Carboxylic Acids, Esters, and Fats

1.6

Oranges, lemons, and tomatoes are all foods that naturally contain citric acid. Sour candies get their sour taste from ascorbic acid. Compounds with functional groups that make them acidic give foods a tart flavour.

Carboxylic Acids

A **carboxylic acid** is an organic compound that contains a **carboxyl group**, –COOH (**Figure 1**). When a carboxylic acid is in aqueous solution, a hydrogen ion may be removed from the carboxyl group relatively easily. As you know, a solution that contains hydrogen ions is acidic. These compounds are therefore weak acids. Citrus fruits, crabapples, rhubarb, and other foods that contain carboxylic acids have a sour, tangy taste. Police routinely use tracking dogs to aid in their police work. The dogs, with their acute sense of smell, are able to pick up and follow the trail of a scent. One scent that the dogs can track is the carboxylic acid in the molecules of a person's sweat.

carboxylic acid a weak organic acid containing at least one carboxyl group

carboxyl group a carbon atom that is double-bonded to 1 oxygen atom and single-bonded to a hydroxyl group

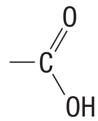


Figure 1 A carboxyl group

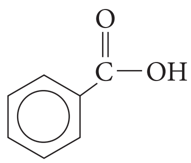
Naming Carboxylic Acids

The functional group of carboxylic acids, –COOH, combines two smaller groups: a hydroxyl group and a carbonyl group. To name organic compounds containing a carboxylic group, start with the alkane name for the longest chain, including the carbon atom in the carboxyl group. Drop the *-e* suffix of the root compound and replace it with the suffix *-oic*, followed by the word *acid*. For example, a carboxylic acid with 3 carbon atoms is propanoic acid (**Figure 2**(**a**)).

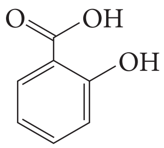
The simplest carboxylic acid is methanoic acid (formic acid) (**Figure 2**(**b**)). The molecule has 1 carbon atom that is also part of the carboxylic group. Methanoic acid is used to remove hair from hides and in rubber-recycling processes. It is also the compound that causes a burning sensation when ants bite.

The next carboxylic acid, with 2 carbon atoms, is ethanoic acid (**Figure 2**(**c**)). Vinegar is typically 5 % ethanoic acid by volume, so it has the sour taste that is characteristic of carboxylic acids. Ethanoic acid is used as a preservative in the food industry, and is also used extensively in the textile-dyeing industry.

The simplest aromatic carboxylic acid is benzoic acid, an acid whose common name is the same as its IUPAC name. The sodium salt of benzoic acid, sodium benzoate, is used as a preservative in foods and beverages. Note that, in a compound that combines an alcohol and a carboxylic acid, the alcohol is indicated as a substituent group: *hydroxy.*



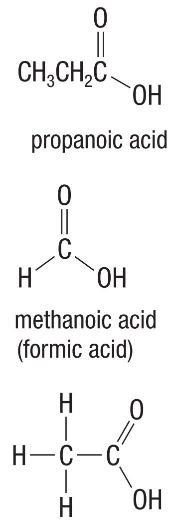
benzoic acid



2-hydroxybenzoic acid

Some carboxylic acids have more than one carboxyl group. When naming an acid with two carboxyl groups, use the suffix *dicarboxylic acid*. Citric acid is an example of a compound with three carboxylic groups (**Figure 3**).

Formic acid, acetic acid, and benzoic acid are acceptable IUPAC names that do not follow the systematic rules for naming acids. In the following tutorial, you will practise naming and drawing carboxylic acids according to the systematic IUPAC rules.

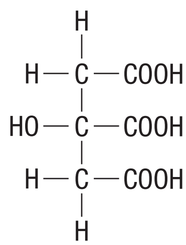


(a) propanoic acid

(b) methanoic acid (formic acid)

(c) ethanoic acid (acetic acid)

Figure 2 Three common carboxylic acids



2-hydroxypropane-1,2,3-tricarboxylic acid (citric acid)

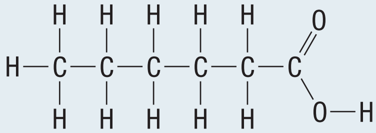
Figure 3 A tricarboxylic acid

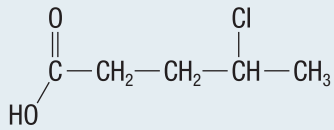
Tutorial 1 Naming and Drawing Carboxylic Acids

Naming and drawing carboxylic acids requires first identifying the part of the compound that includes the carboxyl group, then accounting for any substituents.

