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

LIPIDS

Fatty acids

- Eicosanoids
- Triacylglycerols
- Waxes
- Sphingolipids

Steroids
Lipid vitamins
Terpenes

- Isoprenoids

Glycerophospholipids

- Plasmalogen
- Phosphatidates
- Sphingomyelins

- Phosphatidyl-ethanolamines
- Phosphatidyl-serines
- Phosphatidyl-cholines
- Phosphatidyl-inositol
- Other phospholipids

Ceramides

- Cerebrosides
- Gangliosides
- Other glycosphingolipids
- Glycosphingolipids
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 myelin sheaths)
- Glycosphingolipids – 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

\[
\text{Glycerol} + 3 \text{ Fatty acids} \rightarrow \text{Triglyceride}
\]

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

- 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

<table>
<thead>
<tr>
<th>Carbon Number</th>
<th>Trivial name</th>
<th>IUPAC name</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:0</td>
<td>butyric</td>
<td>butanoic</td>
<td>-5.3</td>
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<tr>
<td>6:0</td>
<td>caproic</td>
<td>hexanoic</td>
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<td>8:0</td>
<td>caprylic</td>
<td>heptanoic</td>
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<tr>
<td>10:0</td>
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<td>decanoic</td>
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<tr>
<td>12:0</td>
<td>lauric</td>
<td>dodecanoic</td>
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<tr>
<td>14:0</td>
<td>myristic</td>
<td>tetradeconoic</td>
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<tr>
<td>16:0</td>
<td>palmitic</td>
<td>hexadeconoic</td>
<td>63</td>
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<tr>
<td>18:0</td>
<td>stearic</td>
<td>octadeconoic</td>
<td>70</td>
</tr>
<tr>
<td>20:0</td>
<td>arachidic</td>
<td>eicosanoic</td>
<td>75</td>
</tr>
<tr>
<td>22:0</td>
<td>behenic</td>
<td>docosanoic</td>
<td>81</td>
</tr>
<tr>
<td>24:0</td>
<td>lignoceric</td>
<td>tetracosanaic</td>
<td>84</td>
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</table>

*IUPAC: International Union of Pure and Applied Chemistry*
## Common unsaturated fatty acids

<table>
<thead>
<tr>
<th></th>
<th>common name</th>
<th>IUPAC name</th>
<th>melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:0</td>
<td>palmitate</td>
<td>hexadecanoate</td>
<td>63</td>
</tr>
<tr>
<td>16:1 Δ⁹</td>
<td>palmitoleate</td>
<td>cis-Δ⁹-hexadecanoate</td>
<td>-0.5</td>
</tr>
<tr>
<td>18:0</td>
<td>stearate</td>
<td>octadecanoate</td>
<td>70</td>
</tr>
<tr>
<td>18:1 Δ⁹</td>
<td>oleate</td>
<td>cis-Δ⁹-octadecanoate</td>
<td>13</td>
</tr>
<tr>
<td>18:2 Δ⁹,₁₂</td>
<td>linoleate</td>
<td>cis-Δ⁹,₁₂-octadecanoate</td>
<td>-9</td>
</tr>
<tr>
<td>18:3 Δ⁹,₁₂,₁₅</td>
<td>linolenate</td>
<td>cis-Δ⁹,₁₂,₁₅-octadecanoate</td>
<td>-17</td>
</tr>
<tr>
<td>20:0</td>
<td>arachidate</td>
<td>eicosanoate</td>
<td>75</td>
</tr>
<tr>
<td>20:4 Δ⁵,₈,₁₁,₁₄</td>
<td>arachindonate</td>
<td>cis-Δ⁵,₈,₁₁,₁₄-eicosatetraenoate</td>
<td>-49</td>
</tr>
</tbody>
</table>
Unsaturated fatty acids

