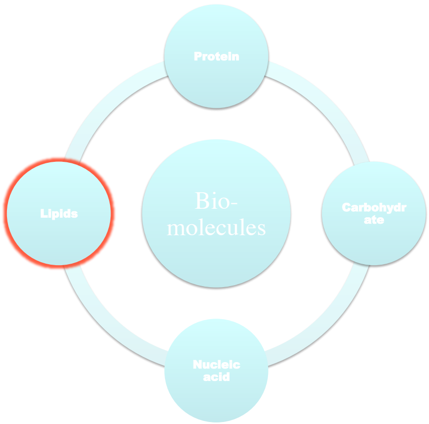


Chapters 10, 11, 12

- Lipid
  - Structure and function (Chapter 10)
- Made from lipids
  - Membrane (Chapter 11)
- Communication across membrane（膜蛋白）
  - Signal transduction (Chapter 12)

2

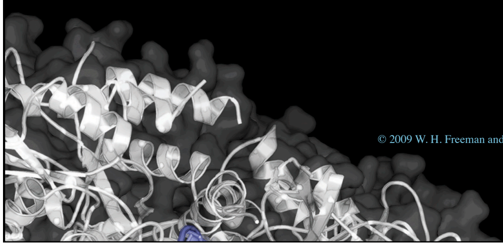
LEHNINGER
PRINCIPLES OF BIOCHEMISTRY

David L. Nelson
Michael M. Cox

FIFTH EDITION

Lecture Connections

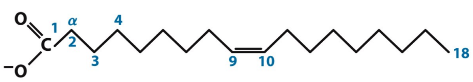
10 | Lipids



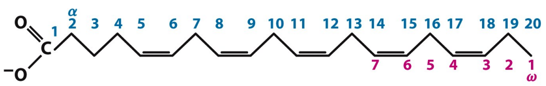
Key points for lipid chemistry

- To love water or do not love water
  - Hydrophilic
  - Hydrophobic
- Temperature environment
  - Presence of double bond
  - Numbers of carbon
- Diversified chemical structures give functions

4



(a) 18:1(Δ^9) *cis*-9-Octadecenoic acid



(b) 20:5($\Delta^{5,8,11,14,17}$) Eicosapentaenoic acid (EPA), an omega-3 fatty acid

Figure 10-1
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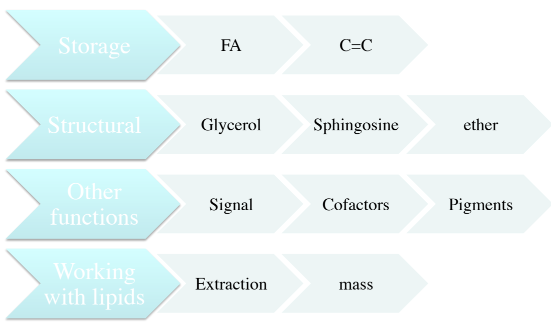


CHAPTER 10
Lipids

Key topics:

– Biological roles of lipids
– Structure and properties of storage lipids
– Structure and properties of membrane lipids
– Structure and properties of signaling lipids

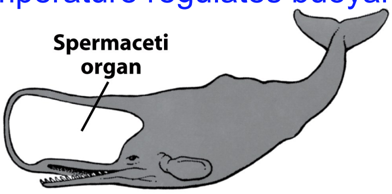
Lipids: Structurally Diverse Class

- Low solubility in water
- Good solubility in nonpolar solvents

Biological Functions of Lipids

- Storage of energy
  - Reduced compounds: lots of available energy
  - Hydrophobic nature: good packing
- Insulation from environment
  - Low thermal conductivity
  - High heat capacity (can “absorb” heat)
  - Mechanical protection (can absorb shocks)
- Water repellant
  - Hydrophobic nature: keeps surface of the organism dry
    - Prevents excessive wetting (birds)
    - Prevents loss of water via evaporation
- Buoyancy control and acoustics in marine mammals
  - Increased density while diving deep helps sinking (just a hypothesis)
  - Spermaceti organ may focus sound energy: sound stun gun?

