

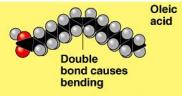


Lipids



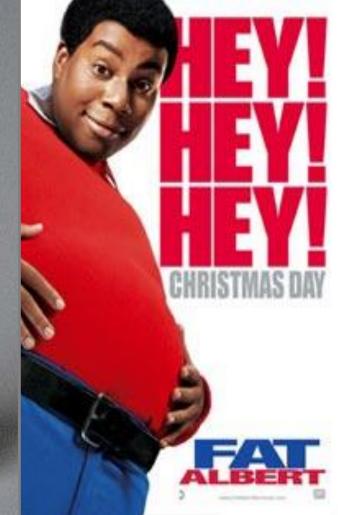






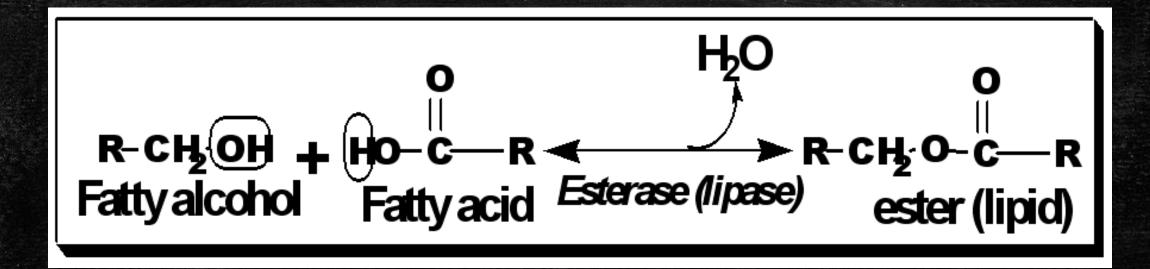
(b) Unsaturated fat and fatty acid





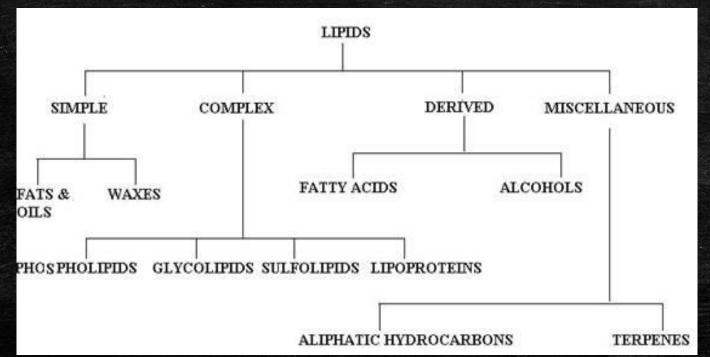
Definition & General Properties

- A heterogeneous class of naturally occurring organic compounds
- Amphipathic
- Insoluble



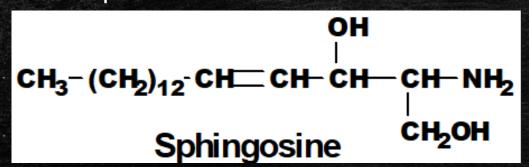
Classification

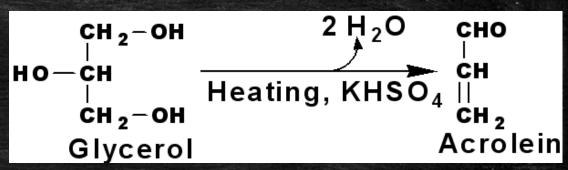
- Open chain vs. cyclic structures
- Simple vs. compound, conjugated, and complex lipids
- Function: storage, support, signaling



Alcohols

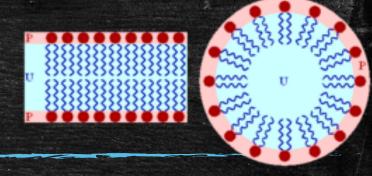
- Glycerol: glycerin, glucose derived
 - Colorless viscous oily liquid with sweet taste но-сн
 - Heating
 - Trinitroglycerin
 - Esterification (mono, di, and triglycerides)
- Sphingosine
 - Monohydric
 - Serine & palmitic acid



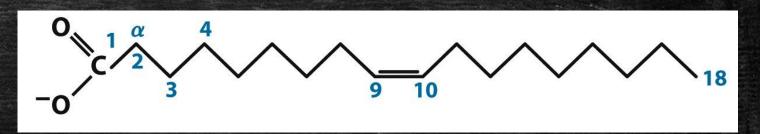




Fatty Acids



- Open chain mono-carboxylic acids
- R-(CH₂)n-COOH (n mostly even)
- Mostly straight chain
- Saturated vs. unsaturated (cis)
- Naming



$$-0$$
 1
 $\frac{\alpha}{2}$
 $\frac{4}{3}$
 $\frac{4}{9}$
 $\frac{10}{10}$

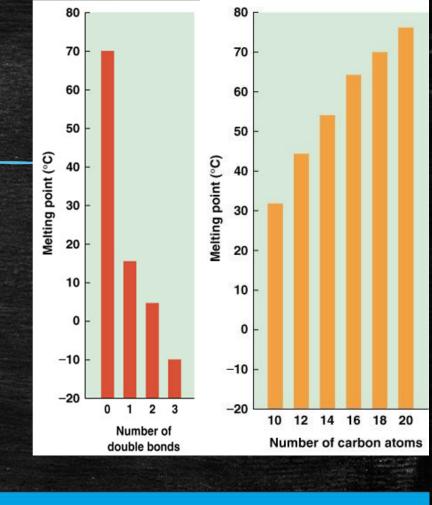
(a) 18:1(Δ^9) cis-9-Octadecenoic acid

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

Physical Properties

Solubility and melting point

| Typical Naturally Occurring Saturated Fatty Acids | | | |
|---|------------------------|---|--------------------|
| Acid | Number of Carbon Atoms | Formula | Melting Point (°C) |
| Lauric | 12 | $\mathrm{CH_{3}}(\mathrm{CH_{2}})_{10}\mathrm{CO_{2}H}$ | 44 |
| Myristic | 14 | $\mathrm{CH_{3}}(\mathrm{CH_{2}})_{12}\mathrm{CO_{2}H}$ | 58 |
| Palmitic | 16 | $\mathrm{CH_{3}(CH_{2})_{14}CO_{2}H}$ | 63 |
| Stearic | 18 | $\mathrm{CH_{3}(CH_{2})_{16}CO_{2}H}$ | 71 |
| Arachidic | 20 | $\mathrm{CH_{3}}(\mathrm{CH_{2}})_{18}\mathrm{CO_{2}H}$ | 77 |



