Food Lipids

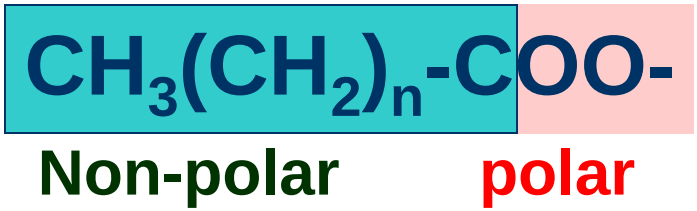
Lipids

- “Lipids consist of a board group of compounds that are generally soluble in organic solvents but only sparingly soluble in water….” “…Glycerol esters of fatty acids, which make up 99% of the lipids of plant and animal origin have traditionally been called fats and oils”

Nawar, “Lipids” Food Chemistry, Fennema Ed. 1996

Lipids are non-polar (hydrophobic) compounds, soluble in organic solvents.

Fatty acids consist of a hydrocarbon chain with a carboxylic acid at one end.

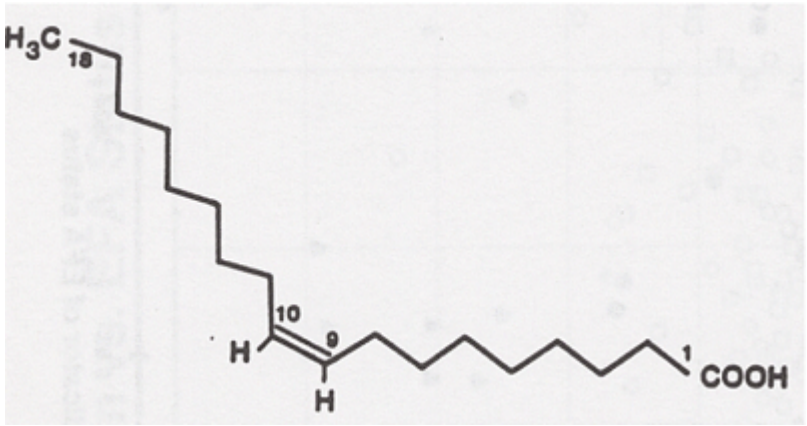


Saturated Fatty Acids

Systematic name	Trivial name	Shorthand designation	Molecular wt.
butanoic	butyric	4:0	88.1
pentanoic	valeric	5:0	
hexanoic	caproic	6:0	116.1
octanoic	caprylic	8:0	144.2
nonanoic	pelargonic	9:0	158.2
decanoic	capric	10:0	172.3
dodecanoic	lauric	12:0	200.3
tetradecanoic	myristic	14:0	228.4
hexadecanoic	palmitic	16:0	256.4
heptadecanoic	margaric (daturic)	17:0	270.4
octadecanoic	stearic	18:0	284.4
eicosanoic	arachidic	20:0	312.5
docosanoic	behenic	22:0	340.5

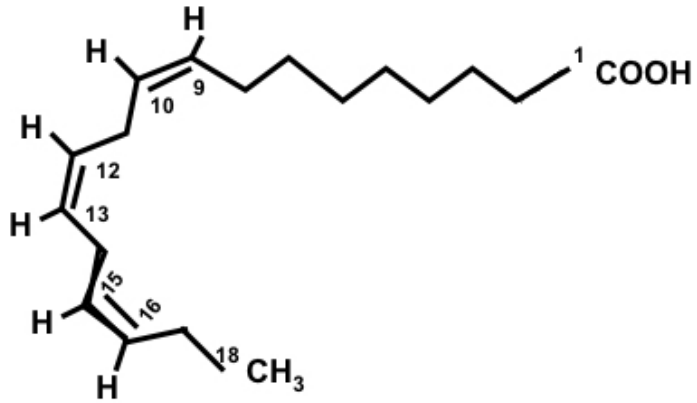
Mono-Unsaturated Fatty Acids

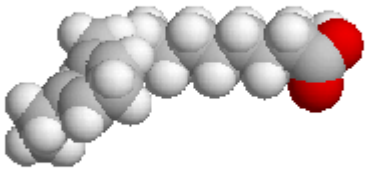
Systematic name	Trivial name	Shorthand designation	Molecular wt.
cis-9-tetradecenoic	myristoleic	14:1(n-5)	226.4
cis-9-hexadecenoic	palmitoleic	16:1(n-7)	254.4
cis-9-octadecenoic	oleic	18:1(n-9)	282.4
tr-9-octadecenoic	elaidic	tr18:1(n-9)	282.4
cis-11-octadecenoic	vaccenic (asclepic)	18:1(n-7)	282.4
cis-11-eicosenoic	gondoic	20:1(n-9)	310.5
cis-13-docosenoic	erucic	22:1(n-9)	338.6



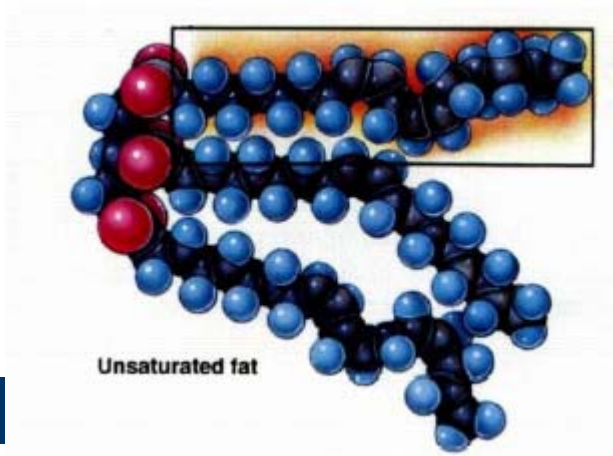
Poly-Unsaturated Fatty Acids

Systematic name	Trivial name	Shorthand designation	Molecular wt.
9,12-octadecadienoic	linoleic	18:2(n-6)	280.4
6,9,12-octadecatrienoic	γ-linolenic	18:3(n-6)	278.4
9,12,15-octadecatrienoic	α-linolenic	18:3(n-3)	278.4
6,9,12,15-octadecatetraenoic	stearidonic	18:4(n-3)	276.4
5,8,11,14-eicosatetraenoic	arachidonic	20:4(n-6)	304.5
5,8,11,14,17-eicosapentaenoic	EPA	20:5(n-3)	302.5
4,7,10,13,16,19-docosahexaenoic	DHA	22:6(n-3)	328.6



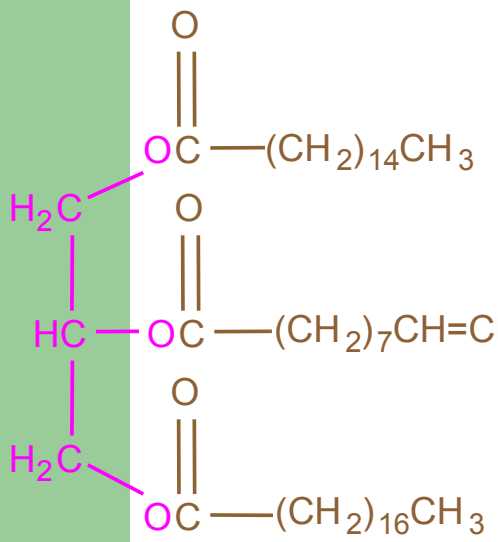


Lipids



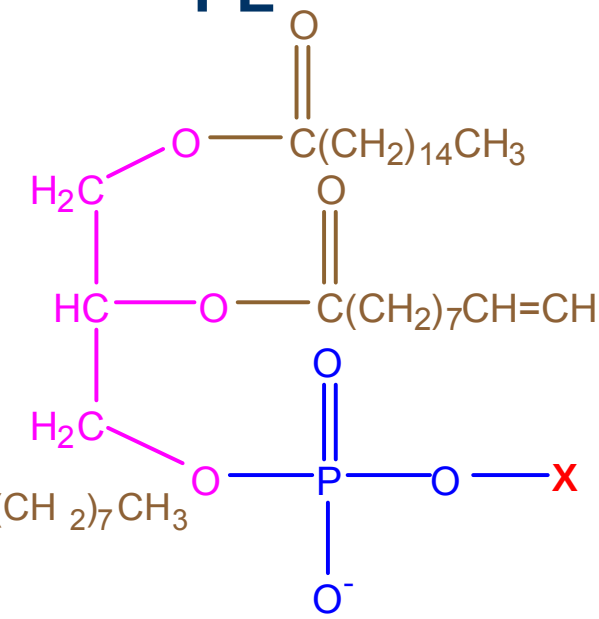
Storage (neutral)

TAG

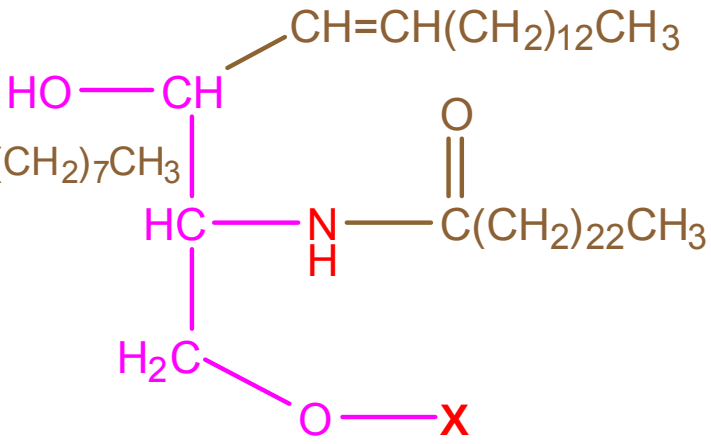


Membrane (polar)

PL

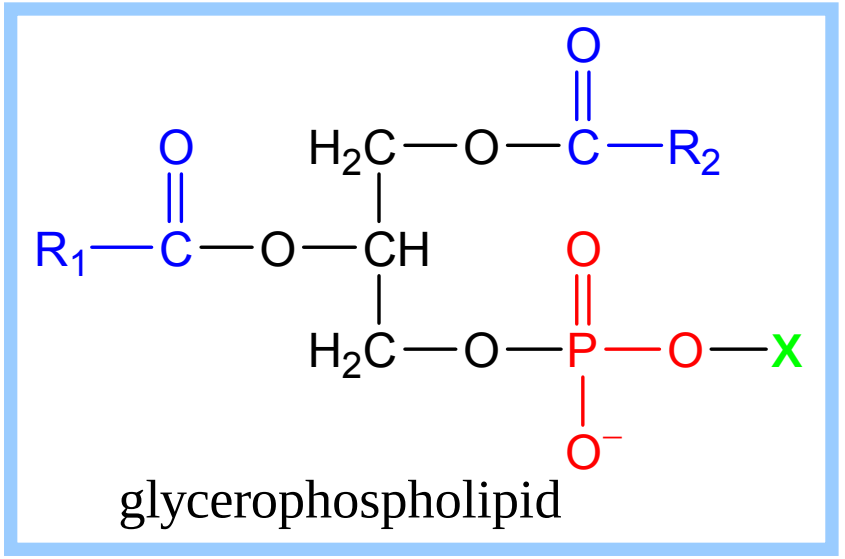


GL

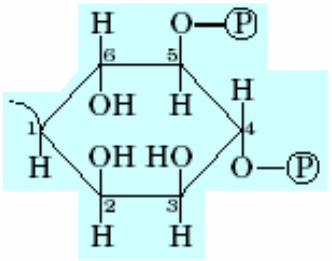
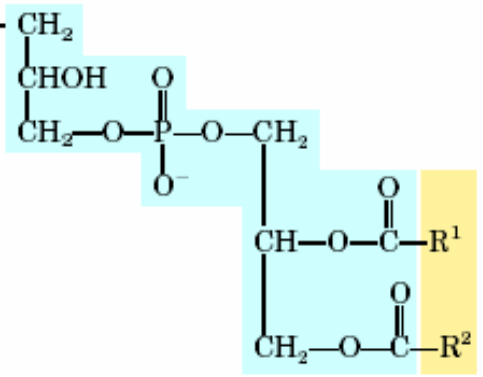


Phospholipids

- **P_i** is in turn esterified to **OH** of a **polar head group** (**X**): e.g., **serine, choline, ethanolamine, glycerol, or inositol**.
- The 2 fatty acids tend to be non-identical. They may differ in length and/or the presence/absence of double bonds.