Density adjustment according to temperature regulates buoyancy



Box 10-1
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More Functions

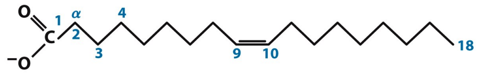
- Membrane Structure
  - Main structure of cell membranes
- Cofactors for enzymes
  - Vitamin K: blood clot formation
  - Coenzyme Q: ATP synthesis in mitochondria
- Signaling molecules
  - Paracrine hormones (act locally)
  - Steroid hormones (act body-wide)
  - Growth factors
  - Vitamins A and D (hormone precursors)
- Pigments
  - Color of tomatoes, carrots, pumpkins, some birds
- Antioxidants
  - Vitamin E

Classification of Lipids

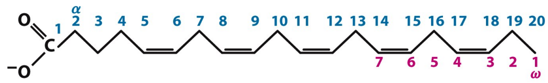
- Based on the structure and function
  - Lipids that do not contain fatty acids: cholesterol, terpenes, …
  - Lipids that contain fatty acids (complex lipids)
    - Storage lipids and membrane lipids

Fatty Acids

- Carboxylic acids with hydrocarbon chains containing from 4 to 36 carbons
- Almost all natural fatty acids have an even number of carbons
- Most natural fatty acids are unbranched
- Saturated: no double bonds between carbons in the chain
- Monounsaturated: one double bond between carbons in the alkyl chain
- Polyunsaturated: more than one double bond in the alkyl chain



(a) 18:1(Δ^9) *cis*-9-Octadecenoic acid



(b) 20:5($\Delta^{5,8,11,14,17}$) Eicosapentaenoic acid (EPA), an omega-3 fatty acid

Figure 10-1
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Fatty Acid Nomenclature

TABLE 10–1 Some Naturally Occurring Fatty Acids: Structure, Properties, and Nomenclature

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 to –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		

*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.

Table 10-1
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Solubility and Melting Point of Saturated Fatty Acids

- Solubility decreases as the chain length increases
- Melting point increases as the chain length increases

TABLE 10–1 Some Naturally Occurring Fatty Acids: Structure, Properties, and Nomenclature

Carbon skeleton	Structure*	Systematic name†	Common name (derivation)	Melting point (°C)	Solubility at 30 °C (mg/g solvent) Water	Benzene
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16:1(Δ^9)	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	*cis*-9-Hexadecenoic acid	Palmitoleic acid	1 to –0.5		
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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		

*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.

Table 10-1
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Conformation of Fatty Acids

- The saturated chain tends to adopt extended conformations
- The double bonds in natural unsaturated fatty acids are commonly in cis configuration
- This introduces a kink in the chain

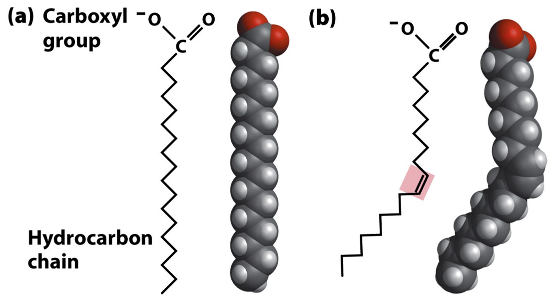

Figure 10-2ab
Lehninger Principles of Biochemistry, Fifth Edition

Melting Point and Double Bonds

- Saturated fatty acids pack in a fairly orderly way
  - extensive favorable interactions
- Unsaturated cis fatty acid pack less regular due to the kink
  - Less extensive favorable interactions
- It takes less thermal energy to disrupt disordered packing of unsaturated fatty acids:
  - unsaturated cis fatty acids have a lower melting point

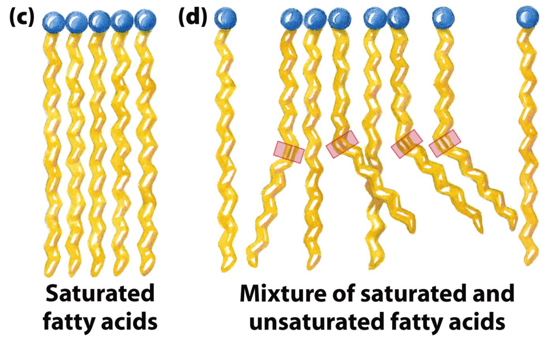

Figure 10-2cd
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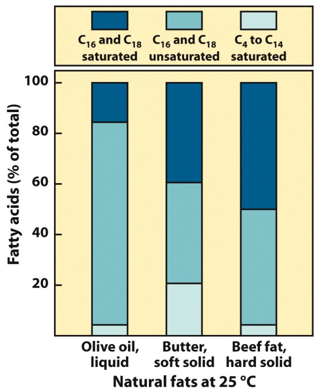


Figure 10-5
Lehninger Principles of Biochemistry, Fifth Edition

Trans Fatty Acids

- Trans fatty acids form by partial dehydrogenation of unsaturated fatty acids
- A trans double bond allows a given fatty acid to adopt an extended conformation.
- Trans fatty acids can pack more regularly, and show higher melting points than cis forms

Trans Fatty Acids in Foods

- Consuming trans fats increases risk of cardiovascular disease
  - Avoid deep-frying partially hydrogenated vegetable oils
  - Current trend: reduce trans fats in foods (Wendy's, KFC)

