

Notes 10/19

Friday, October 19, 2007
10:04 AM



Notes 1019

Audio recording started: 10:04 AM Friday, October 19, 2007

Lipids: Properties Lipoproteins

Oct. 18, 2007

Lecture Slides

- Some instructors charge you \$\$ for their notes
- Making digital lectures (Powerpoint) and loading them online takes *a lot* more effort for me and I don't get paid more for doing it
- The department does not supply most lecturers with a laptop
- I very much appreciate your patience with me

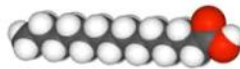
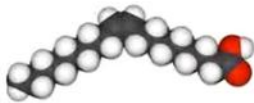
Quick Review of Lipids

- Energy Storage
 - Triacylglycerols
 - Glycerol parent linked to three fatty acids
 - Fatty acids are saturated or unsaturated
- Membrane Lipids
 - Glycerophospholipids
 - Glycerol parent linked to two fatty acids and a polar phosphoryl head group
 - Sphingolipids
 - Ceramide parent linked to R-group
 - Sphingomyelin's R = PC or PE
 - Cerebroside's R = monosaccharide
 - Ganglioside's R = oligosaccharide
 - Steroids
 - Cyclopentanoperhydrophenanthrene parent

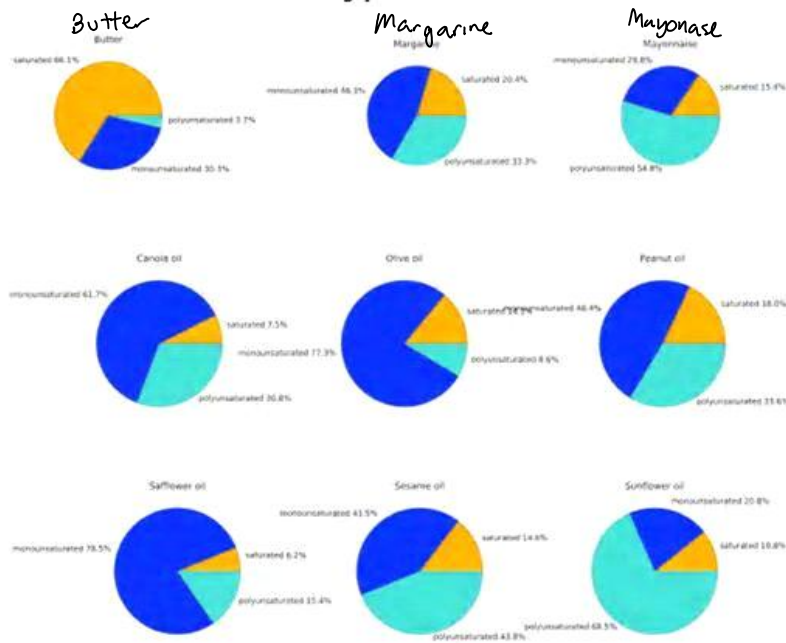
PC- phosphatidyl choline
PE- phosphatidyl

Sources of fats

- | | |
|--|--|
| <ul style="list-style-type: none"> • Monounsaturated Fats <ul style="list-style-type: none"> – Avocados – Canola oil – flaxseed oil – grapeseed oil – Olive oil – Peanut oil and other nuts – Sesame oil | <ul style="list-style-type: none"> • Saturated Fats <ul style="list-style-type: none"> • Fats from animals: <ul style="list-style-type: none"> – beef, veal, lamb, pork, lard, poultry fat, butter, cream, milk, cheeses (All of these contain dietary cholesterol as well) • Foods from plants: <ul style="list-style-type: none"> – coconut, coconut oil, palm oil and palm kernel oil, and cocoa butter. |
|--|--|



Relative amounts of types of fat in selected foods



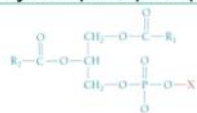
Source: Gebhardt SE, Thomas PG (2002). Nutritive Value of Foods. United States Department of Agriculture, Agricultural Research Service. Home and Garden Bulletin 72

