Lipids- Part 1

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Resources

Campbell and Farrell's Biochemistry, Chapter 8

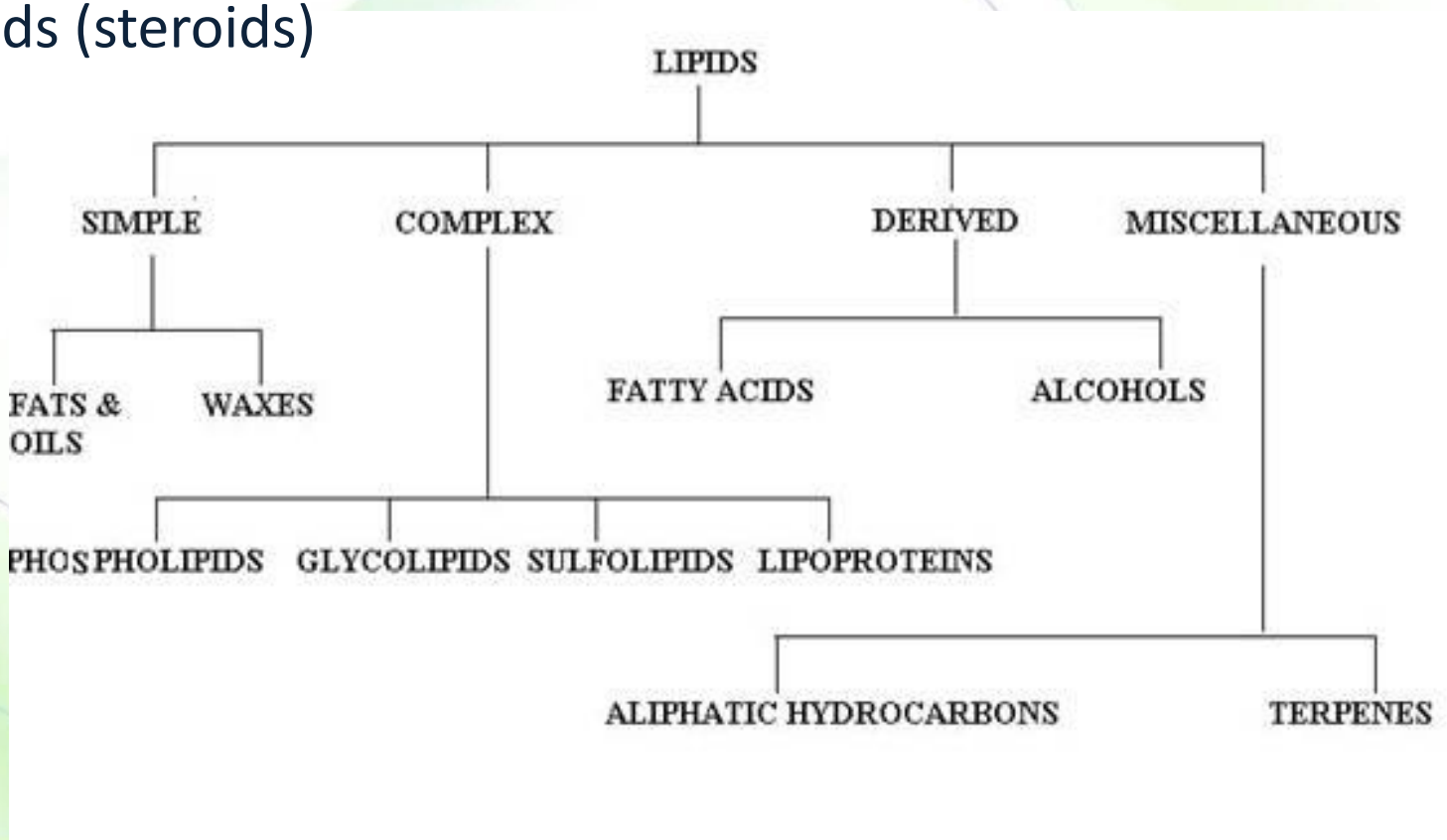
Lipids

- Lipids are a heterogeneous class of naturally occurring organic compounds that share some properties based on structural similarities, mainly a dominance of nonpolar groups.

- They are Amphipathic in nature.
- They are insoluble in water, but soluble in fat or organic solvents (ether, chloroform, benzene, acetone).
- They are widely distributed in plants & animals.

Classes

- Simple lipids (fats, oils, and waxes)
- Complex lipids (glycerides , glycerophospholipids, sphingolipids, glycolipids, lipoproteins)
- Derived lipids (fatty acids, alcohols, eicosanoids)
- Cyclic lipids (steroids)



Lipid Functions

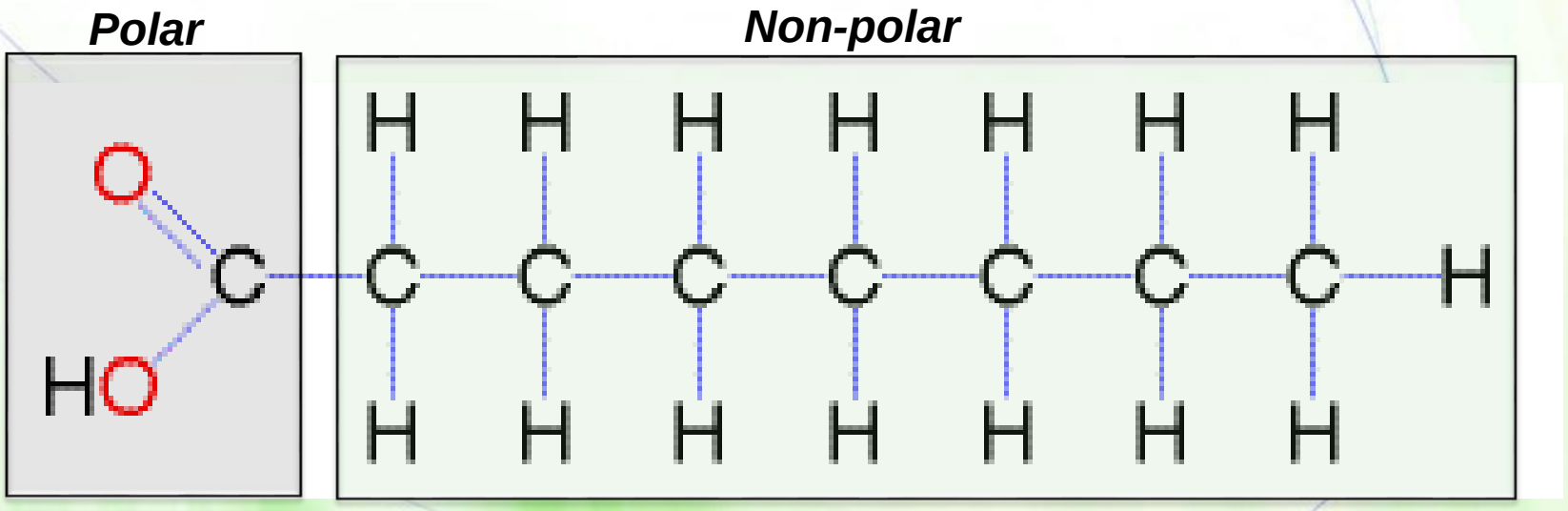
- Lipids include:
  - Storage lipids
  - Structural lipids in membranes
  - Lipids as signals, cofactors & pigments
- They are a major source of energy
  - They are storable to unlimited amount (vs. carbohydrates)
  - They provide considerable amount of energy to the body (25% of body needs) & provide a high-energy value (more energy per gram vs. carbohydrates & proteins)
- Structural components (cell membranes)
- Precursors of hormone and vitamins
- Shock absorbers thermal insulator

Fatty acids

- Aliphatic mono-carboxylic acids
- Formula: **$R\text{-}(CH_2)_n\text{-}COOH$**
- Lengths
  - Physiological (12-24)
  - Abundant (16 and 18)
- Degree of unsaturation
- Amphipathic molecules

