Chem Factsheet

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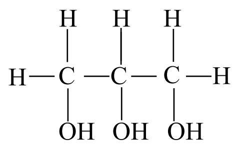
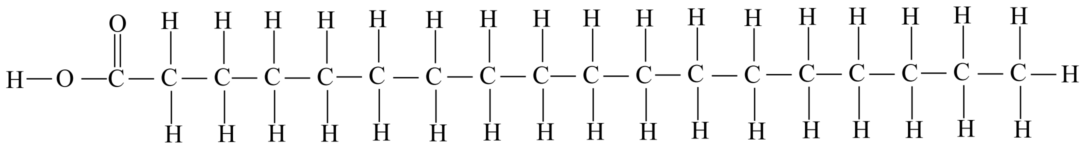
Saturated and Unsaturated Lipids

Lipids are biological molecules that include fats (solid compounds typically derived from animal sources), oils (liquid compounds mainly obtained from plants). Both fats and oils are part of a group of compounds called **triglycerides**, in which a molecule of **glycerol** is bonded to three **fatty acid** chains via **ester linkages** (making a lipid a **triester**).

Glycerol – IUPAC name propane-1,2,3-triol, $CH_2OHCHOHCH_2OH$



Fatty acid – a carboxylic acid (R-COOH) with a long carbon chain, R which is typically 12-18 carbons in length.
e.g., stearic acid, IUPAC name octadecanoic acid, $CH_3(CH_2)_{16}COOH$.



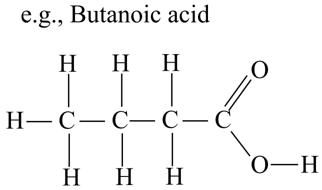
Stearic acid

The long hydrophobic hydrocarbon chain makes these molecules insoluble in water and greasy; hence the name *fatty* acid.
It is important to realise that in most literature (and in this Factsheet), references to the properties and structures of lipids are generally references to the fatty acids rather than the complete triglyceride unit.

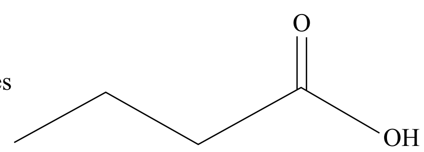
Skeletal formulae

Triglycerides and fatty acids are fairly large molecules that would take a long time to draw if every covalent bond and every atom had to be drawn individually. To expedite the drawing of long carbon and hydrogen-rich compounds, chemists use skeletal structures.
How to interpret a simple skeletal structure:

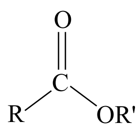
1. Carbon atoms and carbon-linked hydrogen atoms *are not* drawn.
2. All non-carbon and hydrogen atoms *are* drawn
3. Lines to represent the covalent bonds between **carbon** atoms *are* drawn, typically in a zig-zag pattern (which represents the actual shape more closely).
4. Covalent bonds to hydrogen atoms *are not* drawn. It is assumed that each carbon has hydrogens attached to it to give it four bonds.
5. Covalent bonds to all non-carbon and hydrogen atoms *are* drawn.
   e.g., Butanoic acid



becomes

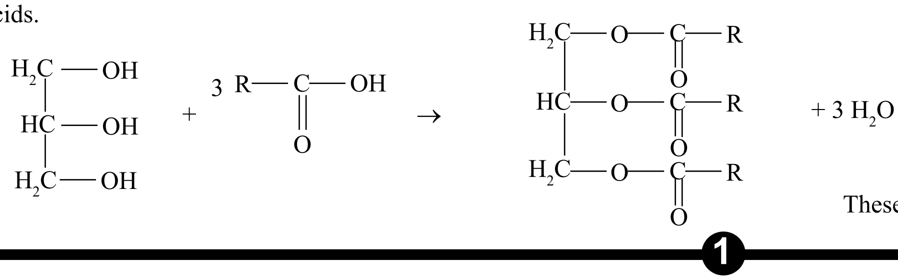


Ester linkage – a type of chemical linkage within a molecule that adopts the structure RCOOR′, where R and R′ are hydrocarbon chains, i.e.,



Triglycerides

As mentioned, triglycerides are triesters formed by each of the OH groups of glycerol forming ester linkages with the COOH groups of 3 fatty acids.



These are the structures that occur in fats and oils.

