Chapter 8
Lipids

Chapter Objectives:
• Learn how to classify lipids.
• Learn the properties of the saturated and unsaturated fatty acids, and how they are linked to form triglycerides (fats and oils).
• Learn how to draw the products of hydrolysis, saponification, and hydrogenation reactions of triglycerides.
• Learn the basic structures of other lipids, including waxes, phosphoglycerides, lecithin, cephalins, sphingolipids, and glycolipids.
• Learn how lipids are important in cell membrane structure.
• Learn about the steroids and steroid hormones, and the prostaglandins.

Chapter 8
Lipids

Lipids

• Lipids are biological molecules that are insoluble in water but soluble in nonpolar solvents.
  – Lipids have a wider spectrum of compositions and structures because they are defined in terms of their physical properties (water solubility).
• Lipids are the waxy, greasy, or oily compounds found in plants and animals.
  – wax coating that protects plants
  – used as energy storage
  – structural components (cell membranes)
  – insulation against cold

Classification of Lipids

• Lipids are divided into:
  – Saponifiable lipids — contain esters, which can undergo saponification (hydrolysis under basic conditions) (waxes, triglycerides, phosphoglycerides, sphingolipids)
  – Nonsaponifiable lipids — do not contain ester groups, and cannot be saponified (steroids, prostaglandins)
• Saponifiable lipids can also be divided into groups:
  – Simple lipids — contain two types of components (a fatty acid and an alcohol)
  – Complex lipids — contain more than two components (fatty acids, an alcohol, and other components)

Fatty Acids

• Fatty acids are long-chain carboxylic acids:

    R—C—OH
    \[ \text{a carboxylic acid} \]

    Nonpolar, hydrophobic tail (water insoluble)
    Polar, hydrophilic head (water soluble)
**Properties of Fatty Acids**
- The long, nonpolar hydrocarbon tails of fatty acids are responsible for most of the fatty or oily characteristics of lipids.
- The carboxyl (COOH) group is hydrophilic under basic conditions, such as physiological pH (7.4):

  ![Carboxylic Acid and Carboxylate Ion](image)

**Characteristics of Fatty Acids**
- They are usually have straight chains (no branches) that are about 10 to 20 carbon atoms in length.
- They usually have an even number of carbon atoms (counting the carboxylic carbon).
- The carbon chains may be saturated (all single bonds) or unsaturated (containing double bonds). Other than the carboxylic group and the double bonds, there are usually no other functional groups.
- Shorter fatty acids usually have lower melting points than longer ones (stearic acid [18C] = 70°C, palmitic acid [16C] = 63°C).
- The double bonds are usually in cis configurations:

  ![Cis Double Bond Configuration](image)

**Essential Fatty Acids**
- Most of the fatty acids we need can be synthesized in the body. Two fatty acids, linoleic acid and linolenic acid, both polyunsaturated fatty acids with 18-carbon chains, cannot be synthesized in the body and must be obtained from the diet. These are **essential fatty acids**. Both are found in plant and fish oils. In the body, they are used to produce hormone-like substances that regulate blood pressure, blood clotting, blood lipid levels, the immune response, and inflammatory reactions.

  ![Linoleic Acid and Linolenic Acid](image)

**Fatty Acid Micelles**
- In aqueous solutions, fatty acids associate with each other in spherical clusters called micelles, in which the hydrocarbon tails tangle each other up through dispersion forces, leaving a “shell” of polar carboxylate ions facing outwards, in contact with the water.
  - Micelles are important in the transport of insoluble lipids in the blood, and in the actions of soaps.

**Saturated and Unsaturated Fatty Acids**
- The cis-double bonds in unsaturated fatty acids put an inflexible “kink” in the carbon chain, preventing the molecules from packing together as tightly as saturated fatty acids do.
  - For example, stearic acid (saturated), oleic acid (one double bond), and linoleic acid (two double bonds) all have 18 carbons in the chain, but their melting points are drastically different:

  ![Fatty Acid Chains](image)

