# Fats and Lipids (Ans570)

# Outlines

- Fats and Lipids – Structure, nomenclature
- Phospholipids, Sterols, and Lipid Derivatives
- Lipid Oxidation
- Roles of fat in food processing and dietary fat
- Lipid and fat analysis: GC method

- Lecture: Mon and Wed
- Discussion: Friday

# Fats and Lipids

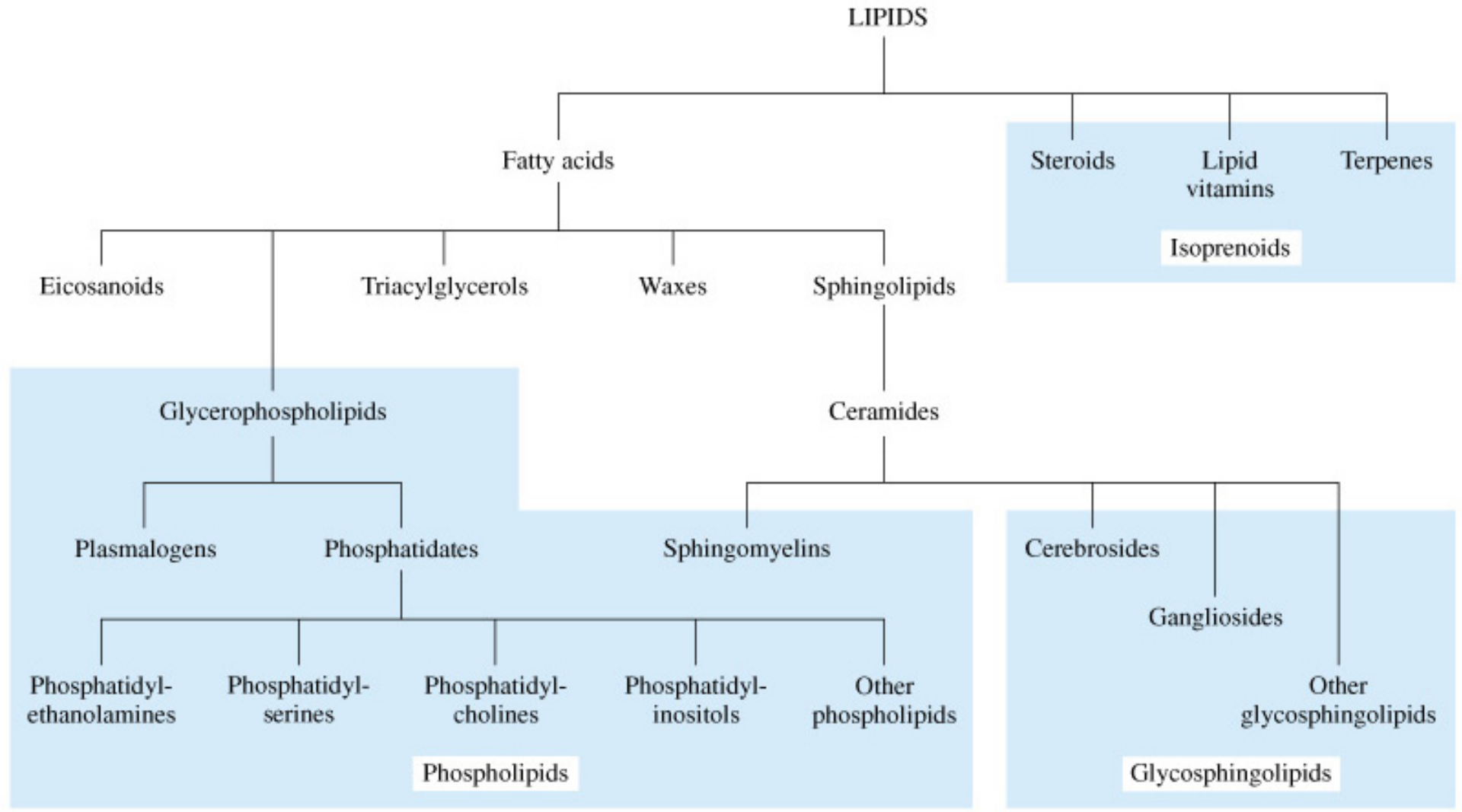
- Definition: water insoluble compounds
  - Most lipids are fatty acids or ester of fatty acid (TG)
  - They are soluble in non-polar solvents such as petroleum ether, benzene, chloroform

- Classification:
  - Neutral lipids (fatty acid esters of glycerol)
  - Phospholipids, sphingolipids, and glycolipids (complex lipids)
  - Sterols (cholesterol and cholesteryl esters)
  - Fatty acids and their eicosanoid derivatives

# Types of Lipids

- Ester of glycerol:
  - Acyl glycerol (glycerides): Mono-, di,-tri-
  - Phosphoglycerides (PA, PC, PE, PI, PG)
  - Glycoglycerides (MGDG, DGDG)
- Esters of other alcohols
  - Diols
  - Sugars: sugar ester
  - Long-chain alcohols: wax ester (C46-C54)
  - Sterols: sterol ester
- Amides of
  - Long-chain bases (sphingosine etc.): ceramide, cerebroside, ganglioside
  - Taurine
  - Serine

# Lipid Subclasses



# Function of major acyl-lipids

- Phospholipids – membrane components
- Triacylglycerols – storage fats and oils
- Waxes – moisture barrier
- Eicosanoids – signaling molecules (prostaglandin)
- Sphingomyelins – membrane component (impt. 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, limonene, terpenene, myrcene, saninene, phelandrene etc.

