Fats and Lipids

What are they?

• Lipids are naturally occurring
• Fatty acids are long chain carboxylic acids
• They are triesters of glycerol and fatty acids
• May be solid or liquid at room temperature
• Usually insoluble in water, soluble in organic solvents

Examples of Fats and Lipids

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Classification of Lipids

Three major types

1. Esters or Amides of Fatty acids
   - Glycerophospholipids
   - Sphingomyelins
   - Glycolipids

2. Steroids: Tetracyclic molecules that act as hormones, e.g. recall the steroid from Ouabain

3. Eicosanoids: Carboxylic acids that work as a chemical messenger

Classification of lipids (contd.)

1. Storage lipids (store energy within fat cells).
   Burning of fats produce 9 Kcal/g of energy and burning of carbohydrates of equal weight produces 4 kcal/g.

2. Membrane Lipids (separate compartments of aqueous solutions from each other)
   Lipids are insoluble in water. This is very important as most proteins and carbohydrates are water soluble. The long alkyl chain in the fatty acid makes them insoluble. Lipids are therefore ‘hydrophobic’.

3. Chemical Messenger lipids. Ex: Steroid hormones, prostaglandins
Lipid classification based on structure

Fatty Acids and their Esters

Natural fatty acids are triesters of glycerol and fatty acids

Example of a triacylglycerol

\[
\begin{align*}
&\text{CH}_2-\text{O-}\text{C-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \quad \text{Palmitic acid} \\
&\text{CH}_2-\text{O-}\text{C-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \quad \text{Oleic acid} \\
&\text{CH}_2-\text{O-}\text{C-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \quad \text{Linoleic acid}
\end{align*}
\]

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Chain lengths may be 16, 18, or 20 carbons long. Most common in vegetable oils and animal fats. Their only functional groups are carboxylic acid groups.
A wax is a simple ester; i.e. a monoester of a fatty acid.

*Example of a wax*

![Diagram of triacontanyl hexadecanoate](image)

A monoester molecule

Generally have higher m.p’s than fats. They are harder. Used as protective Coatings by plants and animals.

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**Saturated and Unsaturated Fatty Acids**

![Structures of saturated and unsaturated fatty acids](image)

A saturated fatty acid (palmitic acid)

A cis unsaturated fatty acid (linoelate acid)
Polyunsaturated Fatty acids have more than one double bond. Melting points of these long chain unsaturated fatty acids depend on the 'degree of unsaturation'.

<table>
<thead>
<tr>
<th>Name</th>
<th>Typical Source</th>
<th>Number of Carbon</th>
<th>Number of Double Bonds</th>
<th>Condensed Formula</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lauric</td>
<td>Coconut oil</td>
<td>12</td>
<td>0</td>
<td>CH₃(CH₂)₇COOH</td>
<td>44</td>
</tr>
<tr>
<td>Myristic</td>
<td>Butter fat</td>
<td>14</td>
<td>0</td>
<td>CH₃(CH₂)₆COOH</td>
<td>58</td>
</tr>
<tr>
<td>Palmitic</td>
<td>Most fats and</td>
<td>16</td>
<td>0</td>
<td>CH₃(CH₂)₁₄COOH</td>
<td>63</td>
</tr>
<tr>
<td>Stearic</td>
<td>Most fats and</td>
<td>18</td>
<td>0</td>
<td>CH₃(CH₂)₁₇COOH</td>
<td>70</td>
</tr>
<tr>
<td>Unsaturated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oleic</td>
<td>Olive oil</td>
<td>18</td>
<td>1</td>
<td>CH₃(CH₂)₆CH═CH(CH₃)₂COOH(cis)</td>
<td>4</td>
</tr>
<tr>
<td>Linoleic</td>
<td>Vegetable oils</td>
<td>18</td>
<td>2</td>
<td>CH₃(CH₂)₆CH═CHCH₂CH═CH(CH₃)₂COOH(all cis)</td>
<td>-5</td>
</tr>
<tr>
<td>Linolenic</td>
<td>Soybean and</td>
<td>18</td>
<td>3</td>
<td>CH₃CH₂CH═CHCH₂CH═CH(CH₂)ₐCOOH(all cis)</td>
<td>-11</td>
</tr>
<tr>
<td>Arachidonic</td>
<td>Lard</td>
<td>20</td>
<td>4</td>
<td>CH₃(CH₂)₈(CH═CHCH₂)₂CH₂COOH(all cis)</td>
<td>-50</td>
</tr>
</tbody>
</table>

Properties: Fats and Oils

The areas with double bonds are rigid. These kinks in the chain, due to cis-conformation prevents the molecules from stacking up. The more double bonds present, the harder to solidify these oils.

