Chapter 11: Lipids

Voet & Voet: Pages 380-394
Lipids are distinguished by their high solubility in non-polar solvents and low solubility in H$_2$O.

- Diverse group of compounds including Fats, Oils, Waxes, some vitamins and hormones and most non-protein components of membranes.

Lipids are amphipathic molecules that can be:

(A) Major components of biological membranes
- membranes define the basic unit of life (cell) and subcellular compartments (eucaryotes)
- includes cholesterol

(B) Major form of stored energy in biological systems
- lipids are largely reduced compounds; complete oxidation of lipids generates lots of energy

(C) Hormones
- signal transduction between cells
Overview of Biological Lipids

**Fatty acids**: principal building blocks of complex lipids

**Waxes**: esters of fatty acids (heat sensitive)

**Triacylglycerols**: membrane precursors, energy storage

**Glycerophospholipids**: membrane components

**Sphingolipids**: brain lipids, membrane components

**Steroids**: cholesterol, bile salts, steroid hormones

**Terpenes**: like turpentine
Fatty Acids

- Composed of a carboxylic acid “head group” and a long hydrocarbon “tail”
  - tail generally contains an even number of carbon atoms
- Hydrocarbon tail can be saturated or unsaturated
  - unsaturated hydrocarbon tails contain one or more double bonds
- Both common and systematic nomenclatures are widely used
  - eg. stearic acid or octadecanoic acid (1CH₃, 16 CH₂ + 1 CO₂H)

General structure of fatty acid, with the carboxylic acid “head group” shown in red
Typical Saturated and Unsaturated Fatty Acids

18:2 (Δ⁹,Δ¹²)

18:1 (Δ⁹)

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## (Some) Important Fatty Acids

<table>
<thead>
<tr>
<th>Carbon skeleton</th>
<th>Structure*</th>
<th>Systematic name†</th>
<th>Common name (derivation)</th>
<th>Melting point (°C)</th>
<th>Solubility at 30°C (mg/g solvent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12:0</td>
<td>CH₃(CH₂)₁₀COOH</td>
<td>n-Dodecanoic acid</td>
<td>Lauric acid (Latin <em>taurus</em>, “laural plant”)</td>
<td>44.2</td>
<td>0.063  2.600</td>
</tr>
<tr>
<td>14:0</td>
<td>CH₃(CH₂)₁₂COOH</td>
<td>n-Tetradecanoic acid</td>
<td>Myristic acid (Latin <em>Myristica</em>, nutmeg genus)</td>
<td>53.9</td>
<td>0.024  874</td>
</tr>
<tr>
<td>16:0</td>
<td>CH₃(CH₂)₁₄COOH</td>
<td>n-Hexadecanoic acid</td>
<td>Palmitic acid (Latin <em>palma</em>, “palm tree”)</td>
<td>63.1</td>
<td>0.0083 348</td>
</tr>
<tr>
<td>18:0</td>
<td>CH₃(CH₂)₁₆COOH</td>
<td>n-Octadecanoic acid</td>
<td>Stearic acid (Greek <em>stear</em>, “hard fat”)</td>
<td>69.6</td>
<td>0.0034 124</td>
</tr>
<tr>
<td>20:0</td>
<td>CH₃(CH₂)₁₈COOH</td>
<td>n-Eicosanoic acid</td>
<td>Arachidic acid (Latin <em>Arachis</em>, legume genus)</td>
<td>76.5</td>
<td></td>
</tr>
<tr>
<td>24:0</td>
<td>CH₃(CH₂)₂₂COOH</td>
<td>n-Tetracosanoic acid</td>
<td>Lignoceric acid (Latin <em>lignum</em>, “wood” + <em>cera</em>, “wax”)</td>
<td>86.0</td>
<td></td>
</tr>
<tr>
<td>16:1(Δ⁹)</td>
<td>CH₃(CH₂)₉CH=CH(CH₂)₇COOH</td>
<td>cis-9-Hexadecenoic acid</td>
<td>Palmitoleic acid (Latin <em>oleum</em>, “oil”)</td>
<td>1-0.5</td>
<td></td>
</tr>
<tr>
<td>18:1(Δ⁹)</td>
<td>CH₃(CH₂)₉CH=CH(CH₂)₇COOH</td>
<td>cis-9-Octadecenoic acid</td>
<td>Oleic acid (Greek <em>linon</em>, “flax”)</td>
<td>13.4</td>
<td></td>
</tr>
<tr>
<td>18:2(Δ⁶,12)</td>
<td>CH₃(CH₂)₉CH=CHCH₃CH=CH(CH₂)₇COOH</td>
<td>cis,cis-9,12-Octadecadienoic acid</td>
<td>Linoleic acid</td>
<td>1-5</td>
<td></td>
</tr>
<tr>
<td>18:3(Δ⁹,12,15)</td>
<td>CH₃(CH₂)₉CH=CHCH₃CH=CHCH₂CH=CH(CH₂)₇COOH</td>
<td>cis,cis,cis-9,12,15-Octadecatrienoic acid</td>
<td>α-Linolenic acid</td>
<td>-11</td>
<td></td>
</tr>
<tr>
<td>20:4(Δ⁶,8,11,13)</td>
<td>CH₃(CH₂)₉CH=CHCH₃CH=CHCH₂CH=CH(CH₂)₇COOH</td>
<td>cis,cis,cis-5,8,11,14-Icosatetraenoic acid</td>
<td>Arachidonic acid</td>
<td>-49.5</td>
<td></td>
</tr>
</tbody>
</table>