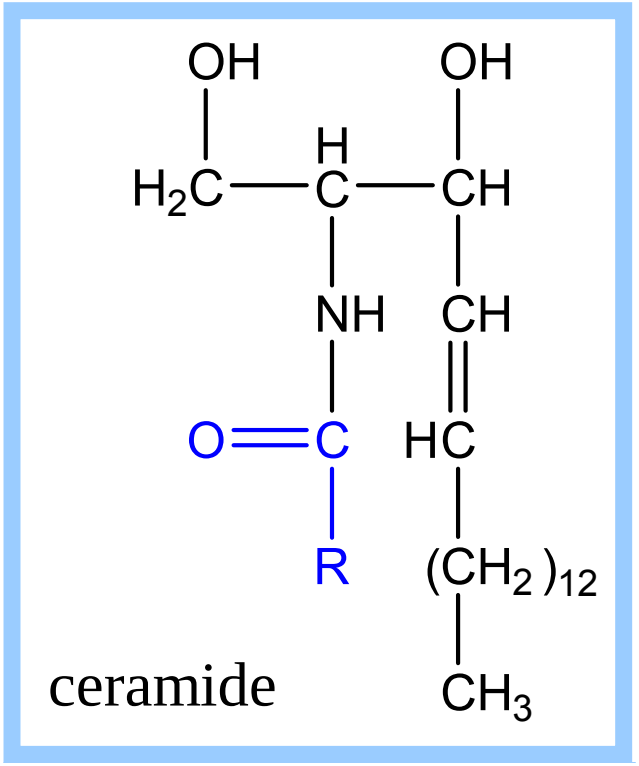


glycerophospholipid

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—$CH(\overset{+}{N}H_3)$—COO^-	−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

Sphingolipids

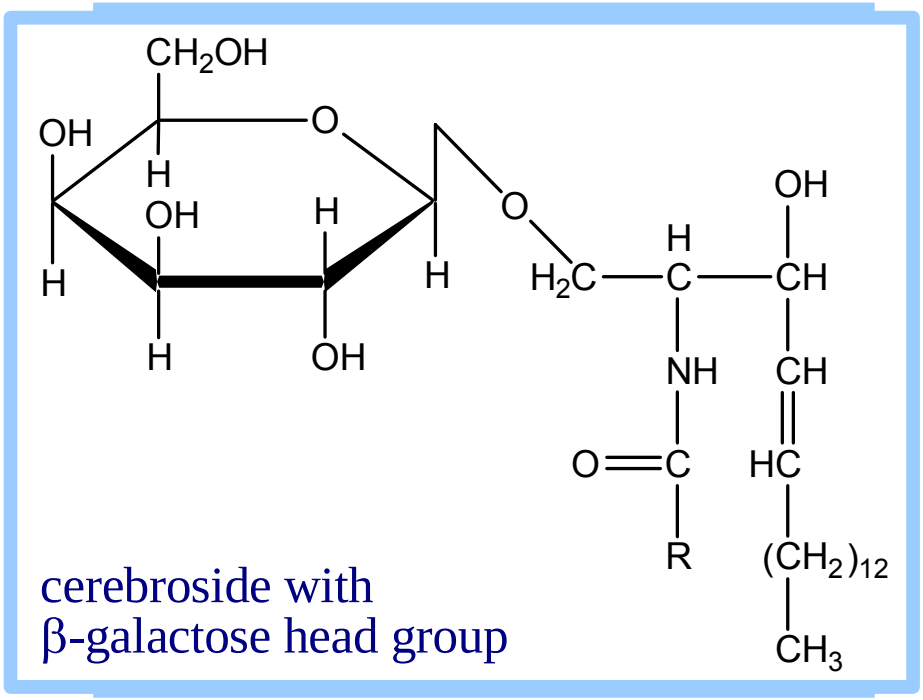
- Sphingolipids are derivatives of the lipid sphingosine, which has a long hydrocarbon tail, and a polar domain that includes an amino group.
- The amino group of sphingosine can form an amide bond with a fatty acid carboxyl, to yield a ceramide.



ceramide

Sphingolipids

- Sphingomyelin, a ceramide with a phosphocholine or phosphethanolamine head group, is a common constituent of plasma membranes
- A cerebroside is a sphingolipid (ceramide) with a monosaccharide such as glucose or galactose as polar head group.



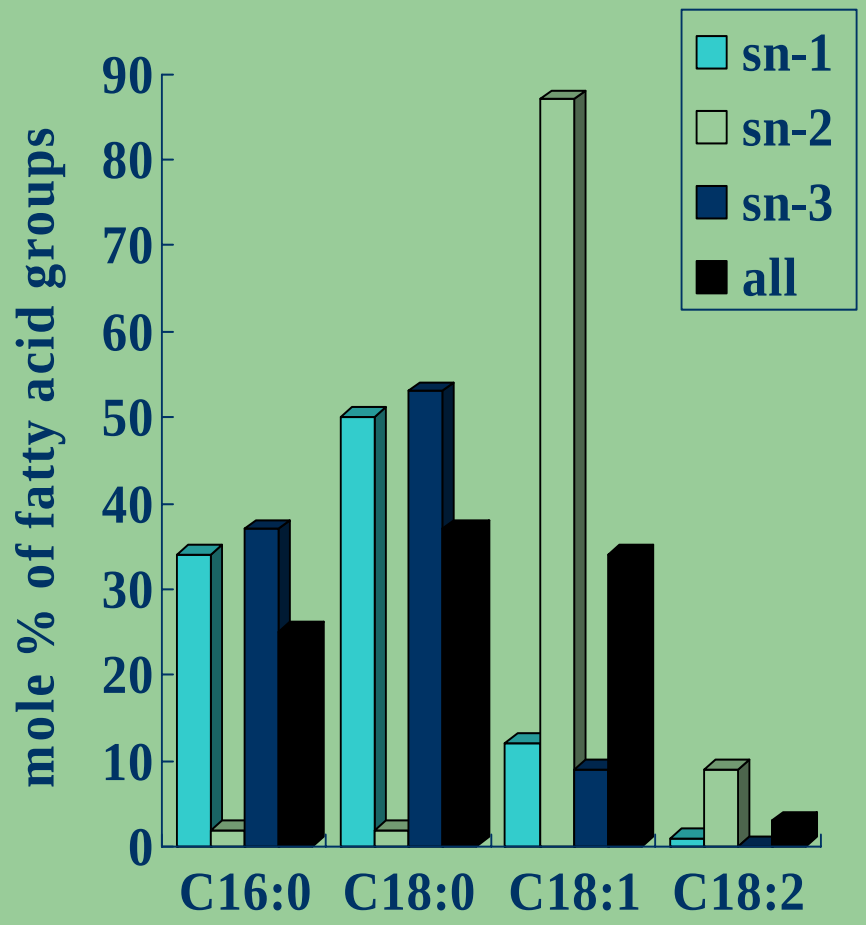
cerebroside with
β-galactose head group

Attributes of Food Lipids

- Three major functions in foods
  - Energy and health
  - Influence food flavors
    - free fatty acids contribute flavors
    - lipids act as solvents for carrying hydrophobic flavors and aromas (and nutrients)
  - Texture
    - Solid vs liquid
    - Emulsions

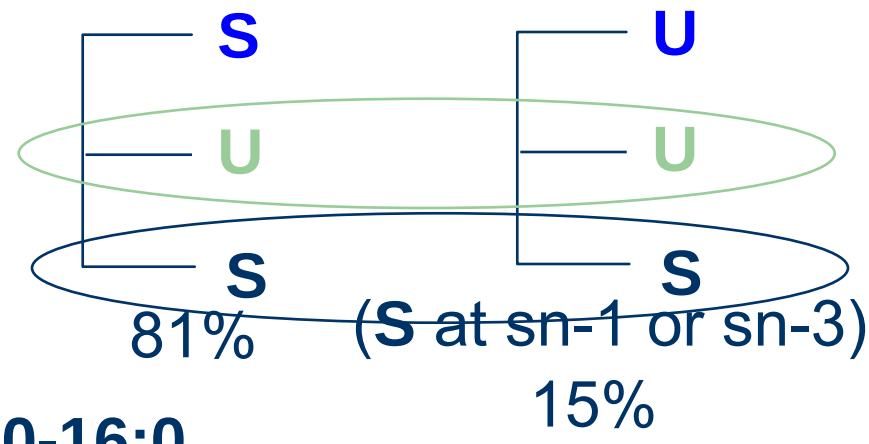
Attributes determined by types and positions of fatty acids on glycerol backbone

Plant Triglycerides



(Belitz and Grosch, 1999; © Springer-Verlag.)

- Cocoa butter
  - ~ equal 16:0, 18:0, 18:1
  - sn-2 primarily unsat'd (U)
  - sn-1,3 mostly sat'd (S)

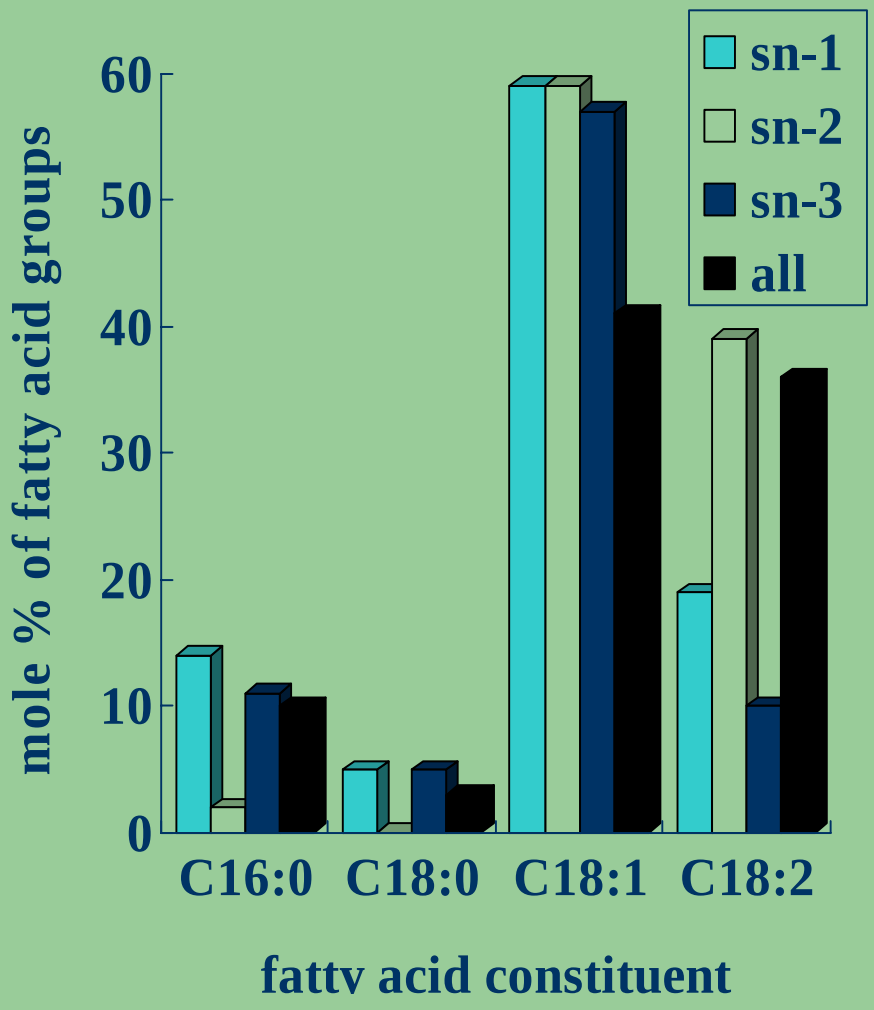


– **Coconut, palm oil richer in 8:0-16:0**

Plant Triglycerides

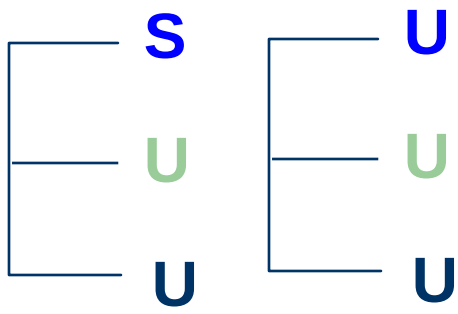
- Coconut oil
  - 80% of triacylglycerols are trisaturated
    - Lauric at sn-2
    - Octanoic at sn-3
    - Myristic or palmitic at sn-1

Plant Triglycerides



(Belitz and Grosch, 1999; © Springer-Verlag.)