Typical Naturally Occurring Unsaturated Fatty Acids

| Acid | Number of Carbon Atoms | Degree of Unsaturation* | Formula | Melting Point (°C) |
|-------------|------------------------|---------------------------|---|--------------------|
| Palmitoleic | 16 | $16:1-\Delta^{9}$ | $CH_3(CH_2)_5CH = CH(CH_2)_7CO_2H$ | -0.5 |
| Oleic | 18 | $18:1-\Delta^{9}$ | $CH_3(CH_2)_7CH = CH(CH_2)_7CO_2H$ | 16 |
| Linoleic | 18 | $18:2-\Delta^{9,12}$ | $CH_3(CH_2)_4CH = CH(CH_2)CH = CH(CH_2)_7CO_2H$ | -5 |
| Linolenic | 18 | $18:3-\Delta^{9,12,15}$ | $CH_3(CH_2CH=CH)_3(CH_2)_7CO_2H$ | -11 |
| Arachidonic | 20 | $20:4-\Delta^{5,8,11,14}$ | $CH_3(CH_2)_4CH = CH(CH_2)_4(CH_2)_2CO_2H$ | -50 |

Classification (saturated)

SHORT CHAIN

- They are <u>liquid in</u> <u>nature</u>
- Water-soluble
- Volatile at room temperature
- Examples: <u>acetic</u>, butyric, & caproic acids

Acetic F.A. (2C) CH_3 -COOH Butyric F.A. (4C) CH_3 -(CH_2)₂-COOH Caproic F.A. (6C) CH_3 -(CH_2)₄-COOH

MEDIUM CHAIN

- Solids at room temperature
- Water-soluble
- Non-volatile at room temperature
- Examples: caprylic& capric F.A.

Caprylic (8 C) CH_3 -(CH_2)₆-COOH Capric (10 C) CH_3 -(CH_2)₈-COOH

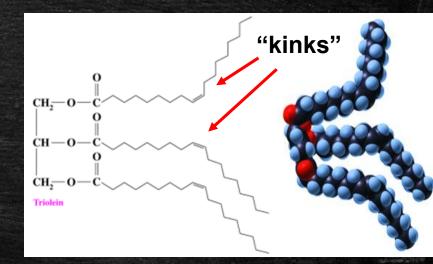
LONG CHAIN

- Occur in <u>hydrogenated</u>
 <u>oils</u>, animal fats, butter &
 coconut & palm oils
- Non-volatile & waterinsoluble
- Examples: <u>palmitic</u>, <u>stearic</u>, & lignoceric F.A.

Palmitic (16C) CH_3 -(CH_2)₁₄-COOH Stearic (18 C) CH_3 -(CH_2)₁₆-COOH Lignoceric (24C) CH_3 -(CH_2)₂₂-COOH

Classification (unsaturated)

- Monounsaturated: Palmitoleic acid, Oleic acid
- Polyunsaturated:
 - More than one double bond
 - Essential fatty acids
 - Linoleic, Linolenic, and Arachidonic
 - $C18:2\Delta^{9,12}$
 - C18:3 Δ 9, 12, 15
 - C20:4 Δ 5, 8, 11, 14
- Do not pack closely (Cis)



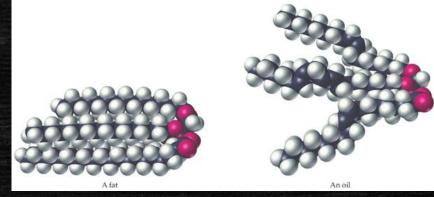
CH₃-(CH₂)₅CH = CH-(CH₂)₇-COOH

CH₃-(CH₂)₇- CH=CH – (CH₂)₇-COOH

Simple lipids Neutral - TAGs

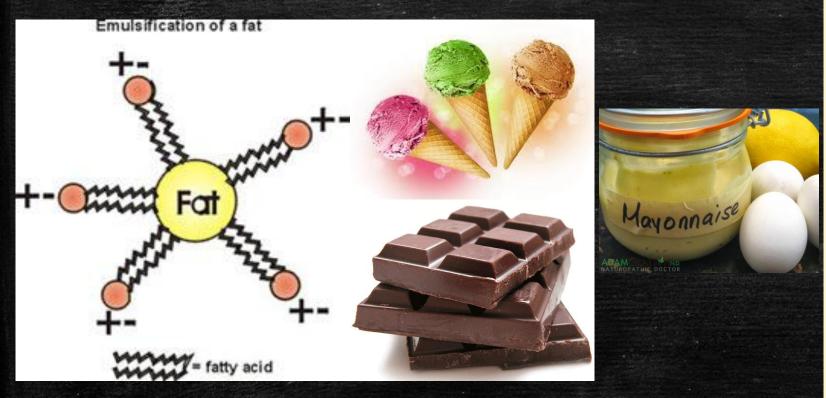
- $\begin{array}{c|c} & O \\ & CH_2-O-\overset{\circ}{C}-(CH_2)_{14}-CH_3 \\ O \\ & CH_3-(CH_2)_{14}-\overset{\circ}{C}-O-\overset{\circ}{C}-H \\ & O \\ & CH_2-O-\overset{\circ}{C}-(CH_2)_{14}-CH_3 \\ & CH_2-O-\overset{\circ}{C}-(CH_2)_{14}-CH_3 \\ & Tripalmitin \\ (simple triacylglycerol) \end{array}$

