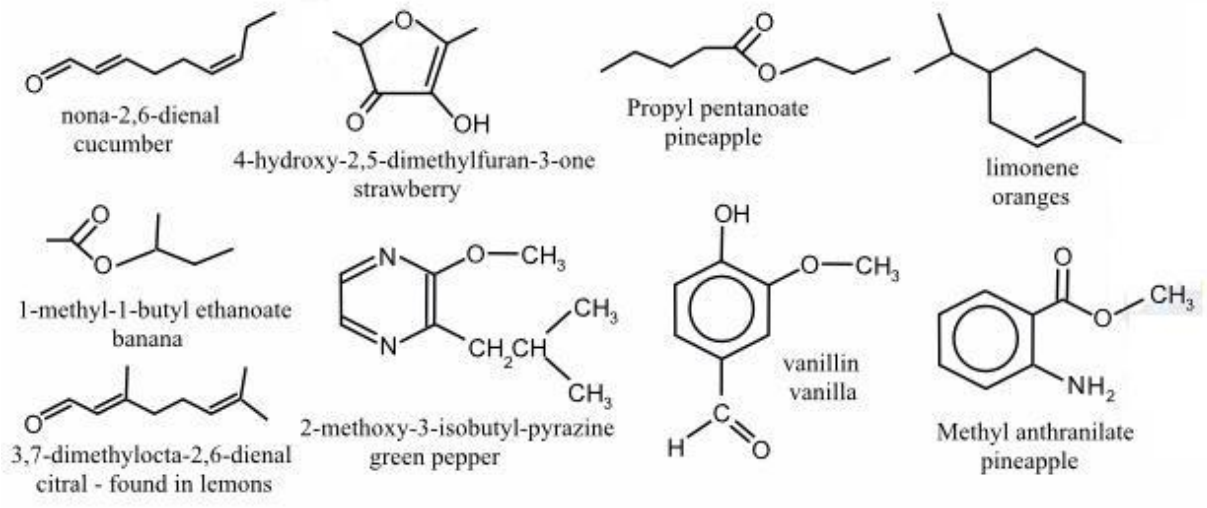
Name _____ Class _____

CfE Higher Chemistry
Unit 2 -Nature's Chemistry



(1) Revision of Hydrocarbon Structures

(Alkanes, alkenes, alkynes, cycloalkanes, cycloalkenes)

(2) Revision of Systematic naming, Isomers, Addition reactions.

(3) New Families and their Reactions

Alcohols are a large group of organic molecules all of which contain at least one **hydroxyl** (OH) **group** as the **functional group**. A functional group allows organic molecules to react. Ethanol is an example of an alcohol and is the second member of its homologous series based on the corresponding alkanes.

Complete the table below for **straight-chain** alcohols with the functional group **at the end** of the molecule:

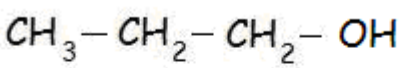
Number of Carbon Atoms	Name of Alcohol	Formula	Full Structural Formula	Shortened Structural Formula

The General Formula for the Alcohols is _____

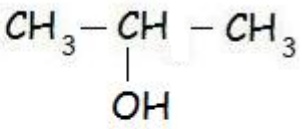
Naming alcohols

Always draw the **full structural formula** before naming any organic molecule. The **oxygen atom** from the hydroxyl group **must** be joined to a carbon atom as per valency rules then apply systematic naming. Note that branching can occur **but** the hydroxyl group has **priority** over branches. From propanol onwards, isomerism can occur because the position of the hydroxyl group can be changed. The rules are:

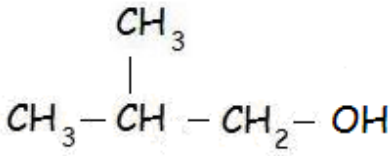
- Select longest hydrocarbon chain containing hydroxyl group and name it
- Number the carbon atoms from the end nearest the OH group
- Name the branches and indicate their positions as shown below

1. 

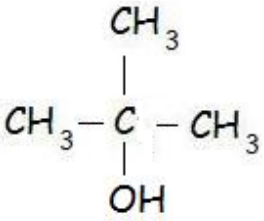
Propan - 1 - ol

2. 

Propan - 2 - ol

3. 

2 - methylpropan - 1- ol

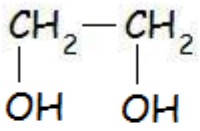
4. 

2 - methylpropan - 2 -ol

No. 2 can also be represented as $CH_3CH(OH)CH_3$

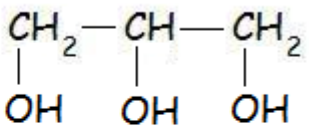
No. 4 can also be represented as $CH_3C(CH_3)(OH)CH_3$

Some alcohols have more than one hydroxyl group:

5. 

ethane-1,2-diol

(ethylene glycol, found in antifreeze)

6. 

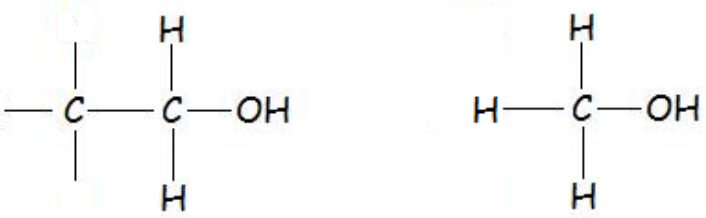
propane-1,2,3-triol

(glycerol)

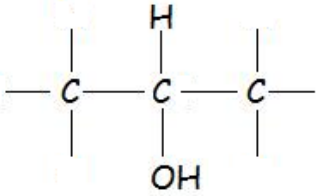
Primary, Secondary and Tertiary Alcohols

There are different types of alcohol: primary, secondary and tertiary alcohols. This is determined by the position of the OH group on the carbon backbone.

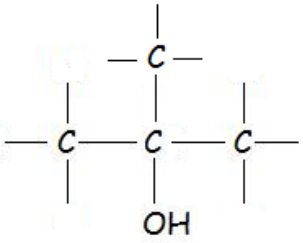
A **primary alcohol** has 2 (or 3) hydrogen atoms attached to the same carbon atom as the hydroxyl group:



A **secondary alcohol** has only 1 hydrogen atom attached to the same carbon atom as the hydroxyl group:

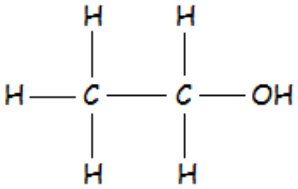


A **tertiary alcohol** does not have any hydrogen atoms attached to the same carbon atom as the hydroxyl group:



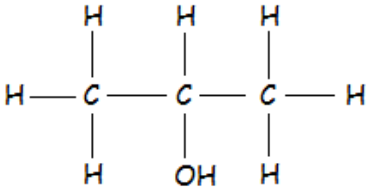
Examples:

Ethanol



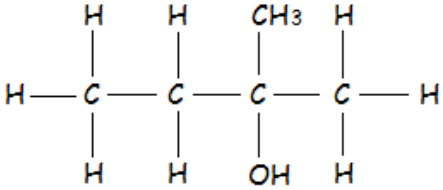
primary

Propan – 2 – ol



secondary

2-Methylbutan – 2 – ol



tertiary

Reactions of Alcohols

All alcohols can be burned (**oxidised**) in a good supply of oxygen to produce _____ _____ and _____. We usually call this a _____ reaction. Combustion is an extreme form of **oxidation**.