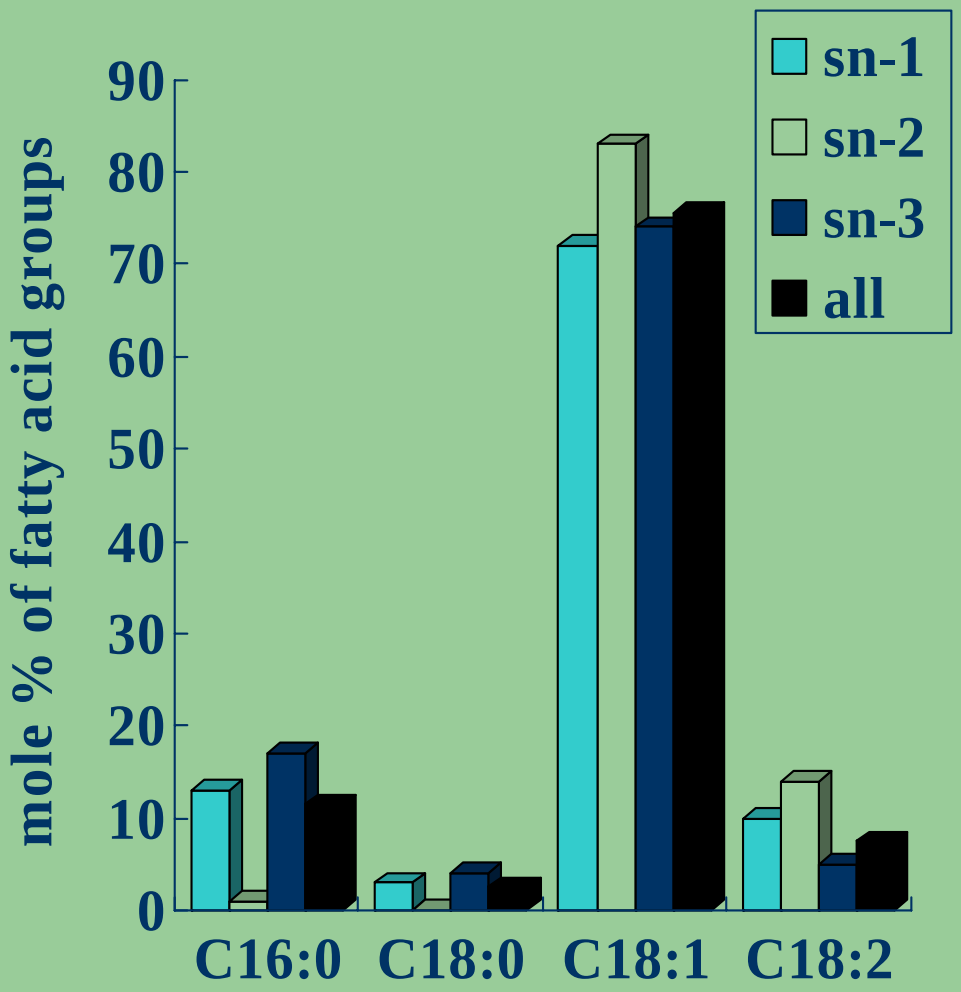
- Peanut Oil
  - ~40% oleic; 40%linoleic
  - sn-2 largely unsat'd



(< 30%) (> 70%)

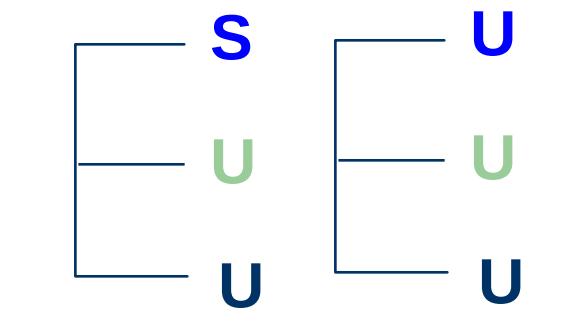
– **Soybean oil similar**

Plant Triglycerides



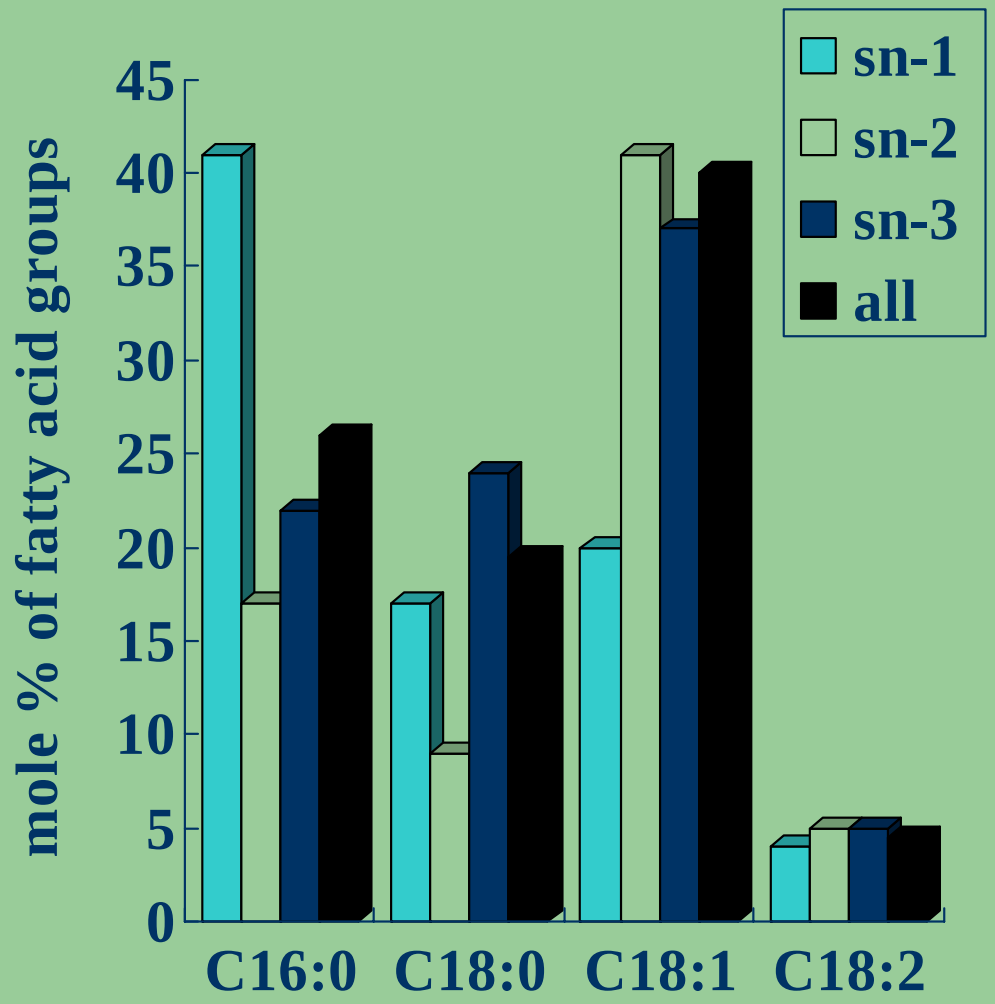
(Belitz and Grosch, 1999; © Springer-Verlag.)

- Olive Oil
  - ~75% oleic
  - sn-2 99% unsat'd
  - homogeneous



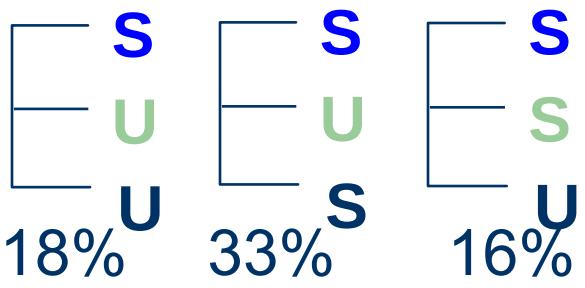
(< 30%) (> 70%)

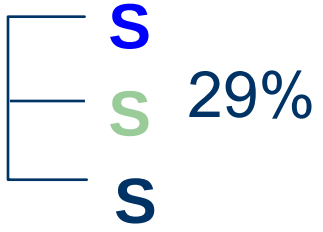
Animal Triglycerides



(Belitz and Grosch, 1999; © Springer-Verlag.)

- Beef Fat (tallow)
  - ~ equal 16:0, 18:0, 18:1
  - sn-1,2,3 sat'd (S) & unsat'd (U)

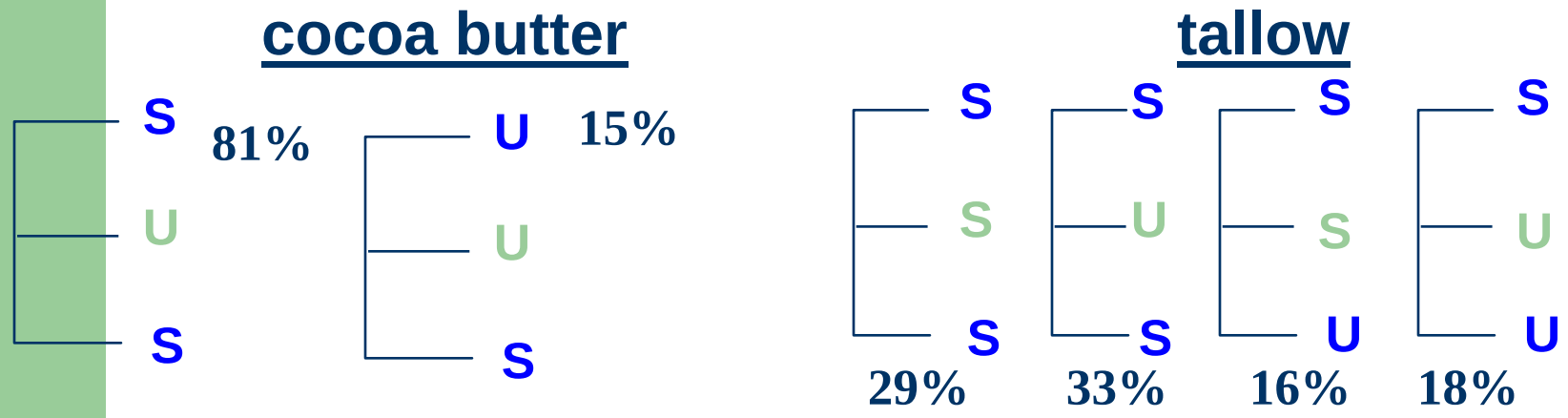




– **Pig fat (lard) similar**

Cocoa Butter *vs* Animal Fat

- Compare cocoa butter vs tallow (beef fat)
  - fatty acid composition quite similar
    - roughly equal C16:0, C18:0, C18:1

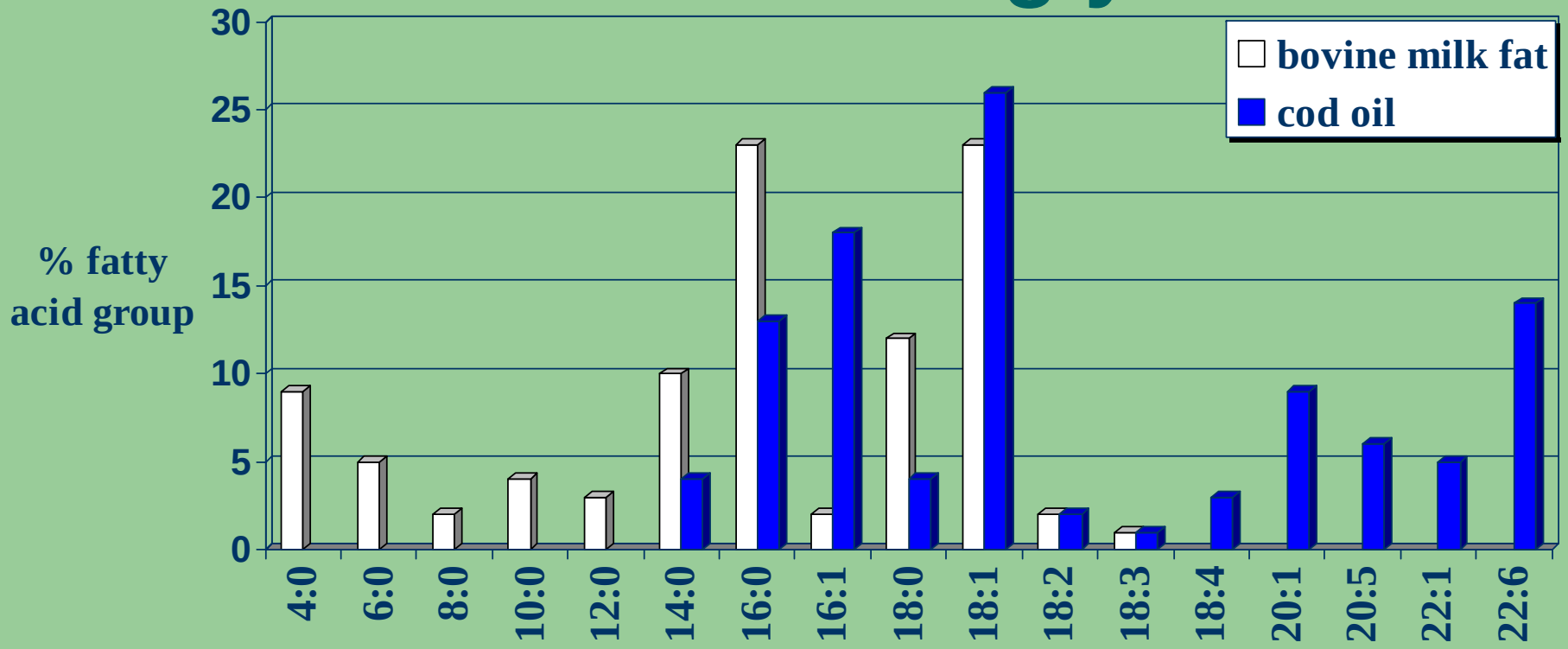


***Cocoa butter homogeneous*: melts sharply at body temp;**

***Tallow heterogeneous*: solid/liquid over wide temp range**

Animal Triglycerides

(Coultate, 1989; © Royal Society of Chemistry)