TABLE 10–2 Trans Fatty Acids in Some Typical Fast Foods and Snacks

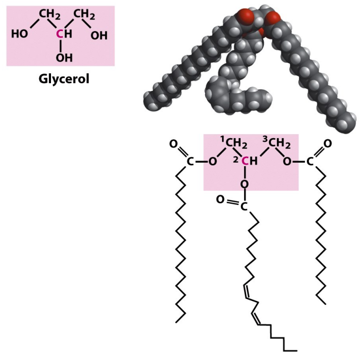
	Trans fatty acid content	
	In a typical serving (g)	As % of total fatty acids
French fries	4.7–6.1	28–36
Breaded fish burger	5.6	28
Breaded chicken nuggets	5.0	25
Pizza	1.1	9
Corn tortilla chips	1.6	22
Doughnut	2.7	25
Muffin	0.7	14
Chocolate bar	0.2	2

Source: Adapted from Table 1 in Mozaffarian, D., Katan, M.B., Ascherio, P.H., Stampfer, M.J., & Willet, W.C. (2006) Trans fatty acids and cardiovascular disease. *N. Engl. J. Med.* 354, 1604–1605.
Note: All data for foods prepared with partially hydrogenated vegetable oil in the United States in 2002.

Table 10-2
Lehninger Principles of Biochemistry, Fifth Edition

Triacylglycerols (fats and oils)

- Majority of fatty acids in biological systems are found in the form of triacylglycerols
- Solid ones are called fats
- Liquid ones are called oils
- Triacylglycerols are the primary storage form of lipids (body fat)
- Triacylglycerols are less soluble in water than fatty acids due to the lack of charged carboxylate group
- Triacylglycerols are less dense than water: fats and oils float



Glycerol

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

Figure 10-3
Lehninger Principles of Biochemistry, Fifth Edition

Fats Provide Efficient Fuel Storage

- The advantage of fats over polysaccharides:
  - Fatty acid carry more energy per carbon because they are more reduced
  - Fatty acids carry less water along because they are nonpolar
- Glucose and glycogen are for short-term energy needs, quick delivery
- Fats are for long term (months) energy needs, good storage, slow delivery

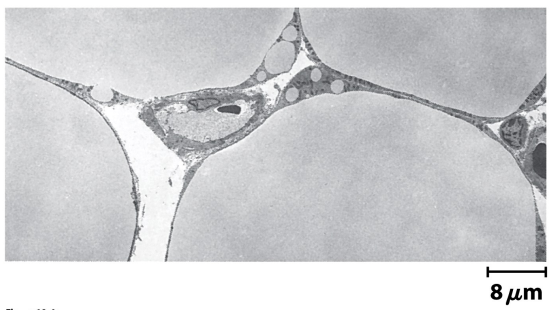


Figure 10-4a
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Waxes

- Waxes are esters of long-chain saturated and unsaturated fatty acids with long-chain alcohols
- Insoluble and have high melting points
- Variety of functions:
  - Storage of metabolic fuel in plankton
  - Protection and pliability for hair and skin in vertebrates
  - Waterproofing of feathers in birds
  - Protection from evaporation in tropical plants and ivy
  - Used by people in lotions, ointments, and polishes

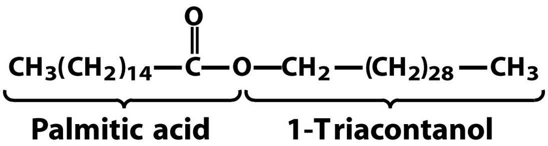

Figure 10-6a
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Wax: the material of the honeycomb

- Beeswax is a mixture of a large number of lipids, including esters of triacontanol, and a long-chain alkane hentiacontane

Figure 10-6b
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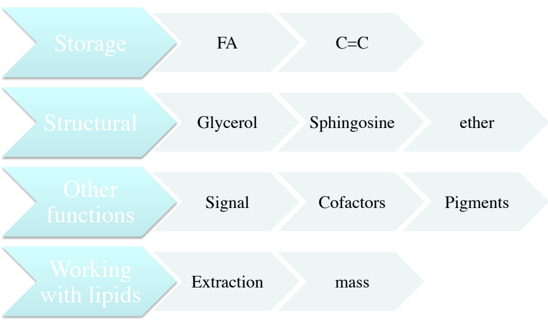
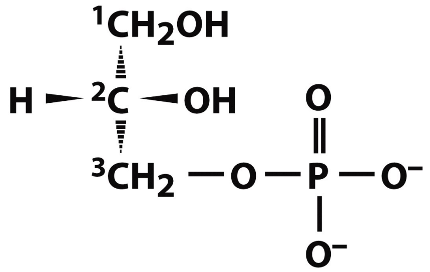


Glycerophospholipids

- Primary constituents of cell membranes
- Two fatty acids form ester linkages with first and second hydroxyl group of L-glycerol-3-phosphate