Sample Problem 1: Naming Carboxylic Acids from Structural Formulas

Write the name of each of the following carboxylic acids:

(a) 

(b) 

Solution (a)

First, identify the compound that forms the root of the acid. This compound contains a 6-carbon chain (including the carboxylic acid carbon), so its root is hexane. There is one carboxyl group in the compound, so its name is hexanoic acid.

Solution (b)

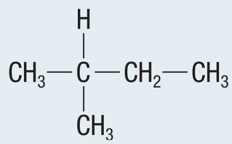
This compound contains a 5-carbon chain: pentane. There is one carboxyl group in the compound, so it is a pentanoic acid. The chlorine substituent is on the fourth carbon, numbering from the carboxyl group, so the compound is 4-chloropentanoic acid.

Sample Problem 2: Drawing Carboxylic Acids

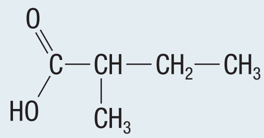
Draw the structure of 2-methylbutanoic acid.

Solution

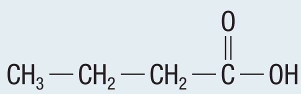
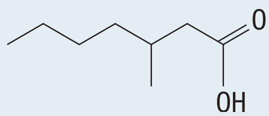
First, draw the root structure, methylbutane.



Next, change a terminal carbon to a carboxyl group. The *2-* prefix indicates that the methyl group is on the second carbon from the carboxyl group, so the carboxyl group must be on the end closest to the methyl group. Therefore, the correct structure is as shown at right:



Practice

1. Name each of the following carboxylic acids: K/U
   (a) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$
   (b) 
   (c) 
2. Draw the structure of each of the following carboxylic acids: K/U C
   (a) octanoic acid
   (b) 3-methylpentanoic acid
   (c) ethanedioic acid

LEARNING TIP

IUPAC and Common Names
You have probably realized that many compounds have both common names and systematic IUPAC names. This textbook mostly uses the systematic names as they help with visualizing the structure of the compound. However, some common names are so familiar that they are also recognized by IUPAC. Acetic acid and formic acid are two such names. You should be familiar with the common names as well as the systematic names of these compounds.

Properties of Carboxylic Acids

Since carboxylic acids have two polar groups—a carbonyl and a hydroxyl—located close together, their molecules are very polar. The carboxyl groups form hydrogen bonds with one another and with polar solvents such as water. Due to this hydrogen bonding, carboxylic acids with 5 or fewer carbon atoms are very soluble in water. Larger carboxylic acids have decreasing solubility due to the large non-polar hydrocarbon group. They are, however, soluble in polar organic solvents, such as alcohols.

Carboxylic acids share many properties with other acids. They affect acid–base indicators, so litmus paper can be used to indicate the presence of carboxylic acids in a mixture of hydrocarbons. Carboxylic acids also react with bases to form ionic compounds and water. Soap is a compound made up of cations of sodium or potassium and anions based on carboxylic acids with multi-carbon alkyl chains.

The melting points of carboxylic acids are higher than their hydrocarbon counterparts because of dipole interactions of the polar carboxyl groups (**Table 1**).

Investigation **1.6.1**

Properties of Carboxylic Acids (page 65)
Now that you have learned about the structures and properties of carboxylic acids, you are ready to explore their properties in the lab.