- Milk Fat - Large number of short-chain fatty acids
  - affects cheese flavor
  - causes milk rancidity

- **Marine Oils**
  - **Long-chain unsaturated fatty acids**

Summary of Fatty Acid Profiles

- Plant fats/oils:
  - sn-2 largely unsaturated fatty acid (C18:1 & C18:2)
  - some plant oils contain high unsaturated fatty acid contents (peanut, soybean, olive, Canola)
  - other plant oils significantly saturated (cocoa butter)
  - coconut and palm oil primarily saturated— rich in C8:0-C16:0
- Animal fats/oils:
  - broader range of fatty acids/triglycerides found
    - milk fat (short chains) vs fish oils (long, polyunsat'd)
  - sn-2 often saturated, greater variation in positions

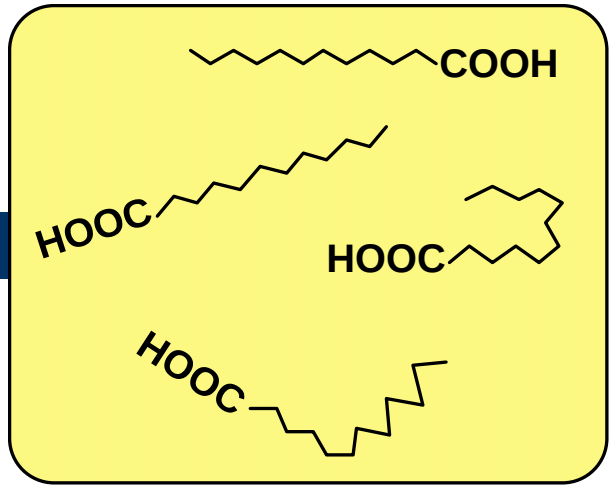
Properties

Crystallization

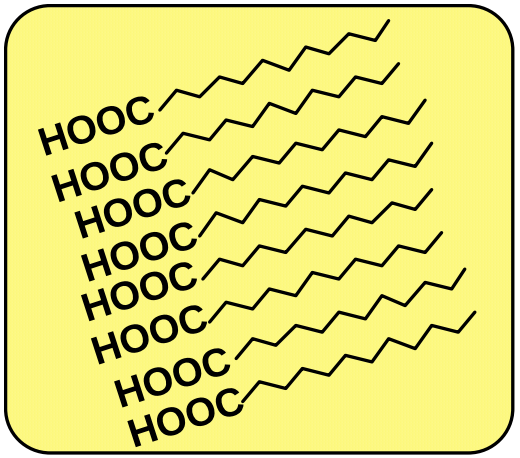
- Crystallization/Melting is balance
  - entropic considerations
    - favor increased molecular motion

  and

  - attractive intermolecular interactions
    - favor packing molecules close together



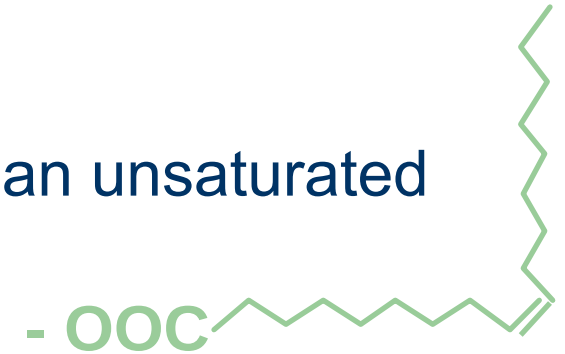
Melt (liquid)



crystal (solid)

Melting Point

- Longer chain fatty acids pack better than shorter chains
  - $M.P._{long} > M.P._{short}$
- Saturated fatty acids pack better than unsaturated
  - $M.P_{sat'd} > M.P._{unsat'd}$



- *Trans* fatty acids pack better than *cis*
  - $M.P_{trans} > M.P._{cis}$
  - hydrogenation increases M.P.

Melting Point Trends

Fatty Acid	Common Name	M.P.
8:0	Caprylic acid	16ºC
16:0	Palmitic acid	63ºC
18:0	Stearic acid	69ºC
20:0	Arachidic acid	75ºC
18:1Δ9 (cis)	Oleic acid	13ºC
18:2Δ9,12 (cis)	Linoleic acid	-5ºC
18:3Δ9,12,15 (cis)	Linolenic acid	-11ºC
18:1Δ9 (trans)	Elaidic acid	46ºC
18:2Δ9,12 (trans)	Linolelaidic acid	28ºC

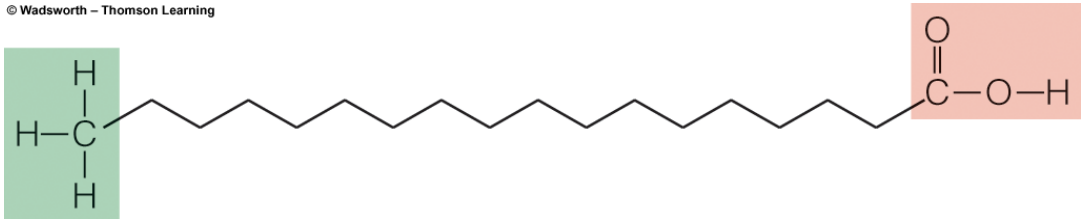
Surfactants (Emulsifiers)

- Surfactants are molecules that lower the surface tension
  - Part of molecule interacts favorably with water
    - Polar or charged (hydrophilic)
  - Part of molecule interacts unfavorably with water
    - Hydrophobic