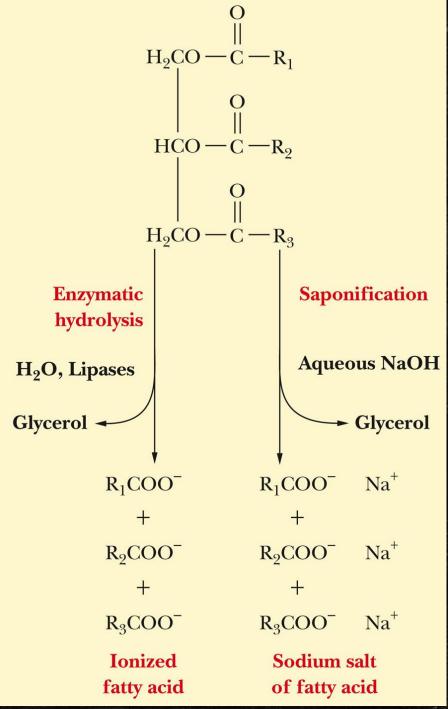
- Uncharged due to absence of ionizable groups in it
- Most abundant lipids in nature
- Either simple or mixed
- Physical:
 - Colorless, odorless & tasteless
 - Specific gravity less than 1
 - Insoluble
 - At room temp. (oils or fat)



Chemical reactions

Hydrolysis and saponification (emulsification)





Chemical reactions

Oils Hydrogen, high pressure, nickel (liquid)

(with unsaturated fatty acids, e.g., oleic)

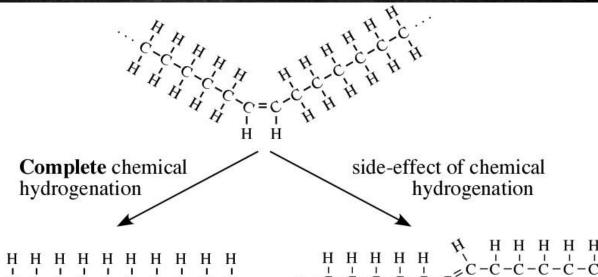
Hard fat
(margarine, solid)
(with saturated)
fatty acids, e.g., stearic)

Hydrogenation: margarine manufacturing

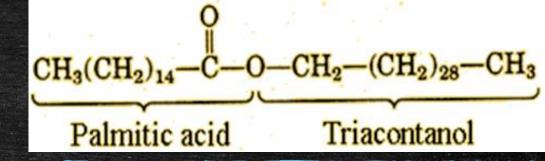


Double bond in the *trans* configuration





Simple lipids Neutral - waxes



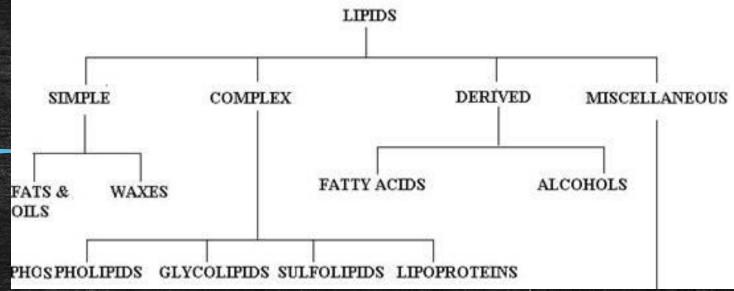
- A monohydric alcohol (C16 ~ C30, higher molecular weight than glycerol) esterified to long-chain fatty acids (C14 ~ C36)
- Insoluble, indigestible, coatings

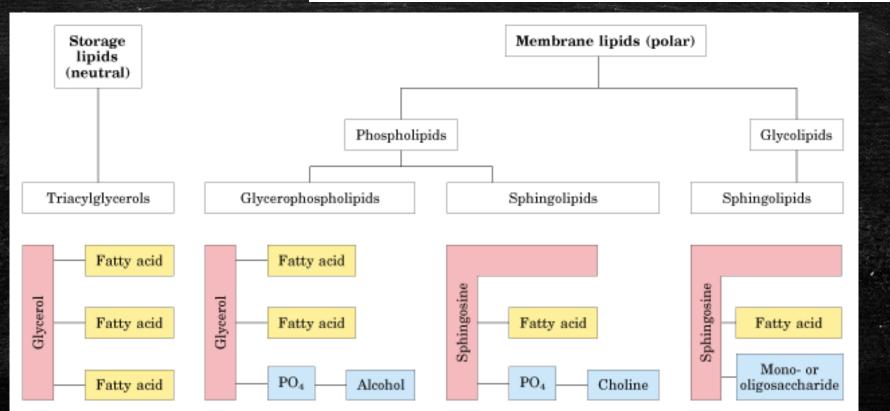
| Туре | Structural Formula | Source | Uses |
|--------------|---|---------------------|--|
| Beeswax | O ∥ CH ₃ (CH ₂) ₁₄ — C — O — (CH ₂) ₂₉ CH ₃ | Honeycomb | Candles, shoe polish, wax paper |
| Carnauba wax | O CH ₃ (CH ₂) ₂₄ — C— O—(CH ₂) ₂₉ CH ₃ | Brazilian palm tree | Waxes for furniture, cars, floors, shoes |
| Jojoba wax | CH ₃ (CH ₂) ₁₈ — C — O — (CH ₂) ₁₉ CH ₃ | Jojoba | Candles, soaps, cosmetics |