Table 1 Comparison of the Melting Points of Carboxylic Acids and Alkanes

Number of carbon atoms	Number of –COOH groups	Compound	Melting point (°C)
1	0	methane	−182
1	1	methanoic acid (formic acid)	8
2	0	ethane	−183
2	1	ethanoic acid (acetic acid)	17
2	2	ethanedioic acid (oxalic acid)	189
4	0	butane	−138
4	1	butanoic acid	−8
4	2	2,3-dihydroxybutanedioic acid (tartaric acid)	206
6	0	hexane	−95
6	1	hexanoic acid	13
6	3	2-hydroxypropane-1,2,3-tricarboxylic acid (citric acid)	153

Esters

Many plants naturally produce esters, which are responsible for many of the odours of fruits, flowers, and perfumes. Synthetic esters are often used as flavourings in processed foods, and as scents in cosmetics and perfumes. An **ester** is characterized by a functional group that is similar to a carboxyl group except that the hydrogen atom is replaced with an alkyl group (**Figure 4**). The letters R and R′ in the formula represent alkyl groups in which a carbon atom attaches to the functional group. CAREER LINK

ester an organic compound that contains a carbonyl group bonded to a second oxygen atom which is bonded to another carbon atom

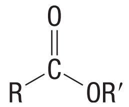


Figure 4 An ester functional group

Naming Esters

Esters are formed by the condensation reaction of a carboxylic acid and an alcohol. To name the resulting ester, determine which part of the molecule was contributed by the alcohol. This is the part that does not include the carbonyl group. In **Figure 5** the alcohol portion of the ester comes from pentan-1-ol. This gives the ester the first part of its name: *pentyl*. The second part of the name comes from the carboxylic acid, butanoic acid. The *-oic acid* part of the name is dropped and replaced with *-oate*: *butanoate*. Therefore, the name of the compound is pentyl butanoate, the ester that gives apricots their aroma. Other esters have different distinctive aromas (**Figure 6**).

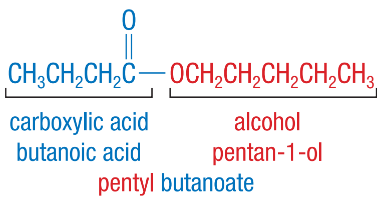


Figure 5 The ester pentyl butanoate is formed by combining a carboxylic acid with an alcohol in a condensation reaction.

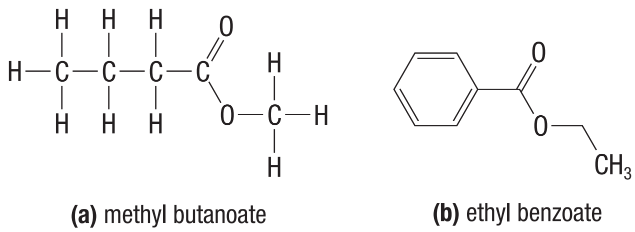


Figure 6 These esters have the aromas of (a) pineapple and (b) cherries.

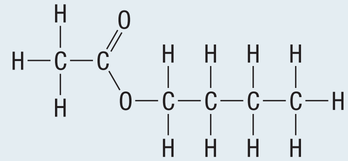
Tutorial 2 Naming and Drawing Esters

When naming esters, follow these steps:

1. Identify the two alkyl groups.
2. Determine which group originated from the carboxylic acid and which originated from the alcohol.
3. Write the name with the alcohol part first and the carboxylic acid part second.

Sample Problem 1: Naming an Ester from Its Structural Formula

Name this ester:



Solution

Step 1. Identify the two alkyl groups.

There is a 2-carbon ethyl group and a 4-carbon butyl group.

Step 2. Determine which group originated from the carboxylic acid and which originated from the alcohol.

The group that includes the carbonyl group originated from the carboxylic acid; in this case, ethanoic acid. The other group originated from the alcohol: butan-1-ol.

Step 3. Write the name with the alcohol part first and the carboxylic acid part second.

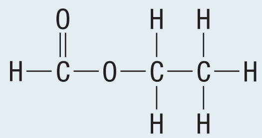
This ester is butyl ethanoate.

Sample Problem 2: Drawing an Ester

Draw the structural formula of ethyl methanoate.