L-Glycerol 3-phosphate
(*sn*-glycerol 3-phosphate)

Figure 10-8
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General Structure of Glycerophospholipids

- Note that unsaturated fatty acids are commonly found to be connected to C2 of glycerol
- The highly polar phosphate group may be further esterified by an alcohol; such substituent groups are called the head groups

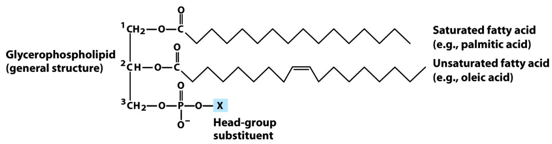

Figure 10-9 part 1
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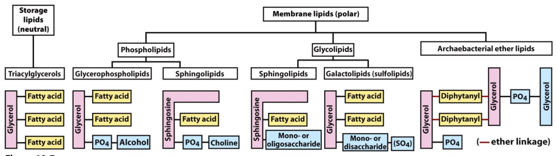


Figure 10-7
Lehninger Principles of Biochemistry, Fifth Edition

How membrane lipids are formed?

- Backbone
  - Glycerol
  - Sphingosine
- Polar head
  - Phosphate
  - Glycol or carbohydrate
- Unique lipids in Archea

Examples of Glycerophospholipids

- The properties of head groups determine the surface properties of membranes
- Different organisms have different membrane lipid head group compositions
- Different tissues have different membrane lipid head group compositions

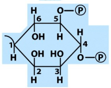
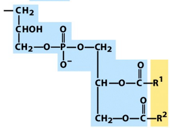
Name of glycerophospholipid	Name of X	Formula of X	Net charge (at pH 7)
Phosphatidic acid	—	—H	– 1
Phosphatidylethanolamine	Ethanolamine	$-CH_2-CH_2-\overset{+}{N}H_3$	0
Phosphatidylcholine	Choline	$-CH_2-CH_2-\overset{+}{N}(CH_3)_3$	0
Phosphatidylserine	Serine	$-CH_2-CH(COO^-)-\overset{+}{N}H_3$	– 1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

Figure 10-9 part 2
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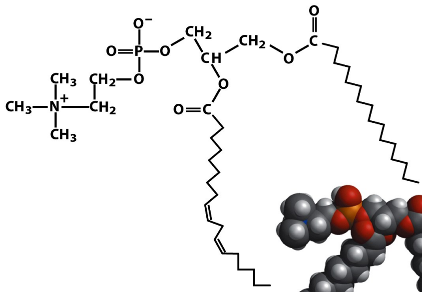
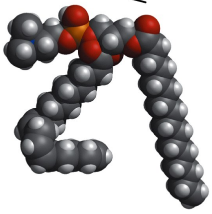
Phosphatidylcholine

- Phosphatidylcholine is the major component of most eukaryotic cell membranes
- Many prokaryotes, including *E. coli* cannot synthesize this lipid; their membranes do not contain phosphatidylcholine

Phosphatidylcholine

Figure 10-14 part 1
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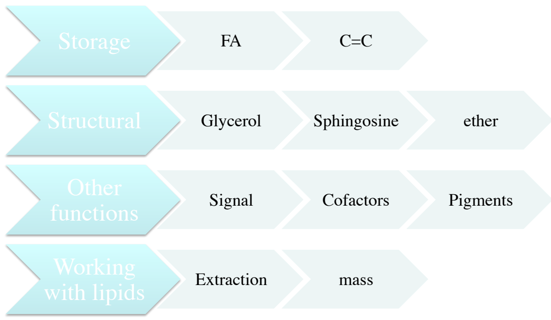
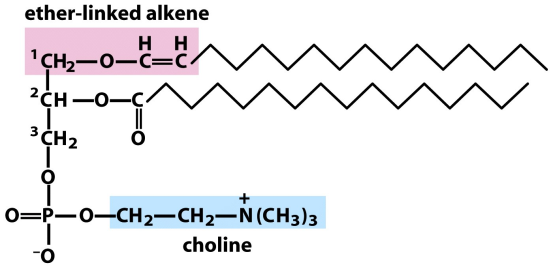


Ether Lipids: Plasmalogen

- Vinyl ether analog of phosphatidylethanolamine
- Common in vertebrate heart tissue
- Also found in some protozoa and anaerobic bacteria
- Function is not well understood
  - Resistant to cleavage by common lipases but cleaved by few specific lipases
  - Increase membrane rigidity?
  - Sources of signaling lipids?
  - May be antioxidants?



