LIPIDS & MEMBRANES

Course: Biochemistry I (BIOC 230)
Textbook:
Principles of Biochemistry, 5th Ed., by L. A. Moran and others. 2014, Pearson. . Chapter 9

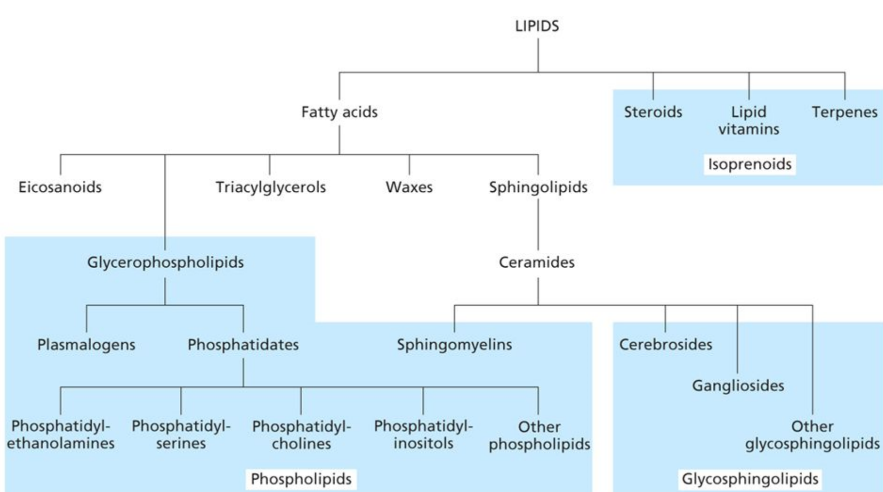
Lipids

- Lipids = fats
- Lipids are compounds that are soluble in non-polar organic solvents, but insoluble in water.
- Can be hydrophobic (non-polar) or amphipathic

Structural and functional diversity of lipids

- Next figure shows major types of lipids
- Simplest lipids are Fatty acids, and has the general formula: R — COOH; R represent a hydrocarbon chain
- Acyl-lipids - contain fatty acid groups as main non-polar group
- Isoprenoids – made up of 5 carbon isoprene units

Fig 9.1 Structural relationships of major lipid classes



Function of major acyl-lipids

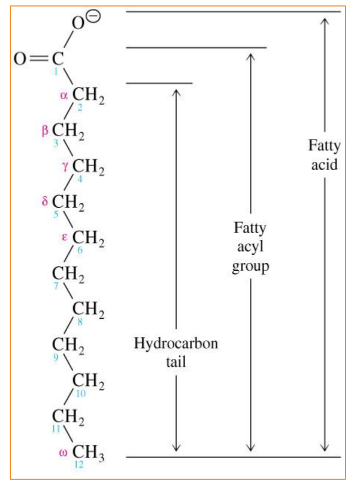
- Phospholipids – membrane components
- Triacylglycerols – storage fats and oils
- Waxes – moisture barrier
- Eicosanoids – signaling molecules (prostaglandin)
- Sphingomyelins – membrane component (in mylein sheaths)
- Glycospingolipids – cell recognition (ABO blood group antigen)

Function of major isoprenoid lipids

- Steroids (sterols) – membrane component, hormones
- Lipid Vitamins – Vitamin A, E, K
- Carotenoids - photosynthetic accessory pigments
- Chlorophyll – major light harvesting pigment
- Plastoquinone/ubiquinone – lipid soluble electron carriers
- Essential oils – menthol

Fatty acids

- Amphipathic molecule
- Polar carboxyl group
- Non-polar hydrocarbon tail
- Diverse structures (>100 different types identified in various species)
- Can contain oxygenated groups
- Most Fatty acids have pKa ~4.5 to 5



Fatty acids differ from one another in

- Differ in chain length
- Differ in degree of unsaturation
- Differ in the position of double bonds

Fatty acids

- Most fatty acids have 12 to 20 carbons
- Most chains have an even number of carbons (synthesized from two-carbon units)
- IUPAC nomenclature: carboxyl carbon is C-1
- Common nomenclature: αβγδε, etc. from C-1
- Carbon farthest from carboxyl is ω

Fatty acid nomenclature

- Short hand nomenclature describes total number of carbons, number of double bonds and the position of the double bond(s) in the hydrocarbon tail.

C18:1 D^9 = oleic acid, 18 carbon fatty acid with a double bond positioned at the ninth carbon counting from and including the carboxyl carbon (between carbons 9 and 10)

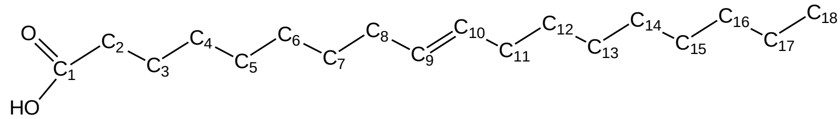


TABLE 10–1 Some Naturally Occurring Fatty Acids: Structure, Properties, and Nomenclature