**Essential:** can not be synthesized by humans
Nutrition and Fatty Acids

- **essential fatty acids**: linoleic and $\alpha$-linolenic fatty acids; must get these from plants

- **“good fats”**: high in polyunsaturated Fats. Typical foods include vegetable oils, like olive, canola, sunflower, etc.

- **“bad fats”**: high in saturated fats. Classic offenders stearic (beef); palm & coconut oils (found in candy)

- **“really bad fats”**: *trans* fatty acids, result from partial hydrogenation of vegetable oils. Margarine has trans fatty acids.

  - difficult to metabolism; lead to increased cholesterol levels in the blood
Triacylglycerols (triglycerides)

- 1 Fatty Acid + Glycerol = monoacylglycerol
- 2 Fatty Acids + Glycerol = diacylglycerol
- 3 Fatty Acids + Glycerol = triacylglycerol
Triacylglycerols

• Most abundant form of fatty acids
• **Not** a part of biological membranes - Major energy reserve in animal
  • Energy yield from burning: 38 kJ/gram, as compared to 17 kJ/gram for carbohydrates (e.g. sugars).

### Stored Metabolic 'fuel' in a 70 kg person

<table>
<thead>
<tr>
<th></th>
<th>Mass (%)</th>
<th>Mass (g)</th>
<th>Energy (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fat (adipose tissue)</td>
<td>37</td>
<td>15,000</td>
<td>555,000</td>
</tr>
<tr>
<td>Protein (muscle)</td>
<td>17</td>
<td>6,000</td>
<td>102,000</td>
</tr>
<tr>
<td>Glycogen (muscle)</td>
<td>16</td>
<td>120</td>
<td>1,920</td>
</tr>
<tr>
<td>Glycogen (liver)</td>
<td>16</td>
<td>70</td>
<td>1,120</td>
</tr>
<tr>
<td>Glucose (extracellular fluid)</td>
<td>16</td>
<td>20</td>
<td>320</td>
</tr>
</tbody>
</table>
Glycerophospholipids

1,2-diacylglycerol (the fatty acids) with a phosphate group at position 3

• Essential components of cell membranes and other cellular structures
• The parent molecule is phosphatidic acid
• You can have additional compounds esterified to the phosphate group
**Glycerophospholipids (examples)**

- **Phosphatidylcholine** (lecithin) and **phosphatidylethanolamine**: common membrane constituents

- **Cardiolipan** = diphosphatidylglycerol (note two phosphates and extra glycerol)