Plasmalogen

Figure 10-10a
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Ether Lipids: Platelets-Activating Factor

- Aliphatic ether analog of phosphatidylcholine
- Acetic acid has esterified position C2
- First signaling lipid to be identified
- Stimulates aggregation of blood platelets
- Plays role in mediation of inflammation

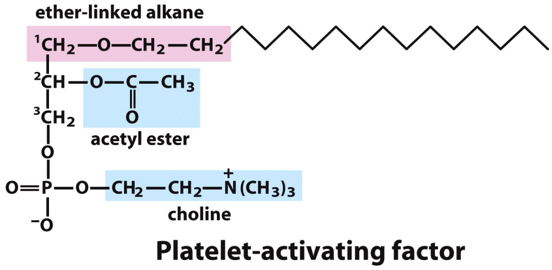

Figure 10-10b
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Unique ether lipid in Archea

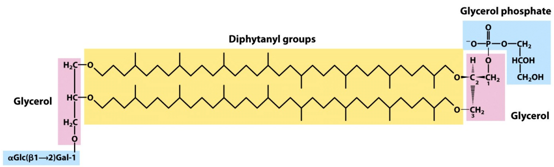

Figure 10-12
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Plants employ more galactolipids than phospholipids

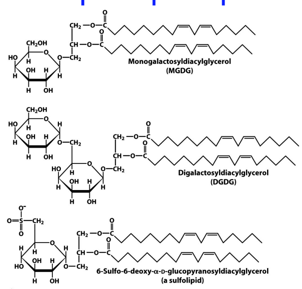

Figure 10-11
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Storage	FA	C=C	
Structural	Glycerol	Sphingosine	ether
Other functions	Signal	Cofactors	Pigments
Working with lipids	Extraction	mass	

Sphingolipids

- The backbone of sphingolipids is NOT glycerol
- The backbone of sphingolipids is a long-chain amino alcohol sphingosine
- A fatty acid is joined to sphingosine via an amide linkage rather than an ester linkage as usually seen in lipids
- A polar head group is connected to sphingosine by a glycosidic or phosphodiester linkage
- The sugar-containing glycosphingolipids are found largely in the outer face of plasma membranes

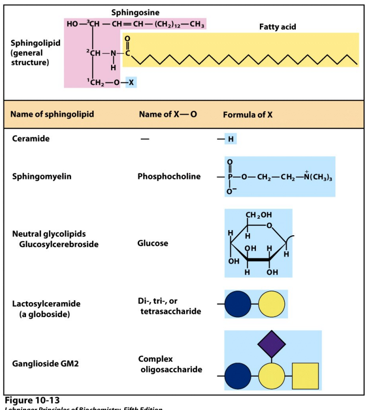

Figure 10-13
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Examples of Sphingolipids

- The properties of head groups determine the surface properties of membranes
- Different organisms have different membrane lipid head group compositions
- Different tissues have different membrane lipid head group compositions

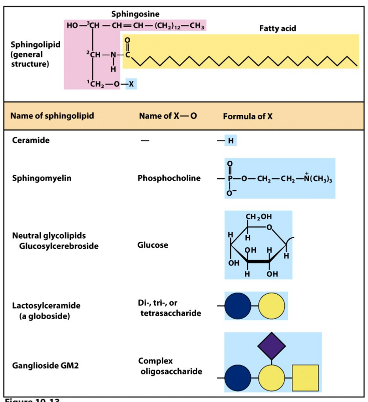

Figure 10-13
Lehninger Principles of Biochemistry, Fifth Edition

Sphingomyelin

- Ceramide (sphingosine + amide-linked fatty acid + phosphocholine
- Sphingomyelin is abundant in myelin sheath that surrounds some nerve cells in animals
- Structurally similar to phosphatidylcholine

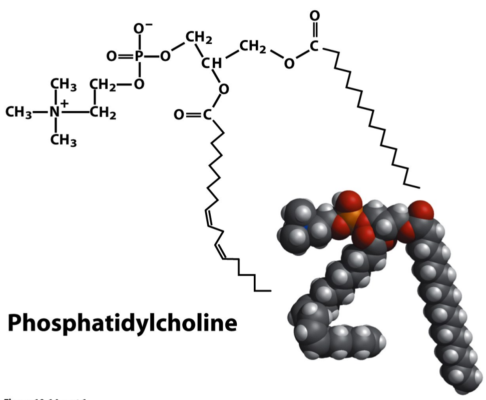

Figure 10-14 part 1
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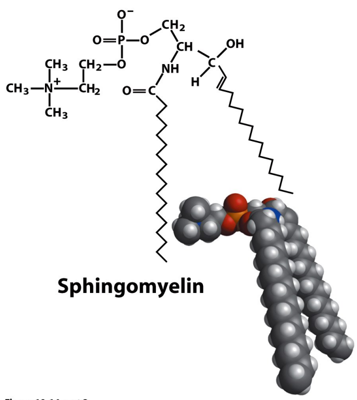

Figure 10-14 part 2
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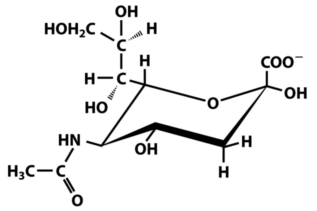
Why sphingomyelin in myelin?