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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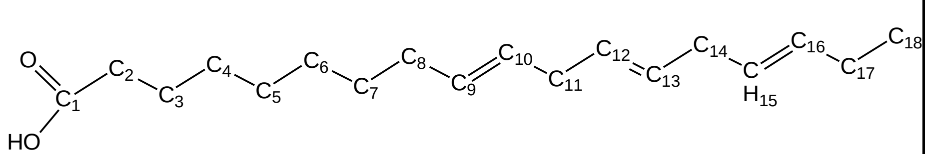
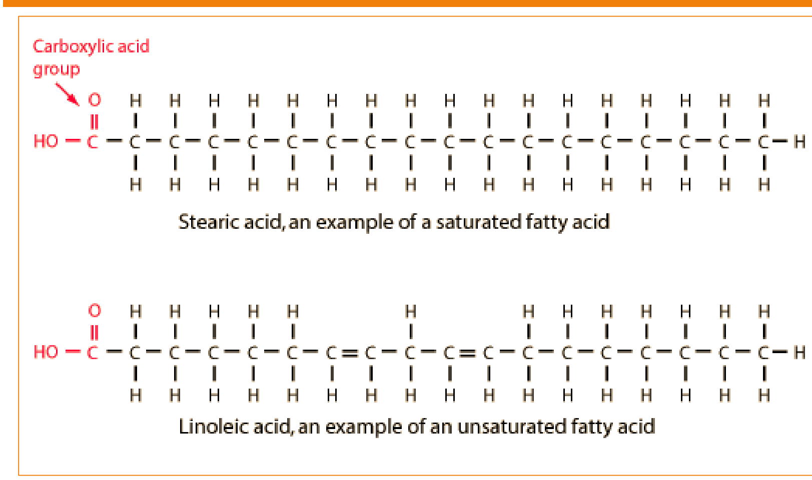
Fatty acid nomenclature

- Omega (ω) notation – counts carbons from end of hydrocarbon chain.
- Omega 3 fatty acids advertised as health promoting
- Linoleate = 18:3 Δ9,12,15 and 18:3 ω3

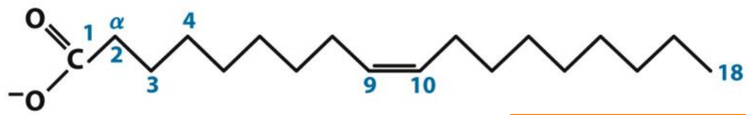


Polyunsaturated fatty acids (PUFAs)

- PUFAs can be alternatively named to stress the presence of first double bond from the methyl end of fatty acid,
- The farthest carbon or the one at the methyl end is given the number 1 and called (ω)
- Why?
- The physiological role of PUFAs is related more to the position of first double bond

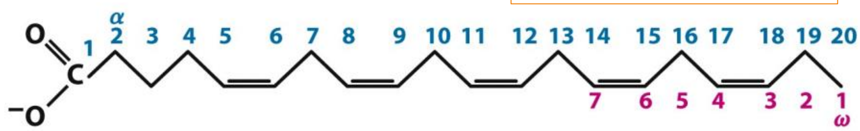


Two conventions for naming fatty acids



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

An omega-9 fatty acid, ω-9



(b) 20:5(Δ[5,8,11,14,17]) Eicosapentaenoic acid (EPA), an omega-3 fatty acid

Figure 10-1
Lehninger Principles of Biochemistry, Fifth Edition

Common saturated fatty acids

	common name	IUPAC name	melting point (C°)
12:0	laurate	dodeconoate	44
14:0	myristate	tetradeconoate	52
16:0	palmitate	hexadeconoate	63
18:0	stearate	octadeconoate	70
20:0	arachidate	eicosanoate	75
22:0	behenate	docosanoate	81
24:0	lignocerate	tetracosanate	84

Common unsaturated fatty acids

	common name	IUPAC name	melting point (Cº)
16:0	palmitate	hexadeconoate	63
16:1 Δ^9	palmitoleate	cis-Δ^9-hexadeconoate	-0.5
18:0	stearate	octadeconoate	70
18:1 Δ^9	oleate	cis-Δ^9- octadeconoate	13
18:2 $\Delta^{9,12}$	linoleate	cis-$\Delta^{9,12}$- octadeconoate	-9
18:3 $\Delta^{9,12,15}$	linolenate	cis-$\Delta^{9,12,15}$- octadeconoate	-17
20:0	arachidate	eicosanoate	75
20:4 $\Delta^{5,8,11,14}$	arachindonate	cis- $\Delta^{5,8,11,14}$-eicosatetraenoate	-49

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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		

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Table 10-1

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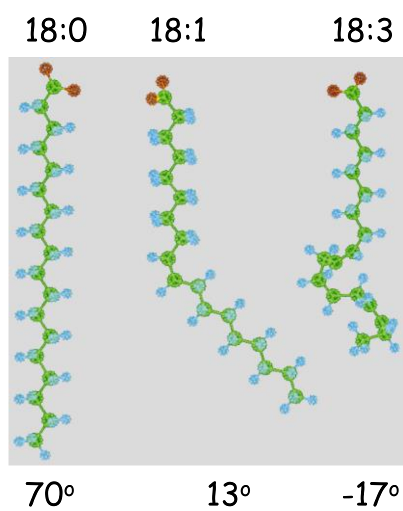
Essential fatty acids: omega-3

- Humans require omega-3 PUFAs (α-linolenic acid, 18:3 ($\Delta^{9,12,15}$), an omega -3 PUFA,
- Humans can use this PUFA to synthesize two other omega-3 PUFAs important in cellular functions, namely;
  - Eicosapentaenoic acid (EPA; 20:5 $\Delta^{5,8,11,14,17}$)
  - Docasahexaenoic acid (DHA; 22:6 $\Delta^{4,7,10,13,16,19}$)

Physical Properties of Fatty acids

- Saturated chains pack tightly and form more rigid, organized aggregates
- Unsaturated chains bend and pack in a less ordered way, with greater potential for motion



Melting points of fatty acids affect properties of acyl-lipids

- Membrane fluidity determined by temperature and the degree of fatty acid unsaturation of phospholipids
- Certain bacteria can modulate fatty acid unsaturation in response to temperature
- Difference between fats and oils
- Cocoa butter – perfect melt in your mouth fat made of triacylglycerol with 18:0-18:1-18:0 fatty acids
- The configuration of most double bonds in unsaturated fatty acids is cis
- Margarine is hydrogenated vegetable oil. Increase saturation of fatty acids. Introduces *trans* double bonds (thought to be harmful)