**Some Important Fatty Acids**

<table>
<thead>
<tr>
<th>#C</th>
<th>Name</th>
<th>Formula</th>
<th>MP</th>
<th>Common Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>Myristic acid</td>
<td>CH(14H2)2CO2H</td>
<td>59°C</td>
<td>Butterfat, coconut oil, tallow oil</td>
</tr>
<tr>
<td>16</td>
<td>Palmitic acid</td>
<td>CH(16H2)2CO2H</td>
<td>58°C</td>
<td>Lard, beef fat, butterfat, coconut oil</td>
</tr>
<tr>
<td>18</td>
<td>Stearic acid</td>
<td>CH(18H2)2CO2H</td>
<td>59°C</td>
<td>Lard, beef fat, butterfat, coconut oil</td>
</tr>
<tr>
<td>20</td>
<td>Arachidonic acid</td>
<td>CH(20H2)2CO2H</td>
<td>59°C</td>
<td>Peanut oil</td>
</tr>
</tbody>
</table>

**Polyunsaturated**
- Linoleic acid  CH(18H2)CH(18H2)2CH(18H2)CH(18H2)CO2H | 5°C | Corn oil, soybean oil, cotton oil, linseed oil |
- Linolenic acid CH(18H2)CH(18H2)2CH(18H2)2CH(18H2)CH(18H2)CO2H | 15°C| Linseed oil, corn oil, cotton oil |
- Arachidonic acid CH(20H2)CH(20H2)2CH(20H2)2CH(20H2)CH(20H2)CH(20H2)CO2H | 5°C | Corn oil, linseed oil, animal tissues |
- Docosanoid acid CH(22H2)CH(22H2)2CH(22H2)2CH(22H2)2CH(22H2)CO2H | 15°C| Fish oil, safflower oil |
- Docosahexaenoic acid CH(22H2)CH(22H2)2CH(22H2)2CH(22H2)2CH(22H2)CH(22H2)CO2H | 15°C| Fish oil, safflower oil |
Examples: Saturated and Unsaturated Fatty Acids

- Indicate whether the following fatty acids are saturated or unsaturated. Which of them are solids and which are liquids at room temperature?

CH₃(CH₂)₁₄COOH

CH₃(CH₂)₄CH=CHCH=CH(CH₂)₄COOH

CH₃(C₁₄H₂₄)COOH

CH₃(C₁₀H₂₀)COOH

The Structure of Fats and Oils

Fats and Oils

- The fatty acids in a triglyceride molecule are usually not all the same; natural triglycerides are often mixtures of many different triglyceride molecules.

- Fats are triglycerides that are solids at room temp.
  - usually derived from animals
  - mostly saturated fatty acids

- Oils are triglycerides that are liquids at room temp.
  - usually derived from plants or fish
  - mostly unsaturated fatty acids

Triglycerides

- Animal fats and vegetable oils are esters composed of three molecules of a fatty acid connected to a glycerol molecule, producing a structure called a triglyceride or a triacylglycerol:

\[
\text{glycerol} \quad \text{fatty acid} \quad \text{fatty acid} \quad \text{fatty acid}
\]

Fats and Oils

Figure 8.7 A comparison of saturated and unsaturated fatty acids in some foods.
**Chapter 8 Lipids**

**Chemical Properties of Fats and Oils**

**Saponification of Triglycerides**

- In *saponification* reactions, triglycerides react with strong bases (NaOH or KOH) to form the carboxylate salts of the fatty acids, called **soaps**:

  ![Soap Diagram]

  - CH₂-O-[(CH₂)ₗCH₃]
  - CH₂-O-[(CH₂)ₗCH₂CH₂CH₃] + 3 NaOH → CH₂-O-[(CH₂)ₗCH₃] Na⁺

  - CH₂-O-[(CH₂)ₗCH₂CH₂CH₃] + 3 NaOH → CH₂-O-[(CH₂)ₗCH₃] Na⁺

**Soaps**

- NaOH produces a "hard" soap, commonly found in bar soaps; KOH produces a "soft" soap, such as those in shaving creams and liquid soaps.

- These salts combine two solubility characteristics:
  - a long, nonpolar, water-insoluble (hydrophobic) hydrocarbon "tail."
  - a charged, water-soluble (hydrophilic) "head."