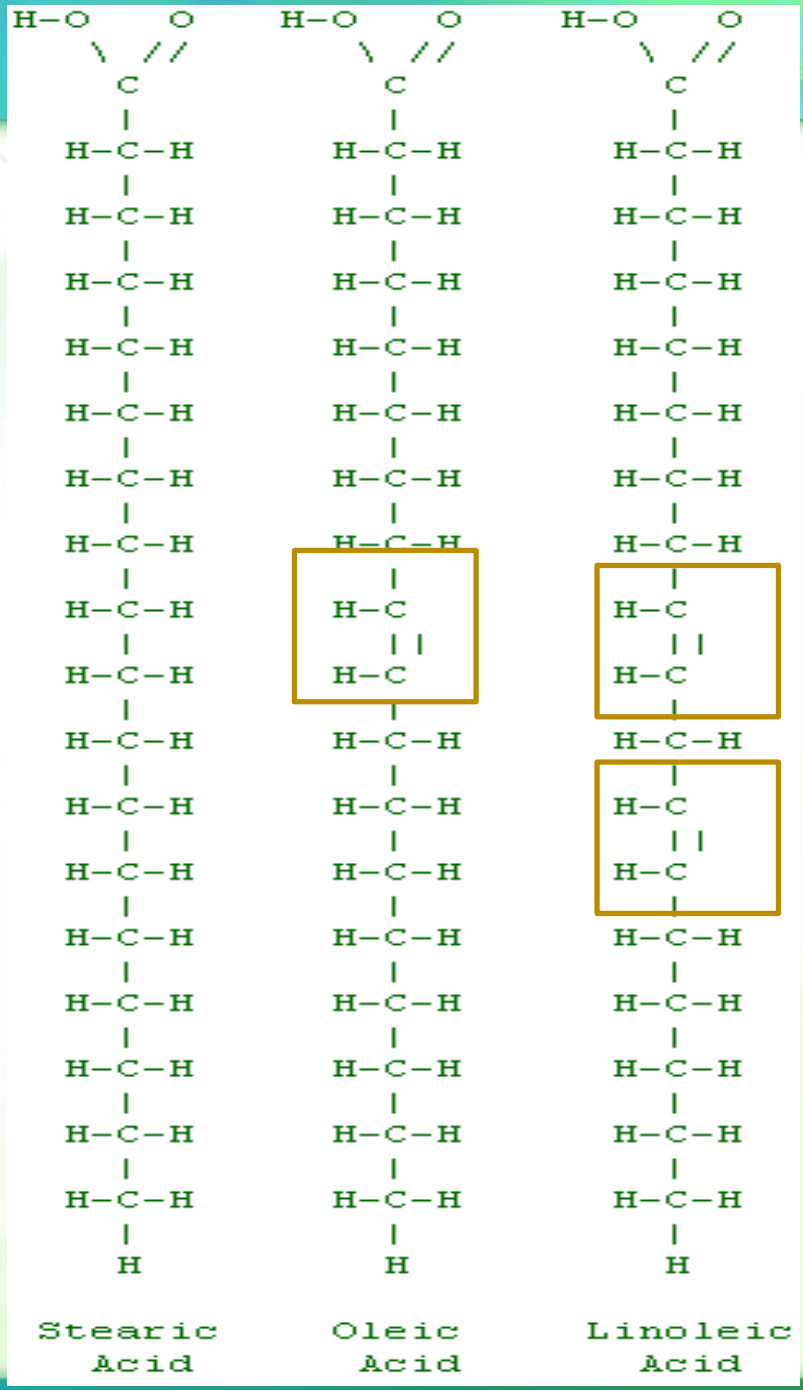
Functions:

- **Building blocks of other lipids**
- **Modification of many proteins (lipoproteins)**
- **Important fuel molecules**
- **Derivatives of important cellular molecules**

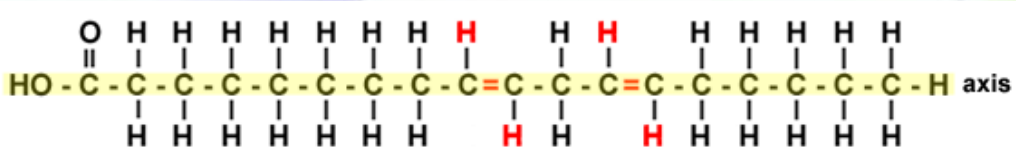


Types of fatty acids

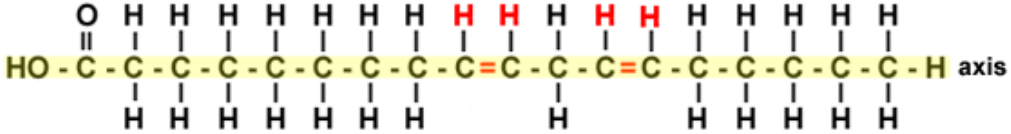
- Saturated fatty acids are those with all of C-C bonds being single.
- Unsaturated fatty acids are those with one or more double bonds between carbons
  - Monounsaturated fatty acid: a fatty acid containing one double bond.
  - Polyunsaturated fatty acids contain two or more double bonds.



Cis vs. trans bonds



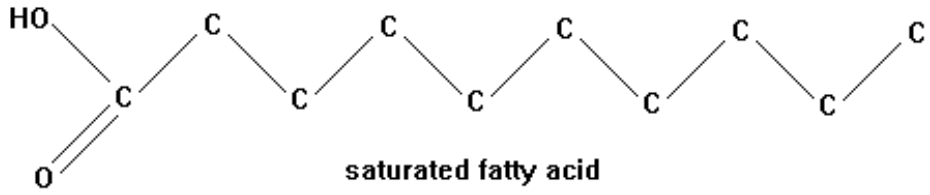
linoleic acid: *trans* configuration (*trans* isomer)



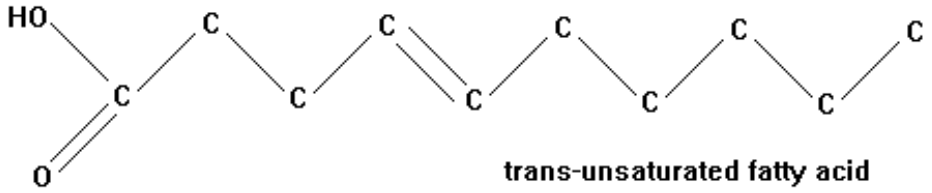
linoleic acid: *cis* configuration (*cis* isomer)

cis isomer predominates; trans is rare

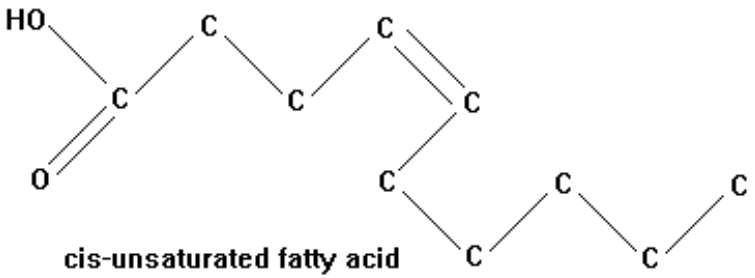
cis- vs. trans-fatty acids



saturated fatty acid



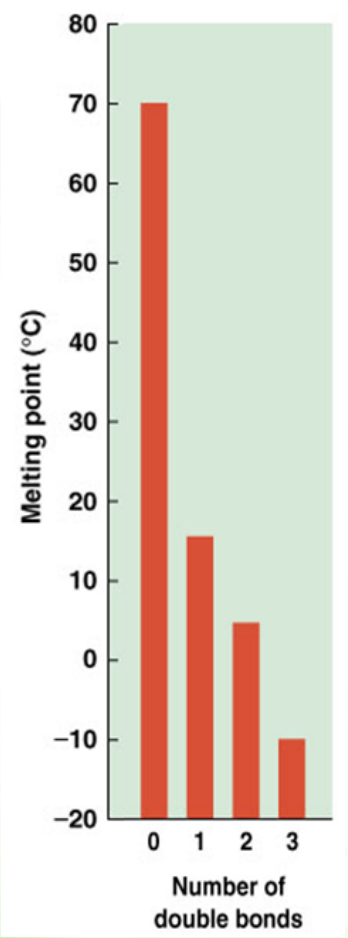
trans-unsaturated fatty acid

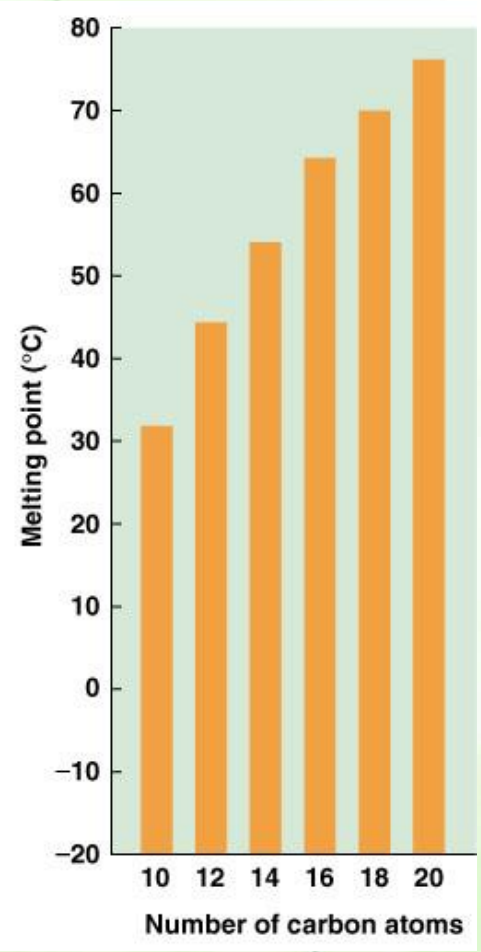


cis-unsaturated fatty acid

Properties of fatty acids

The properties of fatty acids (melting point and solubility) are dependent on chain length and degree of saturation