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
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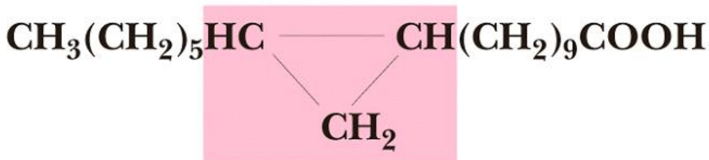
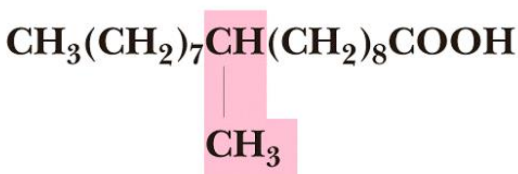
Unusual fatty acids can function analogously to unsaturated fatty acids

Lactobacillic acid



Tuberculostearic acid



Free fatty acids in cells

- Free fatty acids occur only in trace amounts in living cells
- Most fatty acids are esterified to glycerol or other backbone compounds to form more complex lipid molecules
- Complex lipids are named after the parent fatty acid. For example: esters of fatty acid Laurate are called Lauroyl esters
- Relative abundance of fatty acids varies with type of organism, type of organ and food source

Free fatty acids in cells (cont'd)

- The most abundant fatty acids in animals are usually Oleate (18:1), palmitate (16:0) and stearate (18:0)

Fatty acid composition of three food fats

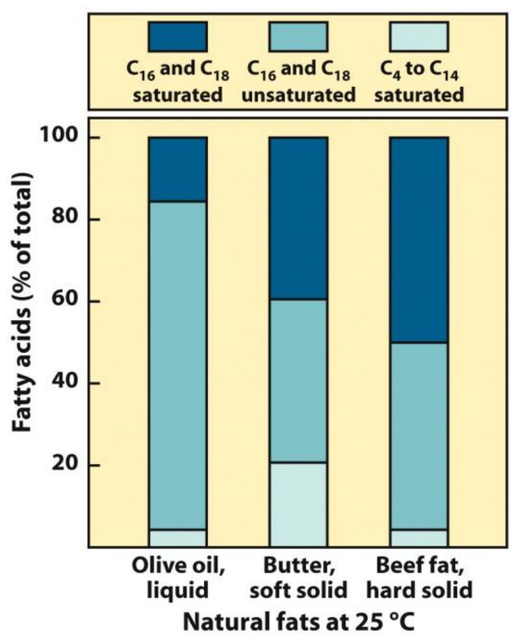


Figure 10-5
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Essential fatty acids

- The body can synthesize most of the fats it needs from the diet.
- **Two essential fatty acids, linoleic acid** (18:2 $D^{9,12}$ or Omega-6) and **alpha-linolenic** (18:3 $D^{9,12,15}$ or Omega-3), cannot be synthesized in the body and must be obtained from food
- Linoleate is abundant in oils and Linolenate is found in plants and fish oils
- Adequate intake of the essential fatty acids results in numerous health benefits.
- Ideally, the ratio of omega-6 to omega-3 fatty acids should be between 1:1 and 4:1

- Most Americans consume these fatty acids at a ratio of omega-6:omega-3 between 10:1 and 25:1, and are consequently unable to reap the benefits of omega-3s.
- This imbalance is due to a reliance on processed foods and oils, which are now common in the Western diet.
- To combat this issue it is necessary to eat a low-fat diet with minimal processed foods and with naturally occurring omega-3 fatty acids.
- A lower omega-6:omega-3 ratio is desirable for reducing the risk of many chronic diseases.

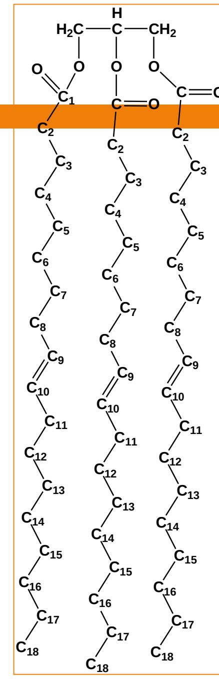
- Deficiencies in these fatty acids lead to a host of symptoms and disorders including abnormalities in the liver and the kidneys, reduced growth rates, decreased immune function, depression, and dryness of the skin.
- Adequate intake of the essential fatty acids results in numerous health benefits.
- Documented benefits include prevention of atherosclerosis, reduced incidence of heart disease and stroke, and relief from the symptoms associated with ulcerative colitis, menstrual pain, and joint pain.
- Omega-3 fatty acid levels have also been associated with decreased breast cancer risk.

Chapter 9 (part 2)

Lipids and Membranes

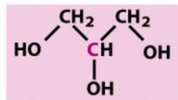
Triacylglycerols (TAG)

- Fats and oils
- Impt source of metabolic fuels
- Because more reduced than carbohydrates, oxidation of TAG yields more energy (16 kJ/g carbo vs. 37 kJ/g TAG)
- Americans obtain between 20 and 30% of their calories from fats and oils; 70% of these calories come from vegetable oils
- Insulation – subcutaneous fat is an important thermo insulator for marine mammals

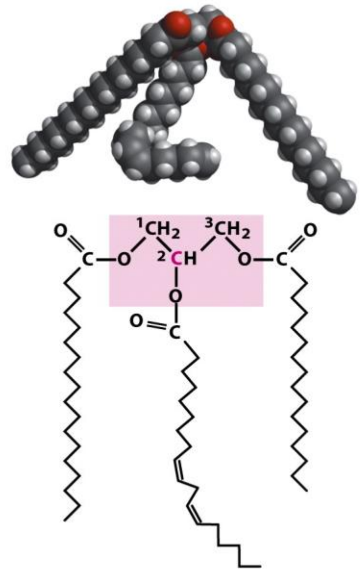


Triacylglycerols (TAG)

- TAGs are fatty acid esters of glycerol
- TAGs are also called Triglycerides, fats or neutral fats
- Those containing same FA in all 3 positions are called simple triacylglycerols and are named after the FA they contain, like 16:0 >tristearin; 18:0> tripalmitin and 18:1> triolein
- Most naturally occurring triacylglycerols are mixed and named after the name and position of each fatty acid
- Most lipids in average human diet are TAGs



Glycerol



Glycerol and a triacylglycerol.