- Think of the polar head
  - No net charge!

Gangliosides, with sialic acid in the polar head termini



***N*-Acetylneuraminic acid (a sialic acid) (Neu5Ac)**

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Glycosphingolipids and Blood Groups

- The blood groups are determined in part by the type of sugars located on the head groups in glycosphingolipids.
- The structure of sugar is determined by a expression of specific glycosyltransferases
  - Individuals with no active glycosyltransferase will have the **O antigen**
  - Individuals with a glycosyltransferase that transfers an N-acetylgalactosamine group have **A blood group**
  - Individuals with a glycosyltransferase that transfers a galactose group to phosphate will have **B blood group**

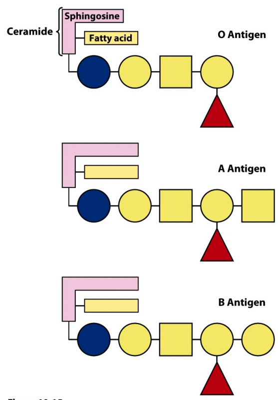

Figure 10-15
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Phosphoipids and sphinoholipids are degraded by lipases

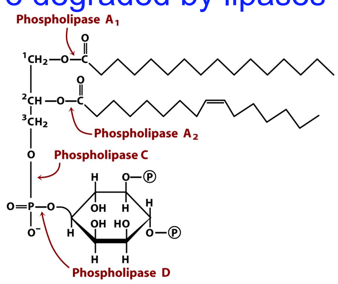

Figure 10-16
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Sterols and Cholesterol

- Sterol:
  - Steroid nucleus: four fused rings
  - Hydroxyl group (polar head) in the A-ring
  - Various non-polar side chains
- The steroid nucleus is almost planar

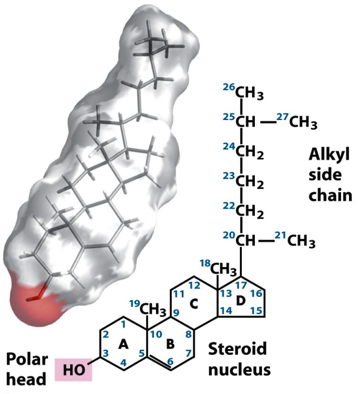

Figure 10-17
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Physiological Role of Sterols

- Cholesterol and related sterols are present in the membranes of most eukaryotic cells.
  - Modulate fluidity and permeability
  - Thicken the plasma membrane
  - Most bacteria lack sterols
- Mammals obtain cholesterol from food and synthesize it *de novo* in the liver
- Cholesterol, bound to proteins, is transported to tissues via blood vessels
  - Cholesterol in low-density lipoproteins tends to deposit and clog arteries
- Many hormones are derivatives of sterols

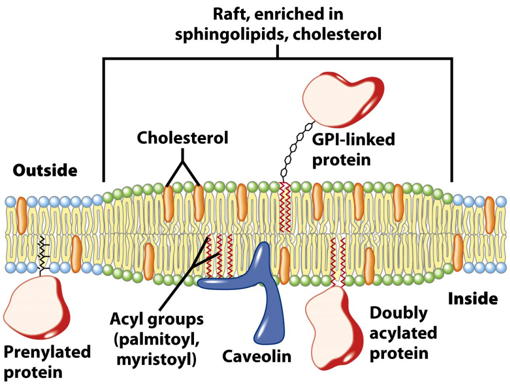

Figure 11-20a
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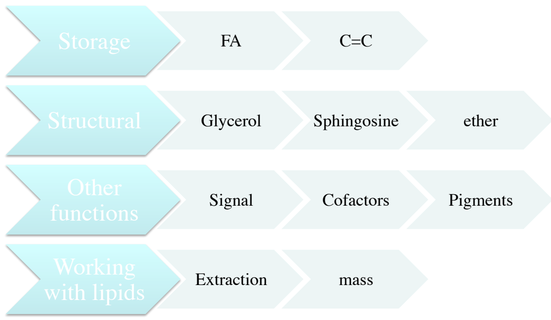

Steroid Hormones

- Steroids are oxidized derivatives of sterols
- Steroids have the sterol nucleus, but lack the alkyl chain found in cholesterol. This makes them more polar than cholesterol.
- Steroid hormones are synthesized in gonads and adrenal glands from cholesterol
- They are carried through the body in the blood stream, usually attached to carrier proteins
- Many of the steroid hormones are male and female sex hormones