The trans- isomer, also known as trans fats stack like the saturated fats. Both saturated fats and trans fats are harder to metabolize and remain stored in the body.
General Properties of Fats and Oils

- No ionic charges, neutral molecules
- Nonpolar therefore hydrophobic
- Solids (Fats) have a higher number of saturated fatty acid side chains
- Oils have higher number of unsaturated fatty acid side chains
Glycerophospholipids (a.k.a phosphoglycerides) are triesters of glycerol that contain charged phosphate diester group/s and are abundant in cell membranes. Together with other lipids, they help to control the flow of molecules into and out of cells.

Note: the third group is always a phosphate ester group (charged).

Phosphotydylserine: found in fish, Green leafy vegetables, soybeans etc

### TABLE 24.3 Some Glycerophospholipids

<table>
<thead>
<tr>
<th>Precursor of X</th>
<th>Formula of X</th>
<th>Name of Resulting Glycerophospholipid Family</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>−H</td>
<td>Phosphatidate</td>
<td>Basic structure of glycerophospholipids</td>
</tr>
<tr>
<td>Choline</td>
<td>−CH₃CH₂N(CH₃)₂</td>
<td>Phosphatidylcholine</td>
<td>Basic structure of lecithin; most abundant membrane phospholipids</td>
</tr>
<tr>
<td>Ethanolamine</td>
<td>−CH₂CH₃NH₂</td>
<td>Phosphatidylethanolamine</td>
<td>Membrane lipids</td>
</tr>
<tr>
<td>Serine</td>
<td>−CH₂−CH⁺NH₃</td>
<td>Phosphatidylserine</td>
<td>Present in most tissues; abundant in brain</td>
</tr>
<tr>
<td>α-glycerol</td>
<td>−OH−OH−OH</td>
<td>Phosphatidylglycerol</td>
<td>Relays chemical signals across cell membranes</td>
</tr>
</tbody>
</table>

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**Sphingomyelins** or **Sphingolipids** are sphingosine derivatives with a phosphate ester group at C1 of sphingosine. The sphingomyelins are major components of the coating around nerve fibers (the myelin sheath) and are present in large quantities in brain tissue.

- The backbone is **NOT** glycerol based, and based on sphingosine molecule
- Associated with diseases such as MS.

**Glycolipids**, complex lipids derived from sphingosine, contains carbohydrate groups;
Cerebrosides occur primarily on the brain and at nerve synapses

Note: Both Phospholipids and Glycolipids are cell-membrane lipids
The glycolipids are also derived from sphingosine. They have a monosaccharide unit attached to the sphingosine backbone and may be classed as sphingolipid.

Cholesterol: another cell membrane lipid. *Member of steroid class of molecules

A flat molecule, hydrophobic except for the –OH group. Within a cell membrane cholesterol molecules remain in the hydrophobic tails of the phospholipids. Maintains structure of cell membrane.
Cholesterols are carried by lipoproteins. Lipoproteins are an assembly of lipids and proteins.

High-Density Lipoproteins (HDL) or the ‘good cholesterol’ contains about 33% protein and about 30% cholesterol.

Low-Density Lipoproteins (LDL) or the ‘bad cholesterol’ contains only 25% proteins and 50% cholesterol.

Very Low-Density Lipoproteins (VLDL) mostly carry triglycerides synthesized by the liver.

Chylomicrons are dietary lipids synthesized in the intestines.

Like all lipids, cholesterols are insoluble in water. High levels of cholesterol in blood serum may cause plaque-like deposits on inner surfaces of arteries which restricts their diameter.

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**Chemical Reactions of Fats and Lipids**

We will look at two major ones:

- **Hydrogenation**
- **Hydrolysis / Saponification**
Hydrogenation Reactions

Hydrogenation of C-C double bonds of fatty acids and directly affects the Degree of unsaturation. Partially hydrogenated fats occur from incomplete Hydrogenation reaction.

