

Lipids & Membranes

Lecture 28

A. Lipids

1. Roles
2. Classes
 - a. Fatty Acids
 - b. Fats
 - c. Waxes
 - d. Membrane lipids
 - e. Terpenes

B. Membranes

1. Introduction
2. The 4 S's
 - a. Size
 - b. Solubility
 - c. Shape
 - d. Stability
3. Models for Membrane structure
 - a. Old Model
 - b. Data
 - c. Fluid Mosaic Model
 - d. Testing the model
4. The Red-Blood Cell Membrane
5. Membrane Asymmetry
6. Membrane Fluidity

(cont.)
(12/2/24)

- Reading: Ch26; 960-964
Ch27, 1006-1013, 1018-1024
Ch27; 1015-1018, 1028-1036
Ch10; 341-348

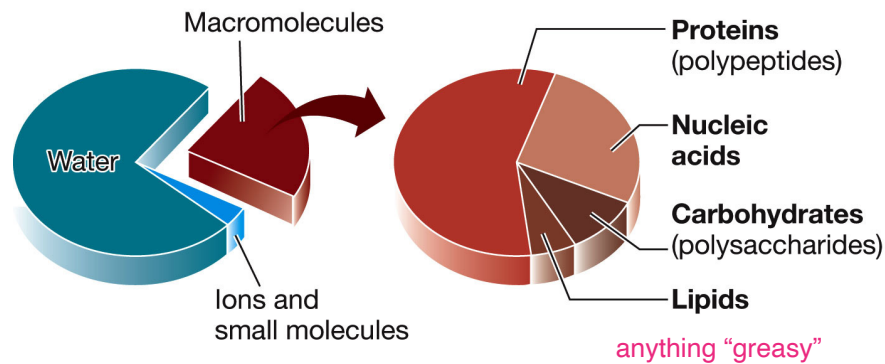
- Homework #29, 30, 31 & 32

NEXT

- Reading: Ch10; 341-348
Ch10; 367-369

Lipids & Membranes

Lipids



Lipids: Roles

- **Membrane structure**
 - main structure of cell membranes
- **Storage of energy**
 - reduced compounds: lots of available energy
 - hydrophobic nature: good packing
- **Signaling molecules**
 - paracrine signals (act locally)
 - steroid hormones (act body-wide)
 - growth factors
 - vitamins A and D (hormone precursors)
- **Vitamins, Cofactors, and secondary products**
 - Vitamins E & K: antioxidant & blood clot formation, resp.
 - coenzyme Q: ATP synthesis in mitochondria
 - Pigments, e.g., tomatoes, carrots, pumpkins, some birds
 - Water repellant in feathers and hides
 - Insulation & bouyancy control in marine mammals (blubber)

Lipids: Roles

Functions of Membranes

- Define the boundaries of the cell
- Allow import and export
 - Selective import of nutrients (e.g. lactose)
 - Selective export of waste and toxins (e.g. antibiotics)
- Retain metabolites and ions within the cell
- Sense external signals and transmit information into the cell
- Provide compartmentalization within the cell
 - separate energy-producing reactions from energy-consuming ones
 - keep proteolytic enzymes away from important cellular proteins
- Produce and transmit nerve signals
- Store energy as a proton gradient
- Support synthesis of ATP

Lipids: Roles

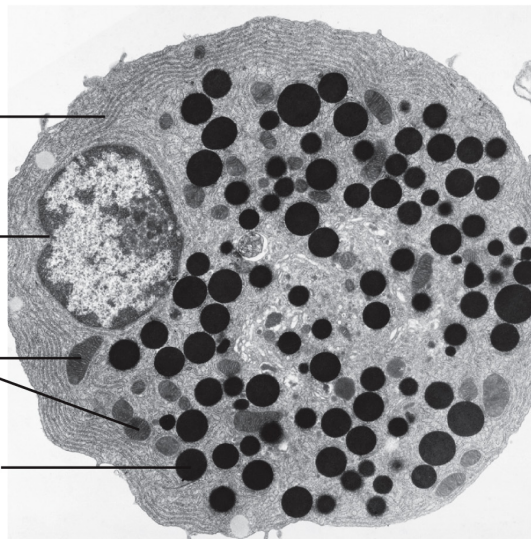
Electron Micrograph of Biological Membranes

**Endoplasmic
reticulum**

**Nuclear
membrane**

Mitochondria

Secretory granule



Pancreas cell

Don W. Favre/Science Source

Lipids: Classes

Biological molecules that are characterized by low solubility in water, that is, are relatively hydrophobic.