# Lipid Molecule

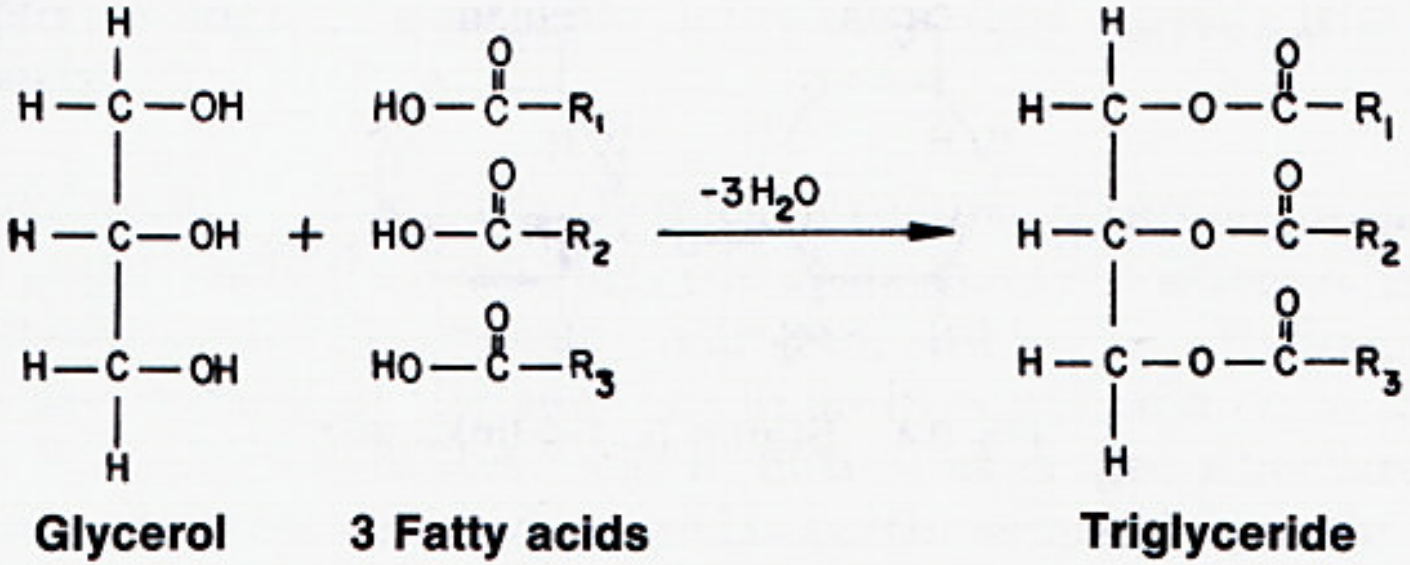
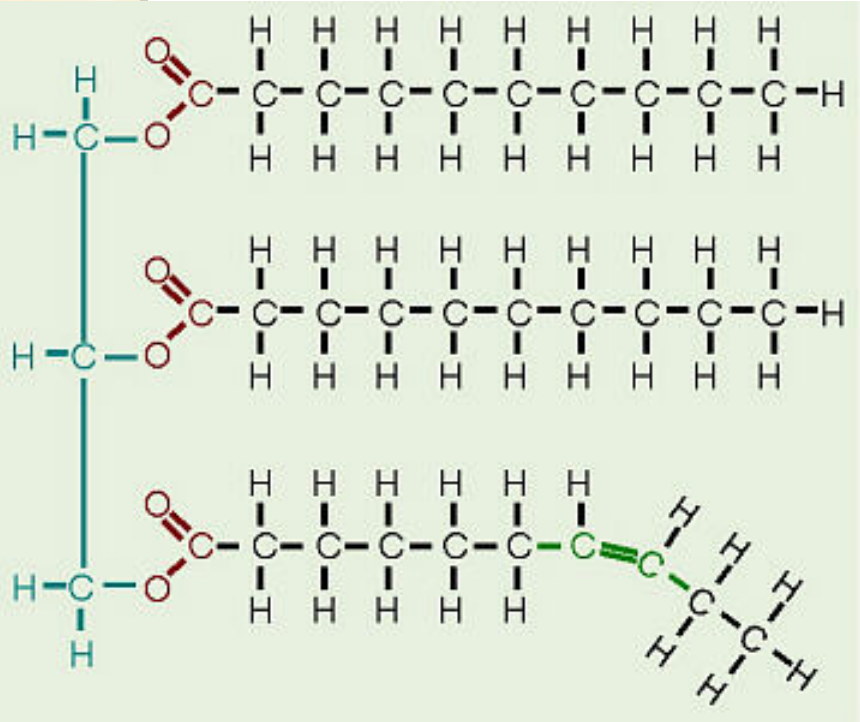