Differences between neutral lipids & waxes

| Property | Waxes | Neutral lipids | |
|------------------------------|--|-----------------------------------|--|
| 1.Digestibility | Indigestible (not hydrolyzed by lipase) | Digestible (hydrolyzed by lipase) | |
| 2-Type of alcohol | Long-chain monohydric alcohol + one fatty acid | Glycerol (trihydric) + 3 F.A | |
| 3-Type of F.A | Mainly palmitic or stearic acid | Long & short chain F.A | |
| 4-Acrolein test | Negative | Positive | |
| 5-Nature at room temperature | Hard solid | Soft solid or liquid | |
| 6-Saponification | Nonsaponifiable | Saponifiable | |
| 7-Nutritive value | No nutritive value | Nutritive | |
| 8-Example: | Bees wax | Butter & vegetable oils | |

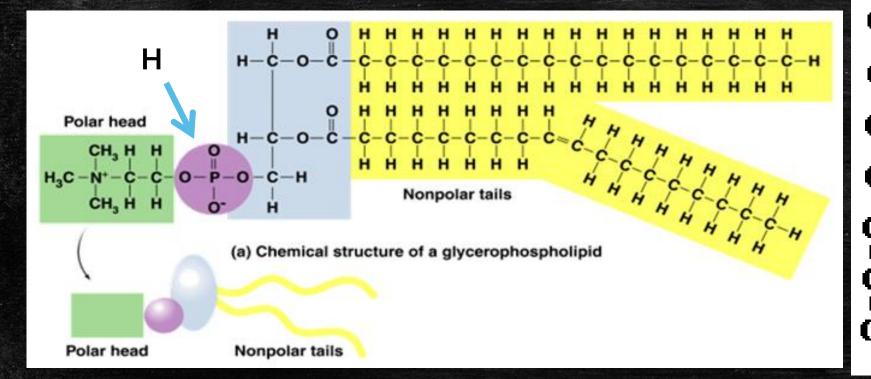
Complex lipids

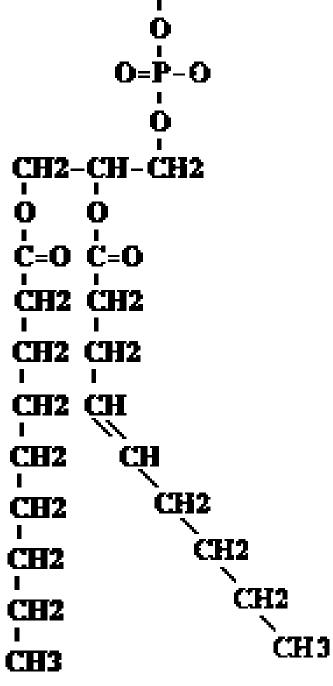




Glycero-phospholipids

Simplest is phosphatidic acid





Lecithins

- CH₂ CH₂ OH

 HO -N -CH₃

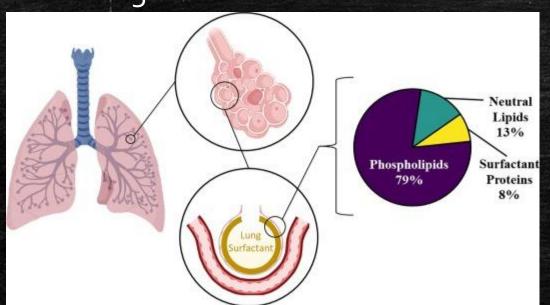
 CH₃

 CH₃
- $\begin{array}{c} O \\ || \\ CH_2 O C R_1 \\ || \\ R C O C C H \\ || \\ CH_3 O P O C C R_1 \\ || \\ CH_3 O P O C C R_1 \\ || \\ CH_2 N CH_3 \\ || \\ CH_3 \end{array}$