They have a high hydrocarbon content

TABLE 10-2 Eight Major Categories of Biological Lipids

Category		Category code	Examples
Fatty acids	①	FA	Oleate, stearoyl-CoA, palmitoylcarnitine
Glycerolipids	②	GL	Di- and triacylglycerols
Glycerophospholipids	④	GP	Phosphatidylcholine, phosphatidylserine, phosphatidylethanolamine
Sphingolipids		SP	Sphingomyelin, ganglioside GM2
Sterol lipids	⑤	ST	Cholesterol, progesterone, bile acids
Prenol lipids		PR	Farnesol, geraniol, retinol, ubiquinone
Saccharolipids		SL	Lipopolysaccharide
Polyketides		PK	Tetracycline, erythromycin, aflatoxin B ₁
Waxes	③		

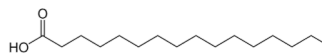
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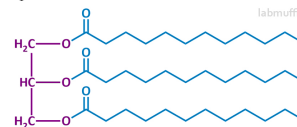
Classes of Lipids

They have a high hydrocarbon content

1. Fatty acids

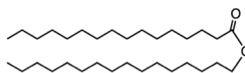


2. Fats (triglycerides)

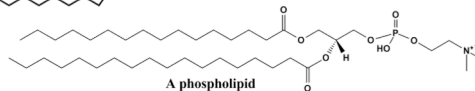


Structure of a fat

3. Waxes

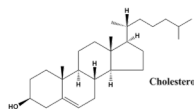


4. Membrane Lipids



A phospholipid

5. Isoprenes

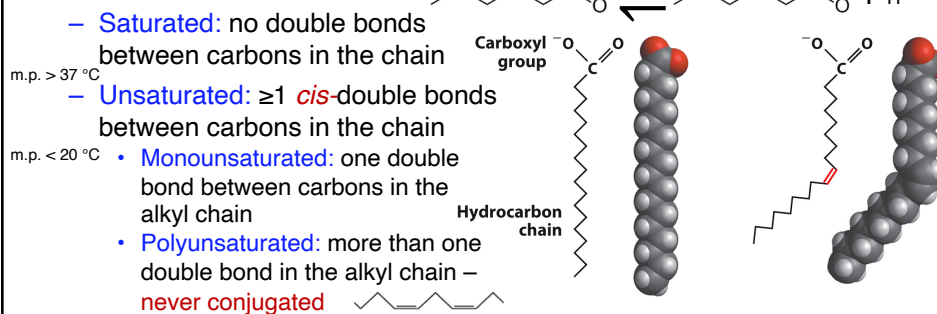


Cholesterol

Lipids: Fatty Acids

- Carboxylic acids with hydrocarbon chains containing between 4 to 36 carbons
 - Almost all natural fatty acids have an **even** number of carbons.
 - Most natural fatty acids are **unbranched**.
- Biologically, most are found in ester linkages as the **pK_a** is ~3.0, and would otherwise be very acidic.