Solution

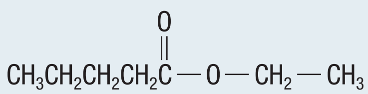
The first part of the name is ethyl, which indicates a 2-carbon alkyl group. The second part of the name, methanoate, indicates a 1-carbon carboxyl part. Therefore, the structure is



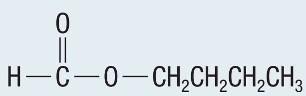
Practice

1. Name each of the following esters: K/U

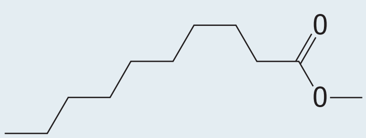
(a)



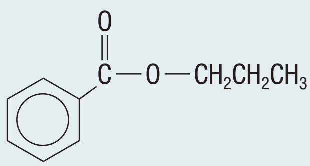
(c)



(b)



(d)



2. Draw the structure of each of the following esters: K/U C

(a) methyl hexanoate (b) methyl benzoate

Properties of Esters

The functional group of an ester is similar to the carboxyl group of an acid, but without the hydroxyl group. As a result, esters are less polar than carboxylic acids and do not form hydrogen bonds. Small esters are soluble in water due to the polarity of their carbon–oxygen bonds. Esters are less soluble in water than carboxylic acids and have lower boiling points. Since their polarities are similar to those of aldehydes and ketones, the melting and boiling points of esters are similar to those of the corresponding aldehydes and ketones. Smaller, low–molecular mass esters are gases at room temperature, but the larger, heavier esters are waxy solids.

Reactions Involving Carboxylic Acids and Esters

Formation of Carboxylic Acids

Carboxylic acids can be formed by the oxidation of aldehydes in the presence of an oxidizing agent. The roadside Breathalyzer test relies on just such a reaction, in which the oxidizing agent changes colour. The dichromate ion, $Cr_2O_7^{2-}$, is the oxidizing agent. It is orange in colour. When a person exhales air containing ethanol into the Breathalyzer tube, the ethanol is oxidized to ethanal, which is then further oxidized to ethanoic acid. The dichromate ion is changed to a different ion, which has a green colour. The extent of the colour change indicates the concentration of alcohol in the exhaled air.

Formation of Esters: Esterification

Esterification is a condensation reaction in which an alcohol and carboxylic acid react to form an ester and water. **Figure 7** shows the general reaction. You have already seen some specific examples of these reactions earlier in this section.

esterification the reaction of a carboxylic acid and alcohol to form an ester and water

$$\mathrm{R\overset{\overset{\displaystyle O}{\|}}{C}{-}OH + R'OH \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} R\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R' + HOH}$$

acid alcohol ester water

Figure 7 The general esterification reaction

Reaction of Esters: Hydrolysis

When esters are treated with an acid or a base, the esterification process can be reversed. The ester splits into the carboxylic acid and alcohol components with the addition of a molecule of water. This reaction is called **hydrolysis**. The general example, shown in **Figure 8**, is carried out in a basic solution. One of the products is the sodium salt of the carboxylic acid and the other is an alcohol.

hydrolysis the breaking of a covalent bond in a molecule by the addition of the elements of water (hydrogen and oxygen); the splitting of an ester into carboxylic acid and alcohol components

$$\mathrm{R\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R' + Na^+ + OH^- \longrightarrow R\overset{\overset{\displaystyle O}{\|}}{C}{-}O^- + Na^+ + R'OH}$$

ester acid alcohol

Figure 8 The general hydrolysis reaction of an ester

Fats and oils are esters of long-chain acids. When these long-chain esters are heated with a strong base, such as sodium hydroxide, the hydrolysis reaction occurs. The sodium salts of this reaction are commonly known as soaps. The reaction is known as saponification. You will learn more about this reaction later in the section.

Tutorial 3 Predicting Reactions Involving Carboxylic Acids

This tutorial reviews some reactions that involve carboxylic acids.

Sample Problem 1: Carboxylic Acid Production

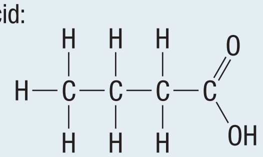
Write equations representing the two chemical reactions that result in the formation of butanoic acid from an alcohol.

Solution

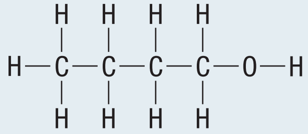
First, consider the reactions that must take place for an alcohol to be converted into butanoic acid. Butanoic acid can be formed from an aldehyde. The first reaction must therefore be the reaction of the alcohol to form an aldehyde; the second must be the reaction of the aldehyde to form the carboxylic acid.