- Choline as a nitrogenous base
- Most abundant membrane lipid

Choline

- Snake venom
- Lung surfactant



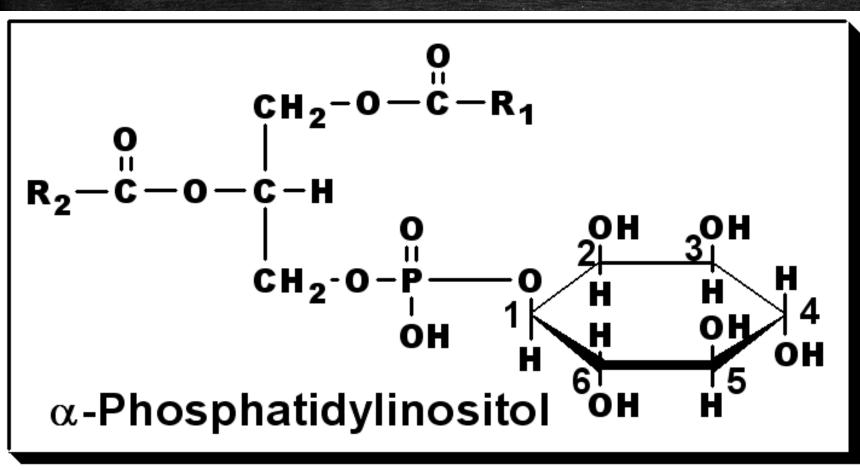


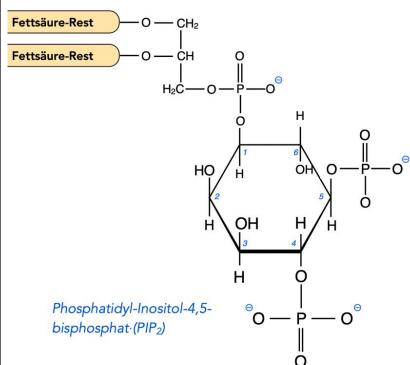
Cardiolipins

- Diphosphatidyl-glycerol
- Inner membrane of mitochondria

Cephalins or Kephalins

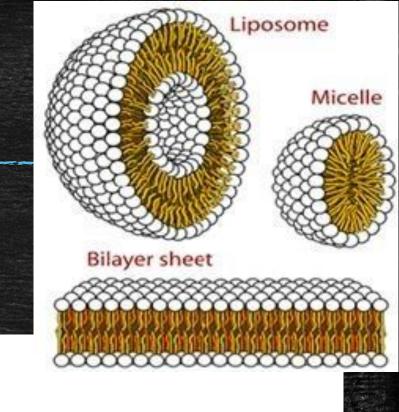
Inositides

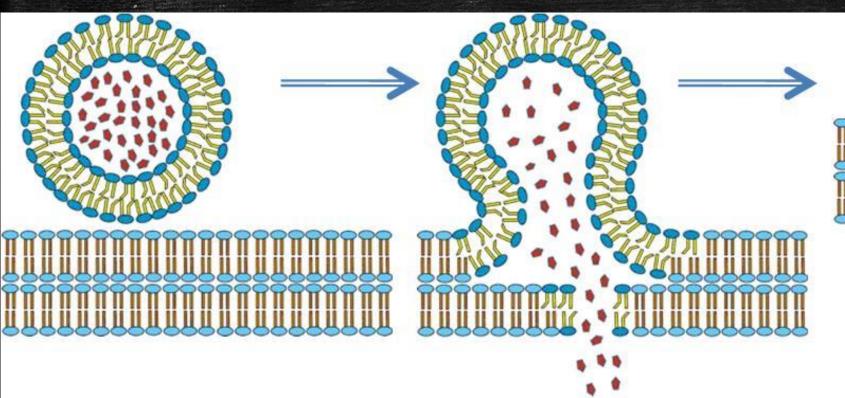


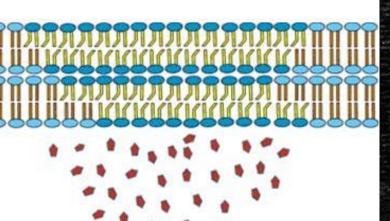


Structures of phospholipids

Uses of liposomes: delivery

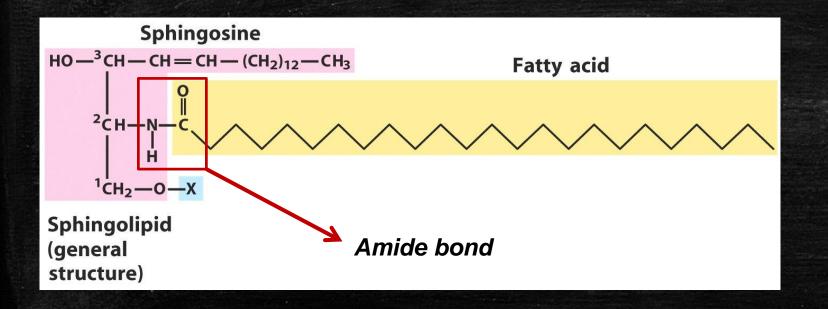


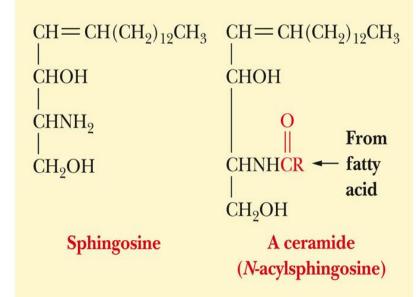


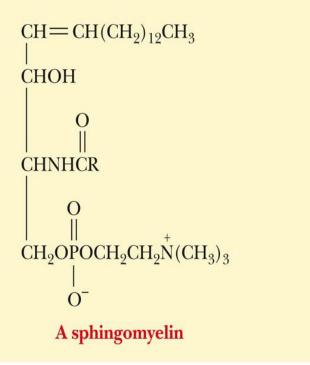


Sphingolipids

- The core: long-chain amino alcohol, sphingosine
- Highest in cells of CNS

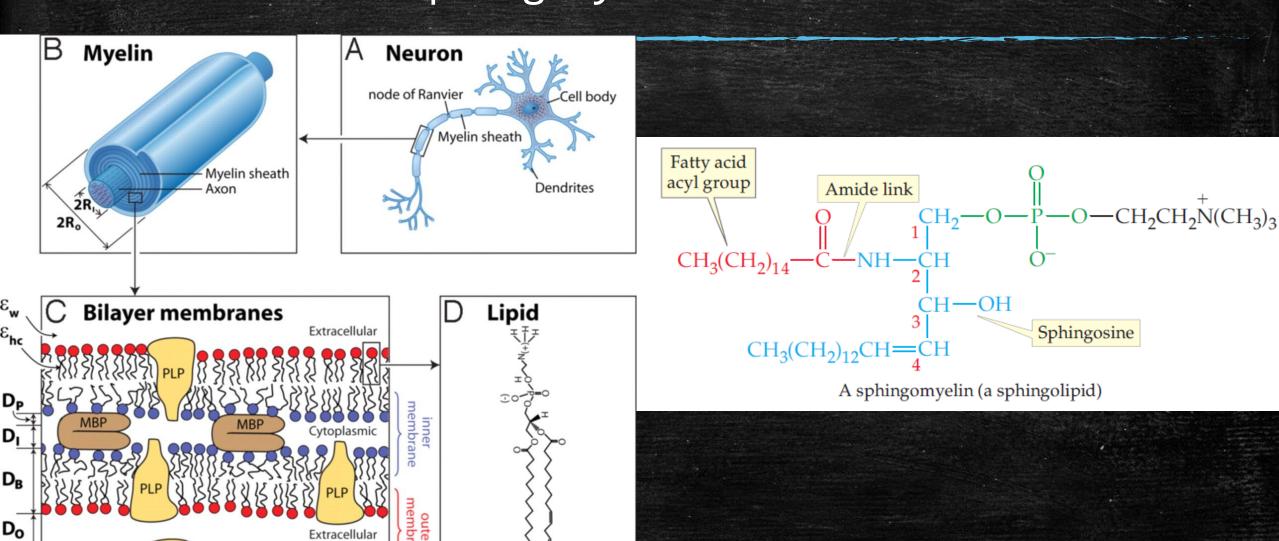






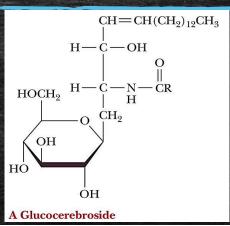
Ceramide **Sphingosine Fatty Acid** H_2O Ceramide (a sphingolipid)