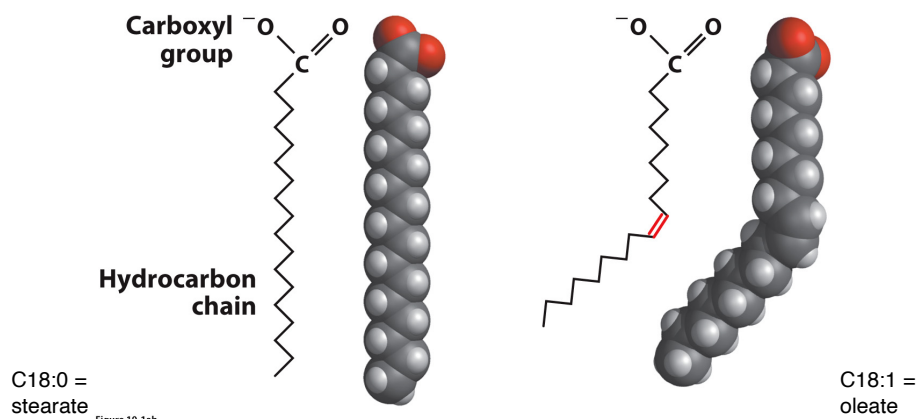
TWO CLASSES



Lipids: Fatty Acids

Conformation of Fatty Acids

- The saturated chain tends to adopt extended conformations.
- The double bonds in natural unsaturated fatty acids are in a **cis** configuration, which **kinks** the chain.



Lipids: Fatty Acids

Fatty Acid Compositions of Some Dietary Lipids*

Source	Lauric and Myristic	Palmitic	Stearic	Oleic	Linoleic
Beef	5	24-32	20-25	37-43	2-3
Milk		25	12	33	3
Turkey	1	18-20	12-14	18-20	25-30
Coconut	74	10	2	7	—
Corn		8-12	3-4	19-49	34-62
Olive		9	2	84	4
Palm		39	4	40	8
Safflower		6	3	13	78
Soybean		9	6	20	52
Sunflower		6	1	21	66

Data from *Merck Index*, 10th ed. Rahway, NJ: Merck and Co., and Wilson et al., 1967, *Principles of Nutrition*, 2nd ed. New York: Wiley.

Saturated FA

Unsaturated FA

Lipids: Fatty Acids

Common Biological Fatty Acids

Number of Carbons	Common Name	Systematic Name	Symbol	Structure
Saturated fatty acids				
12	Lauric acid	Dodecanoic acid	12:0	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
14	Myristic acid	Tetradecanoic acid	14:0	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$
16	Palmitic acid	Hexadecanoic acid	16:0	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
18	Stearic acid	Octadecanoic acid	18:0	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
20	Arachidic acid	Eicosanoic acid	20:0	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$
22	Behenic acid	Docosanoic acid	22:0	$\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$
24	Lignoceric acid	Tetracosanoic acid	24:0	$\text{CH}_3(\text{CH}_2)_{22}\text{COOH}$
Unsaturated fatty acids (all double bonds are cis)				
16	Palmitoleic acid	9-Hexadecenoic acid	16:1 (Δ^9)	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
18	Oleic acid	9-Octadecenoic acid	18:1 (Δ^9)	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
18	Linoleic acid	9,12-Octadecadienoic acid	18:2 ($\Delta^9,12$)	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_2(\text{CH}_2)_6\text{COOH}$
18	α -Linolenic acid	9,12,15-Octadecatrienoic acid	18:3 ($\Delta^9,12,15$)	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_6\text{COOH}$
18	γ -Linolenic acid	6,9,12-Octadecatrienoic acid	18:3 ($\Delta^{6,9,12}$)	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_3\text{COOH}$
20	Arachidonic acid	5,8,11,14-Eicosatetraenoic acid	20:4 ($\Delta^{5,8,11,14}$)	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_4(\text{CH}_2)_2\text{COOH}$
24	Nervonic acid	15-Tetracosenoic acid	24:1 (Δ^{15})	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{15}\text{COOH}$

Need to Know: Common names, structure, symbol

Lipids: Fatty Acids

Nomenclature

- Fatty acids can be described by:

- systematic name: *cis*-9-octadecanoic acid

- common name: **oleic acid**

- delta numbering of carbon skeleton: 18:1 Δ^9

- describes location of the first carbon of the alkene in relationship to the carbonyl carbon

- omega numbering of carbon skeleton: 18:1 ω^9

- describes location of the first carbon of the alkene in relationship to the terminal methyl

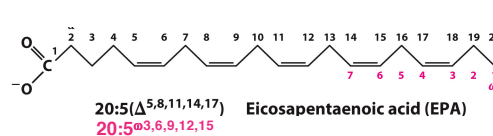
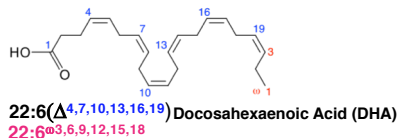
- Omega-3 fatty acids are essential nutrients

- Humans need them: cannot synthesize them.