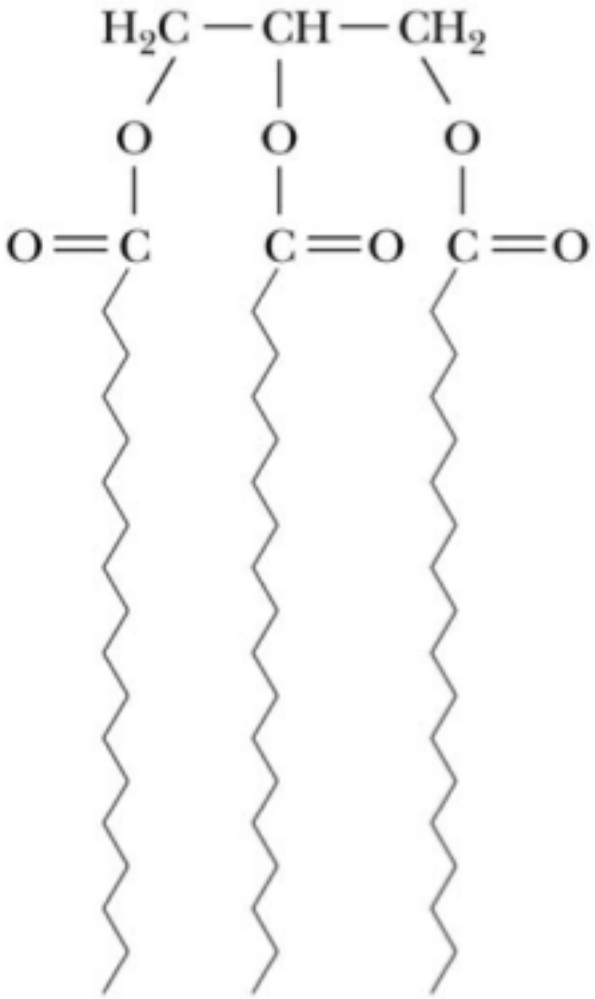

Fig. 2.6. Lipids.

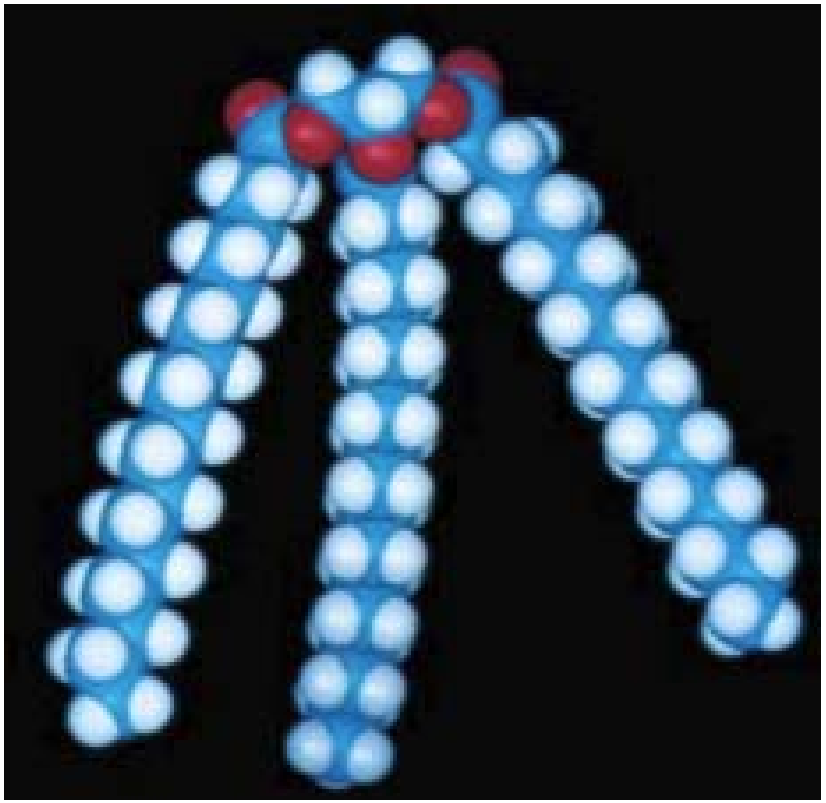
# Structure of Triglycerides



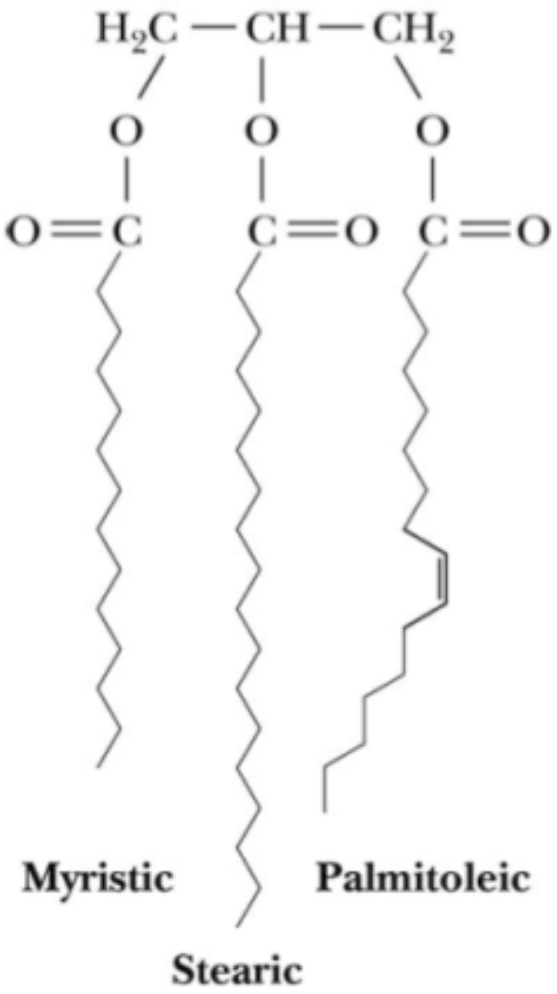
- Triglyceride is a neutral lipid, a glycerol ester of fatty acids.
- Mono- and diglycerols
- Symmetrical and unsymmetrical triglycerols

