LIPIDS: Saturated & Unsaturated Fatty Acids (Part-2)

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Unsaturated Fatty Acids

- Over half of the fatty acid residues of plant and animal lipids are unsaturated (contain double bonds) and are often polyunsaturated (contain two or more double bonds).
- Bacterial fatty acids are rarely polyunsaturated but are commonly branched, hydroxylated, or contain cyclopropane rings.
- Table I indicates that the first double bond of an unsaturated fatty acid commonly occurs between its C9 and C10 atoms counting from the carboxyl C atom. This bond is called a Δ9- or 9-double bond.
- In polyunsaturated fatty acids or PUFA, the double bonds tend to occur at every third carbon atom (e.g., —CH=CH—CH2—CH=CH—) and so are not conjugated (as in —CH=CH—CH=CH—).
- Two important classes of polyunsaturated fatty acids are designated as ω–3 or ω–6 fatty acids, a nomenclature that identifies the last double-bonded carbon atom as counted from the methyl terminal (ω) end of the chain.
- α-Linolenic acid and linoleic acid (Fig. 1) are examples of such fatty acids.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Common Name</th>
<th>Systematic Name</th>
<th>Structure</th>
<th>mp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12:0</td>
<td>Lauric acid</td>
<td>Dodecanoic acid</td>
<td>CH₃(CH₂)₁₀COOH</td>
<td>44.2</td>
</tr>
<tr>
<td>14:0</td>
<td>Myristic acid</td>
<td>Tetradecanoic acid</td>
<td>CH₃(CH₂)₁₂COOH</td>
<td>53.9</td>
</tr>
<tr>
<td>16:0</td>
<td>Palmitic acid</td>
<td>Hexadecanoic acid</td>
<td>CH₃(CH₂)₁₄COOH</td>
<td>63.1</td>
</tr>
<tr>
<td>18:0</td>
<td>Stearic acid</td>
<td>Octadecanoic acid</td>
<td>CH₃(CH₂)₁₆COOH</td>
<td>69.6</td>
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<tr>
<td>20:0</td>
<td>Arachidic acid</td>
<td>Eicosanoic acid</td>
<td>CH₃(CH₂)₁₈COOH</td>
<td>77</td>
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<tr>
<td>22:0</td>
<td>Behenic acid</td>
<td>Docosanoic acid</td>
<td>CH₃(CH₂)₂₀COOH</td>
<td>81.5</td>
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<tr>
<td>24:0</td>
<td>Lignoceric acid</td>
<td>Tetracosanoic acid</td>
<td>CH₃(CH₂)₂₂COOH</td>
<td>88</td>
</tr>
</tbody>
</table>

**Saturated fatty acids (all double bonds are cis)**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Common Name</th>
<th>Systematic Name</th>
<th>Structure</th>
<th>mp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:1n–7</td>
<td>Palmitoleic acid</td>
<td>9-Hexadecanoic acid</td>
<td>CH₃(CH₂)₆CH═CH(CH₂)₇COOH</td>
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<tr>
<td>18:1n–9</td>
<td>Oleic acid</td>
<td>9-Octadecanoic acid</td>
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</tr>
<tr>
<td>18:2n–6</td>
<td>Linoleic acid</td>
<td>9,12-Octadecadienoic acid</td>
<td>CH₃(CH₂)₄(CH═CH(CH₂)₂(CH₂)₆COOH</td>
<td>−5</td>
</tr>
<tr>
<td>18:3n–3</td>
<td>α-Linolenic acid</td>
<td>9,12,15-Octadecatrienoic acid</td>
<td>CH₃(CH₂)₆(CH═CH(CH₂)₂(CH₂)₆COOH</td>
<td>−11</td>
</tr>
<tr>
<td>18:3n–6</td>
<td>γ-Linolenic acid</td>
<td>6,9,12-Octadecatrienoic acid</td>
<td>CH₃(CH₂)₆(CH═CH(CH₂)₃(CH₂)₃COOH</td>
<td>−11</td>
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<tr>
<td>20:4n–6</td>
<td>Arachidonic acid</td>
<td>5,8,11,14-Eicosatetraenoic acid</td>
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<tr>
<td>20:5n–3</td>
<td>EPA</td>
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<tr>
<td>22:6n–3</td>
<td>DHA</td>
<td>4,7,10,13,16,19-Docosahexenoic acid</td>
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<tr>
<td>24:1n–9</td>
<td>Nervonic acid</td>
<td>15-Tetracosenoic acid</td>
<td>CH₃(CH₂)₇CH═CH(CH₂)₁₃COOH</td>
<td>39</td>
</tr>
</tbody>
</table>
Saturated fatty acids

• Saturated fatty acids (which are fully reduced or “saturated” with hydrogen) are highly flexible molecules that can assume a wide range of conformations because there is relatively free rotation around each of their C—C bonds. Nevertheless, their lowest energy conformation is the fully extended conformation, which has the least amount of steric interference between neighboring methylene groups.