- They include **α -linolenic acid (ALA)** (18:3 $\Delta^{9,12,15}$) (18:3 $\omega^{3,6,9}$),

Eicosapentaenoic acid (EPA), and Docosahexaenoic Acid (DHA).

- although DHA (22:6) and EPA (20:5) can be synthesized from ALA



Lipids: Fatty Acids

Solubility and Melting Point of Fatty Acids

- Solubility

- decreases as the chain length increases

- Melting Point

- decreases as the chain length decreases

- decreases as the number of double bonds increases

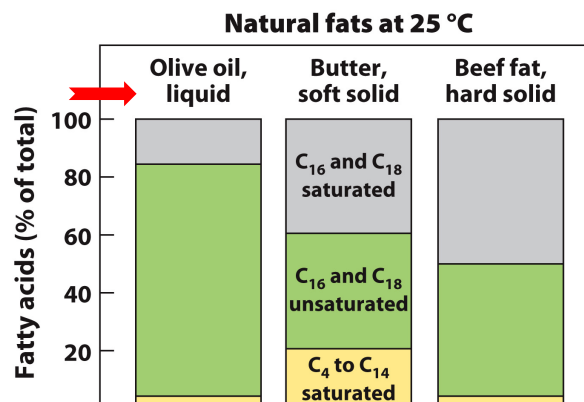


Figure 10-4

Lipids: Fatty Acids

Melting Point and Double Bonds

- Saturated fatty acids pack in a fairly orderly way.
 - extensive favorable interactions What kind of interaction?
- Unsaturated cis fatty acids pack less orderly due to the kink.
 - less-extensive favorable interactions van der Waals
- It takes less thermal energy to disrupt disordered packing of unsaturated fatty acids.
 - Explains the lower melting point of unsaturated cis fatty acids.

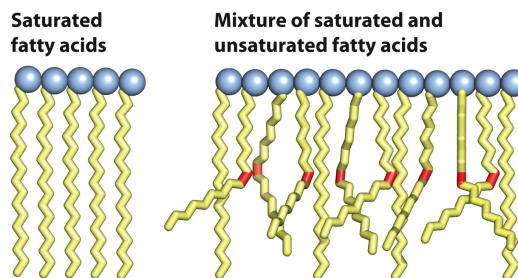
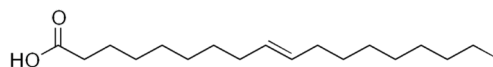


Figure 10-1d
Lehninger Principles of Biochemistry, Seventh Edition
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Lipids: Fatty Acids

Trans Fatty Acids

- Trans fatty acids form by partial hydrogenation (reduction) of unsaturated fatty acids.
 - done to increase shelf life or stability at high temperature of oils used in cooking (especially deep frying)
 - Or to convert plant oils to margarine, a solid fat (partially hydrogenated polyunsaturated oils).
- 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.
- 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).



trans-Oleic acid (Elaidic acid)

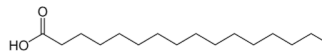
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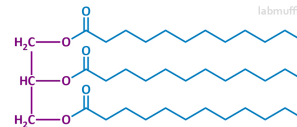
Classes of Lipids

They have a high hydrocarbon content

1. Fatty acids

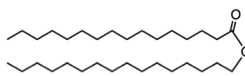


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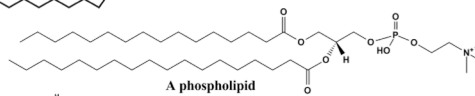


Structure of a fat

3. Waxes

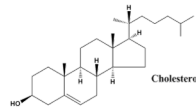


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A phospholipid

5. Isoprenes



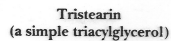
Cholesterol

Lipids: Fat

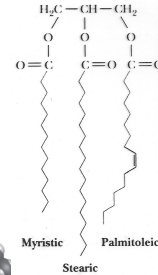
Triacylglycerols (Nonpolar)

- The majority of fatty acids in biological systems are found in the form of triacylglycerols.
 - Solid ones are called **fats**.
 - Liquid ones are called **oils**.
- The primary storage form of lipids (**body fat**)
- Less soluble in water than fatty acids due to the esterification of the carboxylate group
- Less dense than water: **fats and oils float**.