Write the **balanced** formula equations for the complete combustion of 1. methanol, 2. ethanol and 3. propanol below:

1. _____

2. _____

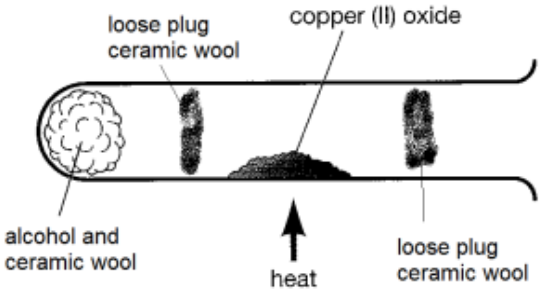
3. _____

Some alcohols undergo **mild oxidation** which does not produce carbon dioxide and water, but produces **new organic molecules** instead. The new products depend on the **type** of alcohol used.

A **mild oxidising agent** is used to oxidise the alcohol while **the oxidising agent is reduced**:

- Acidified potassium dichromate
- Acidified potassium permanganate
- Benedict's solution
- Hot copper (II) oxide

When hot copper (II) oxide is used, the alcohol vapour is passed over the oxidising agent.



As the alcohol is oxidised, the copper (II) ions are reduced to copper atoms as shown in the ion electron equation below:

Copper: _____

Cu^{2+} = _____ agent

Repeat this for the reduction of acidified dichromate ions below using your data book:

Dichromate: _____

$Cr_2O_7^{2-}$ = _____ agent

Which Type of Alcohols Undergo Mild Oxidation?

Acidified potassium dichromate solution can be used to find out which alcohols can undergo mild oxidation. If the alcohol is oxidised, the acidified potassium dichromate will be reduced as follows:

$Cr_2O_7^{2-}(aq)$	+	$14H^+(aq)$ + $6e^-$	→	$2Cr^{3+}(aq)$	+	$7H_2O$
Dichromate Ion				Chromium (III)		
Orange			→	Blue/green		

Why is this a reduction reaction? _____

What happens to the potassium ions in the potassium dichromate solution?

_____

Oxidising Alcohols

Aim

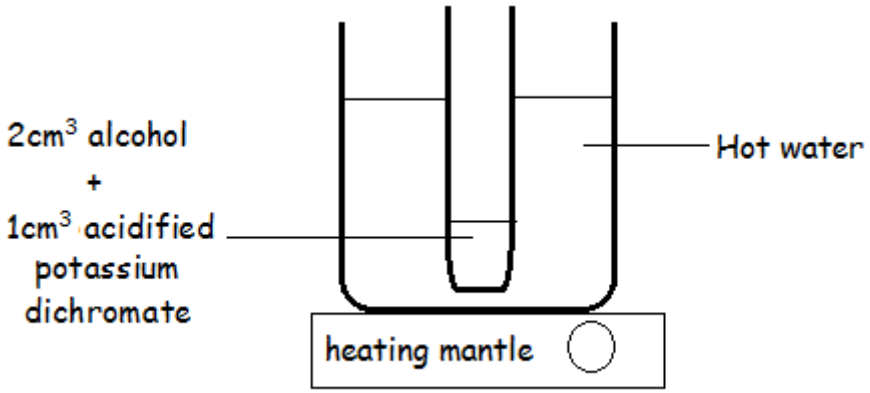
To find out which type of alcohol undergoes oxidation.

Method

1. A 2cm **depth** of each type of alcohol to separate **labelled** test tubes.

2. About 0.5 – 1cm^3 of acidified potassium dichromate solution was **slowly** to each test tube.

3. The mixture was heated in a water bath.



Results

A colour change occurs with _____

Conclusion

_____ and _____ alcohols can be oxidised using a mild oxidising agent but _____ alcohols cannot.

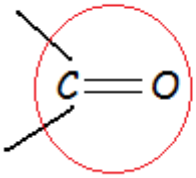
Products of Mild Oxidation

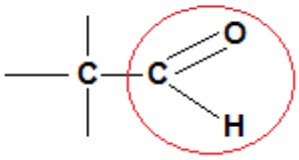
Only primary and secondary alcohols can undergo mild oxidation. These reactions produce new families of organic chemicals:

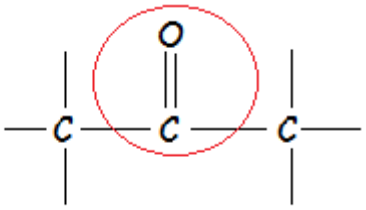
Primary alcohol	→	Aldehyde/Alkanal
ethanol	→	**ethanol**
Secondary alcohol	→	Ketone/Alkanone
propan – 2 – ol	→	**propanone**
Tertiary alcohol	→	**no reaction**

Aldehydes/alkanals)

The **functional group** in aldehydes and ketones is called the **carbonyl group**:







The **position** of the carbonyl group is **different** in aldehydes and ketones:

Aldehydes/alkanals – the carbonyl group is at the **end** of the molecule.

Ketones/alkanones – the carbonyl group is **within** the molecule **linked** to 2 other carbon atoms:

Aldehydes and ketones are further examples of homologous series. Their names are derived from the corresponding alkanes:

- Propane → propanal
- Propane → propanone

- Pentane → pentanal
- Pentane → pentanone

Use this information to complete the 2 tables on the following pages for alkanals and alkanones:

Number of Carbon Atoms	Name of Alkanal	Full Structural Formula	Shortened Structural Formula

Number of Carbon Atoms	Name of Alkanone	Full Structural Formula	Shortened Structural Formula

The General Formula for the aldehydes/alkanals is _____

The General Formula for the ketones/alkanones is _____

Since Aldehydes and Ketones have the same general formula, they must be _____.