• The melting points (mp) of saturated fatty acids, like those of most substances, increase with their molecular mass (Table 1).

• Fatty acid double bonds almost always have the cis configuration (Fig. 1). This puts a rigid 30° bend in the hydrocarbon chain.

• Consequently, unsaturated fatty acids pack together less efficiently than saturated fatty acids. The reduced van der Waals interactions of unsaturated fatty acids cause their melting points to decrease with the degree of unsaturation. The fluidity of lipids containing fatty acid residues likewise increases with the degree of unsaturation of the fatty acids.

• This phenomenon has important consequences for biological membranes.
Triacylglycerols (TAGs) are Major Storage Lipids

- The fats and oils that occur in plants and animals consist largely of mixtures of triacylglycerols (also called triglycerides).
- TAGs are nonpolar, water-insoluble substances, contain three esterified fatty acids or are fatty acid tri-esters of glycerol.
- TAGs function mainly as energy reservoirs in animals and are therefore their most abundant class of lipids even though they are not components of cellular membranes.
- TAGs differ according to the identity and placement of their three fatty acid residues. Most TAGs contain two or three different types of fatty acid residues and are named according to their placement on the glycerol moiety, for example, 1-palmitoleoyl-2-linoleoyl-3-stearoylglycerol.
- Note that the -ate ending of the name of the fatty acid becomes -oyl in the fatty acid ester.
- Fats and oils (which differ only in that fats are solid and oils are liquid at room temperature) are complex mixtures of TAGs whose fatty acid compositions vary with the organism that produced them.
- Plant oils are usually richer in unsaturated fatty acid residues than animal fats, as the lower melting points of oils imply.
Glycerol

Triacylglycerol
Triacylglycerols (TAGs) Function as Energy Reserves.

- Fats are a **highly efficient form to store metabolic energy**. This is because TAGs are **less oxidized than carbohydrates or proteins** and hence **yield significantly more energy per unit mass on complete oxidation**.

- TAGs are **nonpolar, are stored in anhydrous form**, whereas glycogen, for example, binds about twice its weight of water under physiological conditions. *Fats therefore provide about six times the metabolic energy of an equal weight of hydrated glycogen.*

- In animals, **adipocytes (fat cells; Fig. 2) are specialized for the synthesis and storage of TAGs**. Whereas other types of cells have only a few small droplets of fat dispersed in their cytosol, adipocytes may be almost entirely filled with fat globules.

- **Adipose tissue** is **most abundant** in a subcutaneous layer and **in the abdominal cavity**. The fat content of normal humans (21% for men, 26% for women) allows them to survive starvation for **2 to 3 months**. In contrast, the body’s glycogen supply, which functions as a short-term energy store, can provide for the body’s energy needs for less than a day. *The subcutaneous fat layer also provides thermal insulation, which is particularly important for warm-blooded aquatic animals, such as whales, seals, geese, and penguins, which are routinely exposed to low temperatures.*
Adipose Tissue

Adipocytes
*(white adipose cells)*
Consumption of trans fats causes cardiovascular disease

- The **double bonds in unsaturated fats** (fats containing unsaturated fatty acid residues) **slowly react with the oxygen in air to yield aldehydes and carboxylates of shorter chain length, whose increased volatility results in an unpleasant rancid odor.** To increase their stability, commercial oils that are to be used in cooking are **partially hydrogenated** (treated with H2 in the presence of a metallic catalyst at high temperature and pressure). **This eliminates some of their double bonds and increases their melting temperatures** (this is how margarine is produced from vegetable oils). Unfortunately, the conditions under which hydrogenation occurs have the **undesirable side effect** of converting some of the **cis double bonds to trans double bonds**, yielding **trans fats**.

- In recent decades, it has become increasingly clear that the **consumption of significant amounts of trans fats** causes a large **increase in the incidence of cardiovascular disease** by increasing the level of cholesterol in the blood. As a consequence, several **European countries have banned foods containing trans fats**. In the **United States, the trans fat level must be stated on a food’s Nutritional Facts label**, and several municipalities have banned their use by restaurants.

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Formation of trans fats

Complete chemical hydrogenation

Side-effect of chemical hydrogenation

Double bond in the trans configuration
Trans fats causes cardiovascular disease
Reference Book

• Fundamentals of Biochemistry, Life at the Molecular Level, Voet & Voet