Next, draw the structural formulas of the three compounds.

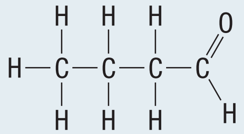
The product is butanoic acid:



To form butanoic acid, start with a primary alcohol with 4 carbon atoms: butan-1-ol.

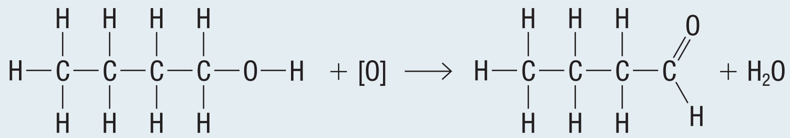


The alcohol reacts with an oxidizing agent to form an aldehyde, butanal.

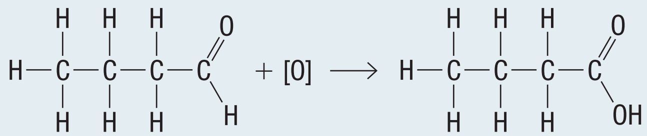


Butanal is oxidized further to form the carboxylic acid, butanoic acid.

Finally, write the equations in the order in which they occur.



butan-1-ol butanal



butanal butanoic acid

Sample Problem 2: Esterification

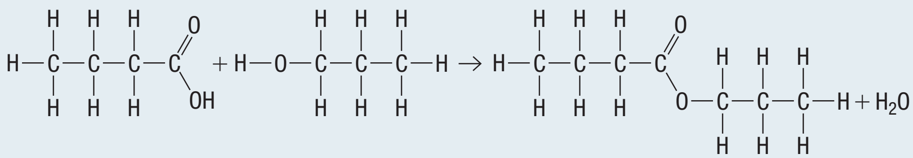
Draw the structural formula equation representing the reaction that forms propyl butanoate. Also write the names of the compounds involved.

Investigation 1.6.2

Synthesizing Esters (page 66)
In this investigation you will synthesize specific esters from their component carboxylic acids and alcohols.

Solution

First, determine the compounds that react to produce the ester. Esters are formed from a carboxylic acid and an alcohol. The last part of the ester name tells you that the carboxylic acid is butanoic acid. The first part of the ester name tells you that the alcohol is propan-1-ol. Esterification reactions are usually written with the carboxylic acid first, followed by the alcohol.



butanoic acid propan-1-ol propyl butanoate water

Sample Problem 3: Hydrolysis of Esters

Write the structural formula equation for the hydrolysis of ethyl propanoate by sodium hydroxide solution.

Solution

The hydrolysis of an ester produces a carboxylic acid and an alcohol. In this case, the carboxylic acid is propanoic acid and the alcohol is ethanol. Draw the part of the compound that includes the carboxyl group on the left side of the reactant molecule.

$$CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}—OCH_2CH_3 + NaOH \longrightarrow CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}—O^- + Na^+ + CH_3CH_2OH$$

Practice

1. Draw structural formula equations illustrating the following reactions. Give the IUPAC name for every compound involved. T/I
   (a) the production of 2-methylpropanoic acid from an aldehyde
   (b) the production of a carboxylic acid from ethanal
   (c) the esterification reaction between propanol and hexanoic acid
   (d) the hydrolysis of methyl butanoate in the presence of sodium hydroxide solution

Fats and Oils

Fats and oils are large ester molecules known as **lipids**. The long-chain carboxylic acid component is called a **fatty acid**. Common fatty acids are listed in **Table 2**. The alcohol component is glycerol. Glycerol is a 3-carbon alcohol with three hydroxyl groups, so it can bond with three fatty acids at once (**Figure 9**). The ester that is formed is called a **triglyceride**. So, fats and oils are triglycerides.

lipid a class of organic compound that includes fats and oils

fatty acid a long-chain carboxylic acid

triglyceride an ester formed from long-chain fatty acids and glycerol

Table 2 Common Fatty Acids

Name	Formula	Source
linoleic acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	vegetable oils (e.g., sunflower seed oil); soya bean oil
oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	most animal fats and vegetable oils (e.g., olive oil)
palmitic acid	$CH_3(CH_2)_{14}COOH$	lard, tallow, palm, and olive oils
stearic acid	$CH_3(CH_2)_{16}COOH$	most animal fats and vegetable oils

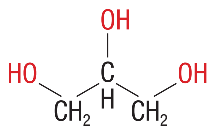


Figure 9 Glycerol

Although the general structure of fats and oils is the same, fats are usually solid at room temperature, while oils are usually liquid. The chain length and degree of unsaturation of the fatty acids generally determine whether a triglyceride is a fat or an oil.