When FAs at C1 and C3 are different, then C2 is a chiral center

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

Figure 10-3
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Fat stores in cells:
each adipocyte contains a large fat droplet that accounts for nearly the entire volume of the cell

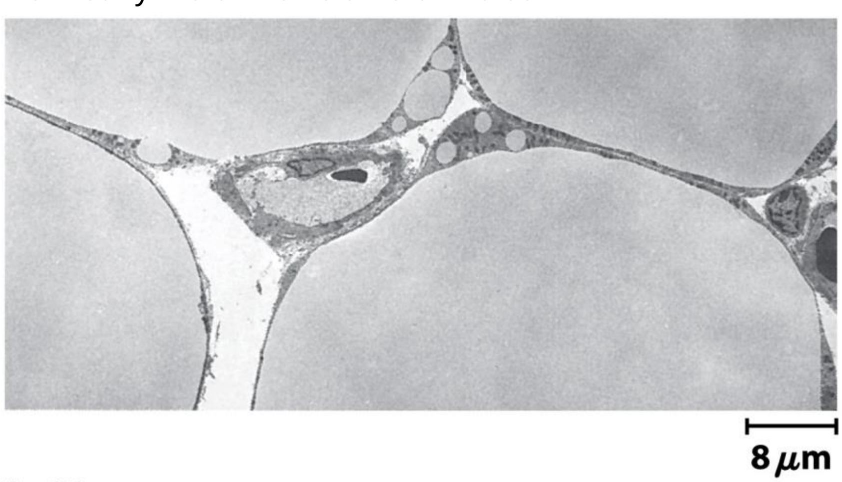

Figure 10-4a
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Structural lipids in membrane

- Five general types of membrane lipids:
  1. Glycerophospholipids: two FAs are joined to glycerol
  2. Galactolipids: two fatty acids are joined to glycerol but lack the phosphate group
  3. Sphingolipids: a single fatty acid is joined to a fatty amine, sphingosine
  4. Archaeal tetraether lipids: two very long alkyl chains are ether-linked to glycerol at both ends
  5. Sterols: has 4 fused hydrocarbon rings

Some common types of storage and membrane lipids:
All the lipid types shown here have either glycerol or sphingosine as the backbone (pink screen), to which are attached one or more long-chain alkyl groups (yellow) and a polar head group (blue).

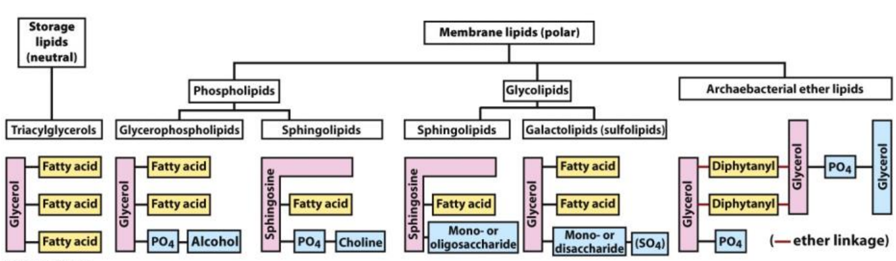

Figure 10-7
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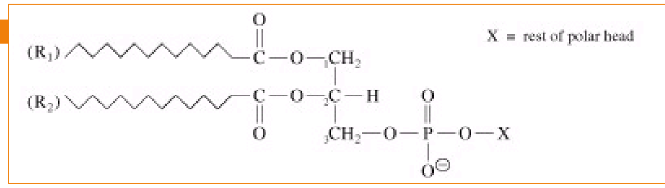
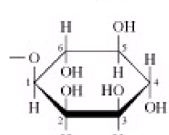
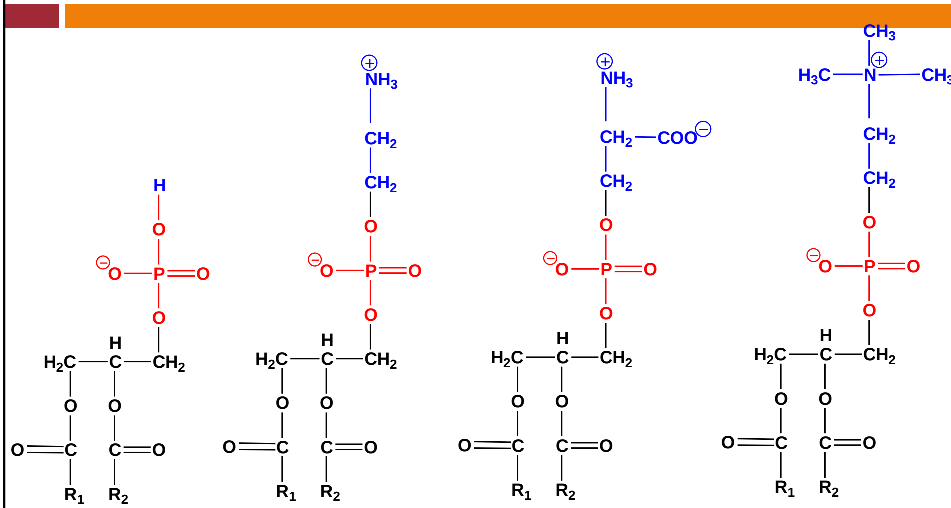
Phospholipids (Glycerophospholipids)