Trans-fatty acids

- Unsaturated fatty acids can be "cis" and "trans."
- We won't study any particular examples of trans-fatty acids but they do exist in nature
- Trans-fatty acids (TFA) are found in small amounts in various animal products such as beef, pork, lamb, dairy products
- TFA are also formed during the process of hydrogenation
- making margarine, shortening, cooking oils and the foods made from them are a major source of TFA in the American diet.
- <http://www.bantransfats.com/>

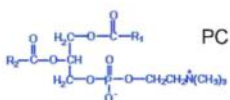


Common Classes of Glycerophospholipids (Oct. 17, slide 23)

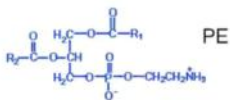


Name of X-OH	Formula of -X	Name of Phospholipid
Water	-H	Phosphatidic acid
Ethanolamine	$-\text{CH}_2\text{CH}_2\text{NH}_3^+$	Phosphatidylethanolamine
Choline	$-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_3^+$	Phosphatidylcholine (lecithin)
Serine	$-\text{CH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-$	Phosphatidylserine
Glycerol	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$	Phosphatidylglycerol

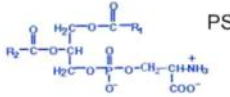
If this table isn't clear to you please look at the next slide...



PC



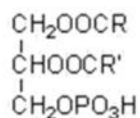
PE



PS



PG



Phosphatidic acid

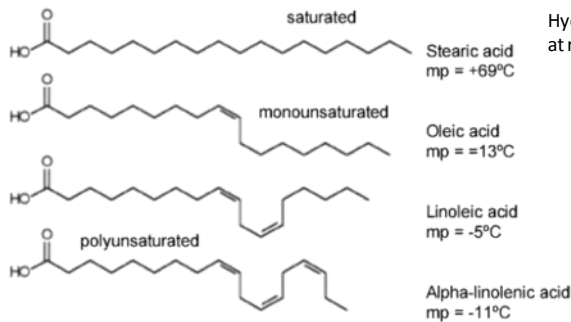
Be able to identify the R groups on these and name entire thing.

Unsaturated fatty acids (Oct. 17, slide 18)



- Double-bond almost always cis configuration
- Rigid 30° bend restricts packing
- Reduced van der Waals interactions
- **m.p. decreases with increasing unsaturation**
- Lard is solid, vegetable oil is liquid at R.T.

m.p. decreases with increasing unsaturation

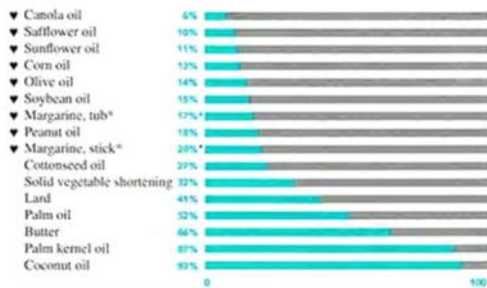


Hydrocarbon tail on stearic acid can pack more tightly and are therefore solid at room temp.

The SatFat Graph

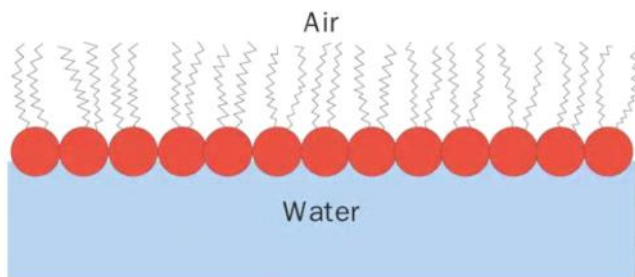
Use this handy graph to help you choose the products with the least amount of saturated fat.

(BLUE) = % SATURATED
(GREY) = % UNSATURATED

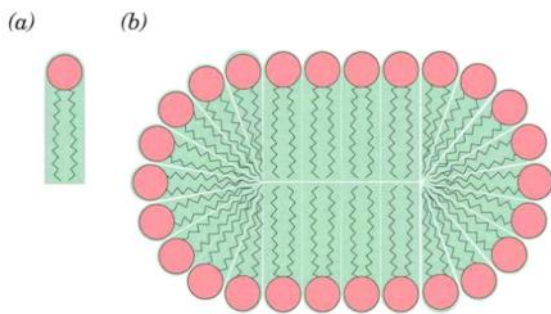


*An average of margarines listing liquid oil as the first ingredient.

