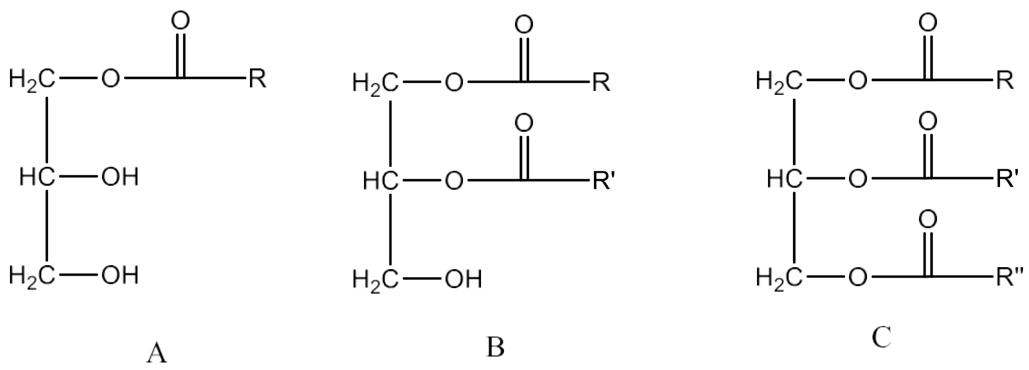
The types of lipids:

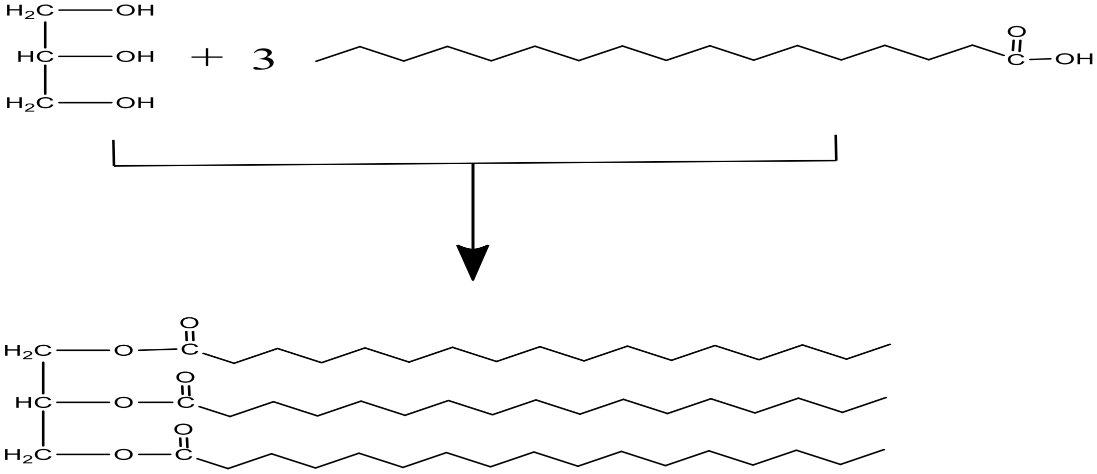
1. triacylglycerols

- Also called triglycerides.
- Made of 3 fatty acyl residues esterified to glycerol.
- Very hydrophobic, neutral in charge ---> can be stored in anhydrous form.
- Long chain, saturated triacylglycerols are solid at RT (fats).
- Shorter chain, unsaturated triacylglycerols are liquid at RT (oils).

- Lipids in our diet are usually ingested as triacylglycerols and broken down by lipases to release fatty acids from their glycerol backbones
  Transported through the body as **lipoproteins**.

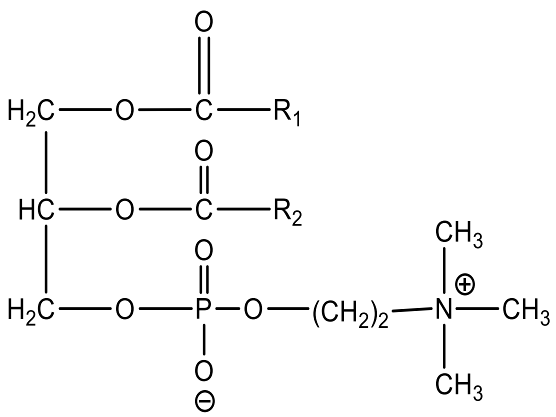
One Fatty Acid + Glycerol = Monoacylglycerol
Two Fatty Acids + Glycerol = Diacylglycerol
Three Fatty Acids + Glycerol = Triacylglycerol