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<table>
<thead>
<tr>
<th>Name of glycerophospholipid</th>
<th>Name of X</th>
<th>Formula of X</th>
<th>Net charge (at pH 7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphatidic acid</td>
<td>—</td>
<td>— H</td>
<td>-1</td>
</tr>
<tr>
<td>Phosphatidylethanolamine</td>
<td>Ethanolamine</td>
<td>CH$_2$—CH$_2$—$\text{NH}_3$</td>
<td>0</td>
</tr>
<tr>
<td>Phosphatidylcholine</td>
<td>Choline</td>
<td>CH$_2$—CH$_2$—N(CH$_3$)$_3$</td>
<td>0</td>
</tr>
<tr>
<td>Phosphatidylserine</td>
<td>Serine</td>
<td>CH$_2$—CH—$\text{NH}_3$</td>
<td>-1</td>
</tr>
<tr>
<td>Phosphatidylglycerol</td>
<td>Glycerol</td>
<td>CH$_2$—CH—CH$_2$—OH</td>
<td>-1</td>
</tr>
<tr>
<td>Phosphatidylinositol 4,5-bisphosphate</td>
<td>myo-inositol 4,5-bisphosphate</td>
<td></td>
<td>-4</td>
</tr>
<tr>
<td>Cardiolipin</td>
<td>Phosphatidylglycerol</td>
<td></td>
<td>-2</td>
</tr>
</tbody>
</table>

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**Glycerophospholipid (general structure)**

1. **Saturated fatty acid** (e.g., palmitic acid)
2. **Unsaturated fatty acid** (e.g., oleic acid)
3. **Head-group substituent**
Other Glycerophospholipids

- **Ether glycerolphospholipids** (e.g. platelet activating factor, an important lipid signaling molecule)

**Galactolipids** found in thylakoid Membranes of chloroplasts. They Make up about 70% to 80% of the Total membrane lipids.
**Sphingolipids**

*Shingolipids* are typically found in brain tissues (*e.g.* brain lipids)

Based upon *sphingosine* (or dihydrosphingosine), an amino alcohol

- Sphingosine is rare in plants and animals while sphingolipids are common

Simplest sphingolipids are ceramides

- Sphingosine + N-linked fatty acid = ceramide

![Diagram of Sphingolipid Structure]
Sphingolipids (types)

<table>
<thead>
<tr>
<th>Name of sphingolipid</th>
<th>Name of X</th>
<th>Formula of X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramide</td>
<td></td>
<td>( \text{---} \rightarrow \text{H} )</td>
</tr>
<tr>
<td>Sphingomyelin</td>
<td>Phosphocholine</td>
<td>( \text{---} \rightarrow \text{H} )</td>
</tr>
<tr>
<td>Neutral glycolipids</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glucosylceribroside</td>
<td>Glucose</td>
<td></td>
</tr>
<tr>
<td>Lactosylceramide (a globoside)</td>
<td>Di-, tri-, or tetrasaccharide</td>
<td></td>
</tr>
<tr>
<td>Ganglioside GM2</td>
<td>Complex oligosaccharide</td>
<td></td>
</tr>
</tbody>
</table>
Gangliosides are complex sphingolipids

- Ceramide + 3 (or more) sugars including one sialic acid

Limited abundance; key tissue specific signaling molecule
Gangliosides determine blood type

- O, A and B antigens that give rise to blood types are gangliosides

The polar “head groups” of these gangliosides differ

Electron Micrograph of Erythrocyte Outer Membrane
Waxes are esters of a fatty acid and a fatty alcohol

- insoluble and water repellent

Weakly polar head group with saturated fatty acid and unsaturated fatty alcohol (typically)

Includes sterols (eg. cholesterol, lanolin, carnuba)
Terpenes are abundant in plants

- Built from 5 carbon isoprene units and do not contain fatty acids
- Monoterpenes contain 2 isoprene units, Diterpenes contain 4, etc.

Generally assembled by a 'head to tail' linkage of isoprene units

- Complex terpenes contain

Common terpenes have varied functions:

- Potent signalling molecules, pigments, chemical sensors, etc
- Intermediates in cholesterol and steroid biosynthesis