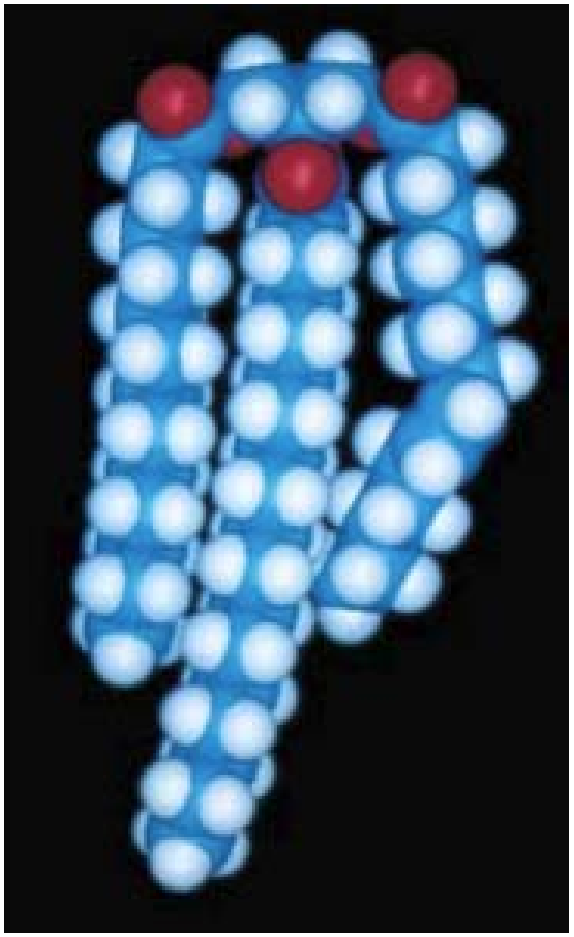
# Tristearin (a simple triacylglycerol).



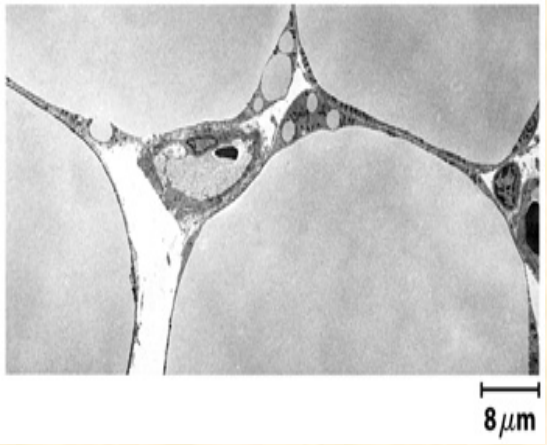



# A mixed triacylglycerol.



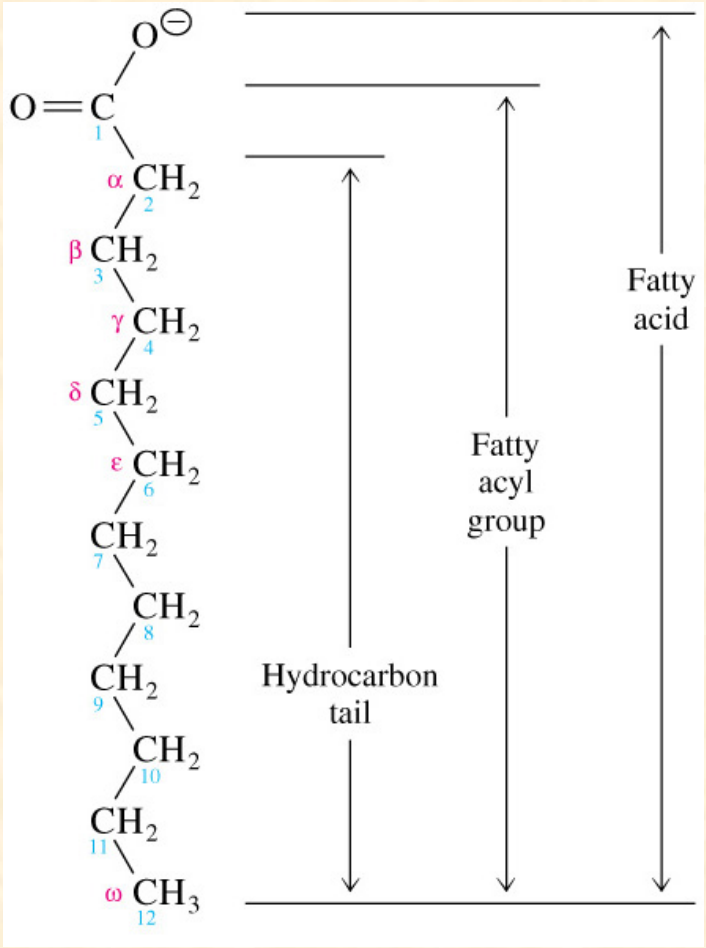
# Fatty Acids




- The fundamental building blocks of lipids
- Consist of long chains of alkyl ($CH_2$) groups
- The major constituent of body fat
- Most fatty acids (>90%) in the body are esterified in triglyceride, phospholipid, sphingolipid, glycolipid and cholesteryl ester
- Small amounts of free (non-esterified) fatty acids can dissolve in cell water, interstitial fluid and the blood compartment