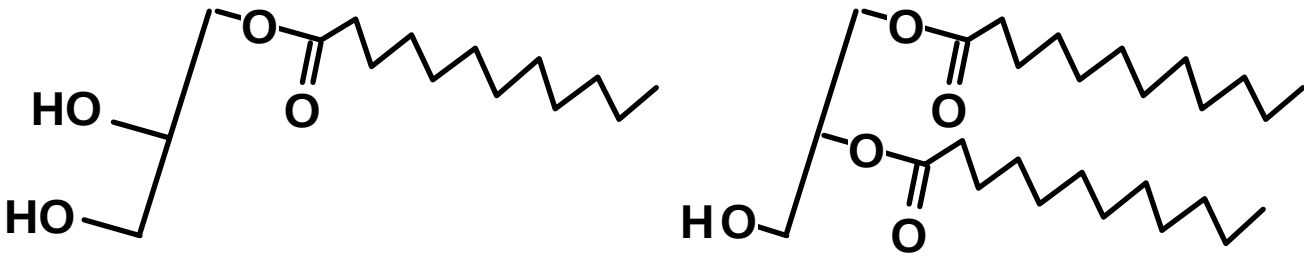
→ **Amphiphilic**

Lipid Surfactants

- Fatty Acids

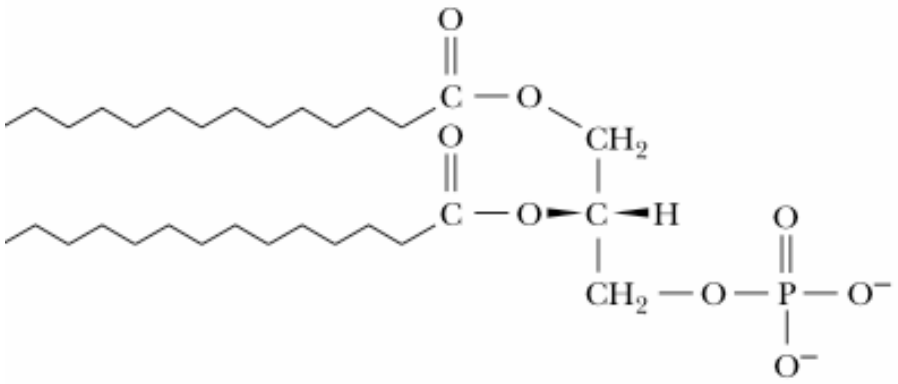


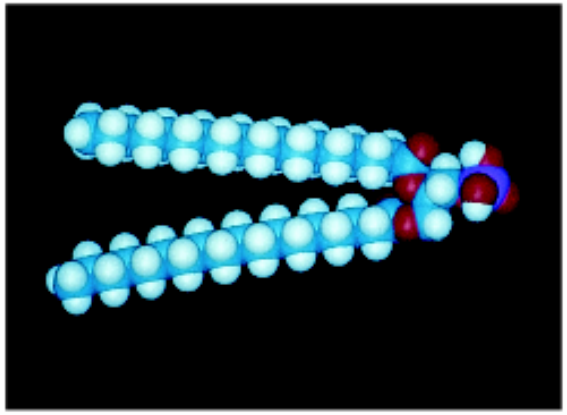
- Monoglycerides and Diglycerides



Lipid Surfactants

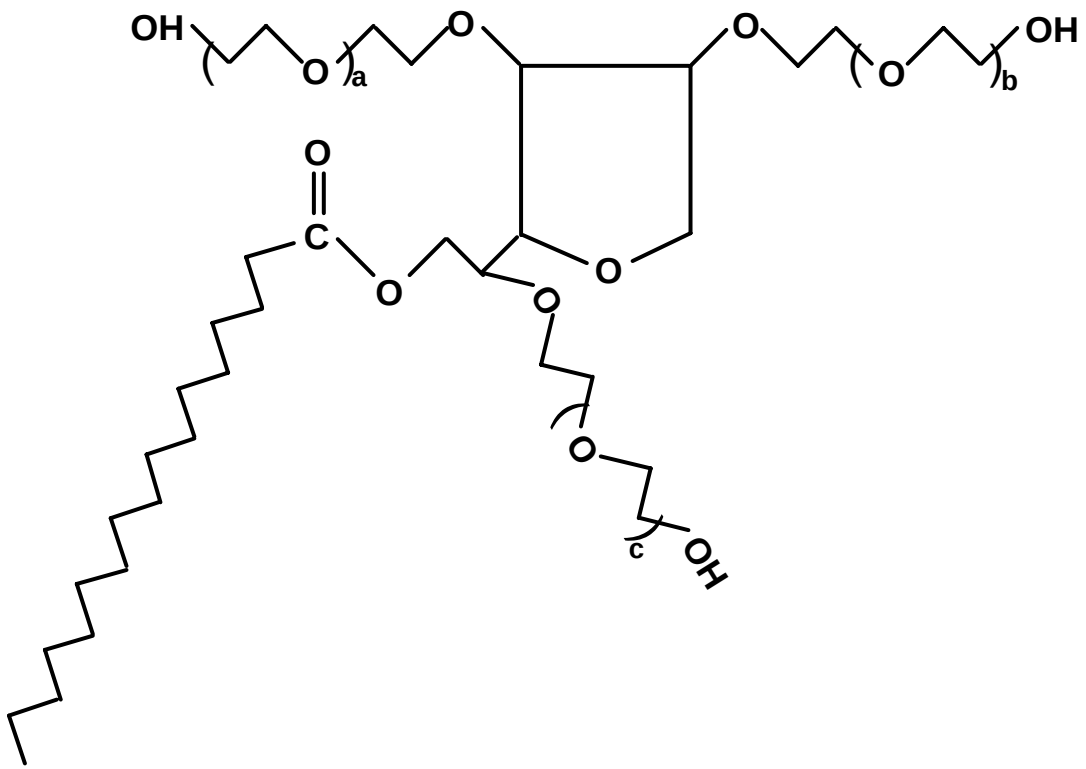
- Phospholipids



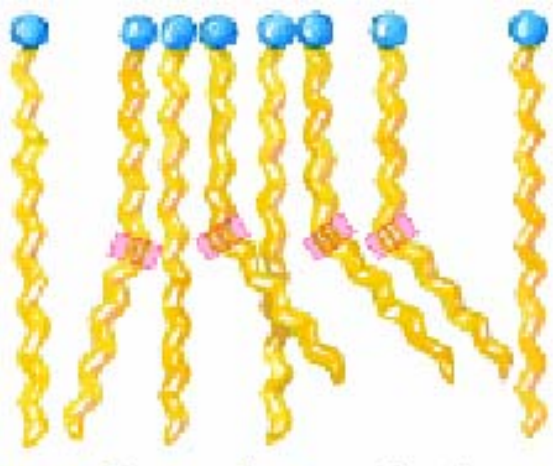


Synthetic Emulsifiers

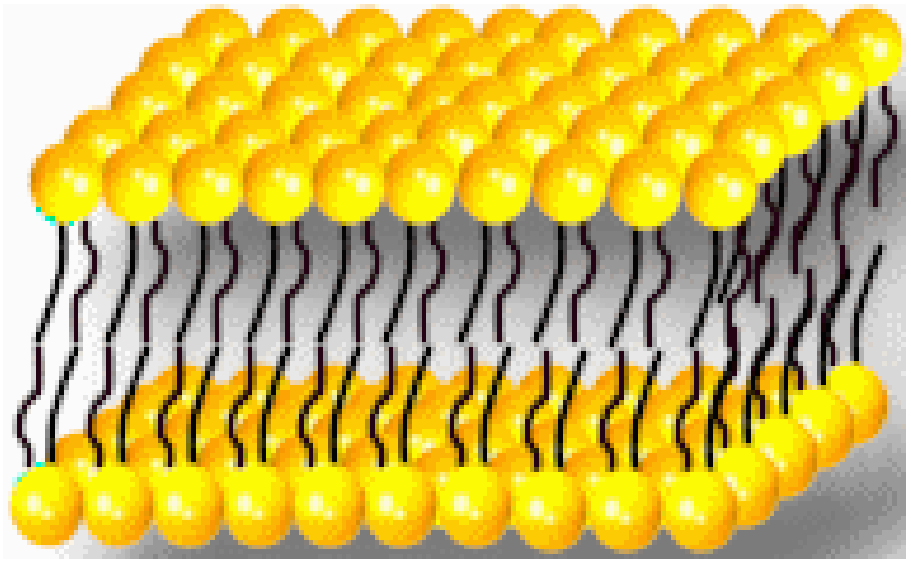
- Tweens

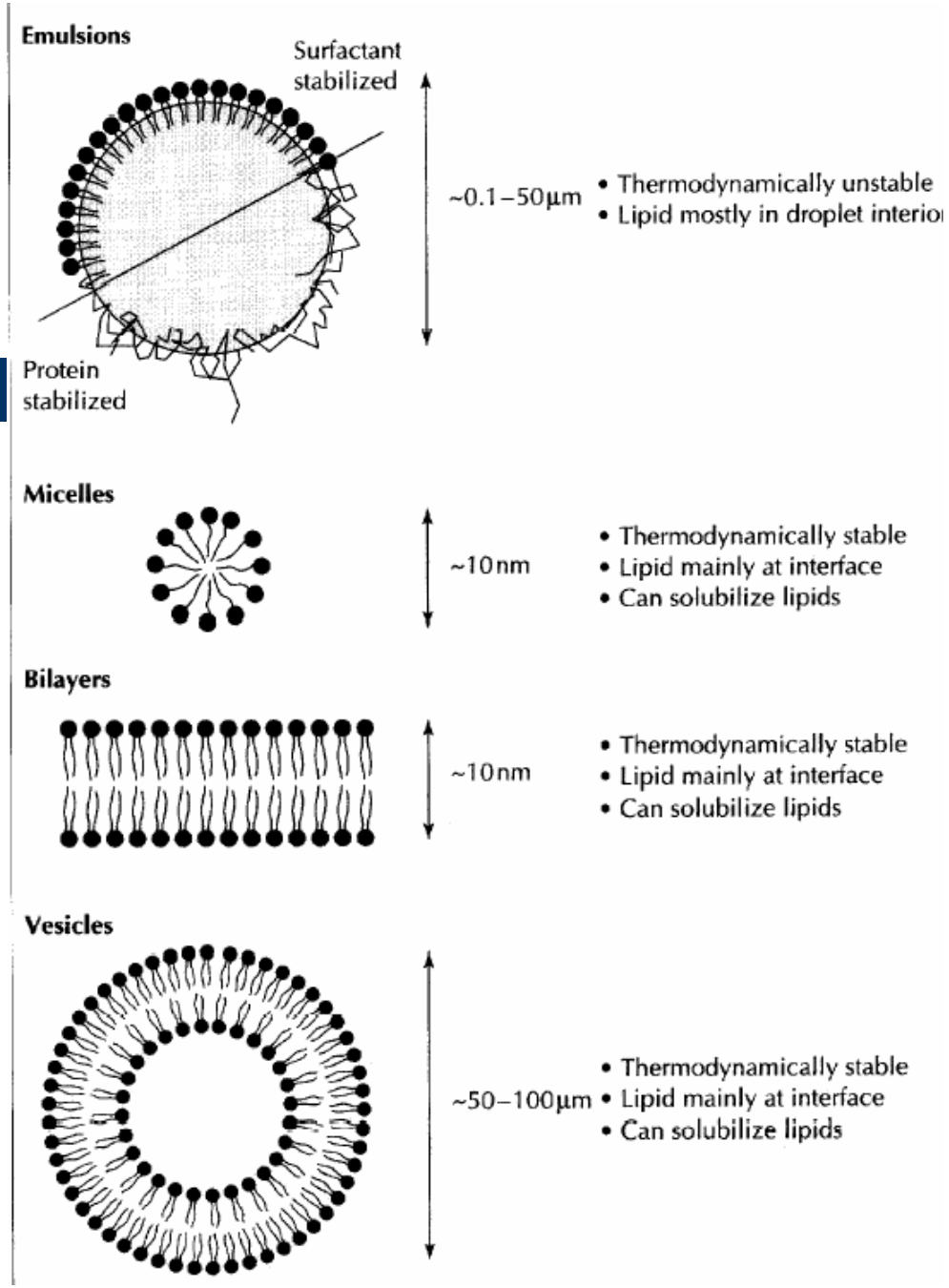


Surfactants



- Mediates interactions between hydrophobic and hydrophilic phases




Emulsions
Surfactant stabilized
Protein stabilized
~0.1–50μm
• Thermodynamically unstable
• Lipid mostly in droplet interio
Micelles
~10nm
• Thermodynamically stable
• Lipid mainly at interface
• Can solubilize lipids
Bilayers
~10nm
• Thermodynamically stable
• Lipid mainly at interface
• Can solubilize lipids
Vesicles
~50–100μm
• Thermodynamically stable
• Lipid mainly at interface
• Can solubilize lipids

Emulsion Breakdown: Creaming

- Density differences between droplets and continuous phase cause droplets to rise or fall
  - In oil-in-water emulsions, droplets typically rise
- Creaming rate depends on
  - droplet size
    - decrease drop size (e.g. homogenized milk)
  - viscosity of continuous phase
    - add macromolecules (termed stabilizers) to increase viscosity

Reactions

Reactions of Triglycerides

- Hydrolysis

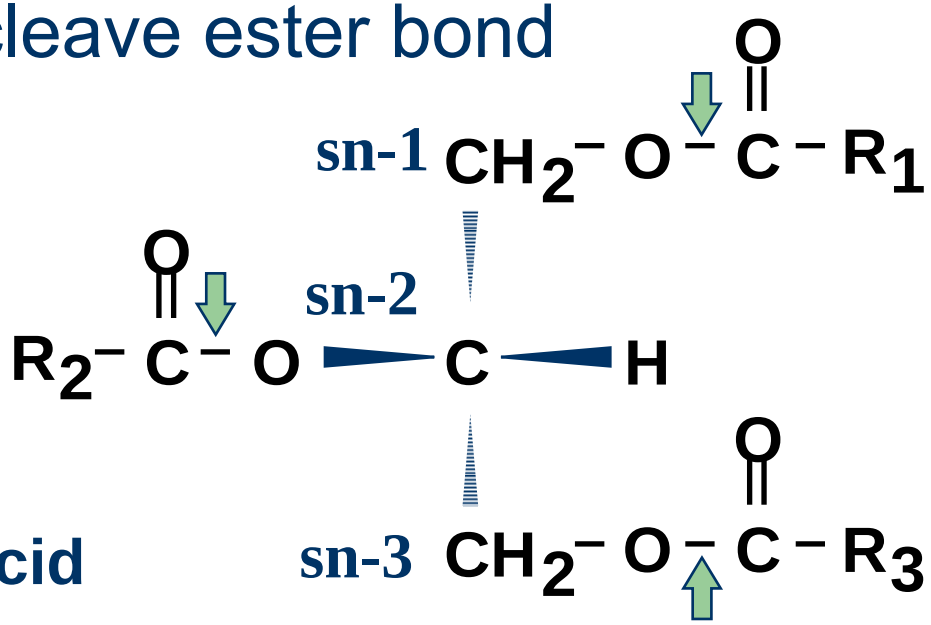
  triglycerides $\xrightarrow{H_2O}$ diglycerides, monoglycerides, glycerol + fatty acids

  - saponification (base catalyzed)
  - enzymatic hydrolysis (lipase catalyzed)
  - interesterification (randomization)
- Hydrogenation

  unsaturated lipids $\xrightarrow{H_2}$ saturated lipids, trans isomers
- Oxidation

Acid Hydrolysis

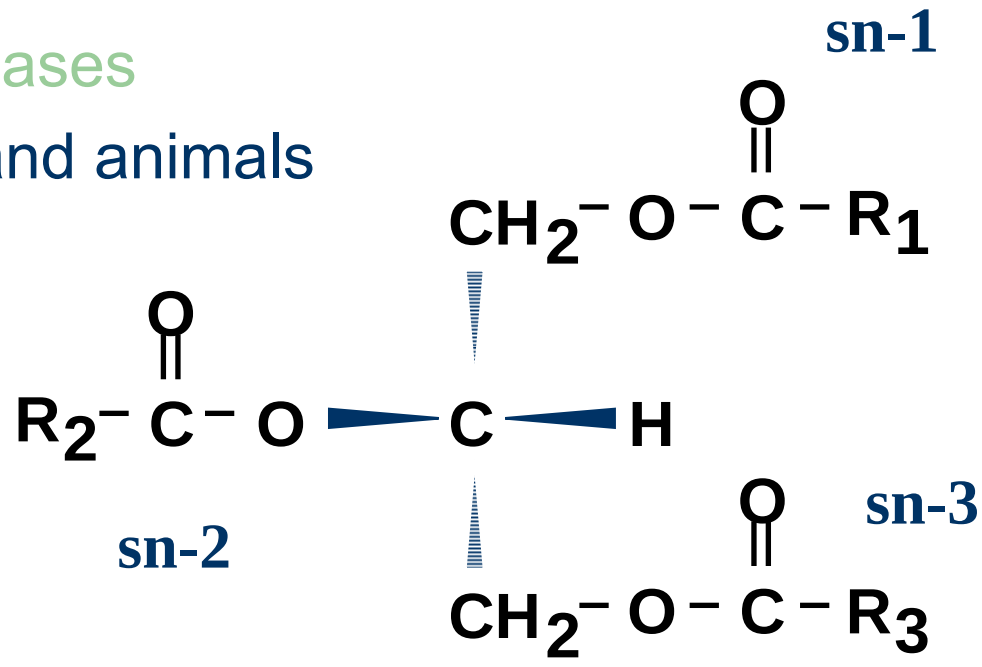
- Addition of water to cleave ester bond
  - **–also called lipolysis**



- **Catalyzed by strong acid**
- **Produces free fatty acids**

Lipases

- Can also be catalyzed by enzymes
  - hydrolases or lipases
  - found in plants and animals
  - *in vivo* digestion