Systematic Naming and Isomers

Aldehydes and ketones are named systematically as before. In aldehydes the **carbonyl** functional group is **always** at the end of the molecule so isomerism can only occur when the position of any branches is altered. Draw 2–methylpentanal and 3–methylpentanal below to illustrate this:

In ketones the position of the **carbonyl** functional group is **never** at the end of the molecule but can be anywhere **within** the molecule. This leads to **isomerism** from _____ onwards.

Draw butanone, pentan–2–one and pentan–3-one to illustrate this:

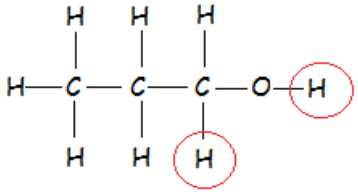
Further isomerism occurs when the position of branches is altered. Draw 2,2-dimethylpentan-3-one and 2,4-dimethylpentan-3-one below to illustrate this:

Summary of Oxidation so far

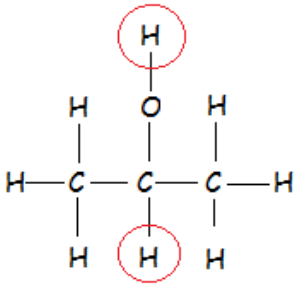
Primary alcohol	→	Aldehyde (Alkanal)
ethanol	→	**ethanal**
Secondary alcohol	→	Ketone (Alkanone)
propan – 2 – ol	→	**propanone**
Tertiary alcohol	→	**no reaction**

Further oxidation?

When primary alcohols are oxidised to alkanals, the hydrogen atom of the hydroxyl group is removed along with one of the hydrogen atoms on the **shared** carbon atom.



When secondary alcohols are oxidised to alkanones, the hydrogen atom of the hydroxyl group is removed along with the only hydrogen atom on the **shared** carbon atom.



Look at structures of aldehyde and ketones. Could any of them be further oxidised?

Aim

To use the mild oxidising agents, acidified potassium dichromate solution, Benedict's solution and Tollens' reagent, to distinguish between an aldehyde and a ketone.

Hypothesis

I think that _____ can be oxidised further because _____

Hazards - **Read all hazards** associated with the chemicals you will use.

- Carbonyl compounds are highly flammable, vapours irritate eyes, skin and lungs!! They are poisonous so do not ingest!!
- 0.1 mol l^{-1} potassium dichromate is toxic if swallowed. It is carcinogenic and very toxic by inhalation. It is also a skin sensitiser and is very toxic to the aquatic environment.
- 1 mol l^{-1} sulphuric acid irritates the eyes.
- Benedict's solution contains copper salts and so is harmful if swallowed.
- Tollens' reagent contains diluted sodium hydroxide which irritates the skin and eyes.

Care

- Wear eye protection and immediately wash off any chemical spillages on the skin.
- When working with Tollens' reagent and carbonyl compounds wear gloves.

Disposal

Dispose of all organic waste in the **organic waste beaker** provided.

Set up all of the reactions at the same time – label all test tubes.

Method 1

1. A hot water bath was set up on a hot plate/heating mantle.
2. 1 cm^3 (1cm depth) of potassium dichromate, 0.1 $moll^{-1}$ was added to 2 test tubes
3. 2 cm^3 (2cm depth) of sulfuric acid, 1 $moll^{-1}$, was added to acidify the potassium dichromate solution.
4. 5 drops of the aldehyde was added to one test tube and 5 drops of the ketone to the other.
5. Both test tubes were placed in the water bath and any changes observed and recorded.

Method 2

1. Benedict's solution was added to two test tubes to a depth of about 3 cm.
2. 5 drops of the aldehyde was added to one test tube and 5 drops of the ketone to the other.
3. Both test tubes were placed in the water bath and any changes observed and recorded.

Method 3

Repeat method 2 but use Tollens' reagent and two **very clean test** tubes instead of benedict's solution.

Results

Test	**Observations with Aldehyde**	**Observations with Ketone**
Acidified potassium dichromate		
Fehling's solution		
Tollens reagent		

Conclusion

_____ can be further oxidised but _____ cannot because _____

Summary so far

Oxidation can be thought of as the gaining of **oxygen** atoms **or** the loss of **hydrogen** atoms resulting in an **increase** in the oxygen : hydrogen ratio.

Reduction can be thought of as the losing of **oxygen** atoms **or** the gain of **hydrogen** atoms resulting in a **decrease** in the oxygen : hydrogen ratio.

Name	**Formula**	**oxygen:hydrogen ratio**	**Answer**
	C_2H_5OH		0.17
	CH_3CHO		
	CH_3COOH		

Oxidation of ethanol → ethanal and oxidation of ethanal → ethanoic acid **increases the O:H ratio**.

Complete Summary of Oxidation Reactions

Primary Alcohol → →

Secondary Alcohol → →

Tertiary Alcohol → →

Reminder

Now that you understand the mechanism of oxidation of organic molecules, is there any new information you can add to your **Research Notes** e.g. changes in O:H ratio for the oxidation of vitamin C??

Carboxylic Acids

_____ but not _____ can be further oxidised to form carboxylic acids using a variety of mild oxidising agents. Alkanoic acids are another **homologous series** based on the corresponding alkane.

They are the oxidation product of aldehydes **so** the functional group must be at the **end of the molecule**. The functional group is the **carboxyl group**:

Number of Carbon Atoms	Name of Acid	Full Structural Formula	Shortened Structural Formula

Branched carboxylic acids.

Branched chain carboxylic acids with no more than 8 carbon atoms in their longest chain should be named from structural formulae. Given the name of a branched chain carboxylic acid structural formulae should be drawn and molecular formula written.

Your teacher will give you some examples to try.

Reduction Reactions

Carboxylic acids can be reduced in stages back to the original parent aldehyde and alcohol:

→ → **Primary Alcohol**

Alkanones can be reduced back to the parent secondary alcohol:

→ **Secondary Alcohol**

What is the effect on the oxygen : hydrogen ratio? _____

Properties and Reactions of Carboxylic Acids

When hydrochloric acid, **a strong acid**, is added to water complete dissociation occurs (single headed arrow). There is no equilibrium; only hydrogen ions and chloride ions are present so there is a high concentration of $H^+(aq)$ and the pH is low:

$$HCl(g) + H_2O(l) \rightarrow H^+(aq) + Cl^-(aq)$$

Acids react with bases to form salts:

$$HCl(aq) + NaOH(aq) \rightarrow Na^+Cl^-(aq) + H_2O(l)$$

Carboxylic acids, like ethanoic acid, are **weak acids** so they only **partially dissociate** in water (double headed arrow). An equilibrium is established in which all 4 molecules are present. At equilibrium there is a low concentration of $H^+(aq)$ so the pH is higher than expected:

$$CH_3COOH(l) + H_2O(l) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Weak acids can still react with bases to form salts:

$$CH_3COOH(l) + NaOH(aq) \rightarrow \_\_\_\_\_(aq) + H_2O(l)$$

More examples

Your teacher will give you some examples to try.