# Fatty acids

- Amphipathic molecule
- Polar carboxyl group
- Non-polar hydrocarbon tail
- Diverse structures (>100 different types)
- Differ in chain length
- Differ in degree of unsaturation
- Differ in the position of double bonds
- Can contain oxygenated groups



# Classification of Fatty Acids I

- According to chain length:
  - Short chain FA: 2-4 carbon atoms
  - Medium chain FA: 6 –10 carbon atoms
  - Long chain FA: 12 – 26 carbon atoms

- Essential fatty acids vs those that can be biosynthesized in the body:
  - Linoleic and linolenic are two examples of essential fatty acid

# Classification of Fatty Acids 2

- **Saturated**: the SFA's of a lipid have no double bonds between carbons in chain
- **Polyunsaturated**: more than one double bond in the chain
- Most common polyunsaturated fats contain the polyunsaturated fatty acids (PUFAs) oleic, linoleic and linolenic acid
- Unsaturated fats have lower melting points
- Stearic (SFA) melts at 70°C, oleic (PUFA) at 26°C

# Names of saturated fatty acids

| | Trivial name | IUPAC name | melting point (C°) |
|---|---|---|---|
| 4:0 | butyric | butanoic | -5.3 |
| 6:0 | caproic | hexanoic | -3.2 |
| 8:0 | caprylic | heptanoic | 16.5 |
| 10:0 | capric | decanoic | 32 |
| 12:0 | lauric | dodeconoic | 44 |
| 14:0 | myristic | tetradeconoic | 52 |
| 16:0 | palmitic | hexadeconoic | 63 |
| 18:0 | stearic | octadeconoaic | 70 |
| 20:0 | arachidic | eicosanoaic | 75 |
| 22:0 | behenic | docosanoaic | 81 |
| 24:0 | lignoceric | tetracosanaic | 84 |

*IUPAC: International Union of Pure and Applied Chemistry

# Common unsaturated fatty acids

| | common name | IUPAC name | melting point ($C^o$) |
|---|---|---|---|
| 16:0 | palmitate | hexadeconoate | 63 |
| 16:1 $\Delta^9$ | palmitoleate | cis-$\Delta^9$-hexadeconoate | -0.5 |
| 18:0 | stearate | octadeconoate | 70 |
| 18:1 $\Delta^9$ | oleate | cis-$\Delta^9$- 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 |

# Unsaturated fatty acids

- Trienoic acids (3 double bonds)
  - 18:3;6,9,12  w6 : g-linolenic acid (all *cis*-6,9,12-octadecatrienoic acid)
  - 18:3; 9,12,15 w3 : a-linolenic acid (all-*cis*-9,12,15-octadecatrienoic acid)
- Tetraenoic acids (4 double bonds)
  - 20:4; 5,8,11,14 w6: arachidonic acid (all-*cis*-5,8,11,14-eicosatetraenoic acid)

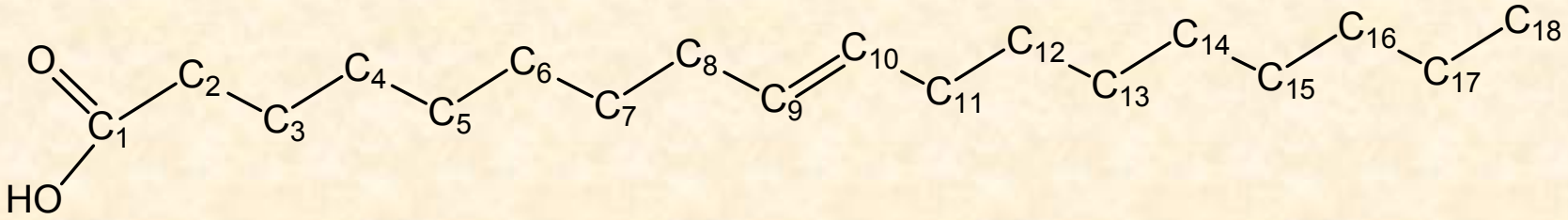
# Unsaturated fatty acids

- Pentaenoic acid (5 double bonds)
  - 20:5; 5,8,11,14,17 ω3: timnodonic acid or EPA (all-*cis*-5,8,11,14,17-eicosapentaenoic acid)
- Hexaenoic acid (6 double bonds)
  - 22:6; 4,7,10,13,16,19 ω3: cervonic acid or DHA (all-cis-4,7,10,13,16,19-docosahexaenoic acid)

# 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 $\Delta^9$ = 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)