Categorising fatty acids

Fatty acids can be categorised according to their chemical structure:

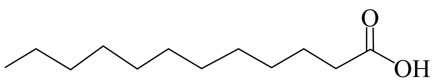
1. **Saturated** – fatty acids that contain only C—C single bonds.
2. **Monounsaturated** – fatty acids that contain exactly one C=C double.
3. **Polyunsaturated** – fatty acids that contain two or more C=C double bonds.

Natural oils and fats normally contain a mixture of triglycerides with a mixture of fatty acids. The overall categorisation of, say, olive oil as monounsaturated is because 70% of the fatty acids present in the triglycerides are monounsaturated (it also contains saturated and polyunsaturated fatty acids to account for the remainder).

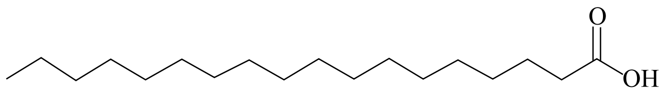
Property	Saturated	Monounsaturated	Polyunsaturated
Source	Mainly animal-derived. but also Palm and coconut oils.	Mainly plant-derived. Seeds and nuts.	Plants and oily fish
Typical state at 25°C	Solid	Liquid	Liquid
Comparative melting point	Highest	Intermediate	Lowest
Stability	Most resistant to rancidification (see later)	Susceptible to rancidification (see later)	Most susceptible to rancidification (see later)
Health considerations	Linked to cardiovascular disease due to build-up of fatty deposits in blood vessels and high cholesterol levels.	*Trans* (see later) isomers are associated with cardiovascular disease and high cholesterol levels.	Evidence of positive benefit to health, e.g., lowering of cholesterol levels.

Predicting melting points of fatty acids

For all three types of fatty acid, as the carbon chain increases in length there is a general trend for the melting point of the fatty acid to increase as well. This is due to an increase in the strength of intermolecular forces (London forces) between the hydrocarbon chains.

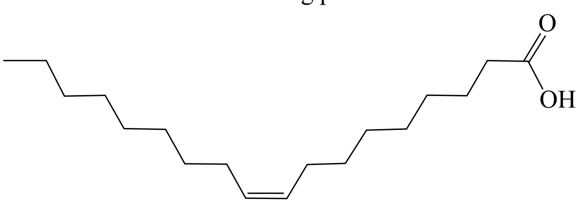


12 carbons – m.p. 44.2 °C

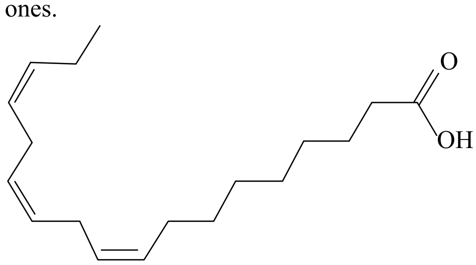


18 carbons – m.p. 69.6 °C

For fatty acids of comparable length, saturated ones tend to have a higher melting point as they adopt a more linear arrangement than unsaturated fatty acids. This allows saturated fatty acids to pack together more effectively which increases the strength of the intermolecular forces.
Most unsaturated fatty acids found in nature adopt the *cis* configuration (see later) which introduces a kink to the carbon chain. These molecules cannot pack as effectively as saturated fatty acids and so the chains are not held together as firmly. The result of unsaturation is a relative decrease in melting point. As the number of C=C double bonds increases, the melting point tends to decrease. This means polyunsaturated fatty acids tend to have even lower melting points than monounsaturated ones.



18 carbons, monounsaturated m.p. 13 °C

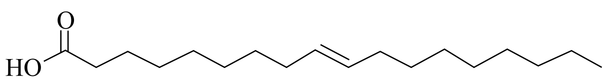


18 carbons, polyunsaturated m.p. -11°C

Cis / Trans Isomerism

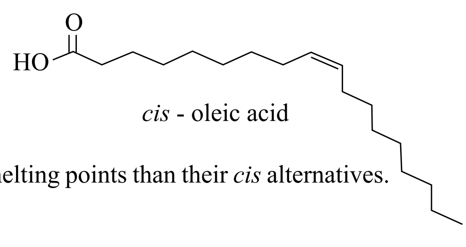
Cis / trans isomerism refers to the geometry about the C=C double bonds in unsaturated fatty acids. In short, in *cis* isomers, the two carbons on either side of the C=C double bond branch from the same side, whereas in *trans* isomers, those carbons branch out from opposite sides.

trans isomer m.p. 44 °C



trans - oleic acid

cis isomer m.p. 13 °C



cis - oleic acid

Trans isomers can pack together more effectively and, thus, have higher melting points than their *cis* alternatives.