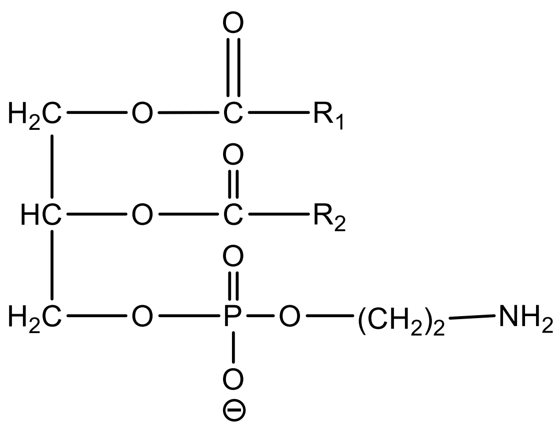


2- glycerophospholipids

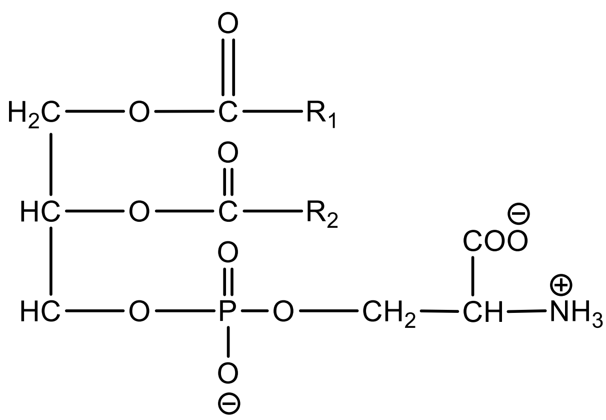
- Main components of cell membranes.
- Are amphipathic and form bilayers.
- All use glycerol 3-phosphate as backbone.
- Simplest is phosphatidate = 2 fatty acyl groups esterified to glycerol 3-phosphate.
- Often, phosphate is esterified to another alcohol to form...
    A. Phosphatidylethanolamine
    B. phosphatidylserine
    C. phosphatidylcholine



Phosphatidyl choline



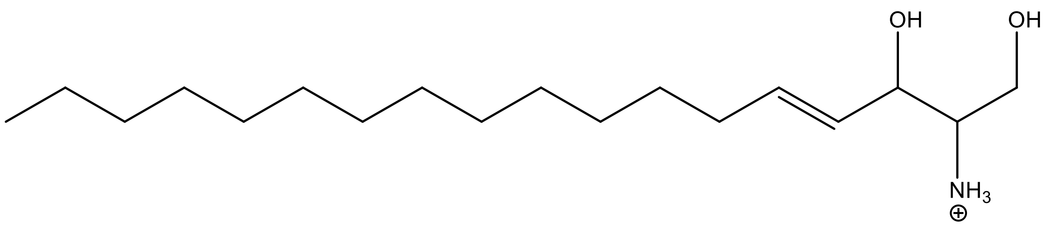
Phosphatidyl ethanolamine



phosphatidylserine

3-Sphingolipids

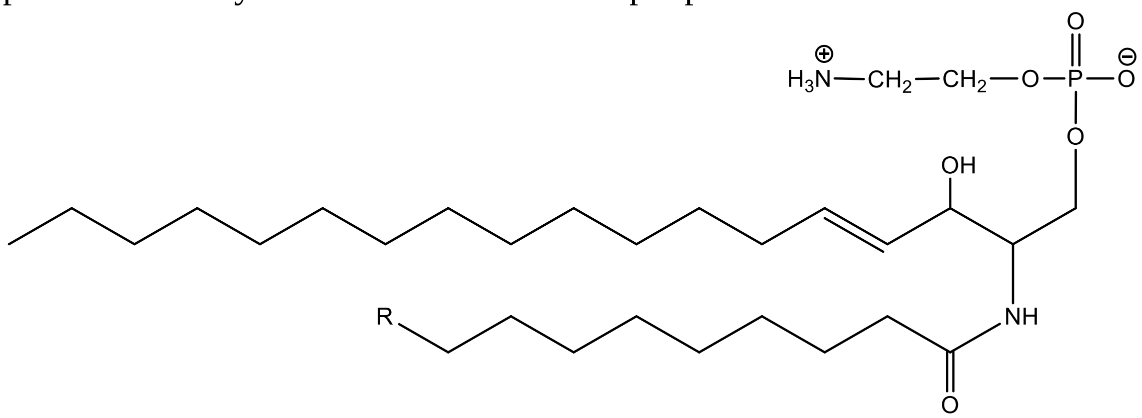
- Second most important membrane constituent.
- Very abundant in mammalian CNS.
- Backbone is **sphingosine** (unbranched 18 carbon alcohol with 1 trans C=C between C-4 and C-5), NH_3^+ group at C-2, hydroxyl groups at C-1 and C-3.