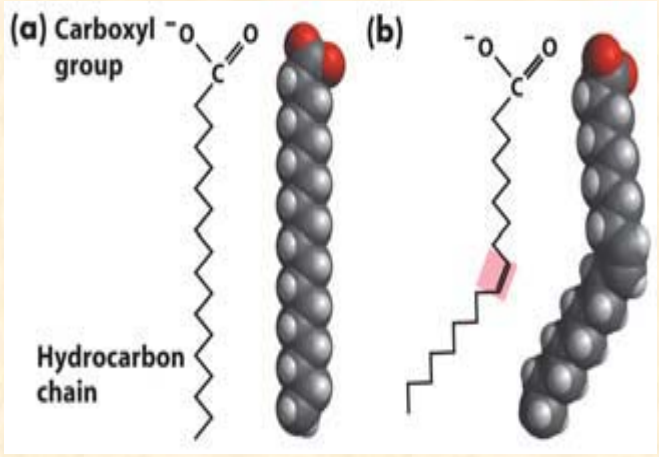


# Fatty acid nomenclature

❖Most natural fatty acids have an even number of backbone carbons (from synthesis in 2-carbon units)

❖ Nomenclature: **Carbon chain length: # of double bonds (position)**

- ❖**20:2(Δ9, 12)** is a FA with 20 carbons and 2 double bonds, between C9-10, C12-13
- ❖ With 2 or more unsaturated double bonds: FAs are rarely conjugated,
- ❖ Double bonds are usually at 3carbon intervals, starting at C9, *e.g. α-linolenic acid is 18:3 (Δ9, 12, 15)*
- ❖ Double bonds are (almost) always in the ***cis*** configuration




**18:0 (Stearic Acid) 18:1(Δ9) (Oleic Acid)**

# Stereospecific numbering

- Carbon 2 of triglycerides is frequently asymmetric since C-1 and C-3 may be substituted with different acyl groups
- By convention we normally draw the hydroxyl group at C-2 to the left and use the designation of sn2 for that particular substituent
- C-1 and C-3 of the glycerol molecule become sn1 and sn3 respectively

# Less common fatty acids

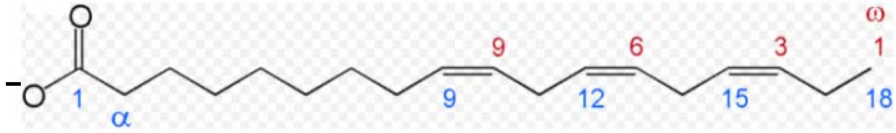
| | common name | Isomeric form | System name |
|---|---|---|---|
| 18:1 | eladic | trans | 9t-octadecenoic |
| 18:1 | petroselinic | cis | 6-octadecenoic |
| 18:1 | *cis*-vaccinic | cis | 11-octadecenoic |
| 18:1 | *trans*-vaccenic | trans | 11t-octadecenoic |
| 20:1 | godoleic | cis | 9-eicosenoic |
| 20:1 | gondoic | cis | 11-eicosenoic |
| 22:1 | - | cis | 5-docosenoic |
| 22:1 | cetoleic | cis | 11-docosenoic |
| 22:1 | erucic | cis | 13-docosenoic |
| 24:1 | nervonic | cis | 15-tetracosenoic |

# Omega-3 fatty acids

Canola oil contains a lot of omega-3 fatty acid; about 10% of the fatty acids in canola oil are omega-3.

"Omega-3" means the first double bond is on the 3rd carbon from the end of the chain.

alpha linolenic acid




Alpha linolenic acid is very abundant in canola oil.

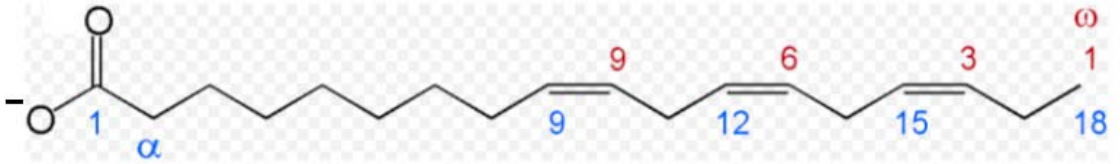
# The Omega (ω) Designation

- The health benefits of these essential fatty acids (EFAs) is in their ability to act as a competitive inhibitor in the production of arachidonic acid (20:4(Δ5,8,11,14), a precursor of the eicosanoids
- These eicosanoids are signaling molecules promote inflammation of the tissues in which they are located.
- The diet of early man was rich in these omega-3 fatty acids
- This is no longer the case, resulting in an increase in a number of diseases called the **diseases of civilization**

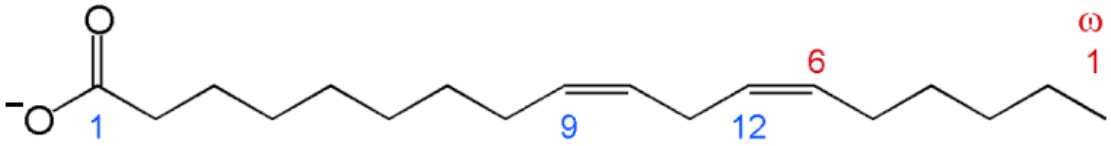
# Essential fatty acids

The human body can make most of the fatty acid types it needs. But you must have some omega-3 and omega-6 fatty acids in your diet.