  ![Soap Micelle Diagram]

**Hydrolysis of Triglycerides**

- Triglycerides can be broken apart with water and an acid catalyst (**hydrolysis**), or by digestive enzymes called **lipases**:

  ![Hydrolysis Equation]

**Hydrogenation**

- In **hydrogenation** reactions, alkenes are converted into alkanes with hydrogen gas (H₂) and a catalyst (Pt, Ni, or some other metal). This process is used to convert unsaturated vegetable oils, which are liquids at room temp., to saturated fats, which are solids at room temp. (shortening, etc.).

  ![Hydrogenation Equation]

- In **partially hydrogenated vegetable oils**, not all of the double bonds are saturated, allowing the texture of the product to be controlled. In the process, this twists some of the naturally-occurring *cis* double bonds into *trans* isomers (trans fats).
Chapter 8 Lipids

Examples: Reactions of Triglycerides

• Write the products of the following reactions:

25

\[
\begin{align*}
\text{CH}_3\text{O} & \text{O} \text{O} \text{O} \text{C} \text{H}_2\text{C} \text{H} \text{C} \text{H}_2\text{CH}_3 \\
\text{CH} & \text{O} \text{O} \text{O} \text{C} \text{H}_2\text{C} \text{H} \text{C} \text{H}_2\text{CH}_3 + 3 \text{H}_2\text{O} \xrightarrow{\text{H}^+} \\
\text{CH}_3\text{O} & \text{O} \text{O} \text{O} \text{C} \text{H}_2\text{C} \text{H} \text{C} \text{H}_2\text{CH}_3 \\
\text{CH} & \text{O} \text{O} \text{O} \text{C} \text{H}_2\text{C} \text{H} \text{C} \text{H}_2\text{CH}_3 + 3 \text{NaOH} \xrightarrow{} \\
\text{CH}_3\text{O} & \text{O} \text{O} \text{O} \text{C} \text{H}_2\text{C} \text{H} \text{C} \text{H}_2\text{CH}_3
\end{align*}
\]

Examples: Reactions of Triglycerides

• Write the products of the following reactions:

26

\[
\begin{align*}
\text{CH}_3\text{O} & \text{O} \text{O} \text{O} \text{C} \text{H}_2\text{C} \text{H} \text{C} \text{H}_2\text{CH}_3 \\
\text{CH} & \text{O} \text{O} \text{O} \text{C} \text{H}_2\text{C} \text{H} \text{C} \text{H}_2\text{CH}_3 + \text{H}_2 \xrightarrow{\text{Ni}} \\
\text{CH}_3\text{O} & \text{O} \text{O} \text{O} \text{C} \text{H}_2\text{C} \text{H} \text{C} \text{H}_2\text{CH}_3
\end{align*}
\]

Waxes

• Waxes are simple lipids contain a fatty acid joined to a long-chain (12-32 carbons) alcohol:

27

\[
\begin{align*}
\text{CH}_3\text{(CH}_2\text{)}_{14} \text{C} \text{O} & \text{O} \text{O} \text{C} \text{H}_2\text{C} \text{H} \text{C} \text{H}_2\text{CH}_3 \\
\text{palmitic acid portion} & \text{myristyl alcohol portion} \\
\text{myristyl palmitate} — \text{found in beeswax}
\end{align*}
\]

28

\[
\begin{align*}
\text{CH}_3\text{(CH}_2\text{)}_{14} \text{C} \text{O} & \text{O} \text{O} \text{C} \text{H}_2\text{C} \text{H} \text{C} \text{H}_2\text{CH}_3 \\
\text{palmitic acid portion} & \text{cetyl alcohol portion} \\
\text{cetyl palmitate} — \text{found in spermaceti oil}
\end{align*}
\]

Waxes

• Waxes are insoluble in water, and not as easily hydrolyzed as fats and oils. They often occur in nature as protective coatings on feathers, fur, skin, leaves, and fruits.

• Sebum, secreted by the sebaceous glands of the skin, contains waxes that help to keep skin soft and prevent dehydration.