Rancidification

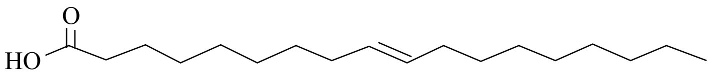
Rancidification describes the process via which a fat or oil is chemically degraded into a number of smaller molecules. These molecules tend to have an unpleasant smell and taste and adversely affect the texture of the lipid. Unsaturated fatty acids are more susceptible to going rancid due to the presence of reactive C=C double bonds.

Two major routes via which rancidification occurs are:
1. **Oxidative rancidification**: oxygen (from the atmosphere) reacts with C=C double bonds to create a mixture of volatile aldehydes, ketones and alcohols. Exposure to light increases the rate of oxidation.
2. **Hydrolytic rancidification**: water present in a food is able to break the ester linkage between fatty acids and the glycerol backbone yielding unpleasant smelling fatty acids.

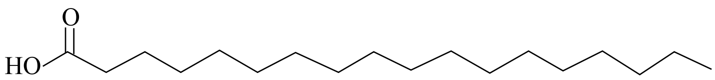
Hydrogenation

Industrially, unsaturated oils may be hydrogenated by **reacting them with hydrogen gas at 150-200°C in the presence of a nickel or copper catalyst**. The hydrogen atoms add across the C=C double bonds and, therefore, decrease the amount of unsaturation present in the lipid. The effect of the reaction is to semi-solidify the oil because the melting point increases. Hydrogenation is used industrially to manufacture "soft" margarine from unsaturated plant oils. e.g.

trans - oleic acid



↓ + H_2(g) ; Ni or Cu catalyst



Note : During the hydrogenation process, some *cis* fatty acids are converted to the less healthy *trans* isomers.

Biological uses of lipids

- energy store: lipids are highly reduced molecules meaning they release a lot of energy when they are oxidised.
- cell membrane components: as phospholipids.
- insulation: both thermal and of nerve cells (myelin).
- organ protection.
- transportation of some vitamins, e.g., A, E and K
- precursor for cell signalling molecules, e.g., arachidonic acid.

Health Effects

Overconsumption of any lipid, whether saturated or unsaturated, may lead to obesity and related conditions due to the extremely high energy content of all lipids.

Saturated and *trans* fatty acids are associated with other negative effects on health such as cardiovascular disease and increased cholesterol levels. Both lead to the build-up of fatty deposits (atherosclerosis) in arteries which increases the chance of strokes and heart attacks. *Trans* fatty acids are poorer substrates for lipase enzymes in the body and are not metabolised as well as *cis* forms. Saturated and *trans* fatty acids increase circulating levels of LDL (low-density lipoprotein) which are responsible for high cholesterol levels as well as fatty deposits. Polyunsaturated and *cis* fatty acids are associated with high levels of HDL (high-density lipoprotein) which scavenges cholesterol from the blood and can reduce the size of fatty deposits.

Practice Questions

1. For each of the following pairs of fatty acids, state and explain which would have the higher melting point

   (a) $CH_3(CH_2)_8CH{=}CH(CH_2)_4COOH$ and $CH_3(CH_2)_{14}COOH$

   (b) $CH_3(CH_2)_8CH{=}CH(CH_2)_4COOH$ and

   $CH_3(CH_2)_4CH{=}CH(CH_2)_3CH{=}CH(CH_2)_4COOH$

   (c) $CH_3(CH_2)_{14}COOH$ and $CH_3(CH_2)_{10}COOH$

2. Explain why unsaturated lipids are less stable than saturated lipids.

3. Explain why consumption of hydrogenated unsaturated lipids may be harmful to health.

Answers

1 (a) $CH_3(CH_2)_{14}COOH$ – saturated (vs unsaturated), molecules pack more effectively (linear vs kinked), stronger intermolecular forces.

(b) $CH_3(CH_2)_8CH{=}CH(CH_2)_4COOH$ – monounsaturated (vs polyunsaturated), molecules less kinked so pack more effectively, stronger intermolecular forces.

(c) $CH_3(CH_2)_{14}COOH$ – longer carbon chain/higher molecular mass, stronger intermolecular forces.

2. Presence of C=C double bond(s), C=C is highly reactive, C=C reacts with oxygen (C—C single bonds do not react with oxygen as easily).

3. Levels of both saturated and *trans* fatty acids increases, increased build-up of fatty deposits, increased levels of LDL / cholesterol.

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