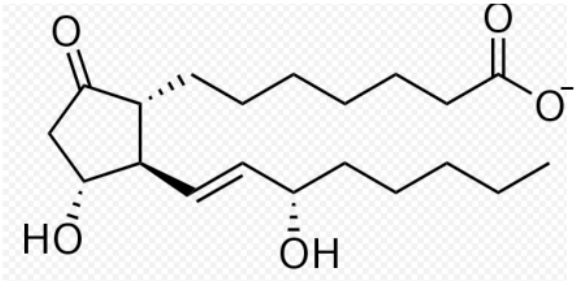
alpha linolenic acid is an example of an omega-3 FA




gamma linoleic acid is an example of an omega-6 FA




The omega-3 and omega-6 FAs are precursors for a number of important molecules.
For example, prostaglandins are hormones that are synthesized from omega-6 fatty acids.



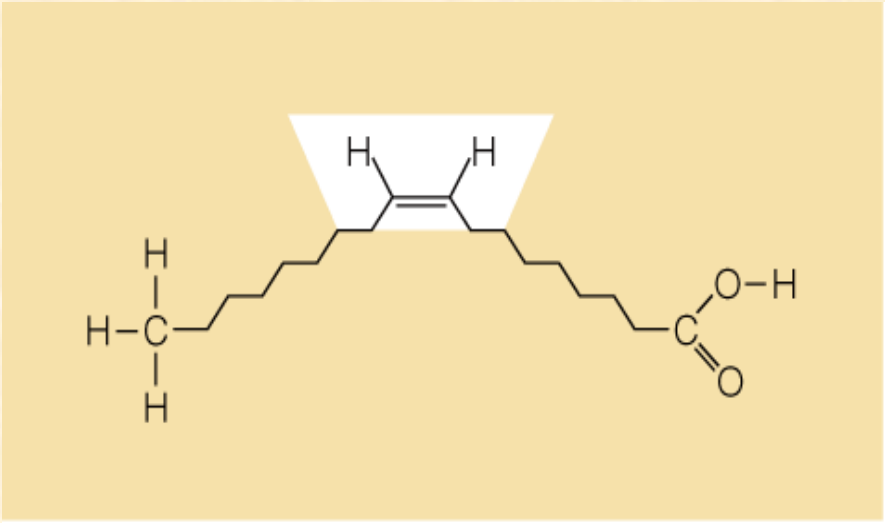

Prostaglandin E1

# Pathways of n-3 and n-6 Fatty Acid Synthesis

| n-6 acids | | n-3 acids |
|---|---|---|
| 18:2 (9,12)a | | 18:3 (9,12,15)e |
| ↓ | 6-desaturase | ↓ |
| 18:3 (6,9,12)b | | 18:4 (6,9,12,15)f |
| ↓ | elongase | ↓ |
| 20:3 (8,11,14)c | | 20:4 (8, 11,14,17) |
| ↓ | 5-desaturase | ↓ |
| 20:4 (5,8,11,14)d | | 20:5 (5,8,11,14,17)g |
| ↓ | elongase | ↓ |
| 22:4 (7,10,13,16) | | 22:5 (7,10,13,16)h |
| ↓ | 4-desaturase | ↓ |
| 22:5 (4,7,13,16) | | 22:6 (4,7,10,13,16,19)i |

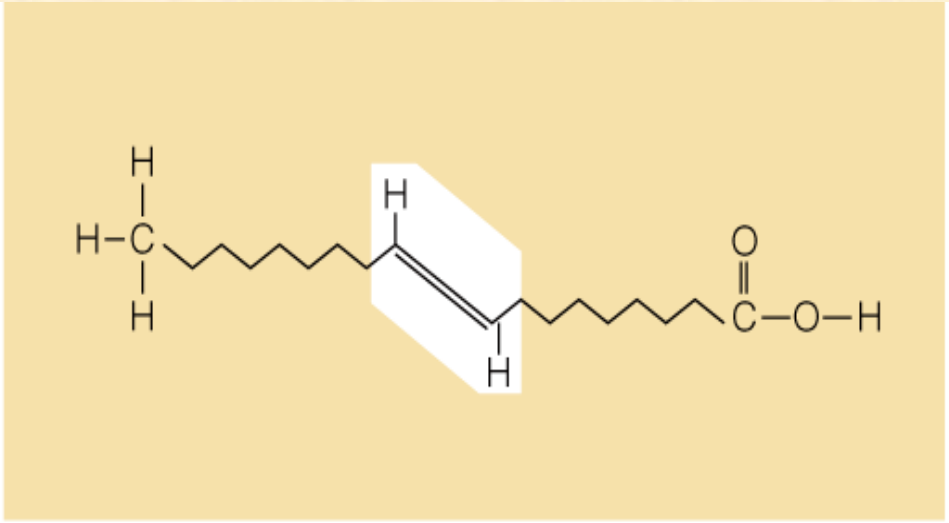
a: linoleic, b: $\gamma$-linoleic, c: dihomom-$\gamma$-linoleic, d: arachidonic, e: $\alpha$-linoleic, f: stearidonic, g: EPA, h: DPA, i: DHA