Sphingosine

- Ceramides are intermediates of sphingolipid synthesis.
- There are three families of sphingolipids:

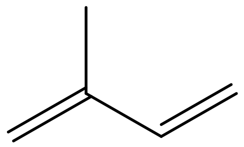
sphingomyelin - phosphocholine attached to C-1 hydroxyl group of ceramide; present in the myelin sheaths around some peripheral nerves.



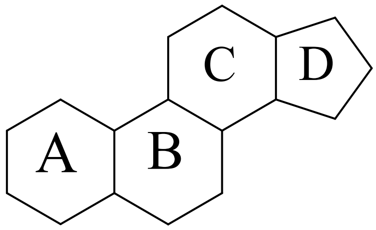
Sphingomyelin

4- Steroids

- Called **isoprenoids** because their structure is similar to isoprene.
- Have 4 fused rings: 3 (6-membered rings) (A, B, C) and 1 (5-membered ring) (D).

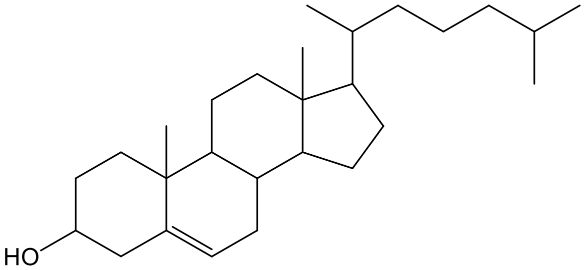


Isoprene



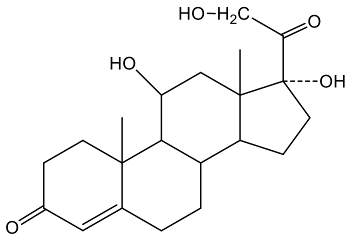
Steroids nuclei

- Cholesterol is an important component of cell membranes of animals, but rare in plants and absent in procaryotes.

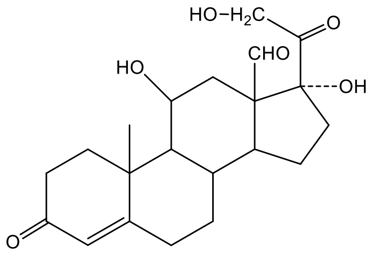


Cholesterol

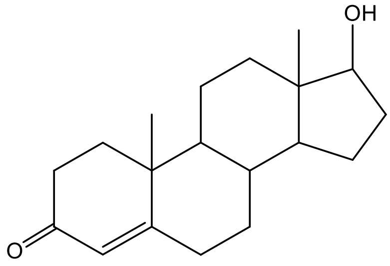
- Also have mammalian steroid hormones (estrogen, androgens) and bile salts.