$$CH_3COOH(l) + KOH(aq) \rightarrow \_\_\_\_\_(aq) + H_2O(l)$$

$$CH_3CH_2COOH(l) + NaOH(aq) \rightarrow \_\_\_\_\_(aq) + H_2O(l)$$

4. Esters, Fats and Oils

An **ester** is the product of the **reaction between the functional groups** in a carboxylic acid and an alcohol. Water is also produced. This is called a _____ reaction and is also known as an _____. The hydroxyl group of the acid reacts with the hydrogen atom of the hydroxyl group in the alcohol to form water. animations - Welcome to the NQ Higher Sciences website

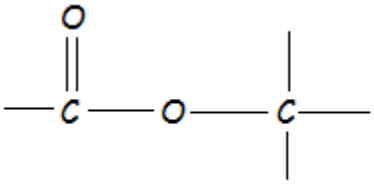
Carboxylic acid functional group:  Alcohols functional group: _____

The name of an ester is found by replacing the –ol ending of the alcohol with the ending -yl (ethanol → ethyl) and replacing the –oic ending of the acid with –oate (methanoic → methanoate)

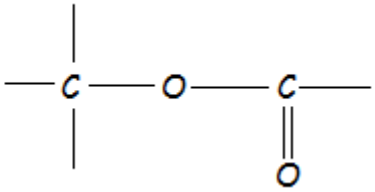
Example: Ethanoic acid + propan – 1 – ol → propyl ethanoate

Example: Propan – 2 – ol + methanoic acid (you would not be expected to name this unless PS)

Esters contain an **ester link** as the functional group as shown in the diagrams below:

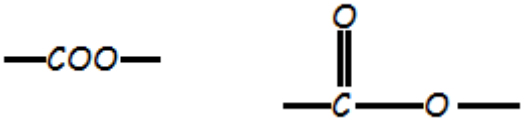


which can also be drawn like this

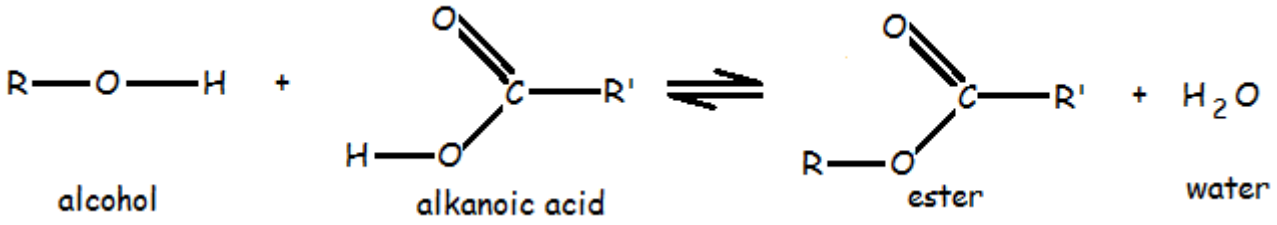


Draw a dotted line through the diagrams to show which part is from the alcohol and the acid.

The ester link can also be shown like this:



More ways to represent the reaction between an alcohol and an alkanoic acid:



The double headed arrow is used to show that these reactions are **reversible**. The R and R' represent different alkyl groups.

Esters can also be represented as shortened structural formulae:

$CH_3COOC_2H_5$ or $C_2H_5OOCCH_3$

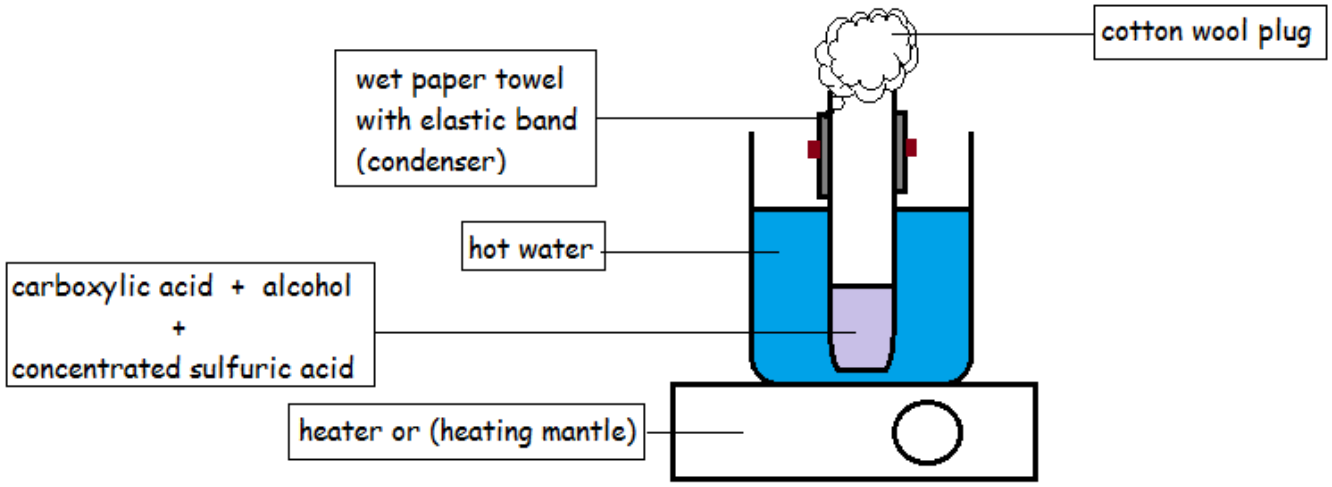
Draw a dotted line through the above formulae to show which part is derived from the alcohol and the acid. **You may find it easier to draw the full structure first!**

You should be able to name an ester from the names of the parent alcohol and alkanoic acid or from full or shortened structural formulae.

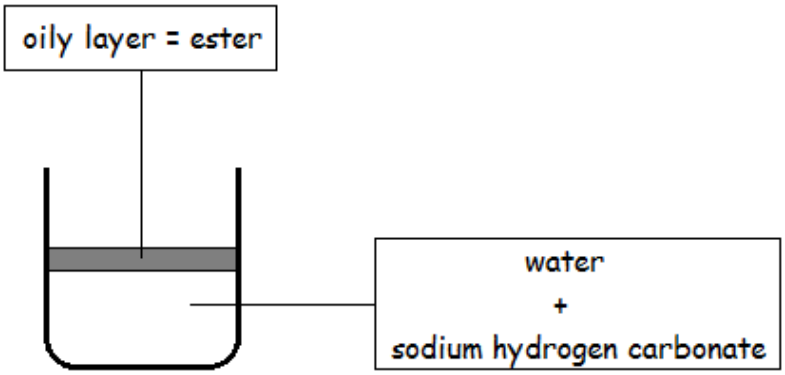
Your teacher will give you more examples to try.