Properties of saturated fatty acids

Short chain F.A.	Medium-chain F.A.	Long chain F.A.
They are liquid in nature	Solids at room temperature	Solids at room temperature
Water-soluble	Water-soluble	Water-insoluble
Volatile at RT	Non-volatile at RT	Non-volatile
Acetic, butyric, caproic FA	Caprylic & capric F.A.	Palmitic and stearic F.A

Naming of fatty acids: Greek number prefix

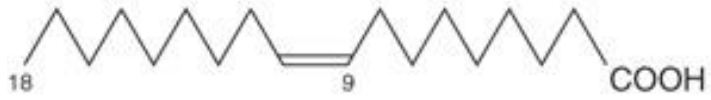
Number	prefix	Number	prefix	Number	prefix
1	Mono-	5	Penta-	9	Nona-
2	Di-	6	Hexa-	10	Deca-
3	Tri-	7	Hepta-	20	Eico-
4	Tetra-	8	Octa-		

Naming of a fatty acid

- Alkane to oic
  - Octadecane (octa and deca) is octadecanoic acid
    - One double bond = octadecenoic acid
    - Two double bonds = octadecadienoic acid
    - Three double bonds = octadecatrienoic acid
- Designation of carbons and bonds
  - 18:0 = a C18 fatty acid with no double bonds
    - stearic acid (18:0); palmitic acid (16:0)
  - 18:2 = two double bonds (linoleic acid)
- Designation of location of bonds
  - Δ^n: The position of a double bond
    - cis-Δ^9 :a cis double bond between C 9 and 10
    - trans-Δ^2:a trans double bond between C 2 and 3

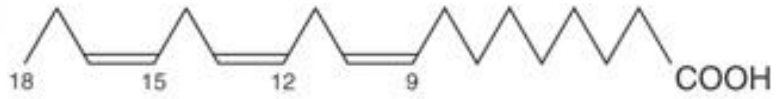
Naming of a fatty acid

Palmitoleic acid (ω7, 16:1, Δ^{9})

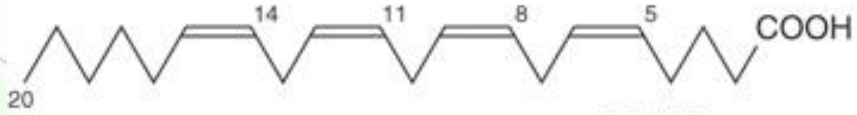


Oleic acid (ω9, 18:1, Δ^{9})

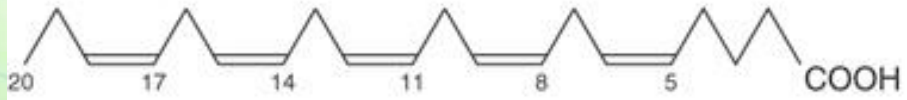
*Linoleic acid (ω6, 18:2, $\Delta^{9,12}$)



*α-Linolenic acid (ω3, 18:3, $\Delta^{9,12,15}$)



*Arachidonic acid (ω6, 20:4, $\Delta^{5,8,11,14}$)



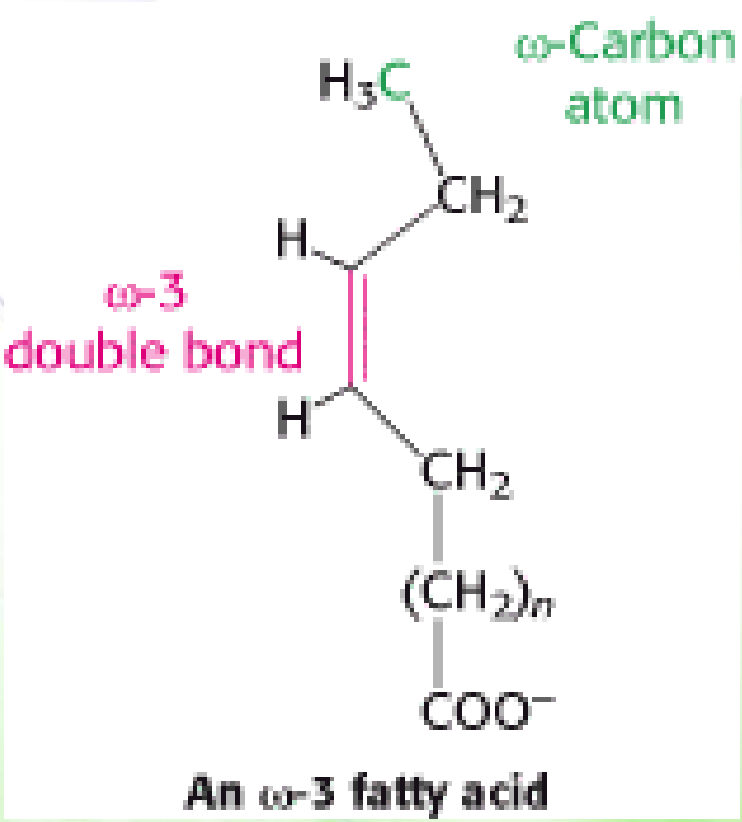
Eicosapentaenoic acid (ω3, 20:5, $\Delta^{5,8,11,14,17}$)

Naming of a fatty acid

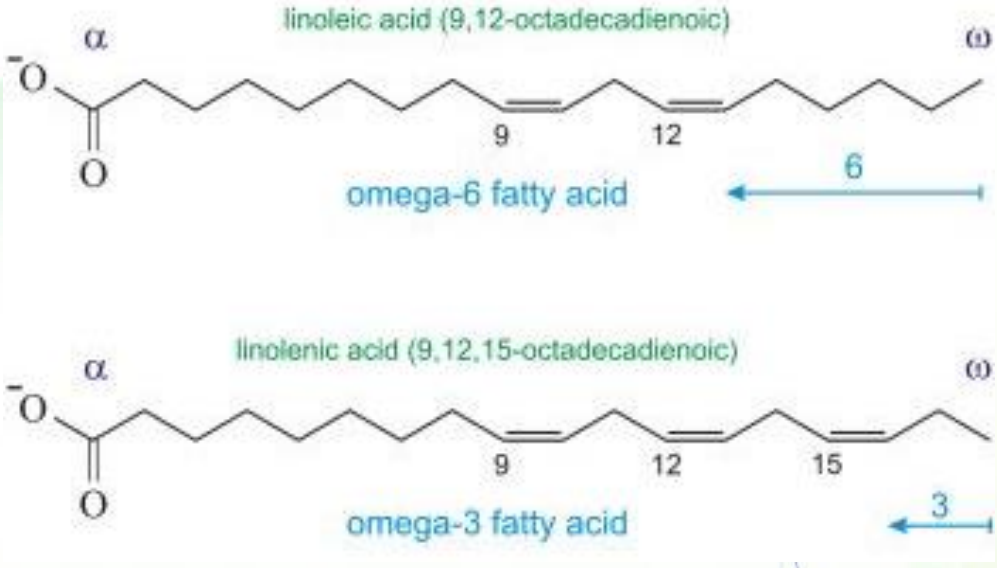
Number of carbons	Number of double bonds	Common name	Systematic name	Formula
14	0	Myristate	n-Tetradecanoate	$CH_3(CH_2)_{12}COO^-$
16	0	Palmitate	n-Hexadecanoate	$CH_3(CH_2)_{14}COO^-$
18	0	Stearate	n-Octadecanoate	$CH_3(CH2)_{16}COO^-$
18	1	Oleate	cis-Δ^9-Octadecenoate	$CH_3(CH_2)_7CH=CH(CH_2)_7COO^-$
18	2	Linoleate	cis,cis-Δ^9,Δ^{12}-Octadecadienoate	$CH_3(CH_2)_2(CH=CHCH_2)_2(CH_2)_6COO^-$
18	3	Linolenate	all-cis-$\Delta^9,\Delta^{12},\Delta^{15}$-Octadecatrienoate	$CH_3CH_2(CH=CHCH_2)_3(CH_2)_6COO^-$
20	4	Arachidonate	all-cis-$\Delta^5,\Delta^8,\Delta^{11},\Delta^{14}$-Eicosatetraenoate	$CH_3(CH_2)_4(CH=CHCH_2)_4(CH_2)_2COO^-$

Another way of naming (Omega)