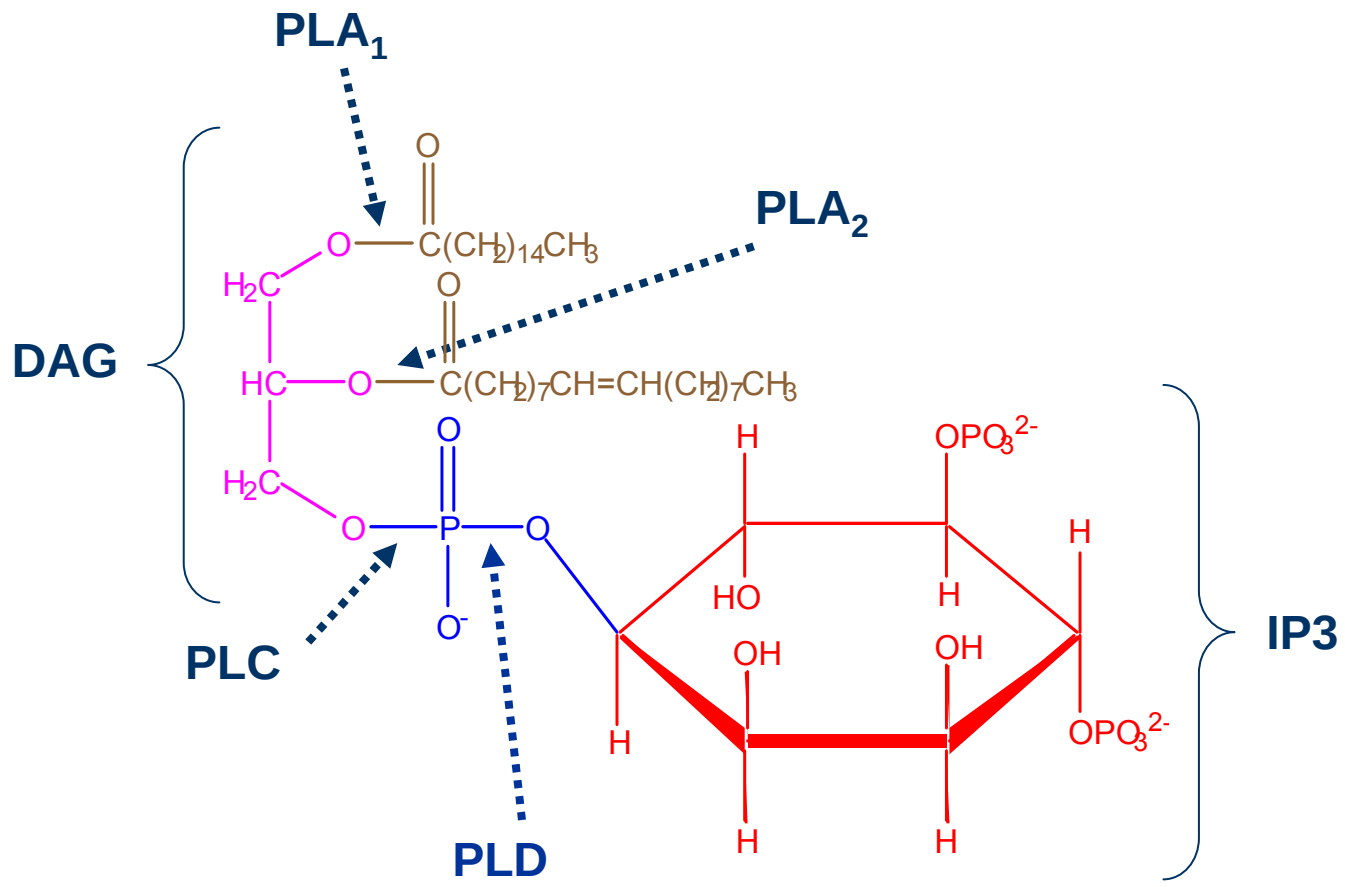

PLA1
PLA2
DAG
PLC
PLD
IP3
O
O
O
C(CH2)14CH3
H2C
HC
O
C(CH2)7CH=CH(CH2)7CH3
H2C
O
P
O
O-
H
OPO3 2-
HO
H
H
OH
OH
OPO3 2-
H
H
H

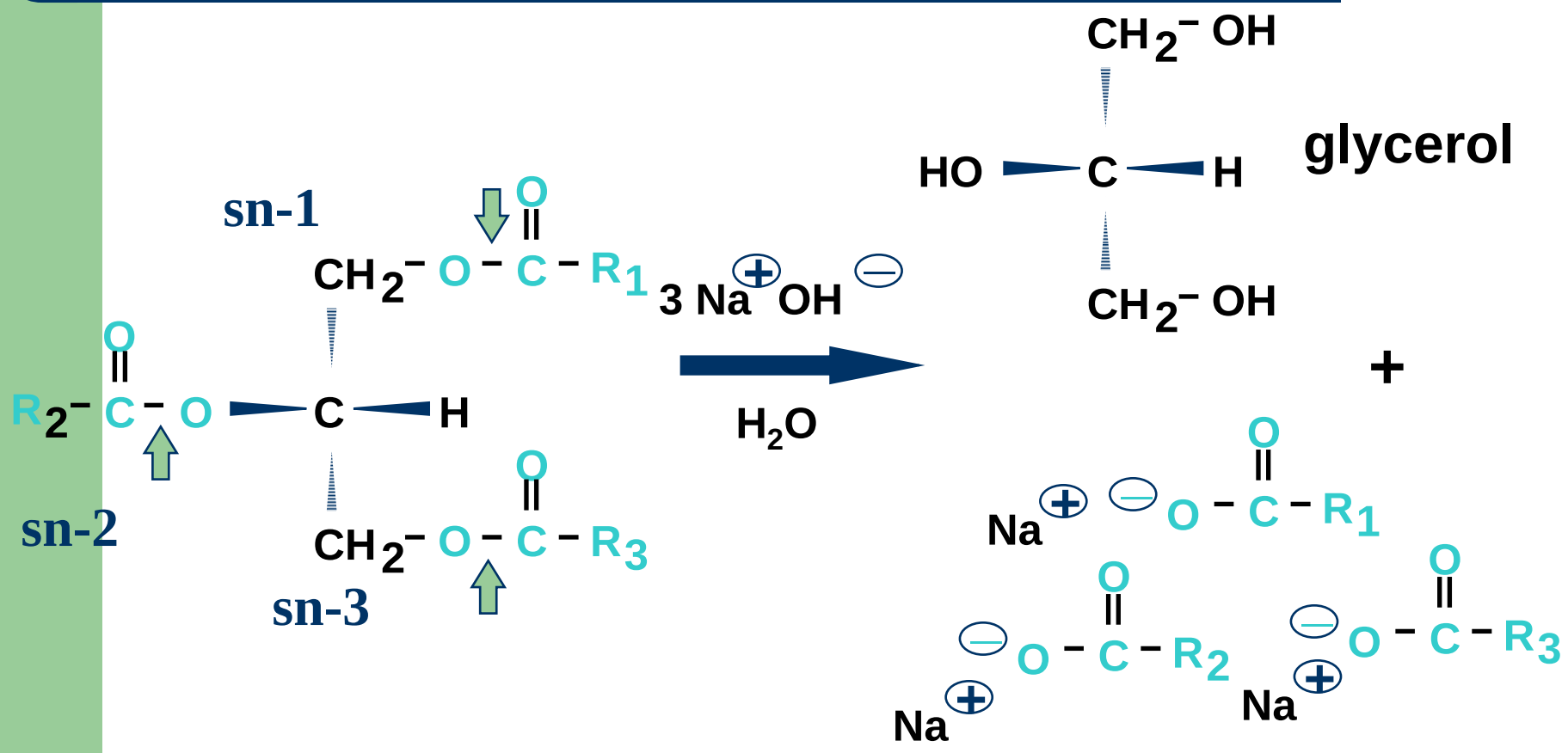
Table 1. Summary of the physiologically important lipases. The roles of these lipases (except lipoprotein and hormone-sensitive lipases) are depicted in Figure 1.
DAG = Diacylglycerol; FFA = Free Fatty Acid

Lipase	Site of Action	Regulation	Preferred Substrate	Carbon Position cleaved	Product(s)
lingual/acid-stable lipase	mouth, stomach	----	triacylglycerol with medium-chain fatty acids	3	FFA+DAG
pancreatic lipase	small intestine lumen	colipase (+)	triacylglycerol with long-chain fatty acids	1 and 3	FFA+2MG
milk lipase	small intestine lumen	bile acids (+)	triacylglycerol with medium-chain fatty acids	1 and 2 and 3	FFA+glycerol
phospholipase A_2 (PLA_2)	small intestine lumen	bile acids (+) Ca^{2+} (+)	phospholipids (lecithin) with unsaturated fatty acid in #2 position	2	unsaturated FFA + lysolecithin
lipoprotein lipase[1]	capillary walls	apo CII (+) insulin (+)	triacylglycerol in chylomicron or VLDL	1 and 2 and 3	FFA+glycerol
hormone sensitive lipase[2]	inside adipose cell	insulin (-) glucagon (+) epinephrine (+)	triacylglycerol stored in adipose cells	3	FFA+DAG

Hydrolysis: Products

- Small quantities of free fatty acids
  - contribute flavors to cheese, milk chocolate
  - cause off-flavors in milk, fruits and vegetables
  - lead to foaming
    - removed during commercial production of food oils