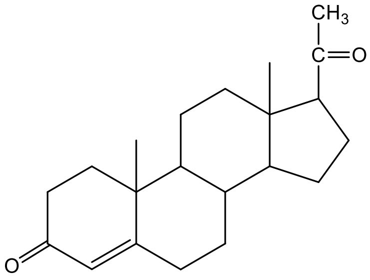
Cortisol



Aldosterone



Testosterone

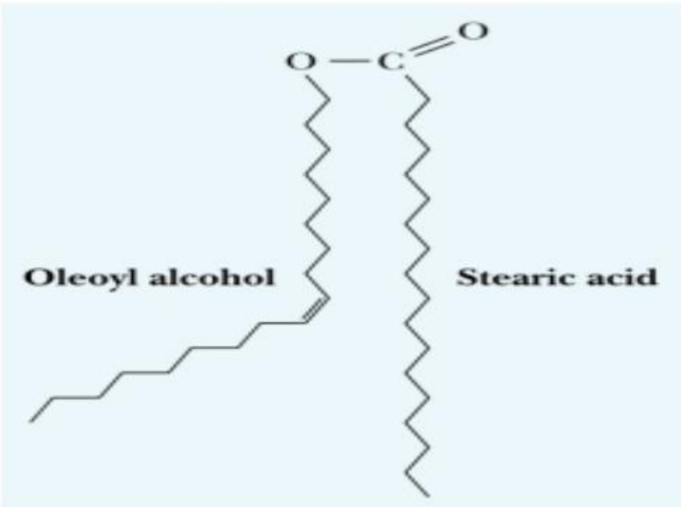


Progesterone

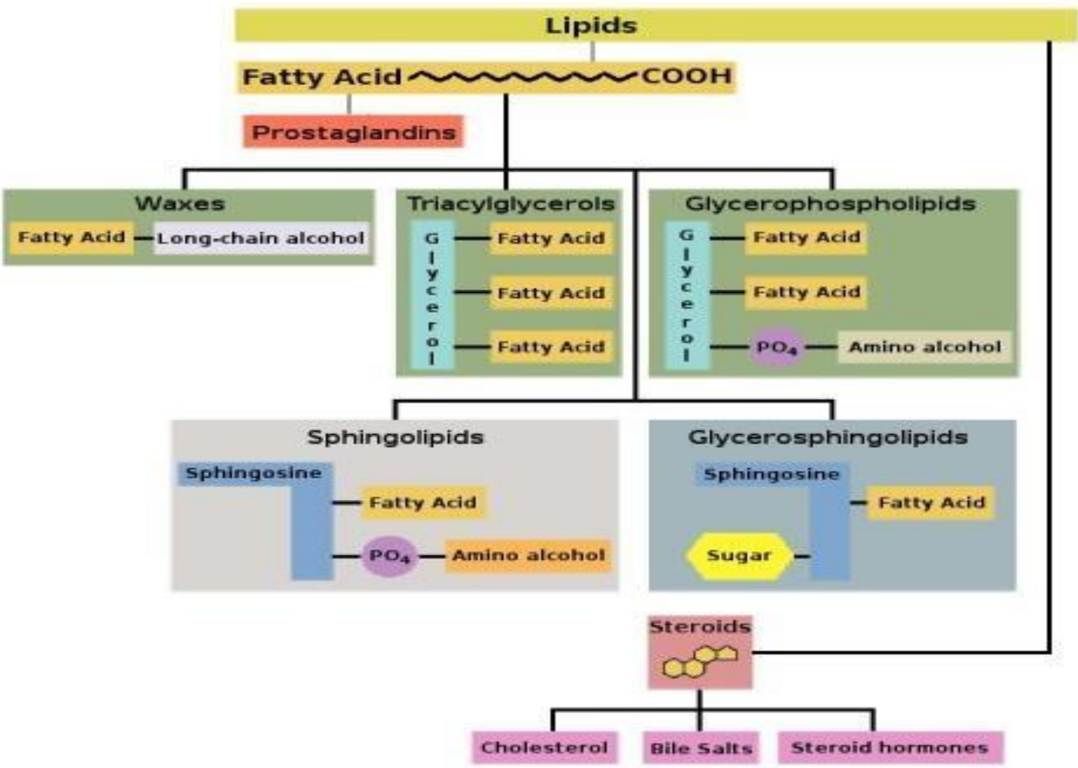
- Cholesterol's role in membranes is to broaden the phase transition of cell membranes ---> increases membrane fluidity because cholesterol disrupts packing of fatty acyl chains.

5- Waxes

Waxes are esters of a long chain of fatty acid and a fatty alcohol insoluble and water repellent, weakly polar head group with saturated fatty acid and unsaturated fatty alcohol (typically)



Overview of Biological Lipids



Rancidity

Rancidification is the process of complete or incomplete autoxidation or hydrolysis of fats and oils when exposed to air, light, moisture, or bacterial action, producing short-chain aldehydes, ketones and free fatty acids.

When these processes occur in food, undesirable odors and flavors can result. Rancidification can also detract from the nutritional value of food, as some vitamins are sensitive to oxidation.

Three pathways for rancidification are recognized

1- Hydrolytic

Hydrolytic rancidity refers to the odor that develops when triglycerides are hydrolyzed and free fatty acids are released. This reaction of lipid with water may require a catalyst (such as a lipase, or acidic or alkaline conditions) leading to the formation of free fatty acids and glycerol.

2-Oxidative

Oxidative rancidity is associated with the degradation by oxygen in the air.

A- Free-radical oxidation

The double bonds of an unsaturated fatty acid can be cleaved by free-radical reactions involving molecular oxygen. This reaction causes the release of malodorous and highly volatile aldehydes and ketones. Because of the nature of free-radical reactions, the reaction is catalyzed by sunlight.

B- Enzyme-catalysed oxidation

A double bond of an unsaturated fatty acid can be oxidised by oxygen from the air in reactions catalysed by plant or animal lipoxygenase enzymes, producing a hydroperoxide as a reactive intermediate, as in free-radical peroxidation. The final products depend on conditions: the lipoxygenase article shows that if a hydroperoxide lyase enzyme is present, it can cleave the hydroperoxide to yield short-chain fatty acids and dicarboxylic acids.

3-Microbial

Microbial rancidity refers to a water-dependent process in which microorganisms, such as bacteria or molds, use their enzymes such as lipases to break down fat. Pasteurization and/or addition of antioxidant ingredients such as vitamin E, can reduce this process by destroying or inhibiting microorganisms.