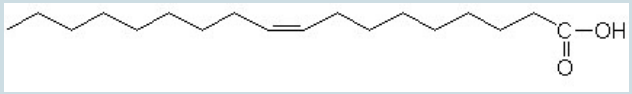
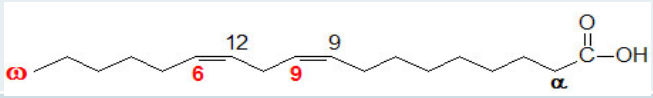
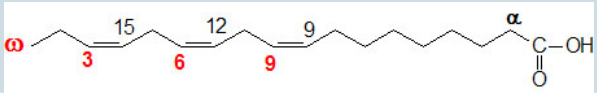
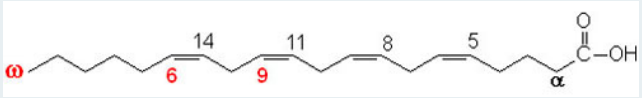
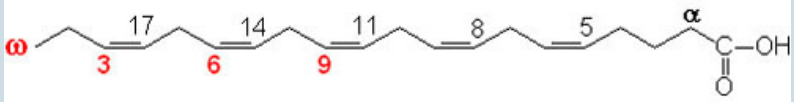
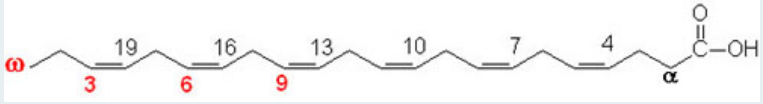
- (ω)-C: distal methyl C as #1



An ω-3 fatty acid



- **Linoleic acid: precursor of arachidonates**
- **Linolenic acid: precursor of EPA and DHA**

Numerical Symbol	Common Name and Structure	Comments
$18:1^{\Delta 9}$	Oleic acid 	Omega-9 monounsaturated
$18:2^{\Delta 9,12}$	Linoleic acid 	Omega-6 polyunsaturated
$18:3^{\Delta 9,12,15}$	α-Linolenic acid (ALA) 	Omega-3 polyunsaturated
$20:4^{\Delta 5,8,11,14}$	Arachidonic acid 	Omega-6 polyunsaturated
$20:5^{\Delta 5,8,11,14,17}$	Eicosapentaenoic acid (EPA) 	Omega-3 polyunsaturated (fish oils)
$22:6^{\Delta 4,7,10,13,16,19}$	Docosahexaenoic acid (DHA) 	Omega-3 polyunsaturated (fish oils)

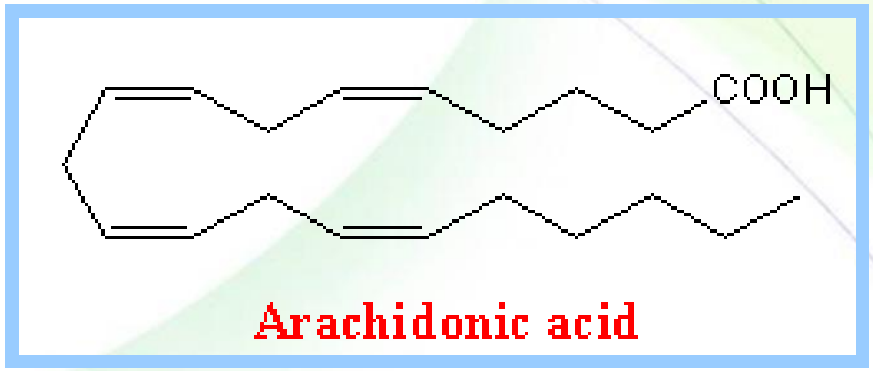
Omega fatty acids

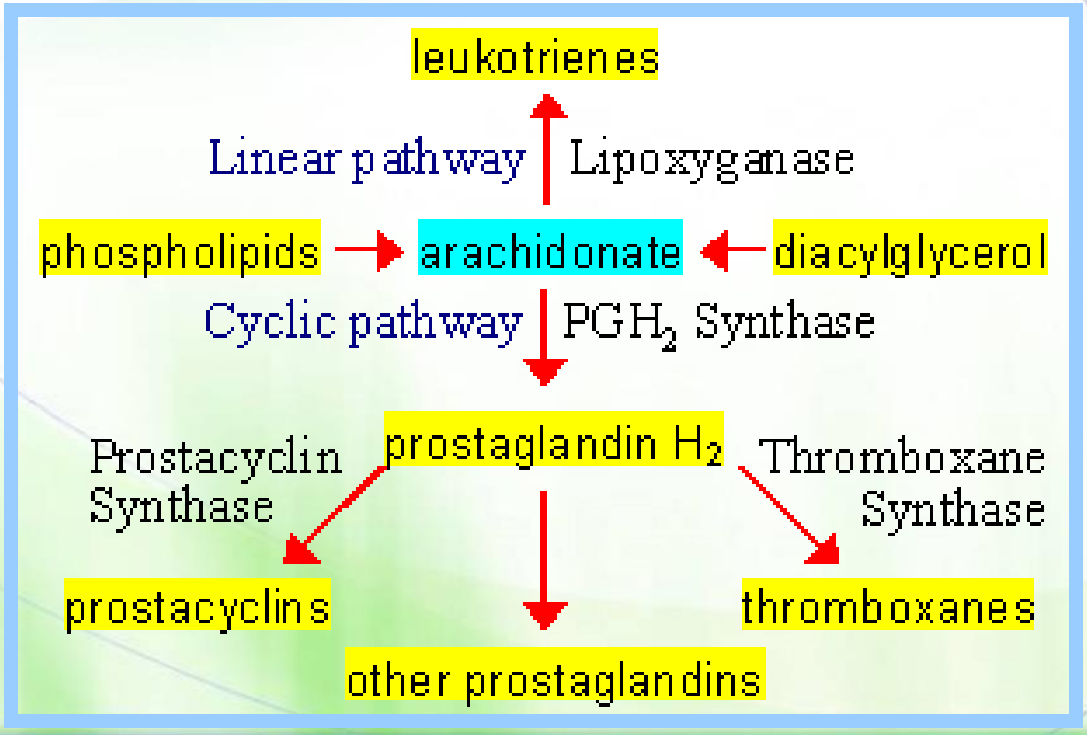
- Omega-3 fatty acids
  - α-linolenic acid → eicosapentaenoic acid (EPA) → docosahexaenoic acid (DHA)
    - They reduce inflammatory reactions by:
      - Reducing conversion of arachidonic acid into eicosanoids
      - Promoting synthesis of anti-inflammatory molecules
- Omega-6 fatty acids:
  - Arachidonic acid
    - stimulates platelet and leukocyte activation,
    - signals pain,
    - Induces bronchoconstriction,
    - regulates gastric secretion
- Omega-9 fatty acids
  - Oleic acid
    - Reduces cholesterol in the circulation

Derived fatty acids: Eicosanoids

Arachidonate

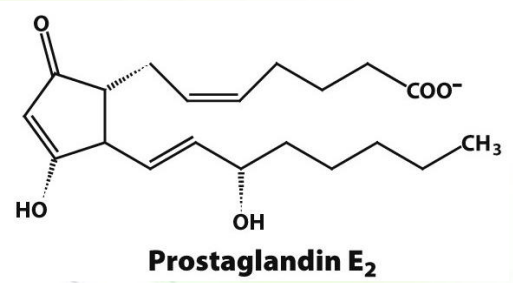
- all *cis*-$\Delta^5,\Delta^8,\Delta^{11},\Delta^{14}$-eicosatetraenoate, $CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COO^-$



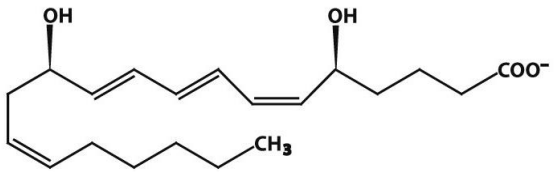


Eicosanoids and their functions

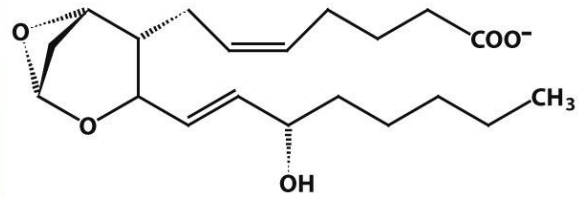
- Prostaglandins
  - Inhibition of platelet aggregation
    - Blood clotting
- Leukotrienes
  - Constriction of smooth muscles
    - Asthma
- Thromboxanes
  - Constriction of smooth muscles
  - Platelet aggregation
- Prostacyclins
  - An inhibitor of platelet aggregation
  - A vasodilator