Classes - Sphingomyelins

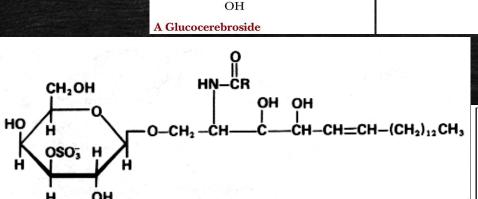


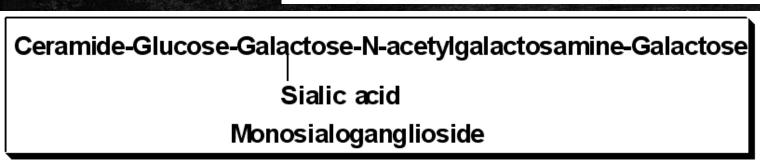
Classes - Glycolipids

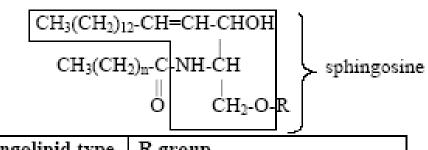
- There are three types of glycolipids
 - Cerebrosides
 - Globosides
 - Gangliosides
 - Sulfatides



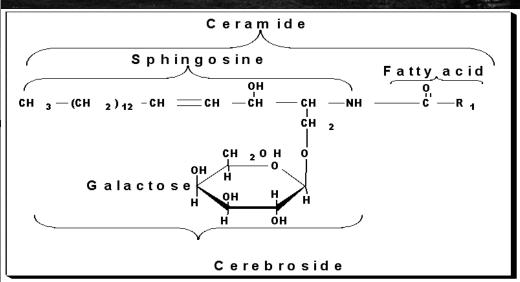
glycolipids-



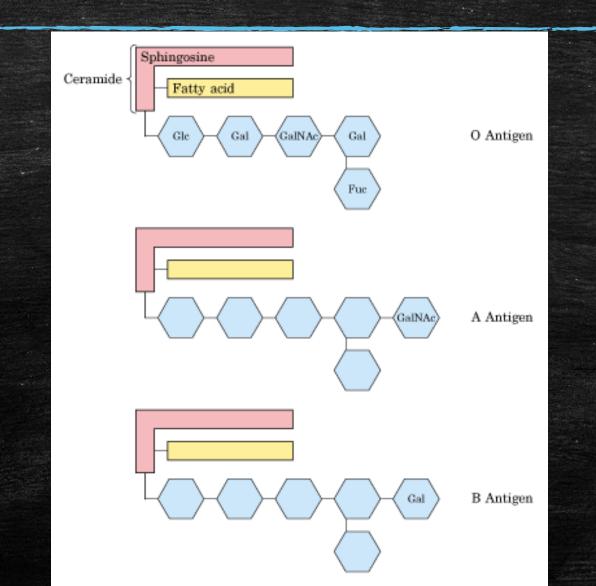




| | Sphingolipid type | R group |
|----|-------------------|--------------------------------|
| | Ceramide | H |
| | Sphingomyelin | phosphocholine |
| _ | Cerebroside | monosaccharide (galactose or |
| | | glucose) |
| | Globoside | two or more sugars (galactose, |
| | | glucose, N-acetylglucosamine |
| | Ganglioside | three or more sugars including |
| ٠. | | at least one sialic acid |

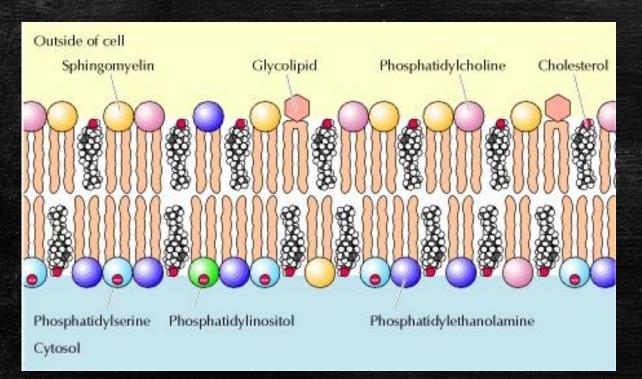


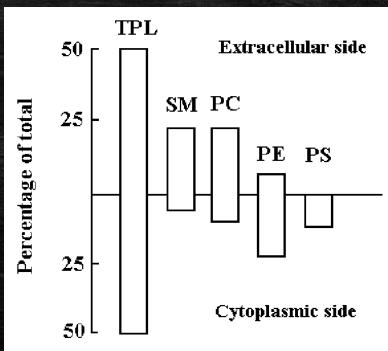
Sphingolipids & blood groups



Phospholipids and membranes distribution

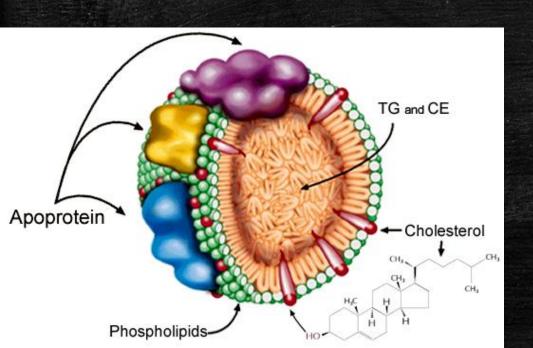
- The outer: phosphatidylcholine, sphingomyelin, and glycolipids(cell recognition)
- The inner: phosphatidylethanolamine, phosphatidylserine, and phosphatidylinositol (signaling)