- Also called phosphoglycerides
- Phospholipids are built on glycerol back bone.
- Two fatty acid groups are attached through ester linkages to carbons one and two of glycerol.
- Unsaturated fatty acid often attached to carbon 2
- A phosphate group is attached to carbon three
- A polar head group is attached to the phosphate (designated as X in figure)

Precursor of X (HO—X)	Formula of —O—X	Name of resulting glycerophospholipid
Water	$-O-H$	Phosphatidate
Choline	$-O-CH_2CH_2\overset{\oplus}{N}(CH_3)_3$	Phosphatidylcholine
Ethanolamine	$-O-CH_2CH_2\overset{\oplus}{N}H_3$	Phosphatidylethanolamine
Serine	$-O-CH_2-CH(\overset{\oplus}{N}H_3)COO^{\ominus}$	Phosphatidylserine
Glycerol	$-O-CH_2CH(OH)-CH_2OH$	Phosphatidylglycerol
Phosphatidyl-glycerol	$-O-CH_2CH(OH)-CH_2-O-P(=O)(O^{\ominus})-O-CH_2-CH(OC(=O)R_4)-CH_2OC(=O)R_3$	Diphosphatidylglycerol (Cardiolipin)
myo-Inositol		Phosphatidylinositol

Common membrane phospholipids



Phophtidate | Phophatidylethanolamine | Phophatidylserine | Phophatidylcholine

Plasmalogens / ether lipids

- Plasmalogens are Ether lipids are phospholipids in which the haydrocarbon tail on C-1 hydroxyl group of glycerol attached by a vinyl ether linkage rather than an ester linkage
- Plasmalogens accounts for ~23% of the phospholipids in human CNS

Ether lipids

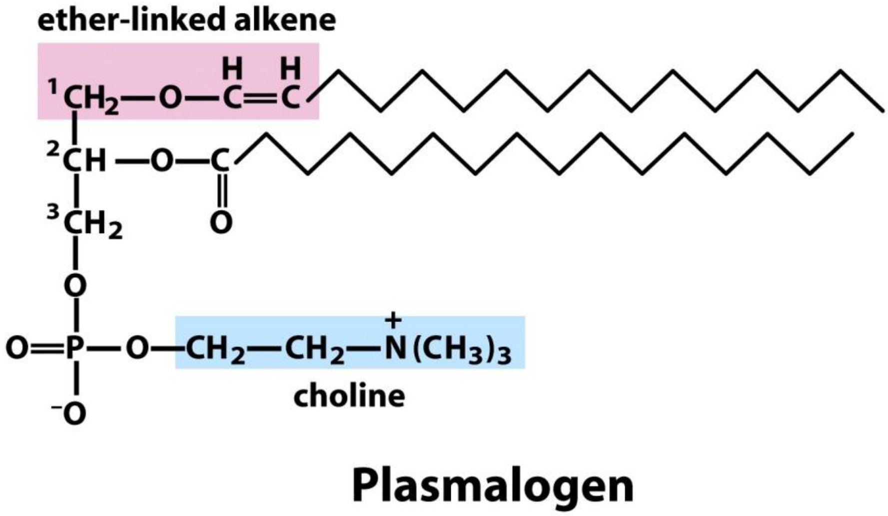


Figure 10-10a
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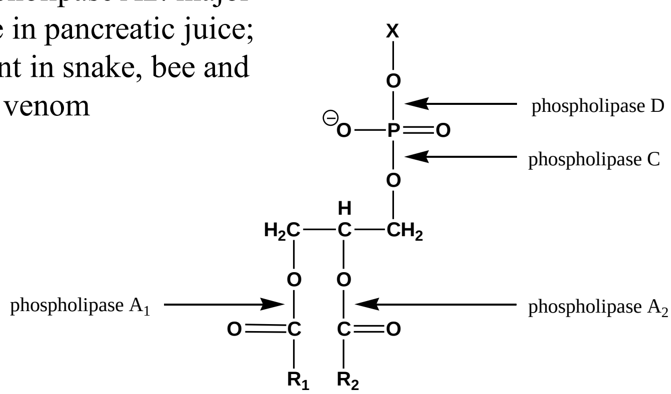
Enzymes used to Dissect Phospholipid Structure

Phospholipase A2: major lipase in pancreatic juice; present in snake, bee and wasp venom



Sphingolipids

- In Sphingolipids, the sphingosine molecule (4-sphingosine or one of its derivatives) replaces glycerol
- Ceramide is the parent compound for this group

Classes of Sphingolipids

- Three classes of sphingolipids: all derived from ceramide and differ in the polar head group
  - Sphingomyelin: contain phosphocholine or phosphoethanolamine as polar head
  - Glycosphingolipids (neutral glycolipids): cerebroside (a single sugar linked to ceramide) and globoside (2 to 4 sugars linked to ceramide)
  - Gangliosides: have oligosaccharides as polar head groups and one or more residues of N-acetylneuraminic acid (NeubAc), a sialic acid