We are mostly water so our lipids must get along with water despite their differences

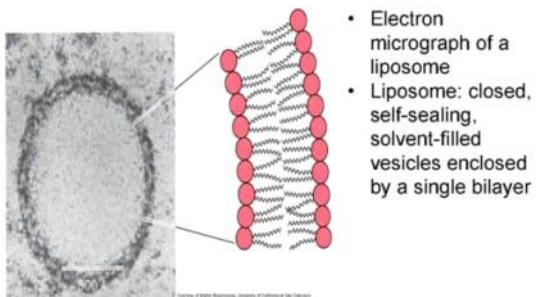


Bilayer formation by phospholipids



Type of micelle

Glycerophospholipids and sphingolipids tend to form bilayers



Biological membranes are rich in lipids

Just understand that these members vary by organism

Lipid	Human Erythrocyte	Human Myelin	Beef Heart Mitochondria	<i>E. coli</i>
Phosphatidic acid	1.5	0.5	0	0
Phosphatidylcholine	19	10	39	0
Phosphatidylethanolamine	18	20	27	65
Phosphatidylglycerol	0	0	0	18
Phosphatidylinositol	1	1	7	0
Phosphatidylserine	8.5	8.5	0.5	0
Cardiolipin	0	0	22.5	12
Sphingomyelin	17.5	8.5	0	0
Glycolipids	10	26	0	0
Cholesterol	25	26	3	0

*The values given are weight percent of total lipid.

Source: Tanford, C., *The Hydrophobic Effect*, p. 109, Wiley (1980).

Biological membranes have other biomolecules as well

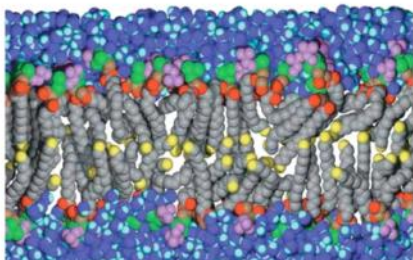
Membrane	Protein (%)	Lipid (%)	Carbohydrate (%)	Protein to Lipid Ratio
Plasma membranes:				
Mouse liver cells	46	54	2-4	0.85
Human erythrocyte	49	43	8	1.1
Amoeba	52	42	4	1.3
Rat liver nuclear membrane	59	35	2.0	1.6
Mitochondrial outer membrane	52	48	(2-4) ^a	1.1
Mitochondrial inner membrane	76	24	(1-2) ^a	3.2
Myelin	18	79	3	0.23
Gram-positive bacteria	75	25	(10) ^a	3.0
<i>Halobacterium</i> purple membrane	75	25		3.0

^aDeduced from the analyses.

Source: Guidotti, G., *Annu. Rev. Biochem.* **41**, 732 (1972).

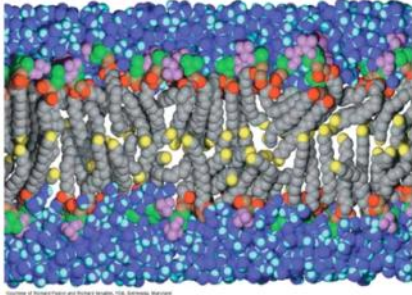
much higher because it serves to insulate charge away from aq. solution