# *Cis* & *Trans*-FA




*cis*-fatty acid

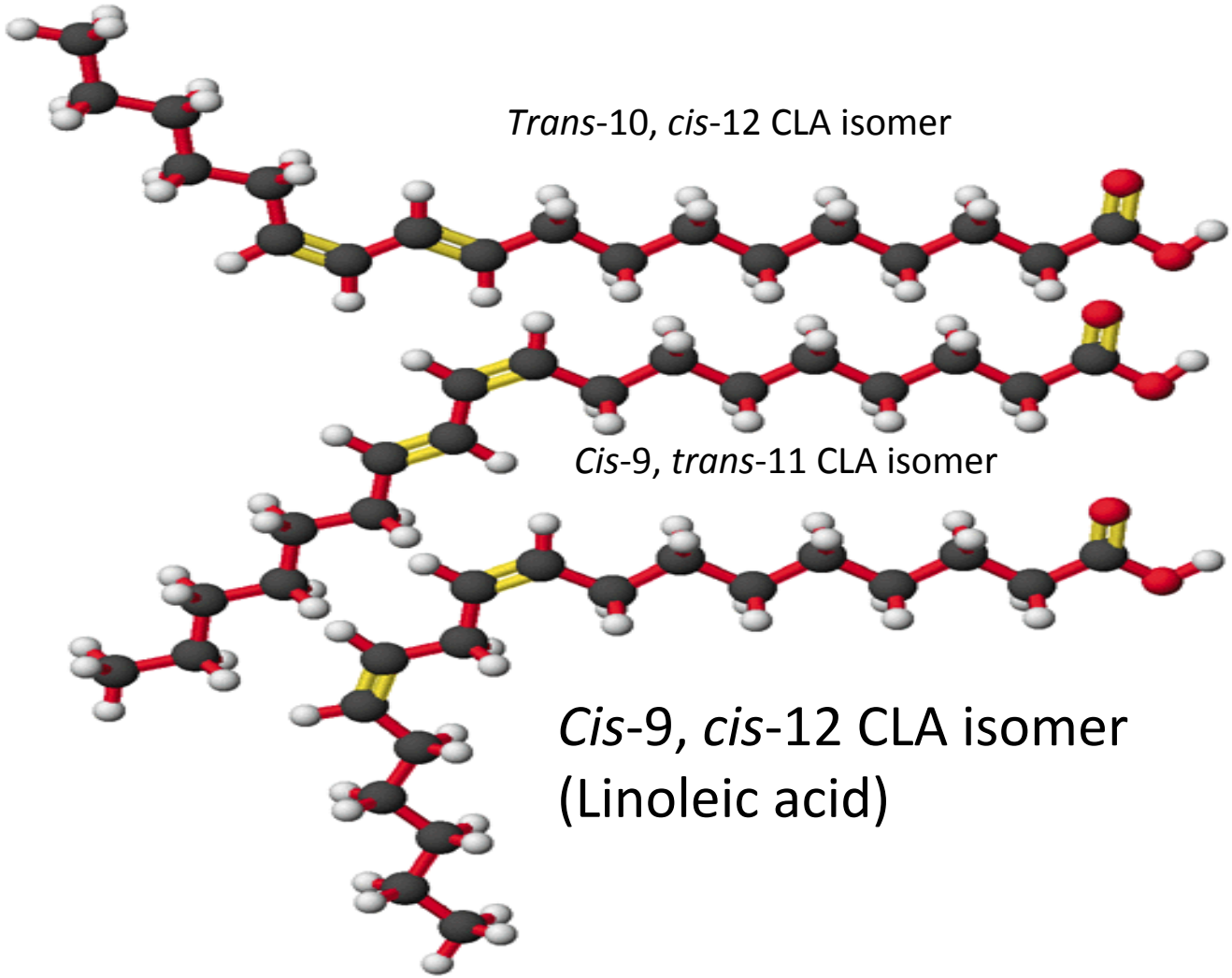
A *cis*-fatty acid has its hydrogens on the same side of the double bond; *cis* molecules fold back into a U-like formation. Most naturally occuring unsaturated fatty acids in foods are *cis*.




*trans*-fatty acid

A *trans*-fatty acid has its hydrogens on the opposite sides of the double bond; *trans* molecules are more linear. The *trans* form typically occurs in partially hydrogenated foods when hydrogen atoms shift around some double bonds and change the configuration from *cis* to *trans*.

# Conjugated Fatty Acids




- Two main CLA isomers suggested to have beneficial biological effects, which are *trans*-10, *cis*-12 CLA isomer and *cis*-9, *trans*-11 CLA isomer.

# Beneficial Effects of CLA

- Reduce fat accumulation. *trans*-10, *cis*-12 CLA isomer > *cis*-9, *trans*-11 CLA isomer
- Prevents or cures cancer, atherosclerosis, and type II diabetes
- Enhances immune response
- Reduces fat in pigs and human
- Increases fat hardness in meat
- Increases storage stability of meat

# Mechanisms of Action

- Trans-10, cis-12 CLA isomer: Body composition changes
  - Reduces lipoprotein lipase activity and inhibits stearyl-CoA desaturase activity
- Cis-9, trans-11 and trans-10, cis-12 CLA isomers: anti-cancer activity and anti-atherogenic effect
  - Modulate the activities of eicosanoid as well as cytokines
  - Activate peroxisome proliferator-activated receptor-gamma (PPAR-gamma) and PPAR-alpha

# Sources of CLA

- Sources of CLA
  - Modified Oil Products: chemical modification
  - Animal Products: Meat (3–8mg total CLA/g fat), Milk (4.3 mg/g butter), Egg
  - Processed Food Products
- Daily CLA Consumption for Health Effects
  - 1.5 to 3.0 g/adult is required for Health Effects