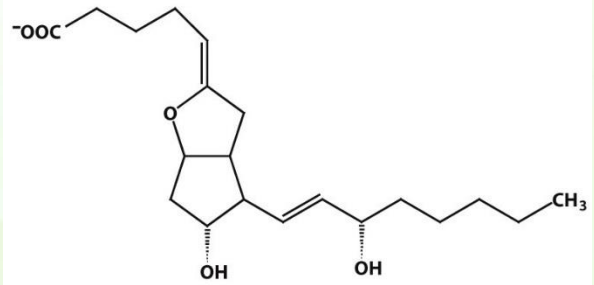
Prostaglandin E_2



Leukotriene B_4

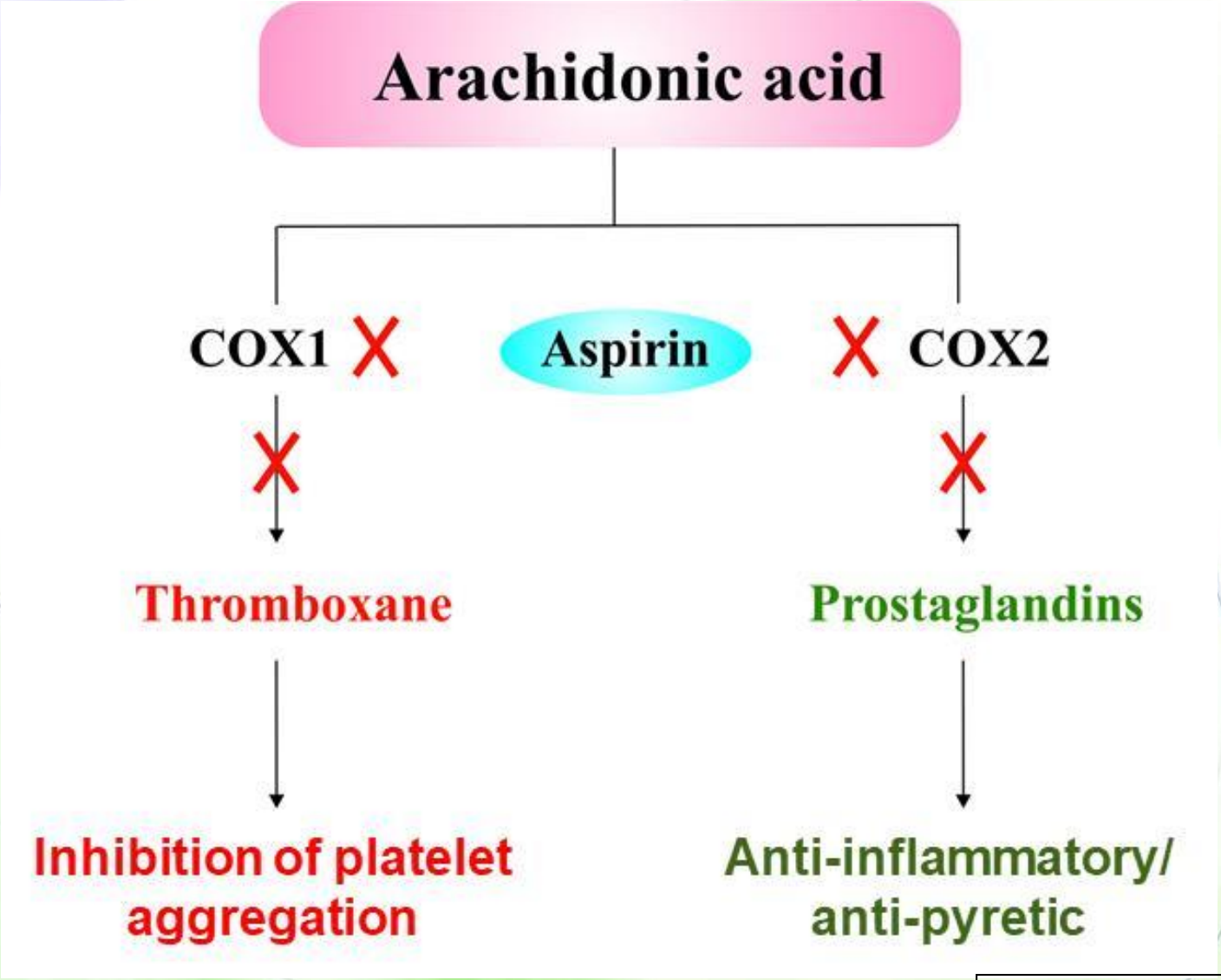


Thromboxane A_2 (TXA_2)



Prostacyclin (PGI_2)