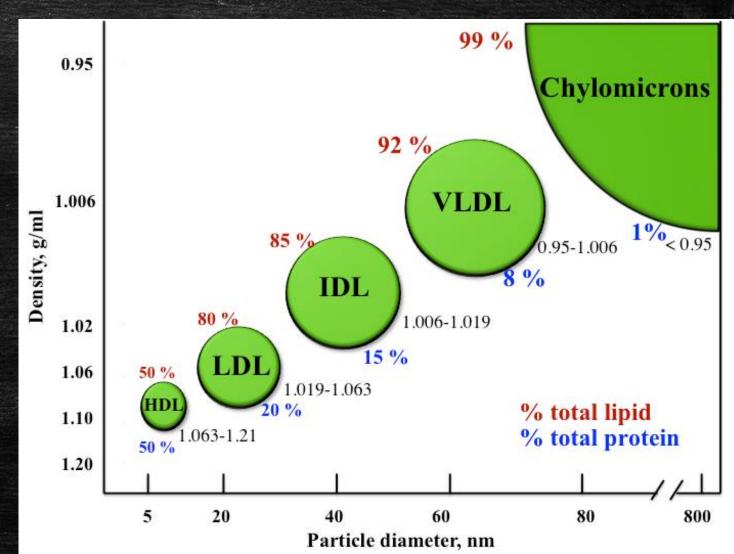




Lipoproteins

- Either structural
 - or transport f different types of lipids (cholesterol, cholesterol esters, phospholipids & triacylglycerols) in blood plasma

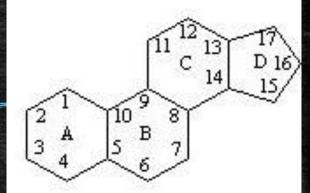




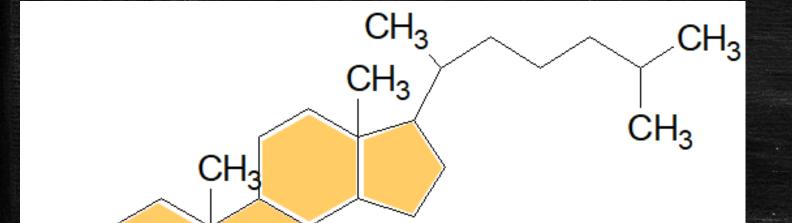
Steroids

The precursor

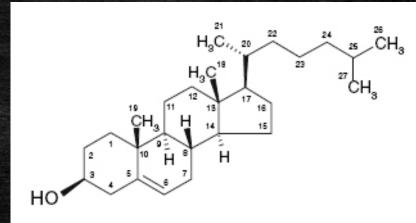
The nucleus



Steroid nucleus

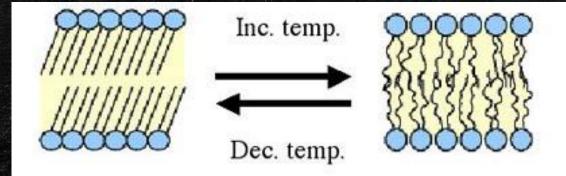


The most common steroid

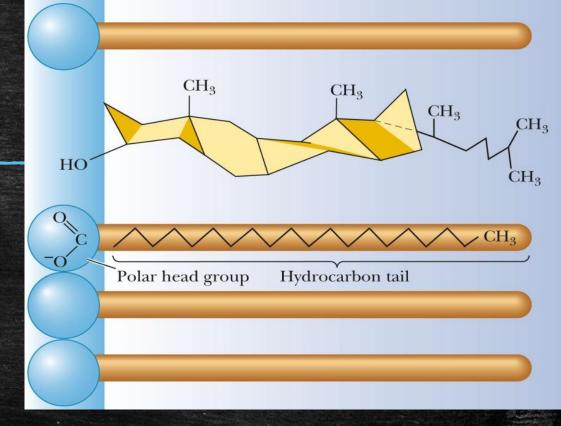


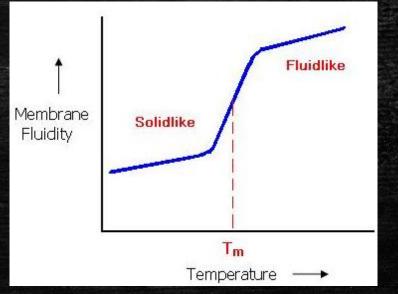
Cholesterol

- Vary among tissues
- Acts as a fluidity buffer in membranes: makes a membrane less solid at low temperatures and more solid at high temperatures



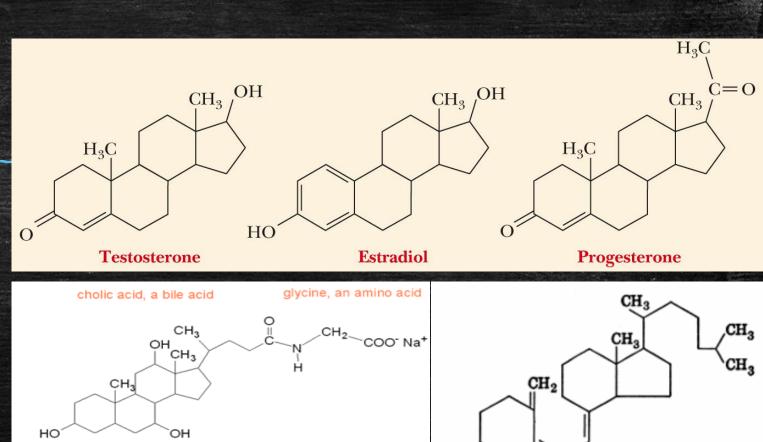
Very regular, Ordered structure Less tightly packed, Hydrocarbon tails Disordered.