<u>Making an Ester</u> Carry out the experiment to make an ester and investigate their properties:

1. Set up a hot water bath.
2. Choose an alkanoic acid and alcohol from the results table on the next page to make an ester.
3. Add 1 cm depth alkanoic acid (or a spatula if solid) to 1cm depth alcohol in a boiling tube.
4. Carefully add 5 drops of concentrated sulfuric acid (dangerous stuff which contains H^+ ions as the catalyst)
5. Wrap a paper towel condenser around the top of the boiling tube and insert a loose cotton wool 'plug'. This will prevent escape of reactant/products when they evaporate.
6. Heat in the water bath for about 20 minutes or longer then put in to a test tube rack to cool down before the next step.



7. Add about 20cm^3 of 1 mol l^{-1} sodium hydrogencarbonate solution to a small beaker.
8. Slowly pour the reaction mixture into the sodium hydrogencarbonate solution. This neutralises the sulfuric acid and any remaining carboxylic acid and removes the smell of the carboxylic acid.
9. Gently swirl the contents of the beaker until it stops bubbling.ee if there is any sign of the ester separating from the aqueous mixture.
10. Check for immiscibility (an oily layer on top of the aqueous layer) and carefully smell the ester.



Results

Carboxylic acid	Alcohol	Ester	Smell of ester
ethanoic acid	$C_5H_{11}OH$		
		$CH_3COOC_2H_5$	
methanoic acid	ethanol		
		propyl methanoate	
salicylic acid	methanol	methyl salicylate	

Problems with Ester Production

Ester formation is slow at room temperature and the **yield** of ester is low because it is a **reversible** reaction. The rate can be increased in 2 ways:

- increase the temperature of the reaction
- use concentrated sulfuric acid as a catalyst to lower the _____
- use concentrated sulfuric acid to remove water from the products to encourage the forward reaction

These issues will be addressed in more detail in the next unit so it is important to learn and understand the reaction and its problems now!

Uses of Esters

Esters are oily liquids which usually have pleasant **fruity** smells. They have a range of uses: **food flavourings**, **perfumes** (characteristic smells) and **solvents**.

Twig - Oil Products: Esters and Perfumes- Learn Chemistry

Food flavourings: pear drops, strawberry 'flavoured' yoghurt, raspberry 'flavoured' ice lolly.

Perfumes: jasmine, rose, citrus.

Solvents: nail varnish remover (ethyl ethanoate or acetone), paints, glues

FYI

Ethyl ethanoate is a **solvent** used to extract caffeine from coffee and tea. Labels on packaging claim that the tea or coffee has been "naturally decaffeinated" because ethyl ethanoate is a chemical found naturally in many fruits. Caffeine ($C_8H_{10}N_4O_2$) is an **alkaloid** and is produced by plants. The name alkaloid means "**alkali-like**".

Natural fruit flavours contain subtle blends of some of the esters in the following table:

Name	Shortened Structural Formula	Odour/Flavour
	$CH_3COO(CH_2)_4CH_3$	Banana
	$CH_3COO(CH_2)_4CH_3$	Orange
Methyl Butanoate		Pineapple
3-Methylbutyl Butanoate	$CH_3(CH_2)_2COO(CH_2)_2CH(CH_3)_2$	Apple
	$CH_3COOC_3H_7$	Pear
Methyl-1-butyl ethanoate	$CH_3COOCH(CH_3)C_4H_9$	Banana
2-Methylpropyl methanoate		Raspberry
	$C_3H_7COOC_5H_{11}$	Apricot, Strawberry
Benzyl ethanoate	$CH_3COOCH_2C_6H_5$	Peach, flowers
Ethyl methanoate		
Methyl 2-aminobenzoate	$C_6H_4(NH_2)COOCH_3$	Grapes
Benzyl butanoate	$C_3H_7COOCH_2C_6H_5$	Cherry

Points to Note

Making an ester is a **reversible** reaction. The **forward** reaction makes an ester using **concentrated sulfuric acid** as a **catalyst**. Concentrated sulfuric acid also slows down the **reverse** reaction.

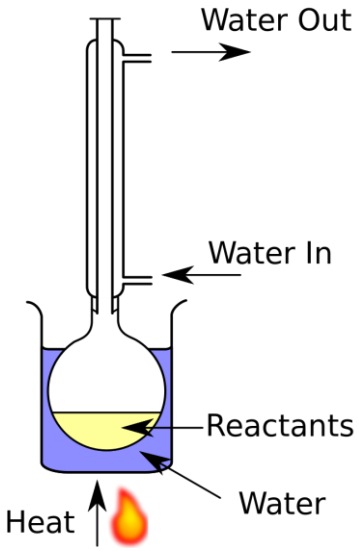
The **reverse** reaction converts the ester back in to an alcohol and alkanoic acid. This is an hydrolysis reaction. **Dilute alkali** e.g. sodium hydroxide or potassium hydroxide is used.

Hydrolysis of Esters

Esters can be hydrolysed (the **reverse** reaction) to produce the parent _____ and the parent _____ by replacing the water which was lost in the **forward** reaction (esterification/condensation reaction).

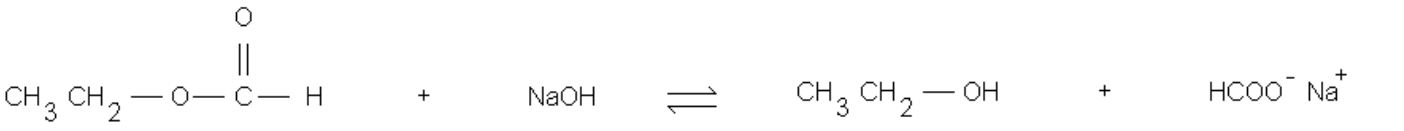
Ester + Water ⇌ Alcohol + Alkanoic Acid

A **dilute alkali** is used to catalyse the reaction and the mixture heated under **reflux**:



Look at this diagram carefully; it is exactly the same as the apparatus you used to make an ester. Look back now. The esterification diagram is on page ___ of this booklet.

The sodium salt of the alkanoic acid is produced if dilute sodium hydroxide is used. The potassium salt of the alkanoic acid is produced if dilute potassium hydroxide is used:



ethyl methanoate + NaOH ⇌ ethanol + sodium methanoate

An inorganic acid like HCl (aq) is then used to displace the organic acid from the salt:

$$HCOO^- Na^+ + HCl \rightarrow HCOOH + NaCl$$

methanoic acid

Your teacher will give you some examples to try.