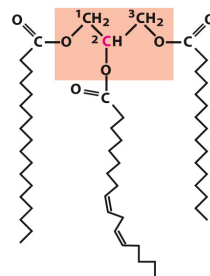
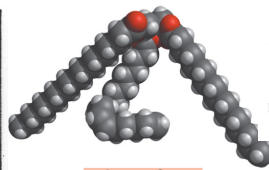
Triacylglycerols



Tristearoyl glycerol



Myristic }
Stearic } Palmitoleic



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



Name?

1-Myristoyl-2-stearoyl-3-palmitoleoyl glycerol

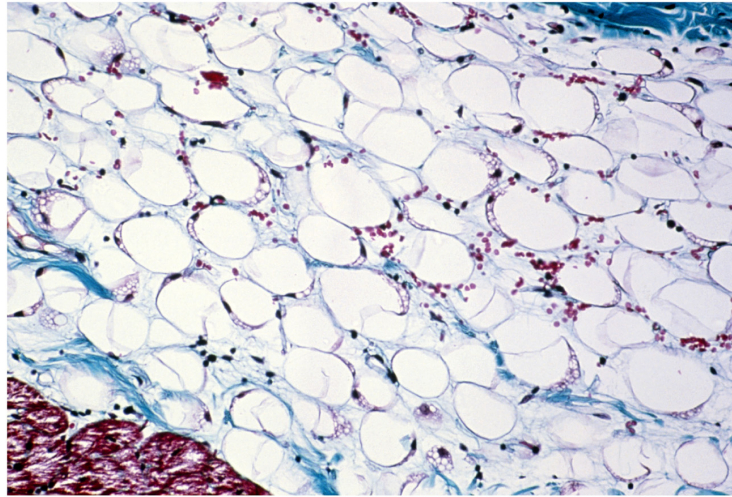
Fats Provide Efficient Fuel Storage

-



Lipids: Fat

Fats Provide Efficient Fuel Storage



Biophoto Associates/Science Source

125 μm

Figure 10-3a

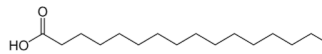
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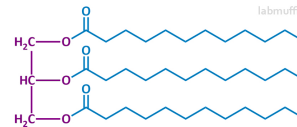
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They have a high hydrocarbon content

1. Fatty acids



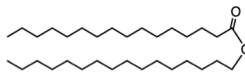
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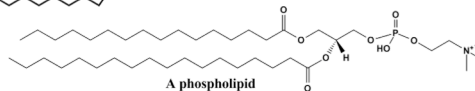
labmuffin

Structure of a fat

3. Waxes

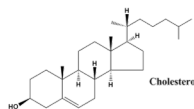


4. Membrane Lipids



A phospholipid

5. Isoprenes



Cholesterol

Lipids: Waxes

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

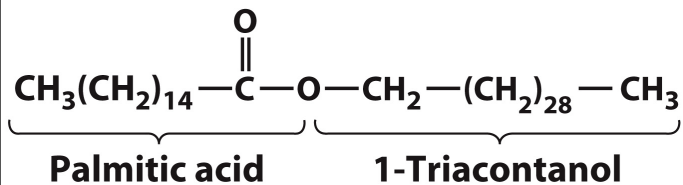
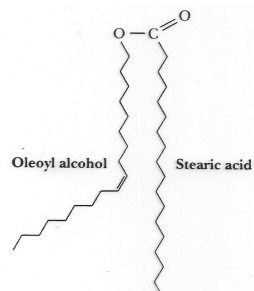


Figure 10-5a



Lipids: Waxes

Wax: The Material of the Honeycomb

Beeswax is a mixture of a large number of lipids, including esters of triacontanol (C30:0) and cerylalcohol (C26:0).



Figure 10-5b