Biological membranes are an exclusive party

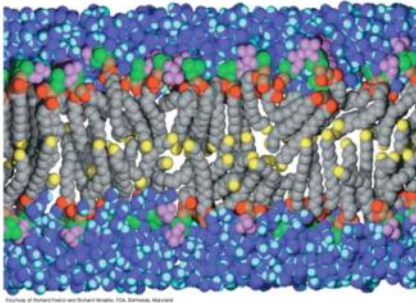


1. solution

Biological membranes are an
exclusive party

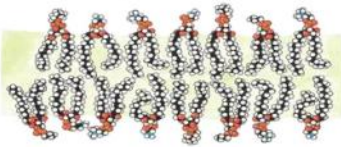


The secret into the party:
You need to be "small" like
water or in polar

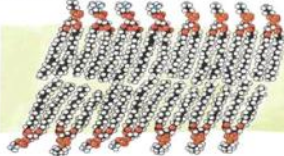


The party dies down on its
own when its cold

(a) Above transition temperature



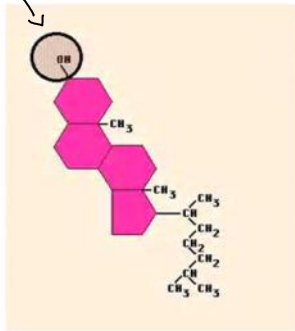
(b) Below transition temperature



- Structure of a lipid bilayer composed of PC and PE
- Bilayer fluidity varies with T
- It loses fluidity below a characteristic transition temperature
- Hydrocarbon chains become fully extended

Cholesterol keeps things moving

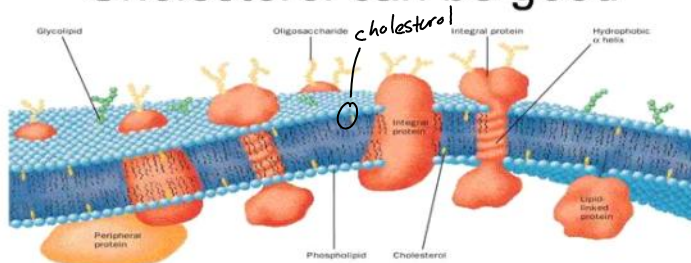
polar



It affects
membrane
fluidity

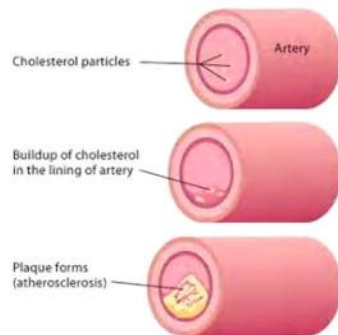
-weakly amphipathic

Cholesterol can be good



- Cholesterol decreases membrane fluidity near the membrane surface due to its rigidity
- At high T cholesterol tends to reduce membrane fluidity, probably by interacting with the hydrocarbon tails of other lipids
- At low temperatures cholesterol helps prevent membranes from freezing and thus tends to maintain membrane fluidity

Cholesterol can be bad...



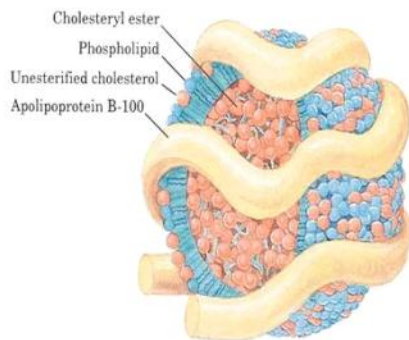
- ...to be continued

Always designate a driver



- Lipids aren't very soluble in aqueous solutions
- How do they travel though the blood stream?
- Lipoprotein "taxis"

Lipoproteins are globular micellelike particles



- nonpolar core of triacylglycerols and cholesterol esters
- surrounded by an amphiphilic coating of protein, phospholipid, and cholesterol

Chapter 2 Problem #8

- Calculate the pH of:

A. 0.1 M HCL $\text{pH} = -\log(.1) = 1$

B. 0.1 M NaOH 13

C. 3×10^{-5} M HNO_3

D. 5×10^{-10} M HClO_4

E. 2×10^{-8} M KOH \downarrow



$$[\text{H}^+][\text{OH}^-] = 10^{-14} \text{ M}$$

$$[\text{H}^+] + [\text{K}^+] = [\text{OH}^-]$$

$$[\text{H}^+]([\text{H}^+] + [\text{K}^+]) = 10^{-14}$$

$$[\text{H}^+]^2 + 2 \times 10^{-8} [\text{H}^+] - 10^{-14} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$[\text{H}^+][\text{OH}^-] = 10^{-14}$$