Edible Fats and Oils

Fats and oils are **natural esters**. Complete the table to show the sources of some fats and oils.

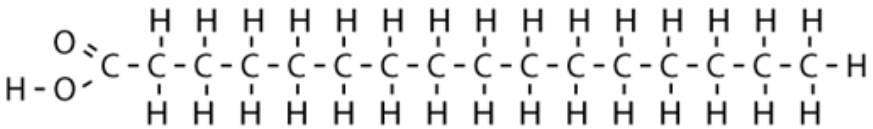
Name of fat or oil	Animal, vegetable or marine
Sunflower oil	
Linseed oil	
Suet	
Cod liver oil	
Lard	
Castor oil	
Palm oil	
Rape seed oil	

Natural oils have vegetable and marine (fish) origins while natural fats have _____ origins. Also, solids fats are mainly from _____; liquid oils are mainly from _____. Fats and oils are an essential part of the **diet** providing us with **energy**. Fats and oils are a more concentrated source of **energy** than _____. They are essential for the transport and storage of fatsoluble vitamins in the body

Fats and oils are **natural esters** from the reaction between long chain carboxylic acids and the alcohol **glycerol**. Glycerol has the systematic name propan 1,2,3 triol. Draw the full structural formula for glycerol below:

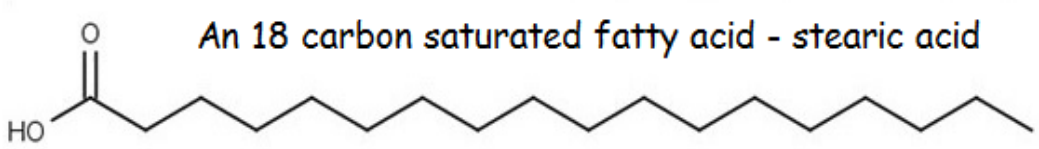
Glycerol is a trihydric alcohol because it contains three alcohol groups. Each molecule of glycerol reacts with ___ molecules of fatty acids. Each fat/oil molecule produced contains ___ ester linkages.

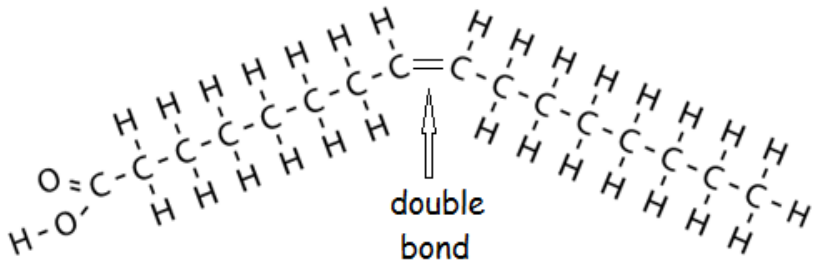
The **long** chain **carboxylic acids** are known as **fatty acids**. They can be saturated or unsaturated:



saturated fatty acid

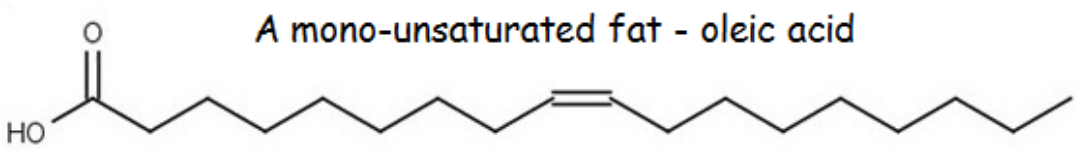
This structures can be represented in a different way:



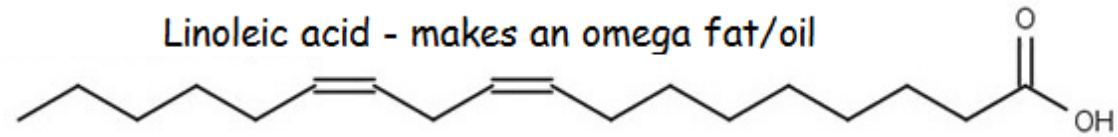


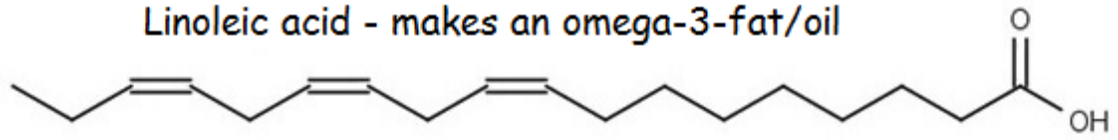
unsaturated fatty acid

This structures can be represented a different way:

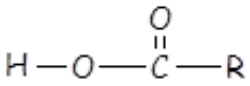


More examples:

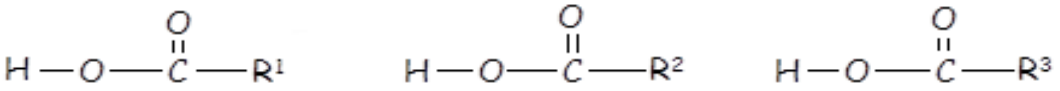




Fatty acid structures are shortened to make them easier to draw:



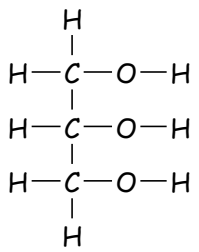
If the carbon chains attached to the carboxyl group are different they may be represented as shown below:



The 3 fatty acids which react with glycerol may all be the same or any combination of different carboxylic acids.

To follow the mechanism of the reaction, glycerol is drawn 'north to south' as shown below:

Complete the reaction mechanism of a molecule of glycerol reacting with 3 molecules of $C_{17}H_{35}COOH$:



_____

Now show the mechanism when a molecule of glycerol reacts with 3 different fatty acids:

Is $C_{17}H_{35}COOH$ a saturated or an unsaturated fatty acid?