Lipids contain long hydrocarbon chains that release a lot of energy when "burned" or oxidized. In this way lipids are similar to fossil fuels. Living cells can "burn" or metabolize lipids to release their stored energy.

Investigation **1.6.3**

Making Soap (Teacher Demonstration) (page 67)
Making soap is a traditional skill. Here you will see soap emerge from the reactants.

Saponification

You have already seen how esters can be hydrolyzed into their component alcohols and acids in a reaction that is the reverse of esterification. In a similar way, a triglyceride can be split to produce glycerol and the sodium salt of the fatty acid when sodium hydroxide is added to the triglyceride. This resulting sodium salt is commonly

saponification the process of making soap by heating fats or oils with a strong base

called soap, so the reaction is called **saponification** (**Figure 10**). Palmitin and stearin from palm oil and olive oil are common triglycerides used for soap making.

$$
\begin{array}{l}
CH_3(CH_2)_{14}COO-CH_2 \\
\qquad\qquad\qquad\quad\;\; | \\
CH_3(CH_2)_{14}COO-CH + 3\,NaOH \xrightarrow[\text{heat}]{} 3\,CH_3(CH_2)_{14}COONa + CH_2(OH)-CH(OH)-CH_2OH \\
\qquad\qquad\qquad\quad\;\; | \\
CH_3(CH_2)_{14}COO-CH_2
\end{array}
$$

palmitin (triglyceride) — sodium palmitate (soap: Na^+ salt of fatty acid) — glycerol

Figure 10 Saponification reactions involve a triglyceride (fat or oil) and a base.

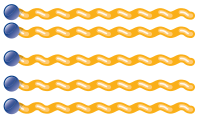
Structure and Properties of Fats and Oils

The best-known property of lipids is their insolubility in water. For example, salad dressing made of oil and vinegar needs to be shaken to mix the two liquids before using. Even so, the two components quickly separate again: oil does not dissolve in the aqueous vinegar. Lipids are not water soluble because of the non-polar nature of the long fatty acid chains in the triglyceride molecules. These long, non-polar chains overcome the polarity of the carbon–oxygen bonds in the ester groups.

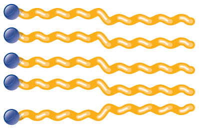
The hydrocarbon chains in fatty acids affect the physical state of the lipid. The shape of the fatty acids determines how tightly the lipid molecules can be packed together. This affects their melting point. Saturated hydrocarbon chains rotate freely around the single carbon–carbon bonds. Each long hydrocarbon chain is a flexible structure that allows the chains to find an optimal packing position. This maximizes the van der Waals interactions between molecules. More thermal energy is required to overcome the attractive forces and separate the molecules, which causes lipids made from saturated fatty acids to have a relatively high melting point. These triglycerides are solids at room temperature.

Unsaturated hydrocarbon chains contain double bonds. These double bonds limit the amount of rotation around the carbon–carbon bonds. Fatty acid chains that contain double bonds can have a *cis* formation or a *trans* formation. *Cis* formations produce kinks in the fatty acid chains and prevent them from packing together tightly (**Figure 11**). The van der Waals interactions are weaker, so it takes less thermal energy to separate the fatty acid chains. Therefore, the melting point of a given unsaturated compound is lower than that of its saturated counterpart. Triglycerides made from unsaturated fatty acid chains with *cis* double bonds are likely to be liquids at room temperature.