• Waxes are used commercially to make cosmetics, candles, ointments, and protective polishes.
**Phosphoglycerides**

- Phosphoglycerides are complex lipids that are major components of cell membranes. Phosphoglycerides and related compounds are also called phospholipids.

  \[
  \begin{align*}
  &\text{CH}_2-O-\stackrel{\circ}{C}-R \\
  &\text{CH}_2-O-\stackrel{\circ}{C}-R' \\
  &\text{CH}_2-O-\stackrel{\circ}{P}-OR \quad \text{phosphate and an aminoalcohol} \\
  &\text{a phosphoglyceride}
  \end{align*}
  \]

**Aminoalcohols in Phosphoglycerides**

- The most abundant phosphoglycerides contain the alcohols *choline*, *ethanolamine*, or *serine* attached to the phosphate group:

  \[
  \begin{align*}
  &\text{HO-CH}_2\text{CH}_2-\text{N(CH}_3)_3 \\
  &\text{HO-CH}_2\text{CH}_2-\text{NH}_3 \\
  &\text{HO-CH}_2\text{CH}-\text{NH}_3
  \end{align*}
  \]

  - choline (a quaternary ammonium cation)
  - ethanolamine
  - serine

**Lecithin**

- Phosphoglycerides that contains the aminoalcohol choline are called *lecithins*:

  \[
  \begin{align*}
  &\text{CH}_2-O-\text{C}-(\text{CH}_2)_16\text{CH}_3 \\
  &\text{CH}-O-\text{C}-(\text{CH}_2)_7\text{CH}-\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CH}_3 \\
  &\text{CH}_2-O-\text{P}-O-\text{CH}_2\text{CH}_2-\text{N}(\text{CH}_3)_3
  \end{align*}
  \]

  - The fatty acids at the first and second positions are variable, so there are a number of different possible lecithins.

**Cephalin**

- Phosphoglycerides that contains the aminoalcohols ethanolamine or serine are called *cephalins*:

  \[
  \begin{align*}
  &\text{CH}_2-O-\text{C}-(\text{CH}_2)_7\text{CH}_3 \\
  &\text{CH}-O-\text{C}-(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_2\text{CH}_3 \\
  &\text{CH}_2-O-\text{P}-O-\text{CH}_2\text{CH}_2-\text{N}\text{H}_3
  \end{align*}
  \]

  - Cephalins are found in most cell membranes, and are particularly abundant in brain tissue. They are also found in blood platelets, and play a role in blood clotting.

**Lecithin**

- Because lecithins contain negatively charged oxygen atoms in the phosphate group and positively charged nitrogen atoms in the quaternary ammonium salt group, that end of the molecule is highly hydrophilic, while the rest of the molecule is hydrophobic.

- This allows lecithin to act as an emulsifying agent:
  - forms an important structural component of cell membranes.
  - forms micelles which play a role in the transport of lipids in the blood stream.
  - Commercially, lecithin extracted from soybeans is used as an emulsifying agent in margarine and candies to provide a smooth texture.
Chapter 8 Lipids

**Sphingolipids**

• **Sphingolipids** are complex lipids that contain sphingosine instead of glycerol.

\[ \text{CH}_2\text{(CH}_2\text{)}_2\text{CH}=-\text{CH}--\text{CH}--\text{OH} \]

- Sphingosine
- \( \text{CH}=-\text{NH}_2 \)
- \( \text{CH}_3\text{OH} \)

• One important type of sphingolipids are the **sphingomyelins**:

\[ \text{CH}_3\text{(CH}_2\text{)}_2\text{CH}=-\text{CH}--\text{CH}--\text{OH} \]

- Choline
- Fatty acid
- \( \text{O} \text{P} \text{O} \text{CH}_2\text{CH}_2\text{N(CH}_3\text{)}_3 \)
- \( \text{O} \text{CH}_2\text{OH} \)

**Glycolipids**

• **Glycolipids** are sphingolipids that contain carbohydrates (usually monosaccharides). They are also referred to as **cerebrosides** because of their abundance in brain tissue.

\[ \text{CH}_3\text{(CH}_2\text{)}_2\text{CH}=-\text{CH}--\text{CH}--\text{OH} \]

- Fatty acid
- D-galactose

**Cell Structure**

• Cells are tiny membrane-enclosed units of fluid.
• **Prokaryotic cells** are found in bacteria and cyanobacteria. They lack a nucleus or organelles.
• **Eukaryotic cells** make up the tissues of other organisms. They are more complex cells, containing a nucleus and other organelles.
• The external cell membrane acts as a selective barrier between the cell and its environment, enclosing the cellular fluid (cytoplasm) and organelles.
• Internal membranes enclose the **organelles**, creating cellular compartments that have separate organization and functions.
### Cellular Organelles