<u>Melting points of Fats and Oils</u>

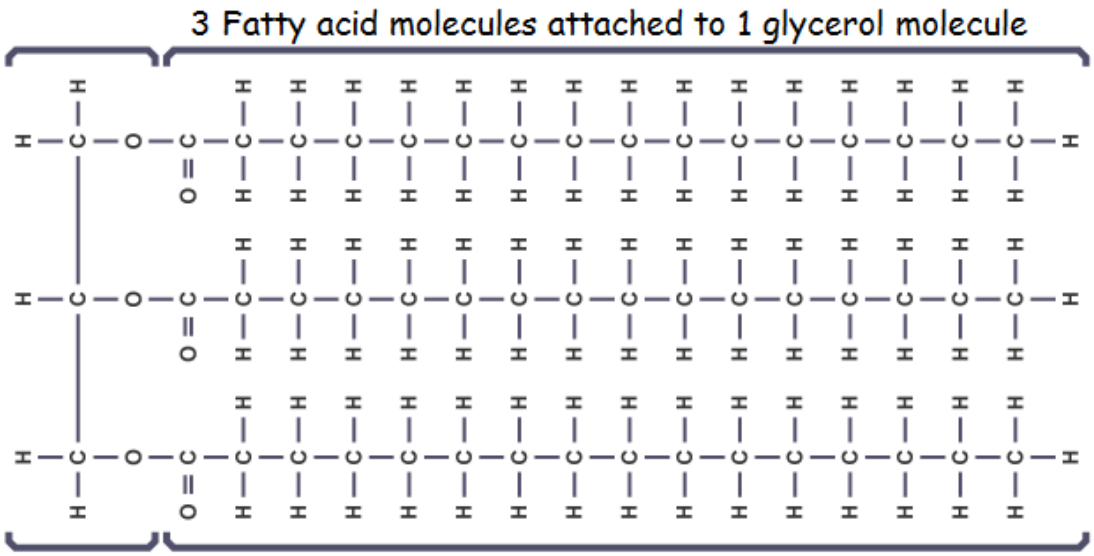
Fats and oils are also known as triglycerides (an ester made from glycerol and three fatty acids). Most fats and oils in nature are mixtures of triglycerides in which the fatty acid molecules may or may not be identical. The properties of a fat or an oil depend on the fatty acids which are combined with the glycerol in each triglyceride. Fats are _____ at room temperature while oils are _____.

Fatty acids are saturated or unsaturated straight chain carboxylic acids which range in size from C_4 to C_{24} carbon atoms, but mainly C_{16} and C_{18}.

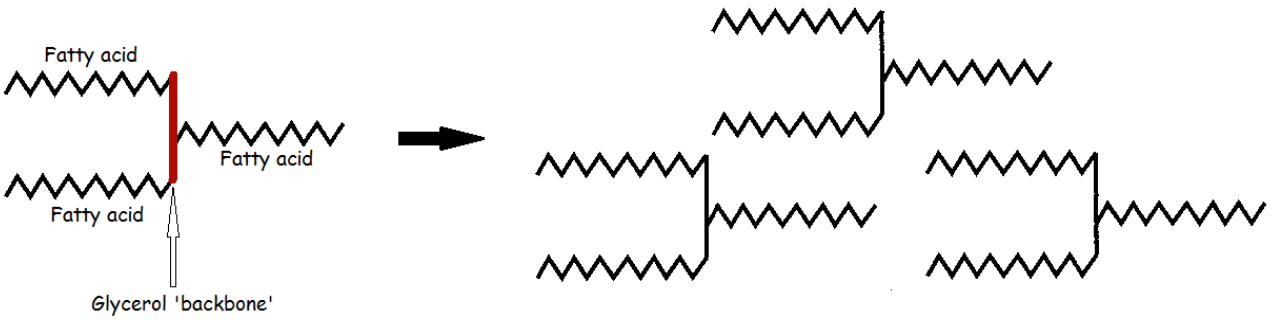
Fatty acid	Formula	Saturated or unsaturated
palmitic acid		
stearic acid		
linoleic acid		
oleic acid		

The Structure of Fats and Oils

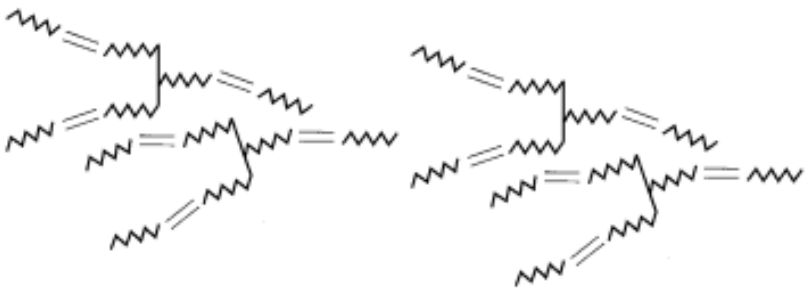
The structure below represents a fat molecule containing 3 **saturated** fatty acids:



This structure can be simplified to a 'tuning fork' structure to show how molecules pack closely together in a fat. Molecules which can **pack closely together** have **stronger** Van der Waals forces **between** molecules so are **solid** at room temperature. **Fats** have **higher melting points** than oils.



Just **one** carbon to carbon double bond in a fatty acid causes a **distortion** in the tuning fork shape. Molecules **cannot pack closely together** due to their irregular structure have **weaker** Van der Waals forces between the molecules and thus lower melting points. **Oils have lower melting points than fats** so are **liquid** at room temperature:



Marine animals living in cold oceans mostly contain body oils rather than fats because solid fats cannot be transported round the body.

Margarine

Margarine is just an **oil** which has been 'hardened'. The oil is **reacted with hydrogen** to remove/reduce the number of carbon to carbon double bonds. This is an _____ reaction which converts unsaturated compounds into (more) saturated ones. A **nickel** catalyst is used to _____.

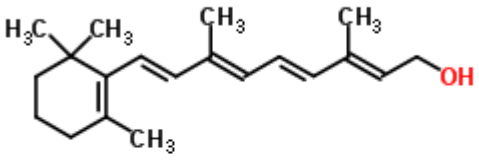
The degree of hydrogenation, use of additives and blending can produce margarines with different properties such as improved taste and appearance. Additives include:

- Flavouring to make margarine taste like butter
- Vitamin A and D to make margarine as healthy as butter*
- Colouring to make margarine look like butter

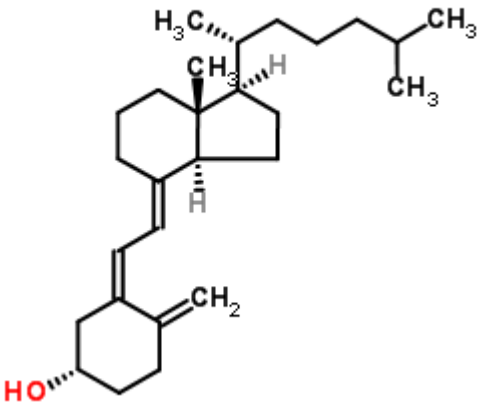
*Vitamin A, known as **retinol,** has many important functions; efficient immune system, good eyesight (so you do need to eat **carrots** and take **cod liver oil**!!!)