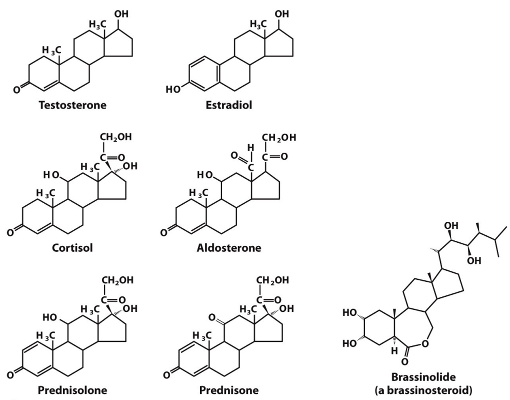

Figure 10-19
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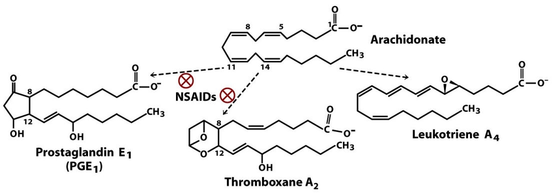
Signaling Lipids

- Paracrine lipid hormones are are present in small amounts but play vital roles as signaling molecules between nearby cells
- Enzymatic oxidation of arachidonic acid yields
  - prostaglandins,
  - thromboxanes, and
  - leukotrienes

Arachidonic Acid Derivatives as Signaling Lipids

- Variety of functions:
  - Inflammation and fever (prostaglandins)
  - Formation of blood clots (thromboxanes)
  - Smooth muscle contraction in lungs (leukotrienes)
  - Smooth muscle contraction in uterus (prostaglandins)



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Vitamins A, D are hormone precursors

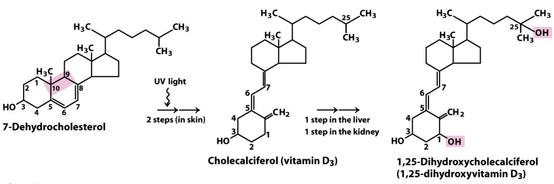

Figure 10-20a
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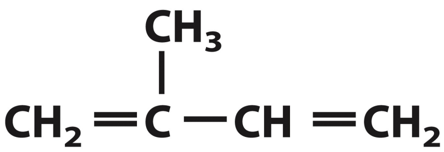
Plants produce volatile signals

- Used as plant signal
- Jasmonate
  - Characteristic of jasmine
  - Plant defense
- Certainly perfume

Vitamins A, D, E, K, Jasmine etc. have same precursor



Isoprene

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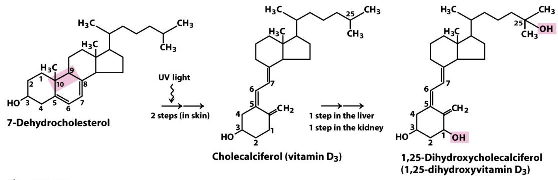

Figure 10-20a
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Figure 10-20b
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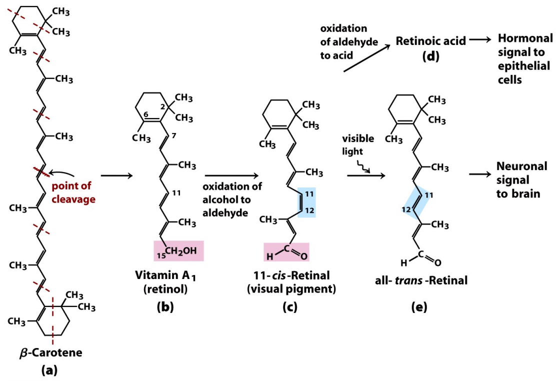

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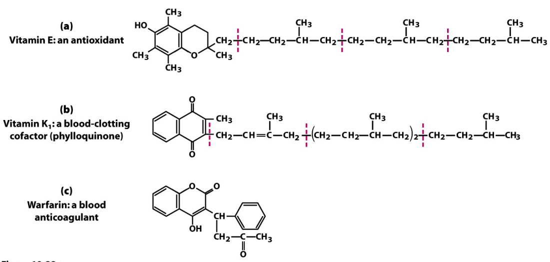

Figure 10-22a-c
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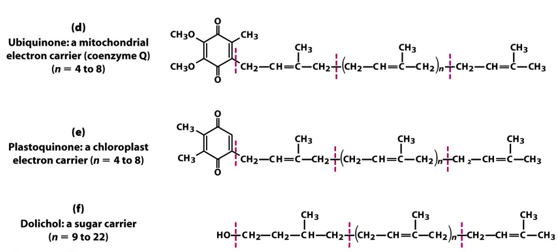