- Trienoic acids (3 double bonds)
  - 18:3;6,9,12 w6 : g-linolenic acid (all \textit{cis}-6,9,12-octadecatrienoic acid)
  - 18:3; 9,12,15 w3 : a-linolenic acid (all-\textit{cis}-9,12,15-octadecatrienoic acid)

- Tetraenoic acids (4 double bonds)
  - 20:4; 5,8,11,14 w6: arachidonic acid (all-\textit{cis}-5,8,11,14-eicosatetraenoic acid)
**Unsaturated fatty acids**

- **Pentaenoic acid (5 double bonds)**
  - 20:5; 5,8,11,14,17 $\omega$3: 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 $\omega$3: 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 3-carbon intervals, starting at C9, e.g. **α-linolenic acid is 18:3 (Δ9, 12, 15)**
  - Double bonds are (almost) always in the **cis** configuration
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

<table>
<thead>
<tr>
<th>common name</th>
<th>Isomeric form</th>
<th>System name</th>
</tr>
</thead>
<tbody>
<tr>
<td>18:1 eladic</td>
<td>trans</td>
<td>9t-octadecenoic</td>
</tr>
<tr>
<td>18:1 petroselinic</td>
<td>cis</td>
<td>6-octadecenoic</td>
</tr>
<tr>
<td>18:1 cis-vaccinic</td>
<td>cis</td>
<td>11-octadecenoic</td>
</tr>
<tr>
<td>18:1 trans-vaccenic</td>
<td>trans</td>
<td>11t-octadecenoic</td>
</tr>
<tr>
<td>20:1 godoleic</td>
<td>cis</td>
<td>9-eicosenoic</td>
</tr>
<tr>
<td>20:1 gondoic</td>
<td>cis</td>
<td>11-eicosenoic</td>
</tr>
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<td>22:1 cetoleic</td>
<td>cis</td>
<td>5-docosenoic</td>
</tr>
<tr>
<td>22:1 erucic</td>
<td>cis</td>
<td>11-docosenoic</td>
</tr>
<tr>
<td>24:1 nervonic</td>
<td>cis</td>
<td>15-tetracosenoic</td>
</tr>
</tbody>
</table>
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.
Pathways of n-3 and n-6 Fatty Acid Synthesis

<table>
<thead>
<tr>
<th>n-6 acids</th>
<th>n-3 acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>18:2 (9,12)a</td>
<td>18:3 (9,12,15)e</td>
</tr>
<tr>
<td>18:3 (6,9,12)b</td>
<td>18:4 (6,9,12,15)f</td>
</tr>
<tr>
<td>6-desaturase</td>
<td></td>
</tr>
<tr>
<td>18:3 (6,9,12)b</td>
<td>18:4 (6,9,12,15)f</td>
</tr>
<tr>
<td>elongase</td>
<td></td>
</tr>
<tr>
<td>20:3 (8,11,14)c</td>
<td>20:4 (8, 11,14,17)</td>
</tr>
<tr>
<td>5-desaturase</td>
<td></td>
</tr>
<tr>
<td>20:4 (5,8,11,14)d</td>
<td>20:5 (5,8,11,14,17)g</td>
</tr>
<tr>
<td>elongase</td>
<td></td>
</tr>
<tr>
<td>22:4 (7,10,13,16)</td>
<td>22:5 (7,10,13,16)h</td>
</tr>
<tr>
<td>4-desaturase</td>
<td></td>
</tr>
<tr>
<td>22:5 (4,7,13,16)</td>
<td>22:6 (4,7,10,13,16,19)i</td>
</tr>
</tbody>
</table>

a: linoleic, b: γ-linoleic, c: dihomom-γ-linoleic, d: arachidonic, e: α-linoleic, f: stearidonic, g: EPA, h: DPA, i: DHA
Cis & Trans-FA

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 occurring unsaturated fatty acids in foods are cis.

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 \textit{trans}-10, \textit{cis}-12 CLA isomer and \textit{cis}-9, \textit{trans}-11 CLA isomer.
Beneficial Effects of CLA

- 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

- 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