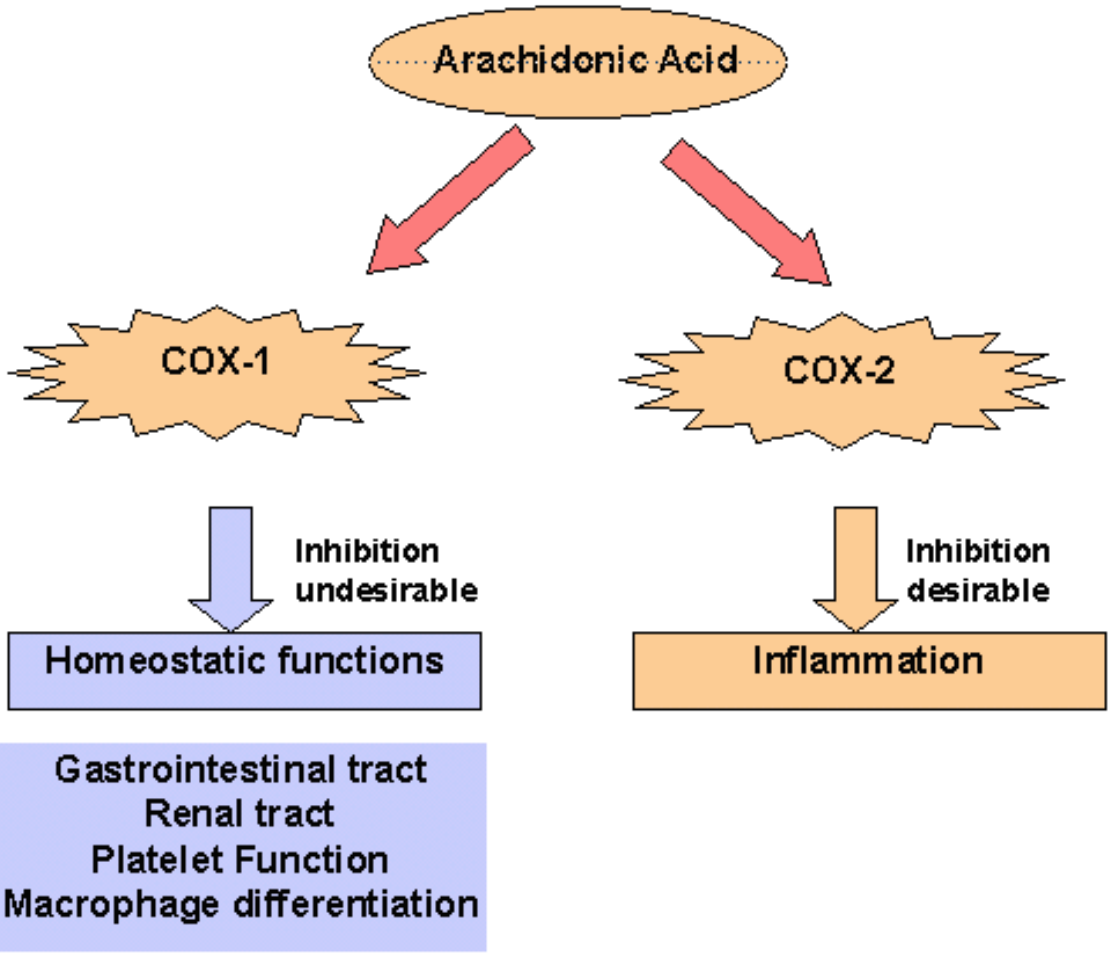
Aspirin and eicosanoids



COX: Cyclooxygenase

Targets of Aspirin

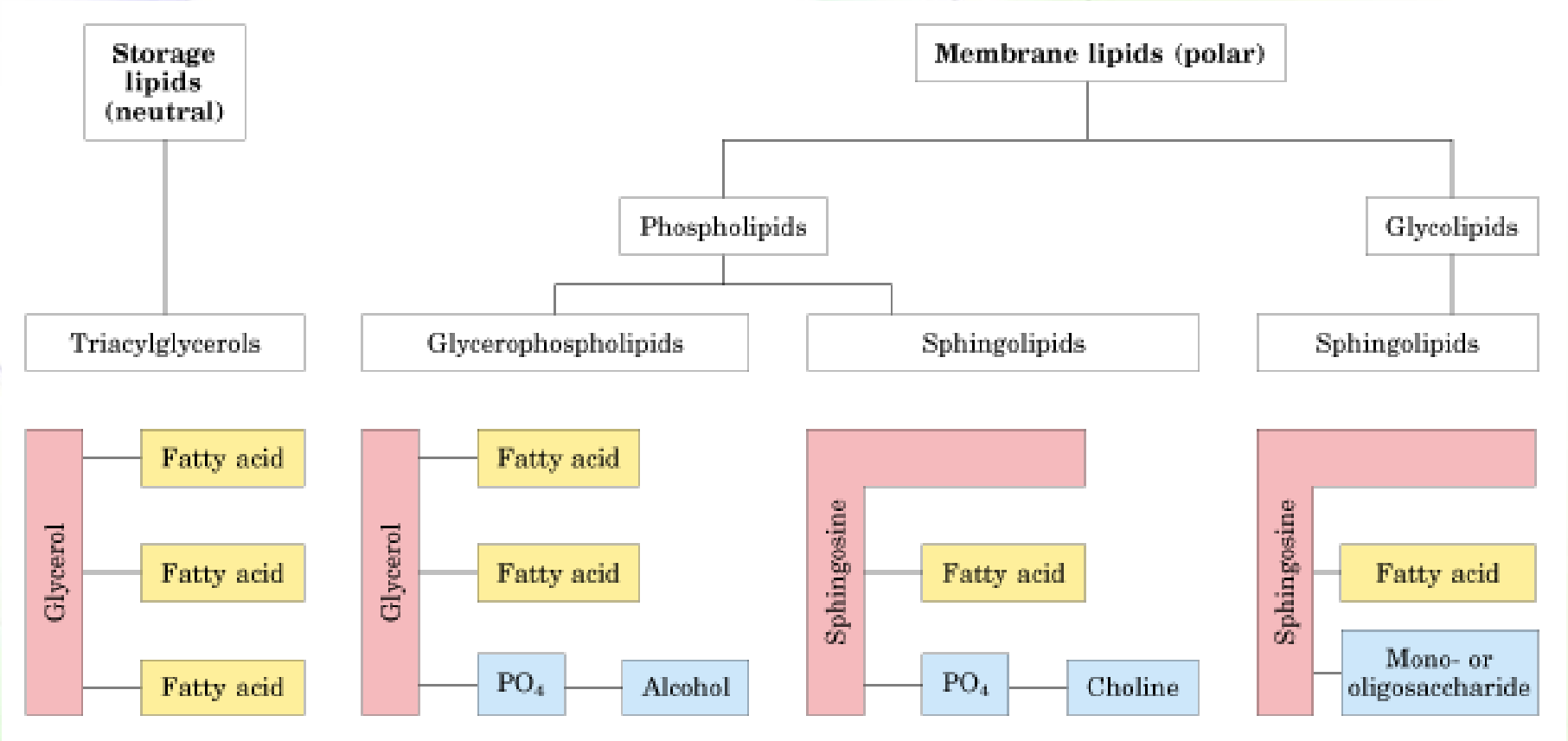
- Cyclooxygenase is present in three forms in cells, COX-1, COX-2, and COX-3.
- Aspirin targets both, but COX-2 should only be the target.



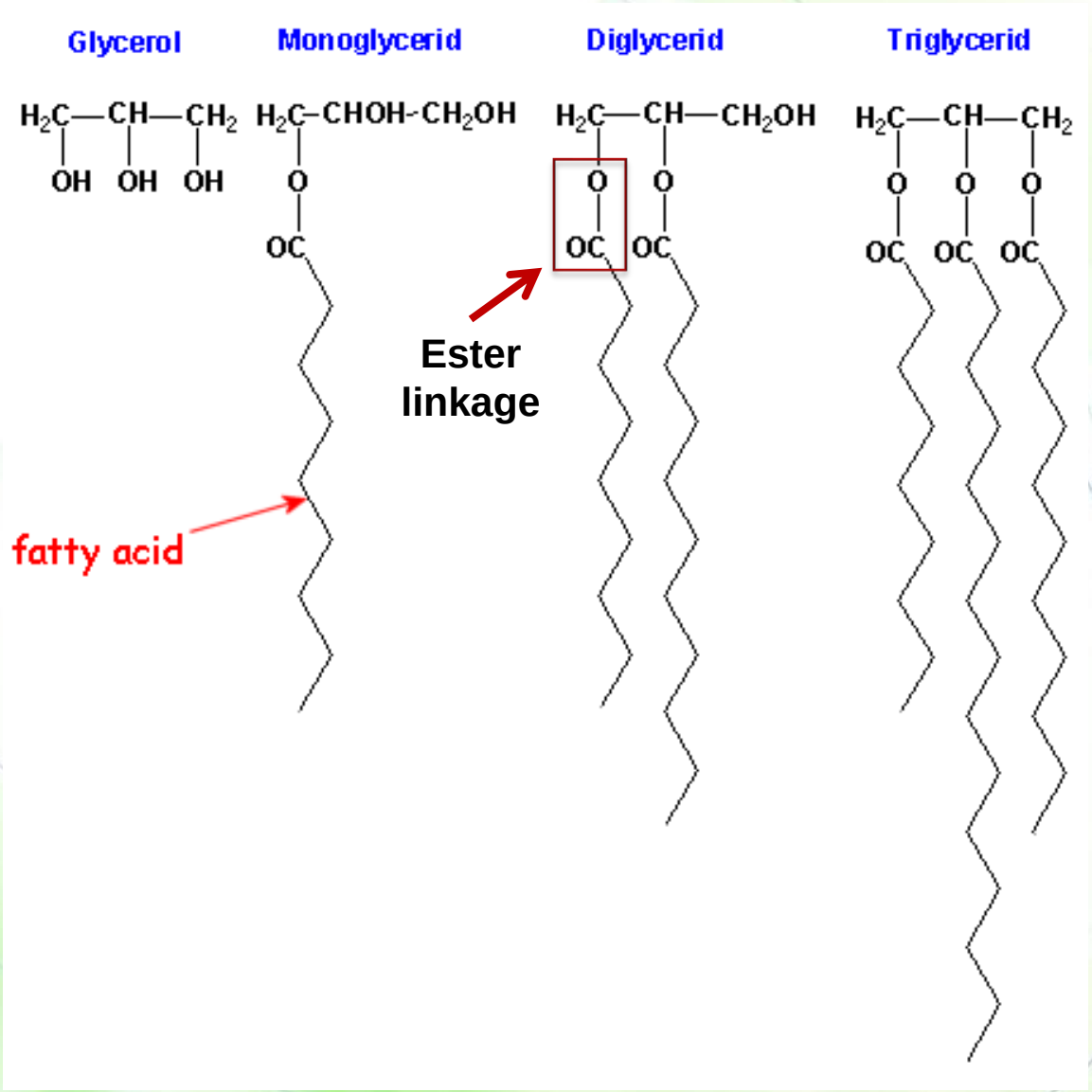
Celebrex

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

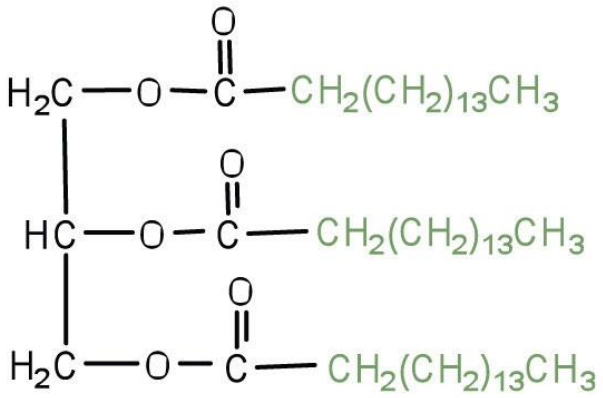
Complex lipids



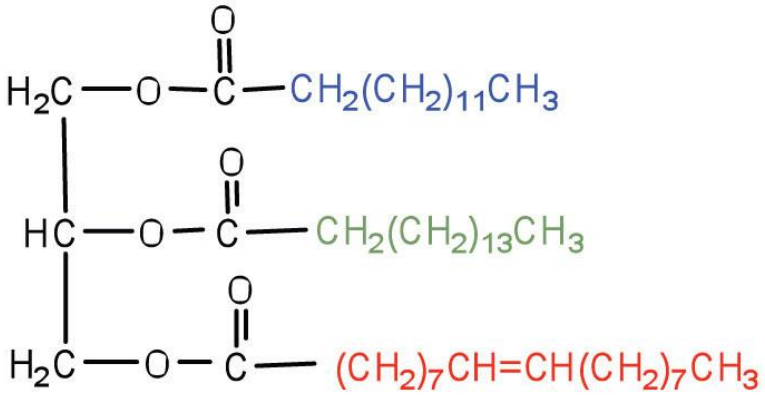
Triglycerides or Triacylglycerols (TAGs)