Sphingolipids

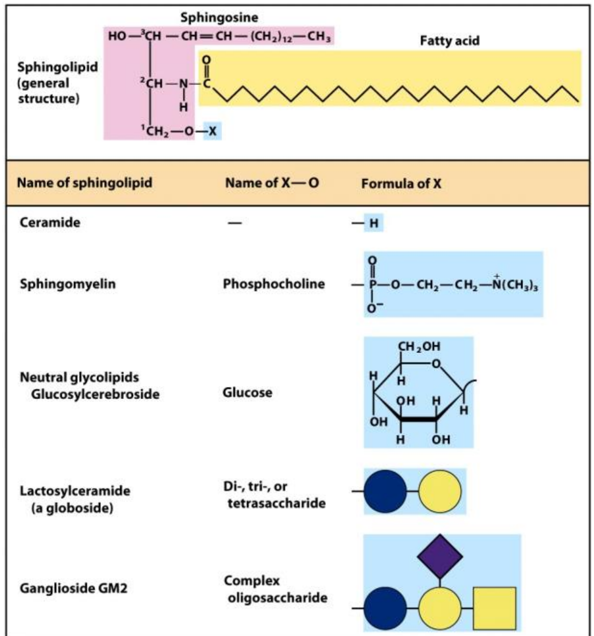


Figure 10-13
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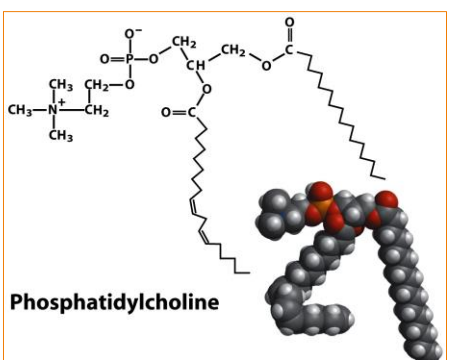

Figure 10-14 part 1
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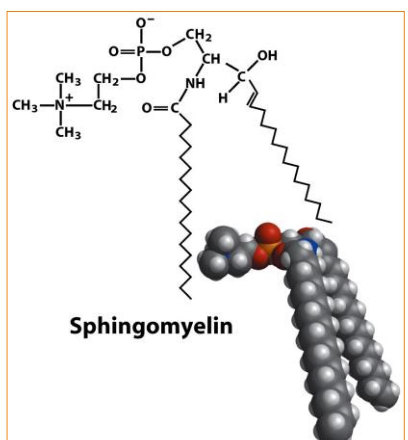

Figure 10-14 part 2
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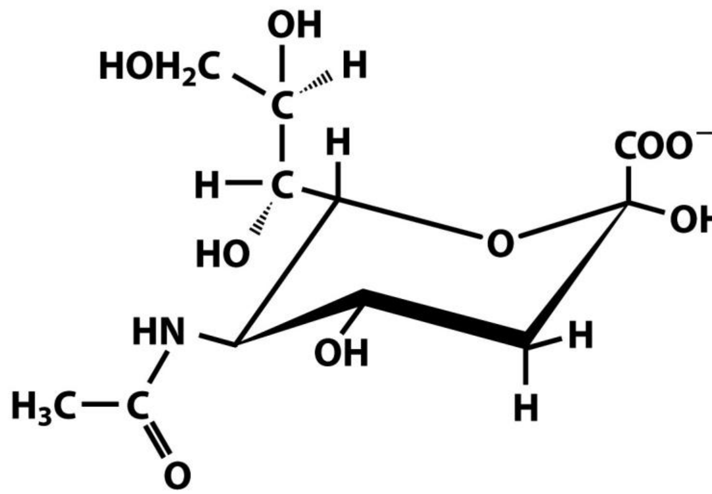
The similarities in shape and molecular structure of phosphatidylcholine (a glycerophospholipid) and sphingomyelin (a sphingolipid)



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

Unnumbered 10 p354
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Sphingolipids at cell surface are sites for biological recognition

- In humans, more than 60 different sphingolipids are found in cellular membranes
- Carbohydrate moieties of certain sphingolipids define the human blood groups
- Gangliosides are concentrated in the outer surface of cells, where they present points of recognition for extracellular molecules or surfaces of neighboring cells
- Very low conc of specific gangliosides induce differentiation of cultured neuronal tumor cells

Glycosphingolipids as determinants of blood groups

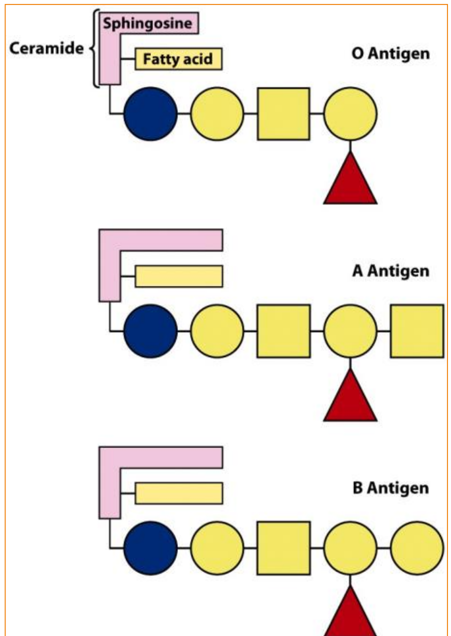

Figure 10-15
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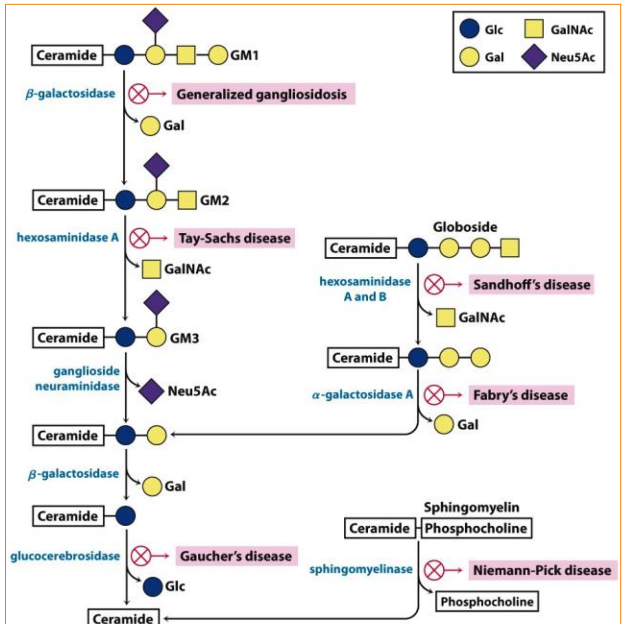
Inherited human diseases resulting from abnormal accumulation of membrane lipids