Figure 10-22d-f
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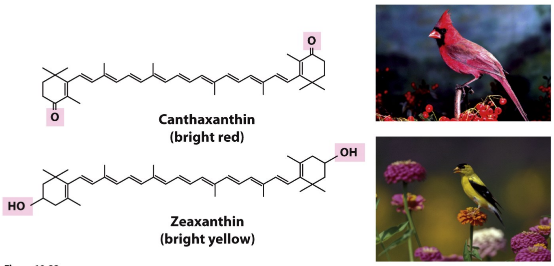

Figure 10-23
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- Storage: FA, C=C
- Structural: Glycerol, Sphingosine, ether
- Other functions: Signal, Cofactors, Pigments
- Working with lipids: Extraction, mass

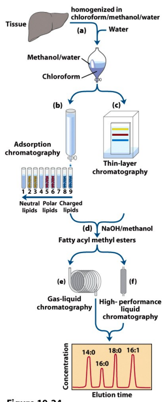

Figure 10-24
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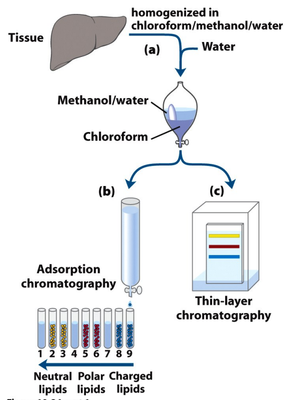

Figure 10-24 part 1
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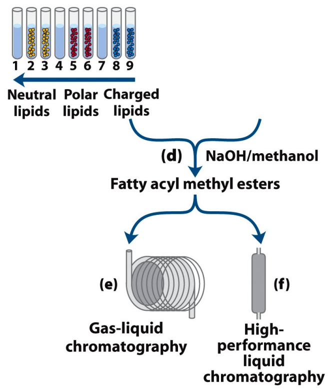

Figure 10-24 part 2
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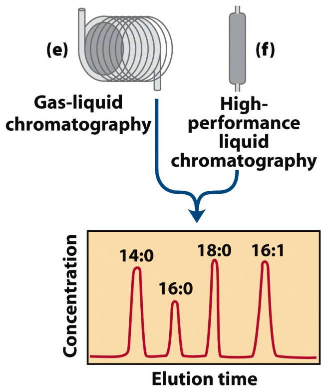

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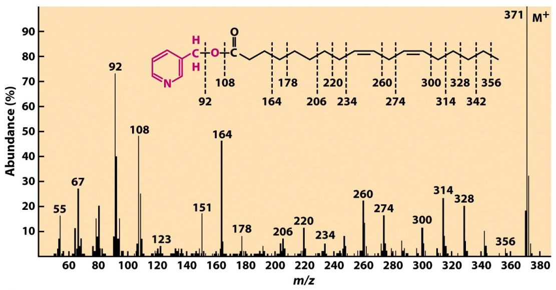

Figure 10-25
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Chapter 10: Summary

In this chapter, we learned that:

- lipids are a structurally and functionally diverse class of molecules that are poorly soluble in water
- triacylglycerols are the main storage lipids
- phospholipids are the main constituents of membranes
- sphingolipids play roles in cell recognition
- cholesterol is both a membrane lipid and the precursor for steroid hormones
- some lipids carry signals from cell to cell and from tissue to tissue

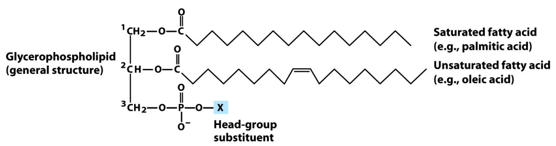

Figure 10-9 part 1
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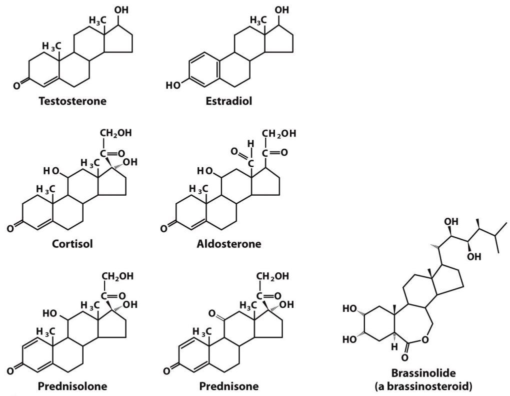

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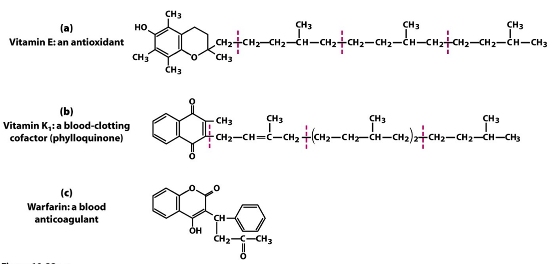

Figure 10-22a-c
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