Types of TAGs



Tristearin
a simple triglyceride

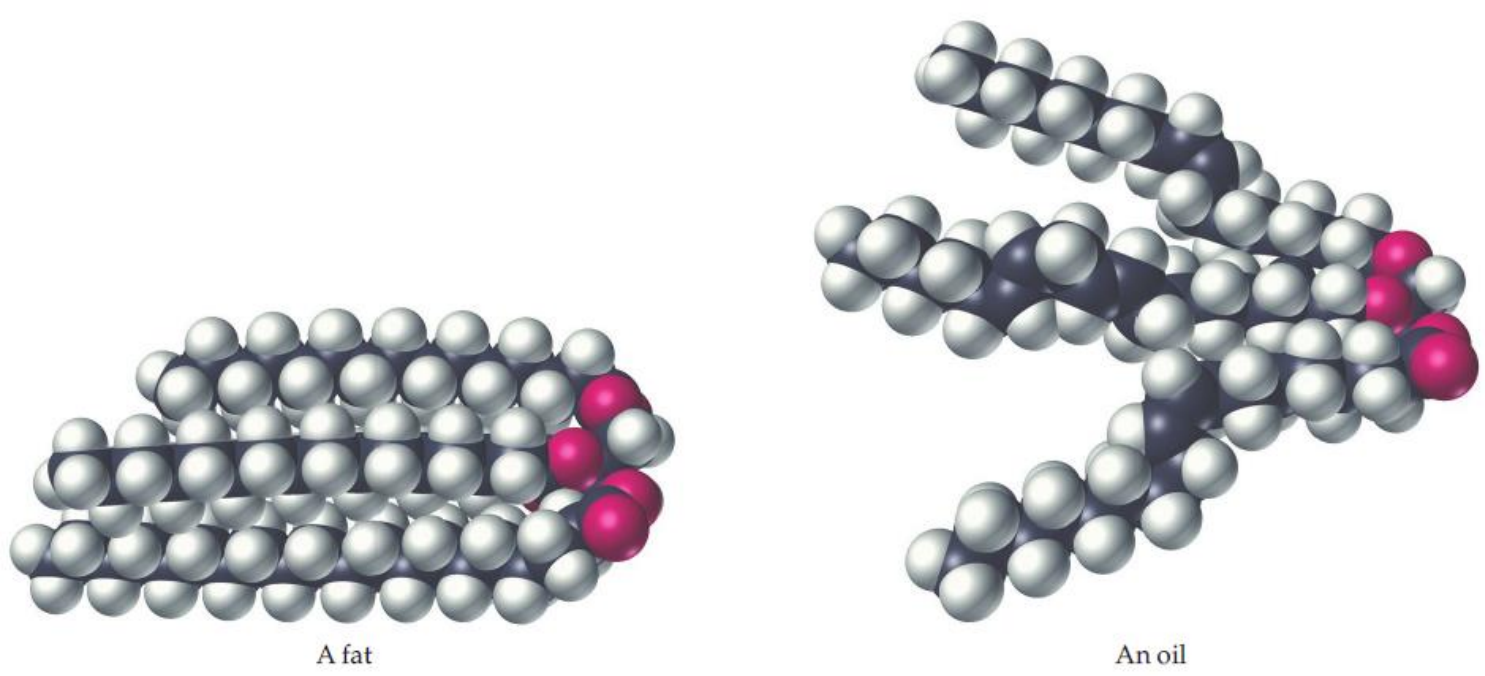


a mixed triglyceride

How soluble will a triglyceride be if fatty acids are unsaturated?

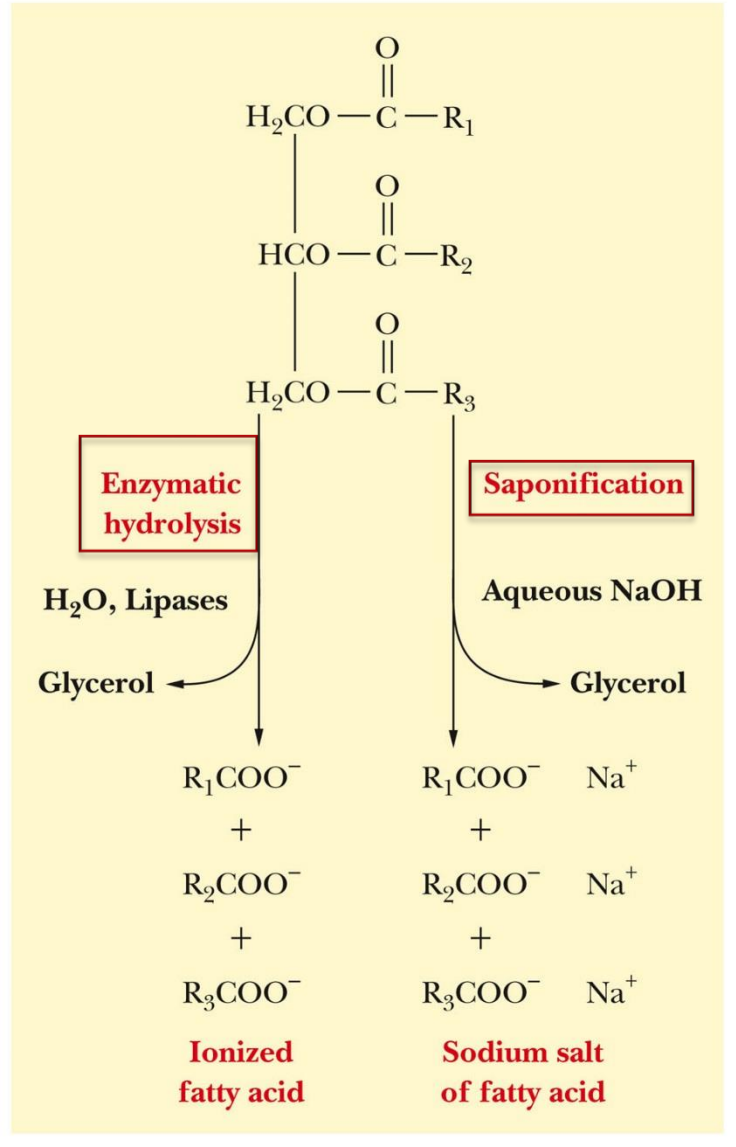
Solid vs. liquid fats

- Vegetable oils consist almost entirely of unsaturated fatty acids, whereas animal fats contain a much larger percentage of saturated fatty acids.
  - This is the primary reason for the different melting points of fats and oils



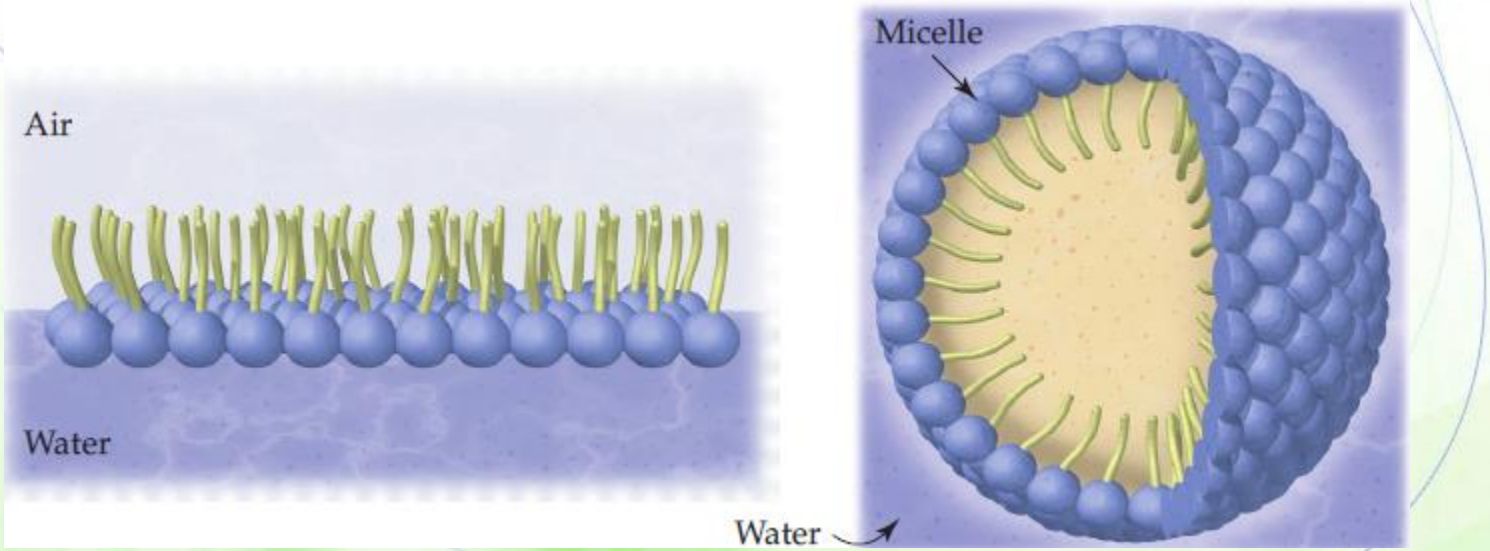
Reactions: Saponification

- Hydrolysis: steam, acid, enzyme (e.g., lipase of pancreas)
- Saponification: Alkaline hydrolysis produces salts of fatty acids (soaps). Soaps cause emulsification of oily material.