- When sphingolipid degradation is impaired by a defect in one of the enzymes (see next figure), partial breakdown products accumulate in the tissues, causing serious diseases
- In Tay-Sachs diseases, GM2 accumulates in lysosomes, which in turn swell leading to tissue enlargement. In CNS, nerve cells die and causes blindness, mental retardation and death

Pathways for the breakdown of sphingolipids



Box 10-2 figure 1
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Steroids

- Steroids have a characteristic steroid nucleus consisting of four fused rings
- Sterols are structural lipids present in membranes of most eukaryotic cells
- Cholesterol is the major sterol in animal tissues
- Similar sterols are found in other eukaryotes, like stigmasterol in plants and ergosterol in fungi
- Bacteria cannot synthesize sterols, a few bacteria can incorporate exogenous sterols in their membranes

Steroids (cont'd)

- Sterols of all eukaryotes are synthesized from simple five carbon isoprene subunits
- Steroid hormones serve many functions in animals - including salt balance, metabolic function and sexual function
- Bile acids are derivatives of cholesterol that act as detergents in the intestine

Cholesterol

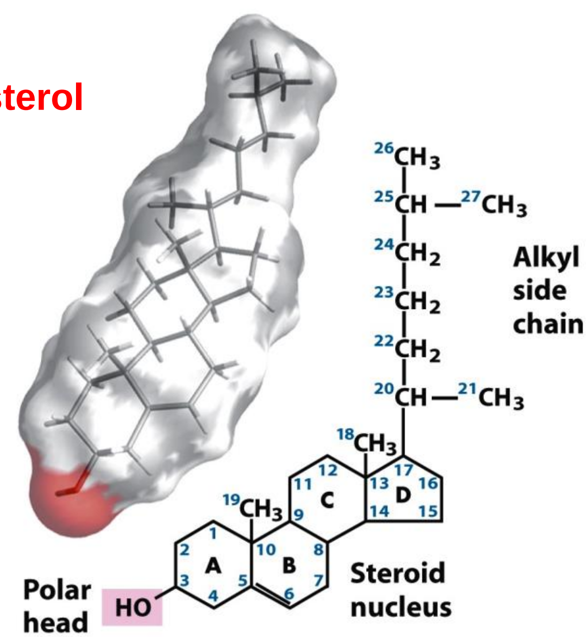

Figure 10-17
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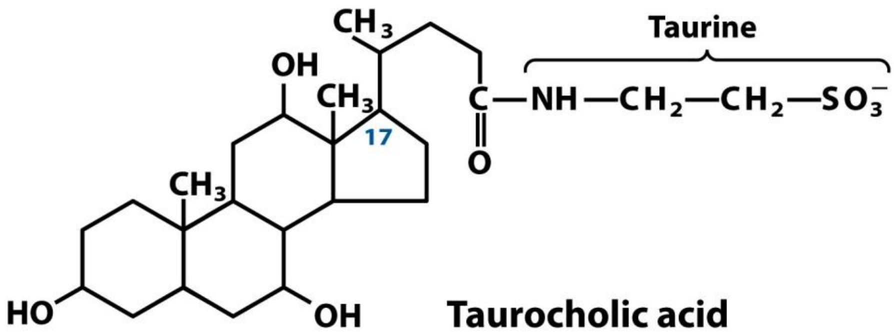

Taurocholic acid
(a bile acid)

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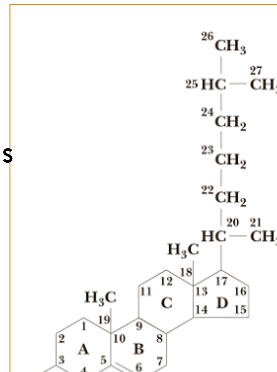
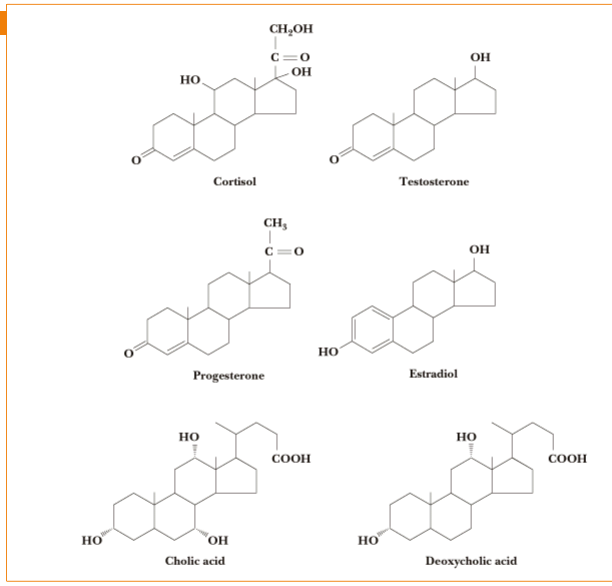
Cholesterol

- Cholesterol is an important membrane component
- Only synthesized by animals
- Accumulates in lipid deposits on walls of blood vessels – plaques
- Plaque formation is linked to cardiovascular diseases