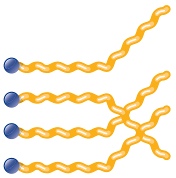
The *trans* form of the fatty acid has a much smaller bend in the chain, so its melting point is closer to that of the unsaturated fat. *Trans* fats are widely manufactured and used because they have properties that increase stability and enhance flavours in some foods. In addition, they allow the manufacture of solid margarine from liquid oils. Unfortunately, these fats are not digested by the digestive system in the same way as saturated fats. This can lead to health problems due to buildup of fats and their by-products in blood vessels and internal organs. Health Canada advises us to choose foods that contain little or no *trans* fat.



(a) saturated lipid



(b) unsaturated lipid with *trans* double bonds



(c) unsaturated lipid with *cis* double bonds

Figure 11 (a) Saturated lipids and (b) those that are unsaturated with *trans* double bonds are able to pack tightly together. Their intermolecular forces are quite strong, so these lipids are solid at room temperature. (c) Unsaturated lipids with *cis* double bonds cannot pack tightly together so tend to be liquid at room temperature.

Research This

Banning *Trans* Fat

Skills: Questioning, Researching, Communicating, Defending a Decision

SKILLS HANDBOOK A5.1

To help increase the shelf life of processed food, manufacturers sometimes add hydrogen to oil, creating *trans* fat. Health risks associated with the consumption of *trans* fats have raised the issue of banning *trans* fats from processed foods.

1. Write a list of information that you would like to know in order to make a decision about the banning of *trans* fats.
2. Once you have made a list, conduct research to find the required information.

A. Should *trans* fats be banned from processed foods? Answer this question in a format of your choice, providing specific information from your research that supports your conclusion. C A

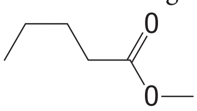
WEB LINK

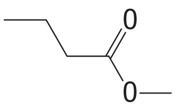
1.6 Review

Summary

- A carboxyl group is a combination of a carbonyl group, C=O, and a hydroxyl group, O–H. Carboxylic acids are named by replacing the *-e* ending of the alkane with *-oic acid*.
- Carboxylic acids are formed by the controlled oxidation of aldehydes.
- An ester's name is derived from the name of the alkyl group of alcohol followed by the name of the alkyl group of the carboxylic acid with the ending *-oate*.
- Esterification is the formation of an ester from a carboxylic acid and an alcohol. Hydrolysis of esters is the breaking down of the ester by a strong base to form the carboxylic acid and alcohol.
- Fats and oils are triglycerides. They are esters made from long chains of fatty acids.
- Saponification is the process by which a fatty acid reacts with a strong base to form a salt of the fatty acid: soap. Saponification is a type of esterification.

Questions

1. Draw the condensed structure or structural formula of the following compounds: K/U C
   (a) 3-methylhexanoic acid
   (b) propyl pentanoate
2. Name the following compounds: K/U C
   (a) 

   (b) 

3. Octyl ethanoate is used in artificial orange flavouring. What molecules could be used to synthesize this ester? Write condensed structural formulas for all the organic molecules in this reaction. K/U C
4. Carboxylic acids, like other organic molecules, are flammable. Write a balanced chemical equation for the combustion of ethanoic acid. K/U
5. Compare the solubility and melting points of ethane, ethanol, and ethanoic acid. Explain. K/U T/I
6. The fatty acid in corn oil is oleic acid:
   $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
   Draw the structure of oleic acid, using this condensed formula. K/U C
7. Given the physical properties of olive oil, would you expect the fatty acid components to be saturated or unsaturated? What process may be necessary to convert olive oil into margarine? T/I
8. Use structural formulas to describe the synthesis of a carboxylic acid using methanol. Name all reactants and products. T/I C
9. Create a flow chart showing the steps needed to transform but-1-ene to butanoic acid. T/I C
10. Table 1 (page 49) lists the melting points of several alkanes and their related carboxylic acids. T/I A
    (a) Predict how the melting point of methanol compares to the melting points of compounds in the table.
    (b) Research the melting point of methanol.
    (c) Give a theoretical explanation for the melting point of methanol, compared to those of the other compounds.
11. Sour milk and yogurt contain a common carboxylic acid. Research the identity of this compound, its structure, and how it is produced industrially. Prepare a poster of your findings. T/I C A
12. Research at least two examples of saponification reactions taking place in the environment. Do you think that these reactions are, on balance, beneficial or damaging to the environment? Explain. T/I A

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