Metal catalysts used for regular alkene hydrogenations, such as Pd, Ni also work in fats hydrogenation.

Partial structure of an unsaturated vegetable oil:

\[
\text{O} \overset{\text{H}}{\rightarrow} \text{C} \overset{\text{H}}{\rightarrow} \text{CH}_2\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\]

Partial structure of hydrogenated oil:

\[
\text{O} \overset{\text{H}}{\rightarrow} \text{C} \overset{\text{H}}{\rightarrow} \text{CH}_2\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\]

2 H₂ Pd catalyst

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Hydrogenation Reactions

- Most common example is making of margarine from oils
- A process of hardening a vegetable oil by Hydrogenation (using metal catalysis)
- This process changes the consistency of the fat and raises its melting point
- The process of hydrogenation may be controlled to maintain product consistency
Hydrolysis/Saponification (of a triacyl-glycerol)

Saponification

Strong aqueous base catalyzes fat hydrolysis

\[
\begin{align*}
\text{CH}_2\text{O} & \text{C} \text{R} \\
\text{CH} & \text{O} \text{C} \text{R} \prime \quad \text{NaOH} \\
\text{H}_2\text{O} & \\
\text{CH}_2\text{OH} & \text{CH}_2\text{OH} + \\
\text{CH}_2\text{OH} & \text{R} \text{C} \text{O} - \text{Na}^+ \\
\text{R} \text{C} \text{O} & - \text{Na}^+ \\
\text{R}'' \text{C} & \text{O} - \text{Na}^+ \\
\end{align*}
\]

A fat or oil

Glycerol

Fatty acid salts (soap)

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Hydrolysis/Saponification

- Saponification is ester hydrolysis under basic conditions
- It produces 1 molecule of glycerol and 3 molecules fatty acids (salt form)
- It is also the term used to prepare soap
- The soap formed in the reaction is known as ‘crude soap’
- Most soaps used now are detergents
How Soap Works.....

The ‘soap’ has a hydrophilic (anionic carboxylate head) and a hydrophobic (alkane) tail; the ionic part dissolves into water. The spherical formation known as ‘micelles’ has an inner core consisting of the hydrophobic tails. Oils and grease which are hydrophobic themselves are encapsulated within this micelle and the molecules may be rinsed away with water, thus giving soaps ‘cleaning action’.

Drawing shows how phospholipids, glycolipid molecules form ‘bilayers’

The drawing is of Sphingomyelin molecule. Major components of coating around nerve fibers (myelin sheath) and in brain tissue

Lack of their presence is associated with Multiple sclerosis (refer to text)

Note the charged polar head group (blue) The head group is hydrophilic. The tail is made of a hydrophobic alkane chain. Because of their structure they act as ‘emulsifying agents’

The diagram on the right is a pictorial representation of bilayers using ball and stick method
Polar/nonpolar structures aggregate as sheets. Ionic, polar head groups stay in the aqueous environment on either side. This is a highly stable but flexible arrangement.

A liposome is formed from a spherical aggregate of a bilayer arrangement of phospholipids. The core is aqueous. If the core is not aqueous, then it is a micelle (see soaps). Liposomes are an important class of molecules for drug delivery.

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**Cell Membrane Structure (the Fluid Mosaic Model)**

The membrane is primarily made up of lipid bilayers (phospholipids). The molecules are not bonded to one another but float freely, hence the term 'fluid'. The term 'mosaic' means made from many parts.
Transport Across Cell Membrane

- **Active transport**: Energy must be supplied to move substance into the cell membrane.

- **Passive transport**: When substances move across the membrane freely via diffusion.

- **Facilitated diffusion**: When substance moves in through the membrane with the aid of other biomolecules but without energy. This is a form of passive transport.

Eicosanoids: Prostaglandins and Leukotrienes

**Eicosanoids**: Made via biosynthesis from either $\omega$-3 or $\omega$-6 Essential Fatty Acids (EFA’s). They function as short-lived chemical messengers or local hormones.

**Prostaglandins and Leukotrienes**: These are two classes of Eicosanoid molecules. Prostaglandins contain a 5-membered ring. Both are synthesized from the 20-carbon arachidonic acid.

These molecules are of great interest for therapeutic applications. They have an *extraordinary* range of biological effects.