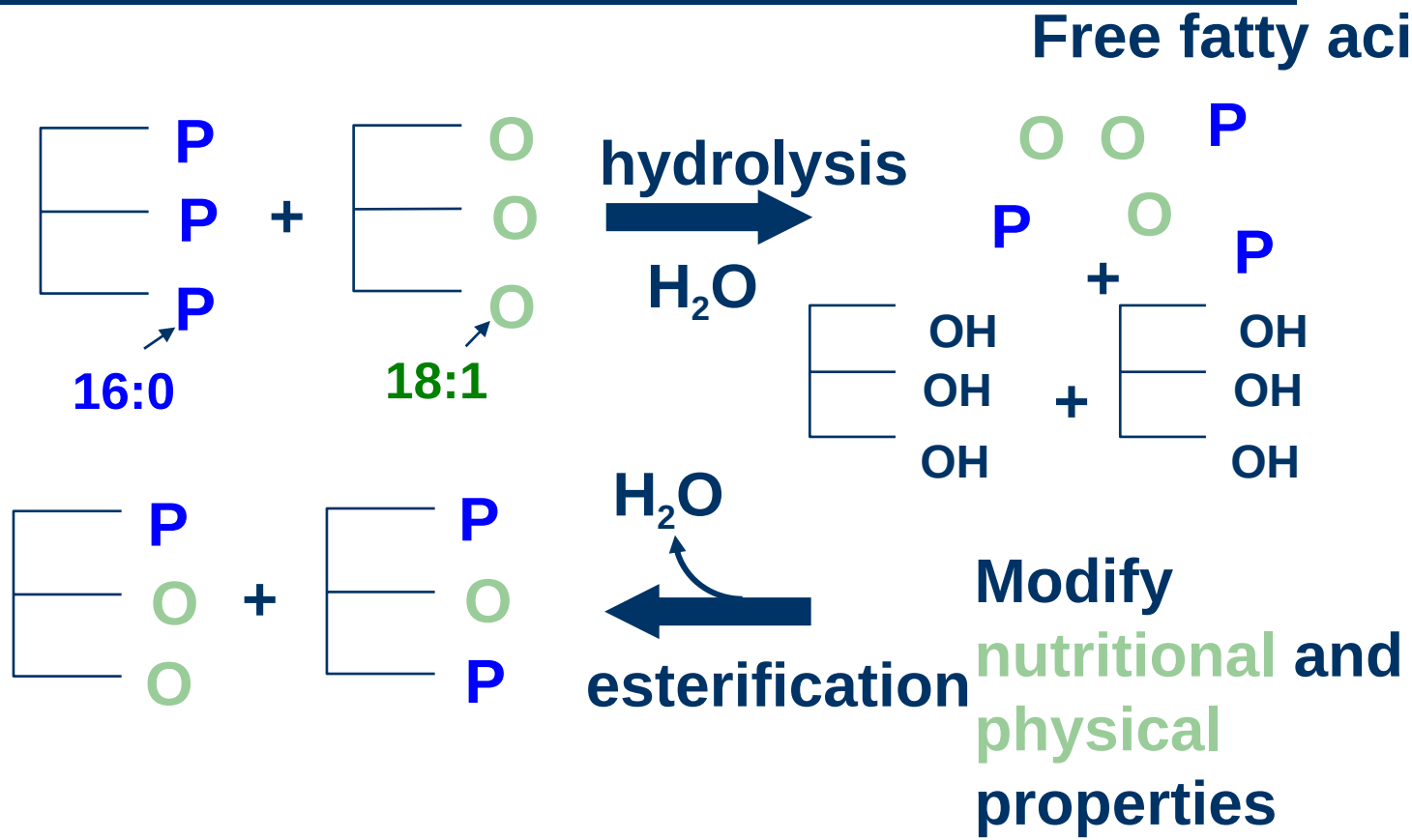
Saponification



Interesterification

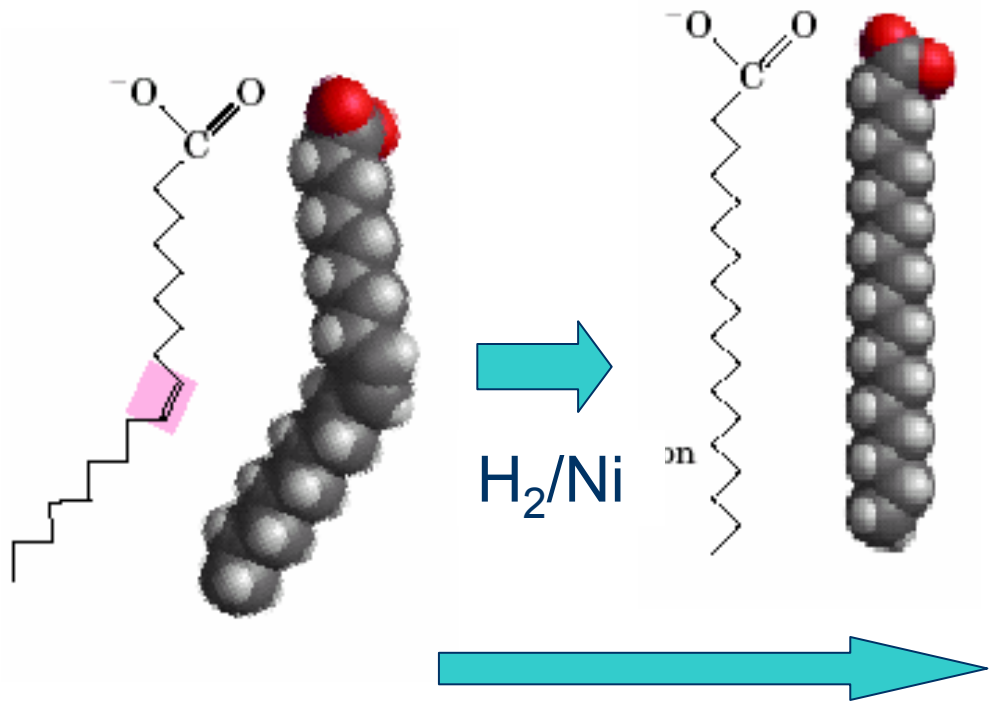
- Rearrange the fatty acids so they become distributed randomly among triacylglycerol molecules of the fat
- Improves consistency of fats
- Applications:
  - Manufacture of shortenings
  - Lard (want ~10% tri-saturated glycerides)
    - Forms large and coarse crystals
    - Shortenings posses grainy consistency and poor baking performances
    - Randomization improves plastic range
  - Production of high stability margarine blends and hard butters with desirable melting qualities and crystallization behavior

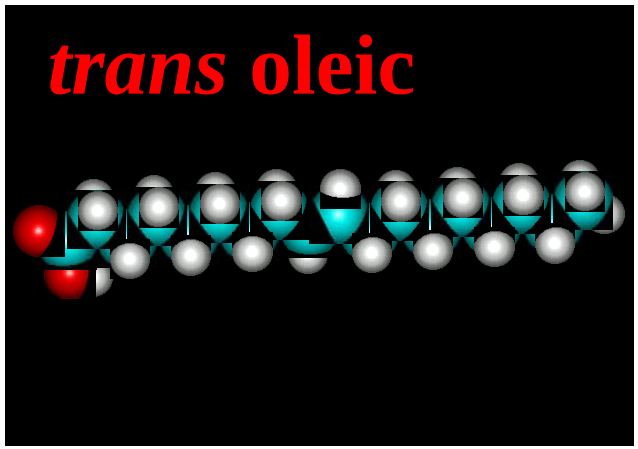
Interesterification



Hydrogenation

- Addition of hydrogen across double bonds





Hydrogenation

- Rate is determined by
  - Nature of substrate
  - Type and concentration of catalyst
  - Pressure (concentration of H_2)
  - Temperature
  - Agitation

Hydrogenation: Products

Produces triglycerides with higher melting points

- **liquid $\Rightarrow$ semi-solid**
- **Convert soft-fats into firmer fats**
  - **Useful in margarine, peanut butter, baked goods**
- **Improves oxidative stability**

Butter

Nutrition Facts

Serving size 1 Tbsp (14g)
Servings Per Container 32

Amount per serving	
Calories 100	Calories from Fat 100
	%Daily Value*
Total Fat 11g	17%
Saturated Fat 7g	36%
Cholesterol 30mg	10%
Sodium 90mg	4%
Total Carbohydrate 0g	0%
Protein 0g	
Vitamin A 8%	

Not a significant source of dietary fiber, sugars, vitamin C, calcium, and iron.

*Percent Daily Values are based on a 2,000 calorie diet.

INGREDIENTS: Cream, salt.

Margarine (stick)

Nutrition Facts

Serving size 1 Tbsp (14g)
Servings Per Container 32

Amount per serving	
Calories 90	Calories from Fat 90
	%Daily Value*
Total Fat 10g	15%
Saturated Fat 2g	10%
Polyunsaturated Fat 2g	
Monounsaturated Fat 3g	
Cholesterol 0mg	0%
Sodium 95mg	4%
Total Carbohydrate 0g	0%
Protein 0g	
Vitamin A 10%	

Not a significant source of dietary fiber, sugars, vitamin C, calcium, and iron.

*Percent Daily Values are based on a 2,000 calorie diet.

INGREDIENTS: Vegetable oil blend (partially hydrogenated and liquid soybean oils), water, sweet cream buttermilk, salt, vegetable mono- and diglycerides, soy lecithin, citric acid, artificial flavor, vitamin A, colored with beta carotene.

Margarine (tub)

Nutrition Facts

Serving size 1 Tbsp (14g)
Servings Per Container 32

Amount per serving	
Calories 90	Calories from Fat 90
	%Daily Value*
Total Fat 10g	15%
Saturated Fat 2g	10%
Polyunsaturated Fat 4.5g	
Monounsaturated Fat 2.5g	
Cholesterol 0mg	0%
Sodium 95mg	4%
Total Carbohydrate 0g	0%
Protein 0g	
Vitamin A 10%	

Not a significant source of dietary fiber, sugars, vitamin C, calcium, and iron.

*Percent Daily Values are based on a 2,000 calorie diet.

INGREDIENTS: Water, liquid soybean oil, partially hydrogenated soybean oil, sweet cream, buttermilk, gelatin, salt, vegetable mono- and diglycerides, soy lecithin, lactic acid, artificial flavor, vitamin A, colored with beta carotene.

Margarine (liquid)

Nutrition Facts

Serving size 1 Tbsp (14g)
Servings Per Container 32

Amount per serving	
Calories 60	Calories from Fat 60
	%Daily Value*
Total Fat 7g	10%
Saturated Fat 1g	6%
Polyunsaturated Fat 4g	
Monounsaturated Fat 1.5g	
Cholesterol 0mg	0%
Sodium 85mg	3%
Total Carbohydrate 0g	0%
Protein 0g	
Vitamin A 10%	

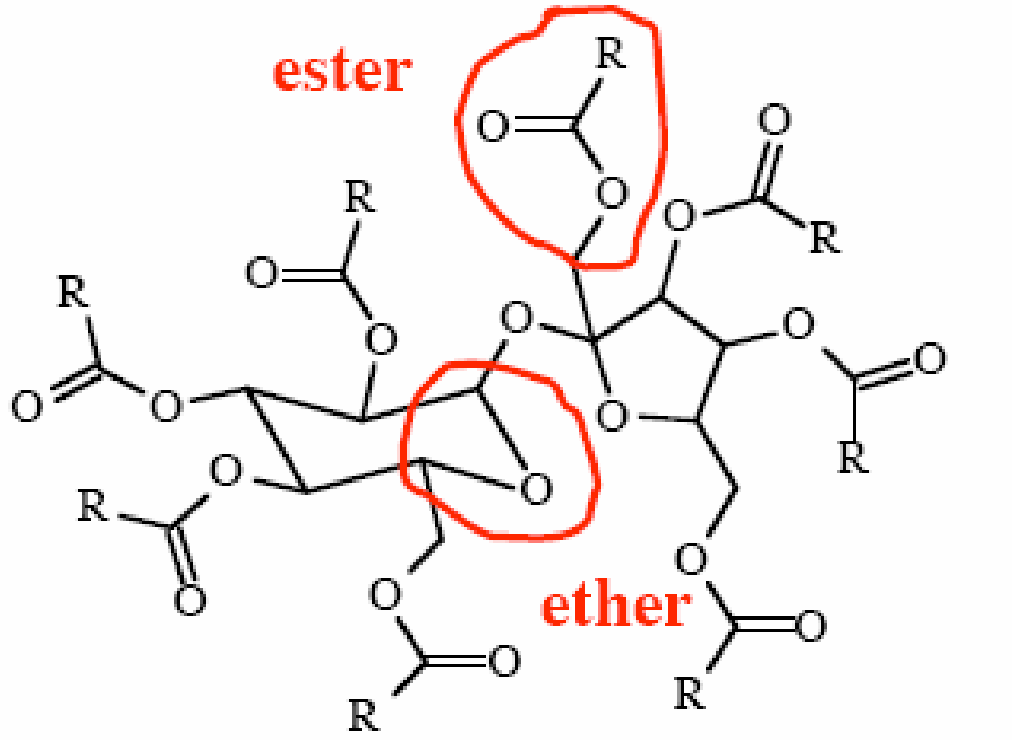
Not a significant source of dietary fiber, sugars, vitamin C, calcium, and iron.

*Percent Daily Values are based on a 2,000 calorie diet.

INGREDIENTS: Liquid soybean oil, water, sweet cream buttermilk, salt, partially hydrogenated cottonseed oil, vegetable mono- and diglycerides, soy lecithin, citric acid, artificial flavor, vitamin A, colored with beta carotene.

Fat Replacers

Olestra, Fat replacer



R = 12–18 hydrocarbon tail

Olestra vs Triglycerides

Calories 75

Fat Calories 0

Total fat 0 g

Saturated fat 0 g

Ingredients: Potatoes, Olestra, Salt, α-Tocopheryl Acetate (Vit E), Vitamin A Palmitate, Tocopherols (to protect flavor), Vitamin K, Vitamin D

Calories 160

Fat Calories 90

Total fat 10 g

Saturated fat 2.5 g

Ingredients: Potatoes, Corn and/or Cottonseed Oil, Salt

(*cf. www.olean.com*)

Lipids and Health

Trans Fatty Acids

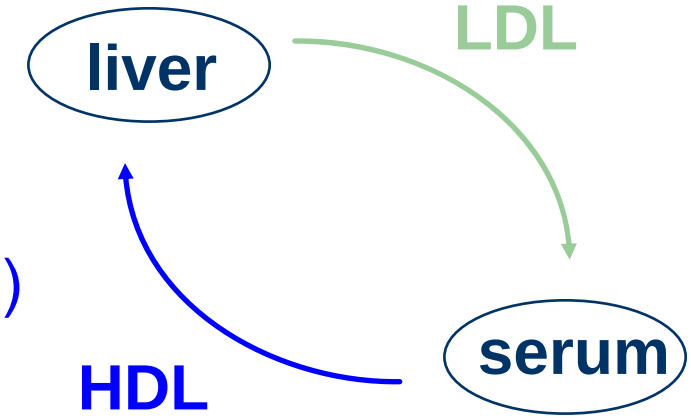
- Trans fats refers to triglycerides containing unsaturated fatty acids in the trans conformation
  - Found in partially hydrogenated fats or oils
  - Help to solidify food (melting point higher than cis)
- FDA adopted new food labeling
    - labels give weight of trans fat
    - restrict low fat definitions by trans fat content
  - Some margarines are sold as ”trans free”
    - No hydrogenation
    - Mix sat’d and unsat’d fats
    - Tend to be soft spreads

Alternatives for *trans*-FA in Foods

- Modification of the hydrogenation process
  - Increase the degree of hydrogenation
- Interesterification
  - Expensive
  - Use 85% un-hydrogenated liquid vegetable oil and 15% fully hydrogenated vegetable oil (hardstock)
- Use of fractions high in solids
  - Derived from coconut, pal and palm kernel oils
  - Prepared by reducing the temperature of an oil sample so that the more saturated fraction solidifies
- Use of trait-enhanced oils
  - High oleic acid oils
  - Plant breeding, sunflower and canola