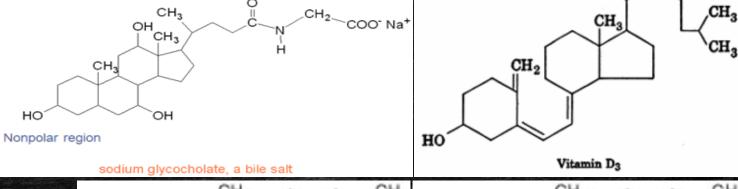


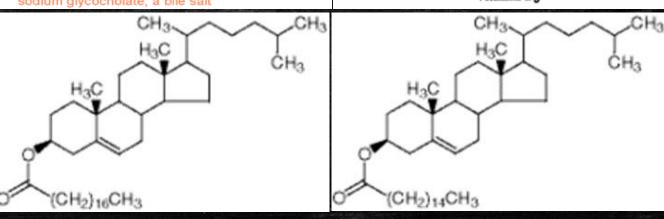


Products of cholesterol

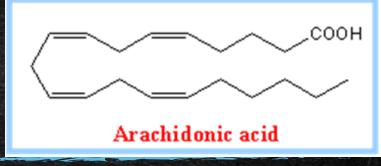
- Sterols
- Adrenal cortical hormones
- Male and female sex hormones
- Vitamin D group
- Bile acids
- Cholesterol esters



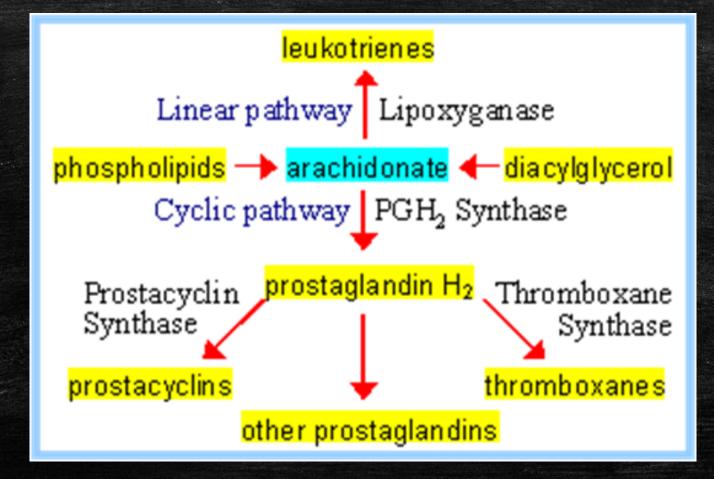




Derived fatty acids: Eicosanoids (icosanoids)

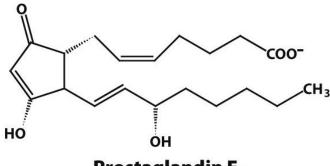


■ all $cis-\Delta^5,\Delta^8,\Delta^{11},\Delta^{14}$ -eicosatetraenoate, $CH_3(CH_2)_4(CH=CHCH_2)_4(CH_2)_2COO-$



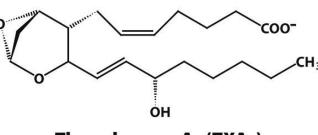
Functions

- Prostaglandins
 - Inhibition of platelet aggregation
 - Blood clotting
- Leukotrienes
 - Constriction of smooth muscles
 - Asthma
- Thromboxanes
 - Constriction of smooth muscles
 - Platelet aggregation
- Prostacyclins
 - An inhibitor of platelet aggregation
 - A vasodilator

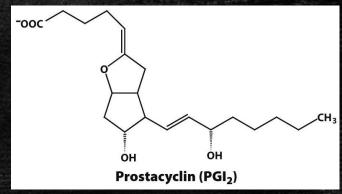


Prostaglandin E₂





Thromboxane A₂ (TXA₂)



Aspirin and NSAIDS

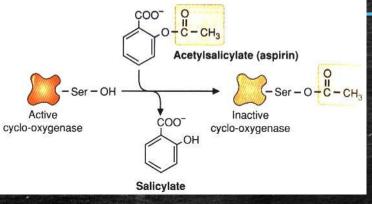


X COX2

Prostaglandins

Anti-inflammatory/

anti-pyretic

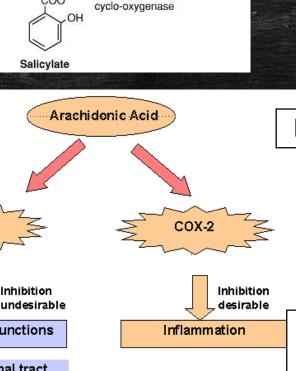


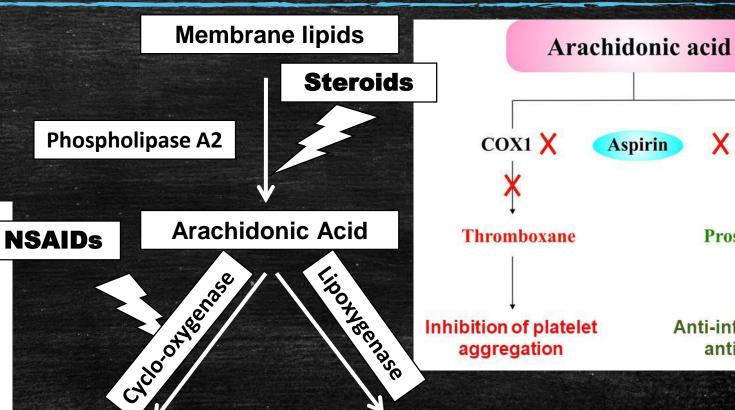
Inhibition

Homeostatic functions

Gastrointestinal tract Renal tract Platelet Function

Macrophage differentiation





Prostaglandins,

thromboxanes

Leukotrienes

COX: Cyclooxygenase

Selectives: Celebrex

 A new generation drug, Celebrex, targets COX2, but is prescribed with a strong warning of side effects on the label