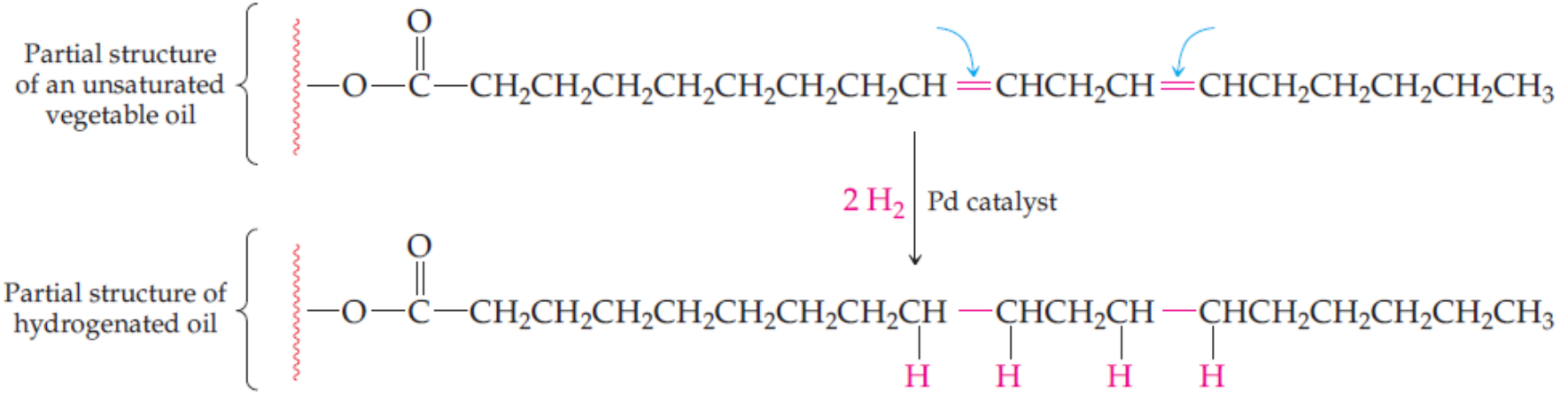
How does soap work?

- When mixed with water, the hydrophobic hydrocarbon tails cluster together to create a nonpolar microenvironment and the hydrophilic ionic heads interact with water.
- The resulting spherical clusters are called **micelles.**
- Grease and dirt are trapped inside micelles and the complex can be rinsed away.



Reactions : Hydrogenation

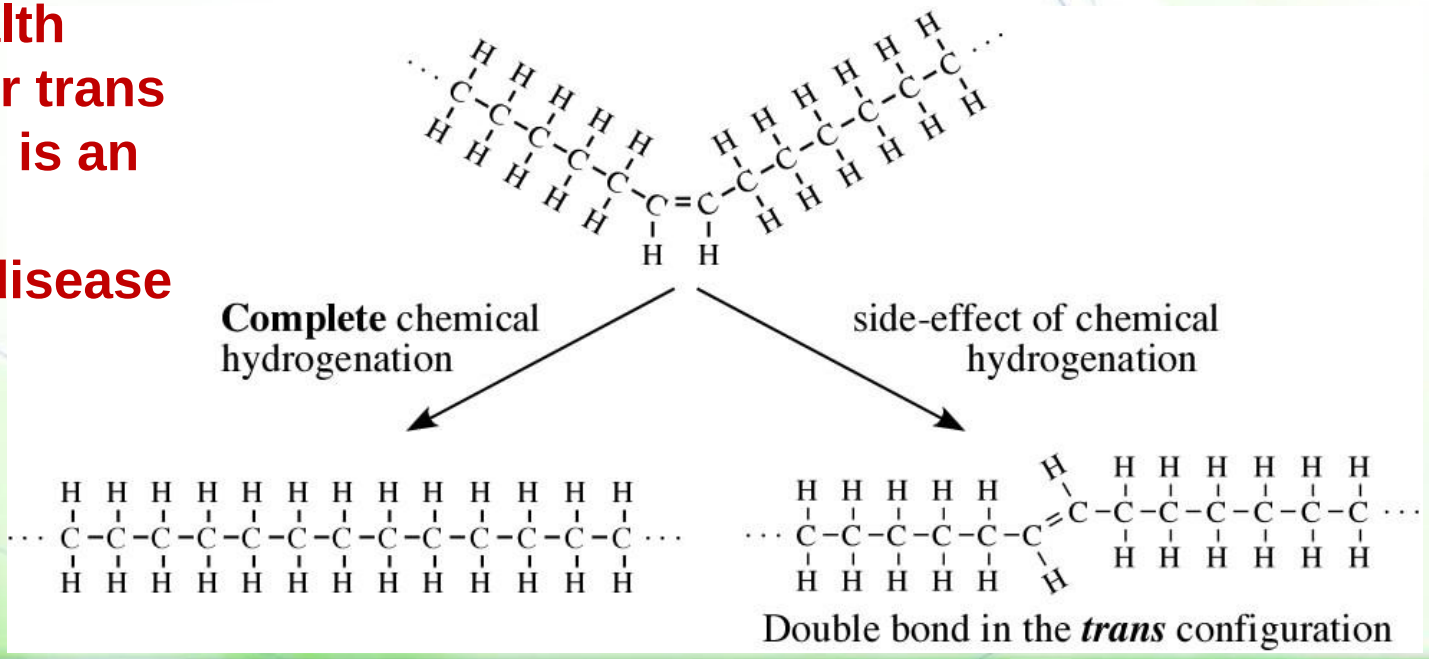
- The carbon-carbon double bonds in vegetable oils can be hydrogenated to yield saturated fats in the same way that any alkene can react with hydrogen to yield an alkane.



Trans fat

- Although the animal fat is unhealthy, it has better cooking properties and better taste.
- Therefore, chemists invented a method of converting unsaturated oil into solid form by partially hydrogenating it.
- Partial hydrogenation converts some, but not all, double bonds into single bonds generating (trans fats).

The primary health risk identified for trans fat consumption is an elevated risk of coronary heart disease (CHD).



Example: margarine

- In margarine, only about two-thirds of the double bonds present in the starting vegetable oil are hydrogenated, so that the margarine remains soft in the refrigerator and melts on warm toast.

Nutrition Facts

Serv Size 1 Tbsp (14g)
Servings: About 24
Calories 80
Calories from Fat 80

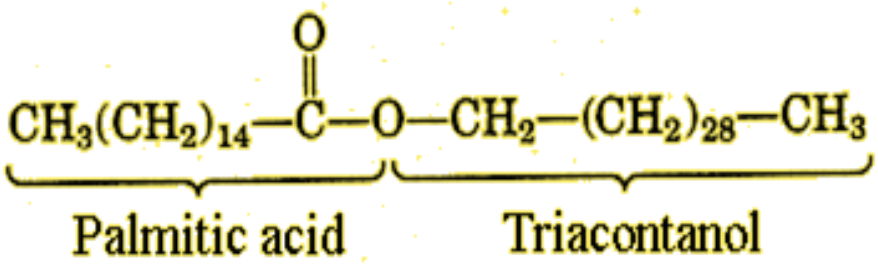
*Percent Daily Values (DV) are based on a 2,000 calorie diet.

Amount/Serving	% DV*	Amount/Serving	% DV*
Total Fat 8g	**12%**	**Cholesterol** 0mg	**0%**
Sat Fat 2.5g	**13%**	**Sodium** 85mg	**4%**
Trans Fat 0g		**Total Carb** 0g	**0%**
Polyunsat Fat 3g		Sugars 0g	
Monounsat Fat 2.5g		**Protein** 0g	

Vitamin A 15% • Vitamin D 15%
Vitamin B6 35% • Vitamin B12 20% • Vitamin E 15%
Not a significant source of dietary fiber, Vitamin C, Calcium and Iron

INGREDIENTS: Natural Oil Blend (palm fruit, soybean, fish, canola and olive oils), water, plant sterols; contains less than 2% of salt, sorbitan esters of fatty acids, monoglycerides of vegetable fatty acids, natural and artificial flavors, TBHQ (to preserve freshness), potassium sorbate, lactic acid, soy lecithin, vitamin B12, vitamin E acetate,vitamin B6, beta carotene (color), vitamin A palmitate, calcium disodium EDTA, Vitamin D3.

Waxes



- Solid simple lipids containing a monohydric alcohol (C16 ~ C30, higher molecular weight than glycerol) esterified to long-chain fatty acids (C14 ~ C36). Examples: palmitoyl alcohol
- Insoluble in water & Negative to acrolein test that tests for the presence of glycerin or fats
- Are not easily hydrolyzed (fats) & are indigestible by lipases
- Are very resistant to rancidity (oxidation or hydrolysis of fats and oils)
- Are of no nutritional value
- Coatings that prevent loss of water by leaves of plants, wetting of feathers and fast deterioration of fruits like apples

Type	Structural Formula	Source	Uses
Beeswax	$CH_3(CH_2)_{14}-C(=O)-O-(CH_2)_{29}CH_3$	Honeycomb	Candles, shoe polish, wax paper
Carnauba wax	$CH_3(CH_2)_{24}-C(=O)-O-(CH_2)_{29}CH_3$	Brazilian palm tree	Waxes for furniture, cars, floors, shoes
Jojoba wax	$CH_3(CH_2)_{18}-C(=O)-O-(CH_2)_{19}CH_3$	Jojoba	Candles, soaps, cosmetics