<table>
<thead>
<tr>
<th>Organelle</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Endoplasmic reticulum</td>
<td>Synthesis of proteins, lipids, and other substances</td>
</tr>
<tr>
<td>Lysosome</td>
<td>Digestion of substances taken into cells</td>
</tr>
<tr>
<td>Microfilaments and microtubules</td>
<td>Cellular movements</td>
</tr>
<tr>
<td>Mitochondrion</td>
<td>Cellular respiration and energy production</td>
</tr>
<tr>
<td>Nucleus</td>
<td>Contains hereditary material (DNA), which directs protein synthesis</td>
</tr>
<tr>
<td>Plastids</td>
<td>Contain plant pigments such as chlorophyll (photosynthesis)</td>
</tr>
<tr>
<td>Ribosome</td>
<td>Protein synthesis</td>
</tr>
</tbody>
</table>

### Membrane Structure

- Most cell membranes contain about 60% lipids and 40% proteins:
  - phosphoglycerides (e.g., lecithin and cephalin)
  - sphingomyelin
  - cholesterol
- The **fluid-mosaic model** of the cell pictures the cell membrane as being composed of a **lipid bilayer**, in which the nonpolar tails of lipids point towards the “interior” of the bilayer, leaving the polar, hydrophilic portions pointing outwards.

### Membrane Structure

- When the membrane is broken, the repulsion between the nonpolar portion and water causes the membrane to re-form.
- Cell membranes also contain unsaturated fatty acid chains that increase the flexibility or fluidity of the membrane.
- Some of the proteins in the membrane “float” in the lipid bilayer like icebergs, while others extend through the bilayer.
- The lipid molecules are free to move laterally within the bilayer like dancers on a crowded dance floor.

### The Fluid-Mosaic Model

- **Steroids** are classified as lipids because they are soluble in nonpolar solvents, but they are non-saponifiable because the components are not held together by ester linkages.
- The basic steroid structure contains four fused rings:
Cholesterol

- **Cholesterol** is the most abundant steroid in the body. It is an essential component of cell membranes, and is a precursor for other steroids, such as the bile salts, sex hormones, vitamin D, and the adrenocorticoid hormones.

- There is apparently a correlation between high levels of cholesterol in the blood and atherosclerosis.

![Cholesterol Structure](image)

Bile Salts

- **Bile** is a yellowish brown or green fluid produced in the liver and stored in the gall bladder.

- Bile salts act like soaps and other emulsifiers: they contain both polar and nonpolar regions, helping to break fats in foods into smaller pieces, allowing them to be hydrolyzed more easily.

![Bile Salts Structure](image)

Gallstones

- Bile salts also emulsify cholesterol in the bile, so it can be removed in the small intestine. If cholesterol levels are too high or the levels of bile salts is too low, the cholesterol precipitates and forms gallstones.

  - Gallstones can block the duct that allows bile to be secreted into the duodenum. Fats are no longer digested properly, and bile pigments absorbed into the blood causes the skin to become yellow and the stool to become gray.

![Gallstones Structure](image)

Adrenocorticoid Hormones

- **Hormones** are chemicals released by cells or glands in one part of the body that send out messages that affect cells in other parts of the body. Many hormones are based on steroids.

- The **adrenocorticoid hormones** are produced in the adrenal glands (located on the top of the kidney).

  - Glucocorticoids such as cortisol affect the metabolism of carbohydrates. Cortisol and its derivatives, cortisone and prednisolone (synthetic) are powerful anti-inflammatory drugs used to treat arthritis and asthma.

![Steroid Hormones and Prostaglandins](image)
Adrenocorticoid Hormones

- Mineralocorticoids regulate ion concentration (mainly Na⁺). Aldosterone influences the absorption of Na⁺ and Cl⁻ in kidney tubules, thus regulating the retention of water in the body.

Sex Hormones

- Sex hormones produced in the testes and ovaries regulate the production of sperm and eggs and aid in the development of secondary sex characteristics.

Prostaglandins

- Prostaglandins are cyclic compounds synthesized from arachidonic acid. Like hormones, they are involved in a host of body processes, including reproduction, blood clotting, inflammation, and fever. (Aspirin works by inhibiting prostaglandin production, alleviating inflammation and fever.)