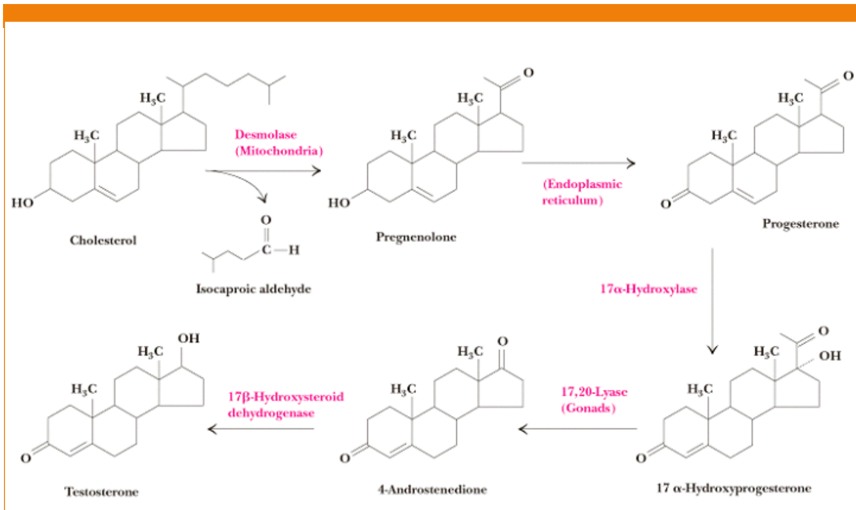


Cholesterol

Steroids



Many steroids are derived from cholesterol



Other biologically important lipids

- Many kinds of lipids are not found in membranes such as waxes, eicosanoids and some isoprenoids

Waxes serve as energy stores and water repellents

- Waxes are esters of long chain (C14-C36) saturated and unsaturated fatty acids with long chain (C16-C30) alcohols
- Their melting points (60-100°C) are generally higher than those of triacylglycerols
- Certain skin glands secrete waxes to protect hair and skin and keep it pliable, lubricated and waterproof

Biological wax

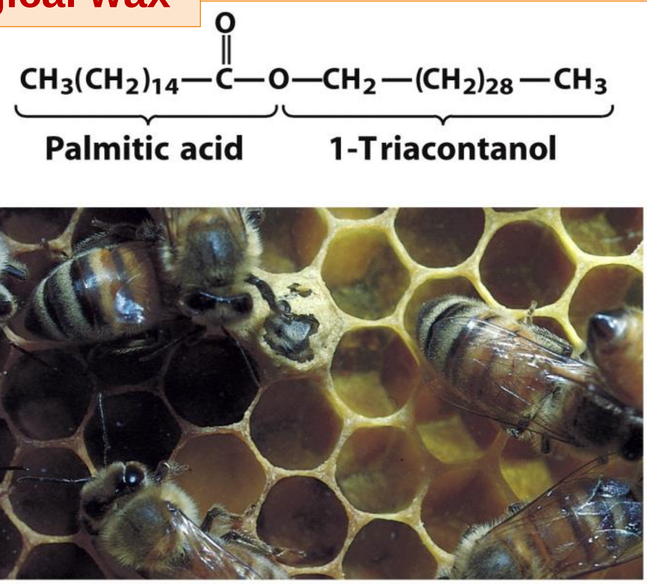


Figure 10-6
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Biological wax:
Triacontanoylpalmitate, the major component of beeswax, is an ester of palmitic acid with the alcohol triacontanol.

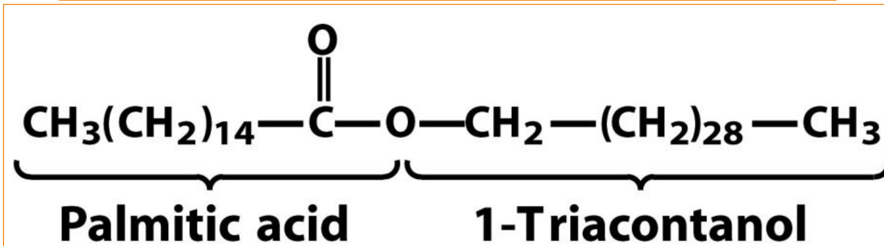

Figure 10-6a
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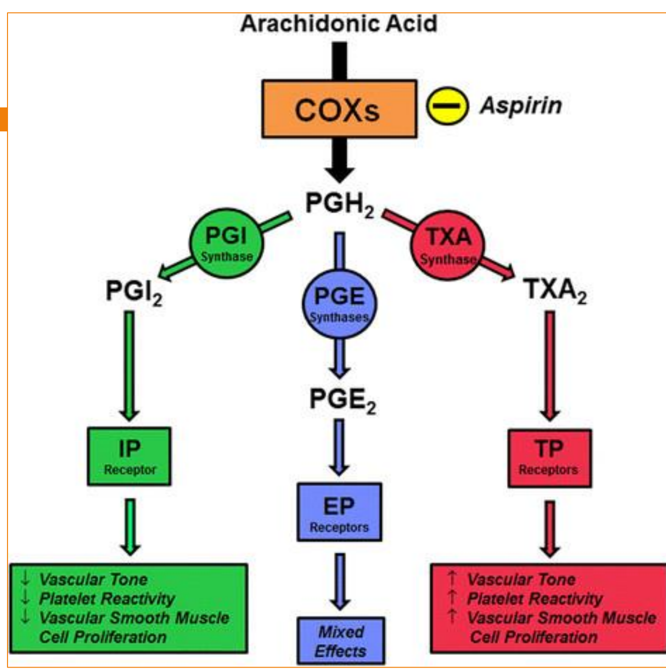
Eicosanoids

- Eicosanoids are oxygenated derivatives of C20 polyunsaturated fatty acids such as arachidonic acid
- Examples include:
  - Prostaglandins E2: causes constriction of blood vessels
  - Thromboxanes A2: involved in formation of blood clots
  - Leukotriene D4: a mediator of smooth muscle contraction and provokes bronchial constriction in asthma
- **Aspirin** alleviates pain, fever and inflammation by inhibiting synthesis of prostaglandins



Isoprenoids

- Includes lipid vitamines A, E and K
- Vitamin D is an isoprenoid derivative of cholesterol