Saturated Fat & Health

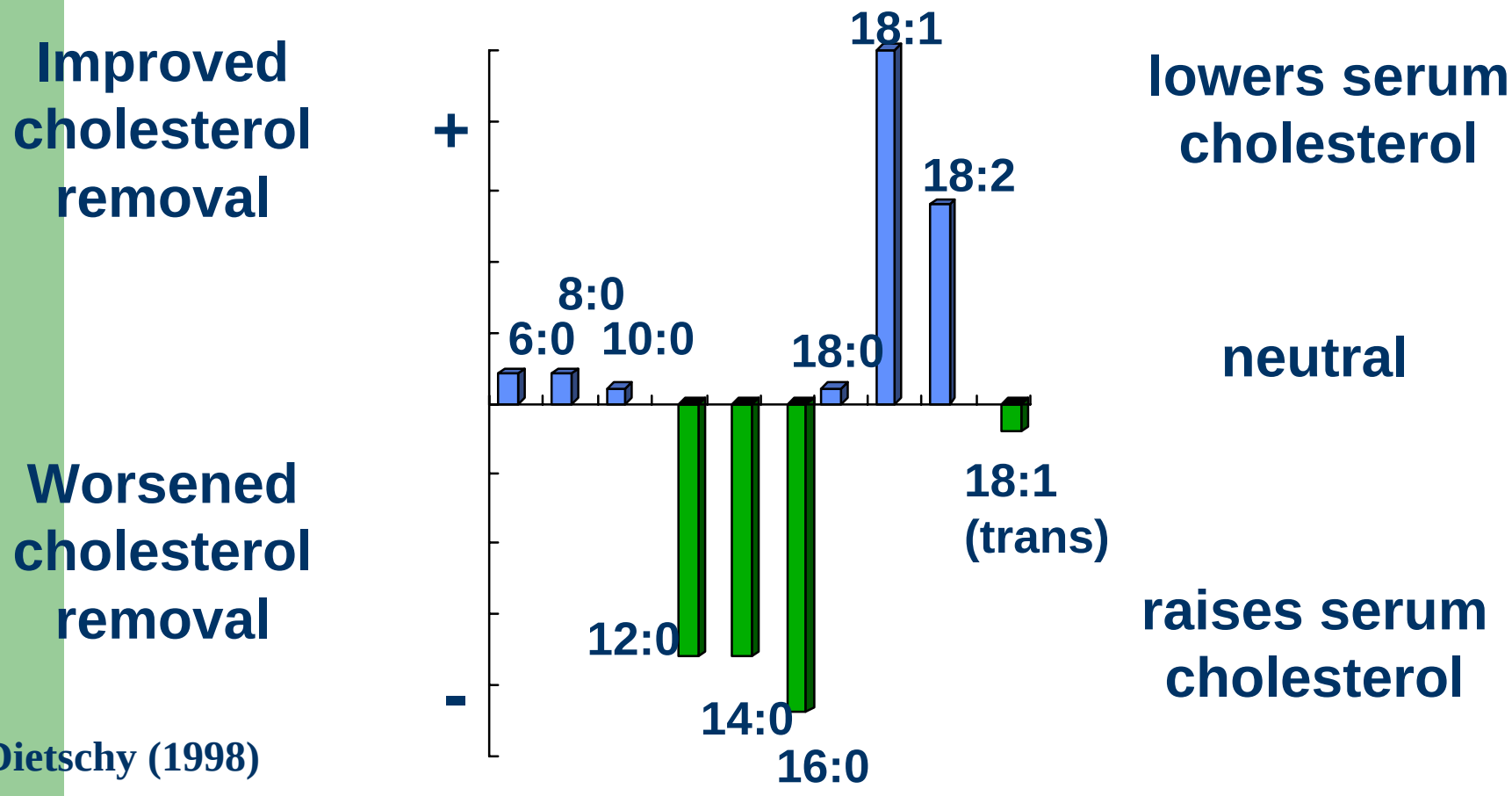
- Risk of heart disease correlates with cholesterol level in bloodstream (serum cholesterol)
  - low density lipoproteins (LDL)
    - carry cholesterol to cells
  - high density lipoproteins (HDL)
    - carry cholesterol away



- Fat affects cholesterol regulation
  - Fat consumption with cholesterol raises serum cholesterol levels

Health

- Depends on what type of saturated/unsaturated fat



Dietschy (1998)

Lipoproteins

VLDL (30-80 nm)

(Vance and Vance, 1996; © Elsevier)

LDL (18-25 nm)

Chylomicron (75-1200 nm) Protein poor Lipid rich

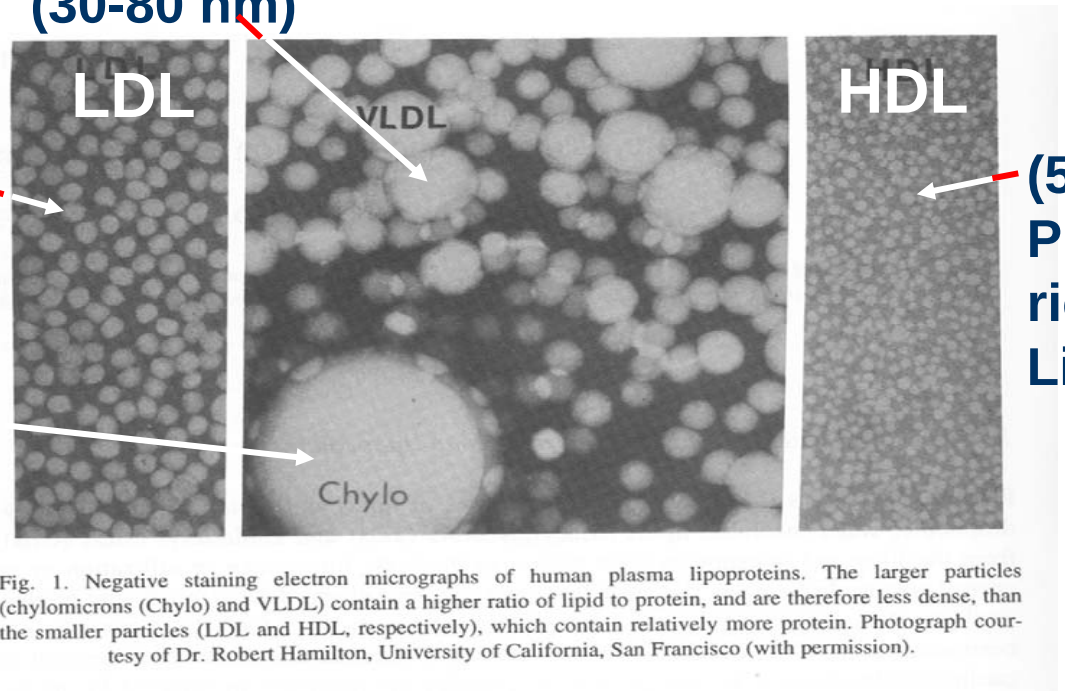
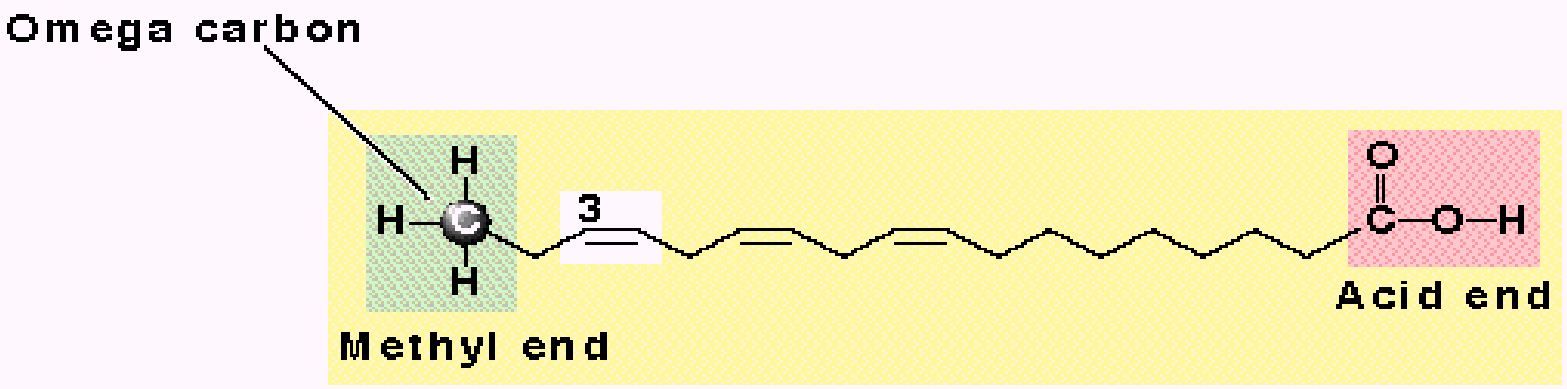


Fig. 1. Negative staining electron micrographs of human plasma lipoproteins. The larger particles (chylomicrons (Chylo) and VLDL) contain a higher ratio of lipid to protein, and are therefore less dense, than the smaller particles (LDL and HDL, respectively), which contain relatively more protein. Photograph courtesy of Dr. Robert Hamilton, University of California, San Francisco (with permission).

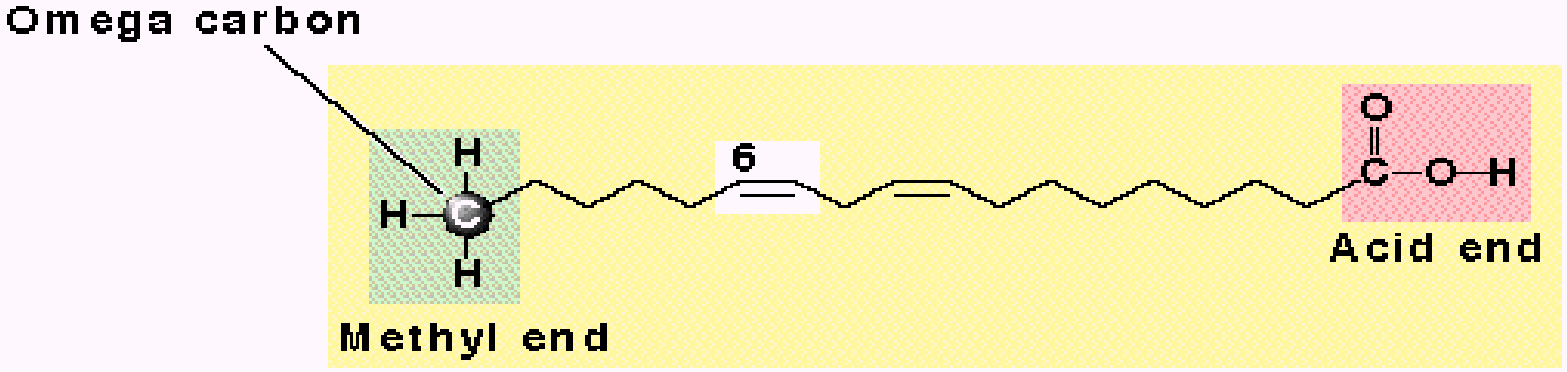
(5-12 nm) Protein rich Lipid poor

Lipoproteins transport lipids throughout body

Essential Fatty Acids



Linolenic acid, an omega-3 fatty acid



Linoleic acid, an omega-6 fatty acid

PUFA requirements

a. should make up to 3% of fatty acid intake
b. PUFA deficiencies cause growth retardation, skin lesions, neurological and visual abnormalities

Role of polyunsaturated fatty acids

ω3 and ω6 fatty acids are precursors to potent bioactive compounds

1. Prostaglandins
    a. Platelet antiaggregate
2. Thromboxanes
    a. Platelet aggregate

TABLE 5-2 Sources of Omega Fatty Acids

Omega-6	
Linoleic acid	Vegetable oils (corn, sunflower, safflower, soybean, cottonseed), poultry fat, nuts, seeds
Arachidonic acid	Meats, poultry, eggs (or can be made from linoleic acid)
Omega-3	
Linolenic acid	Oils (flaxseed, canola, walnut, wheat germ, soybean) Nuts and seeds (butternuts, flaxseeds, walnuts, soybean kernels) Vegetables (soybeans)
EPA and DHA	Human milk
	Pacific oysters and fish[a] (mackerel, salmon, bluefish, mullet, sablefish, menhaden, anchovy, herring, lake trout, sardines, tuna) (or can be made from linolenic acid)

[a] All fish contain some EPA and DHA; the amounts vary among species and within a species depending on such factors as diet, season, and environment. The fish listed here except tuna provide at least 1 gram of omega-3 fatty acids in 100 grams of fish (3.5 ounces). Tuna provides fewer omega-3 fatty acids, but because it is commonly consumed, its contribution can be significant.