***Vitamin D**, known as **cholecalciferol,** is needed for intestinal absorption of calcium (to prevent rickets), iron, magnesium, phosphate and zinc. Very few foods contain vitamin D (mainly oily fish) unless the food is fortified (like margarine). Most Vitamin D is **synthesised** in the **skin** from cholesterol – **UVB radiation** from the sun is **needed** for this process. (See UVB radiation later!)

Vitamin A



Vitamin D



Examine the structure of these vitamins – are they water soluble or fat soluble? Why?

_____

_____

_____

Emulsifiers (mechanism later)

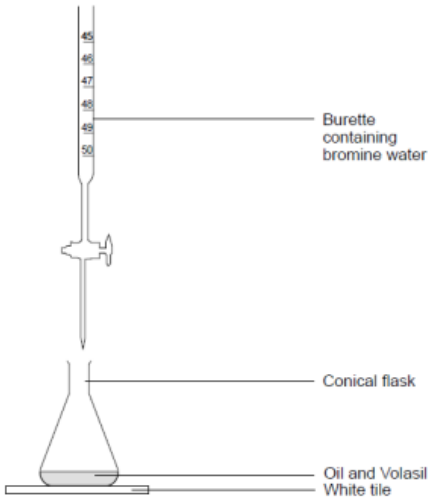
Margarine is a water/oil emulsion – a mixture of water and oil which would separate into layers without an emulsifier e.g. lecithin.

Comparison of unsaturation in fats and oils

The degree of saturation in a fat or oil can be determined by the **Iodine Number** (bromine can also be used). The iodine (or bromine) reacts with the C=C bonds, so the greater the iodine number, the greater the number of double bonds.

Method

1. Using a plastic pipette, add five drops of olive oil to 5 cm^3 of hexane in a conical flask.
2. Use a burette filled with a dilute solution of bromine water (0.02 $moll^{-1}$). **Read the burette.**
3. Run the bromine water slowly into the oil solution while shaking vigorously - the yellow colour of bromine disappears as bromine reacts with the oil.
4. Continue adding bromine water until yellow colour remains – all carbon to carbon double bonds have now been saturated so bromine now unreacted.
5. Obtain titre volume and repeat until concordant results achieved.
6. Repeat the experiment with different oils e.g. soya bean oil (vegetable), lard 'oil' (animal).



Results

Fat or Oil	Average Iodine No.
Butter	40
Beef fat	45
Lard (pig fat)	50
Olive oil	80
Peanut oil	100
Soya bean oil	180

Conclusion and Explanations

Animal fats have **lower** iodine numbers because they are more saturated (fewer C=C bonds) than oils. Vegetable fats (oils) have **higher** iodine numbers because they are more unsaturated (more C=C bonds) than fats.

Fats and oils are just mixtures of saturated and unsaturated **esters**. Each fat or oil will have a different degree of saturation/unsaturation:

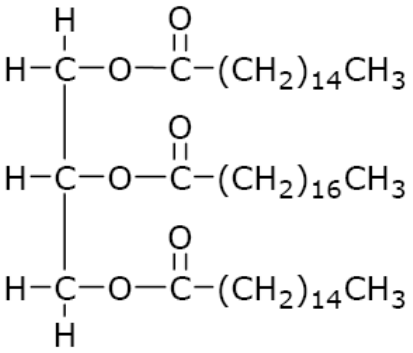
FAT	saturated	unsaturated
OIL	saturated	unsaturated

Hydrolysis of Fats and Oils

Like simple esters, fats and oils, which are esters, can be **hydrolysed** (split using 'water') to produce glycerol and the 3 fatty acid(s).

Hydrolysis of a simple ester **methyl propanoate** (revision):

Hydrolysis of fat or oil. You do not need to know what the molecule is called:



Label the ester links in the above diagram then draw the structure of the 3 fatty acids present in the molecule.

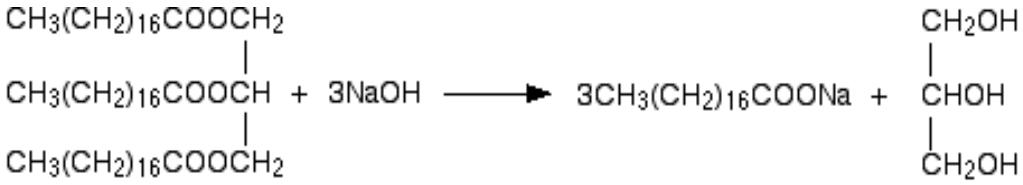
1. 2. 3.

Now draw the fat/oil molecule above using the symbol R instead of the carbon chain.

Hydrolysis can be done simply by treatment with superheated steam. In school labs hydrolysis is carried out using aqueous or alkali. You have already seen this when simple esters were hydrolysed. Look back in your booklet to find this.

(5) Soaps, Detergents and Emulsions

Fats and oils are **esters**. Fats and oils can be **hydrolysed** to make **soaps** using an **alkali**. The products of the reaction are a water-soluble **ionic salt** of the carboxylic acid and **glycerol**. The fatty acid salts are 'salted out' of the reaction mixture by adding a great excess of sodium or potassium chloride and the soap is then filtered off.

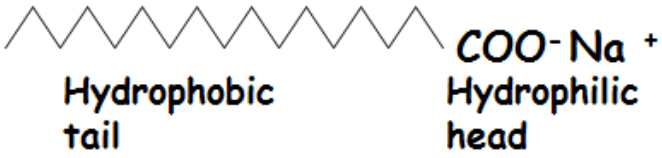


a typical fat or oil

a typical sodium salt found in soap

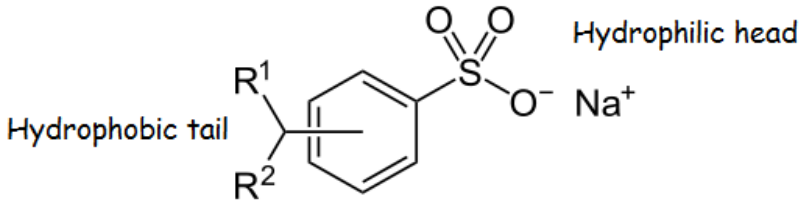
glycerol

Soaps the sodium or potassium salts of fatty acids:



Detergents

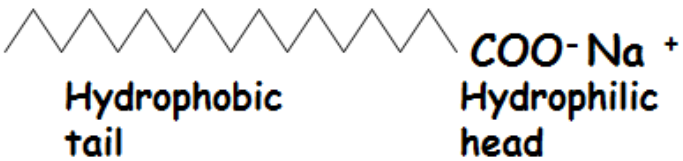
Detergents are produced by the petrochemical industry. They are used in hard water areas because, unlike soaps, they do not produce a scum on the surface of the water.



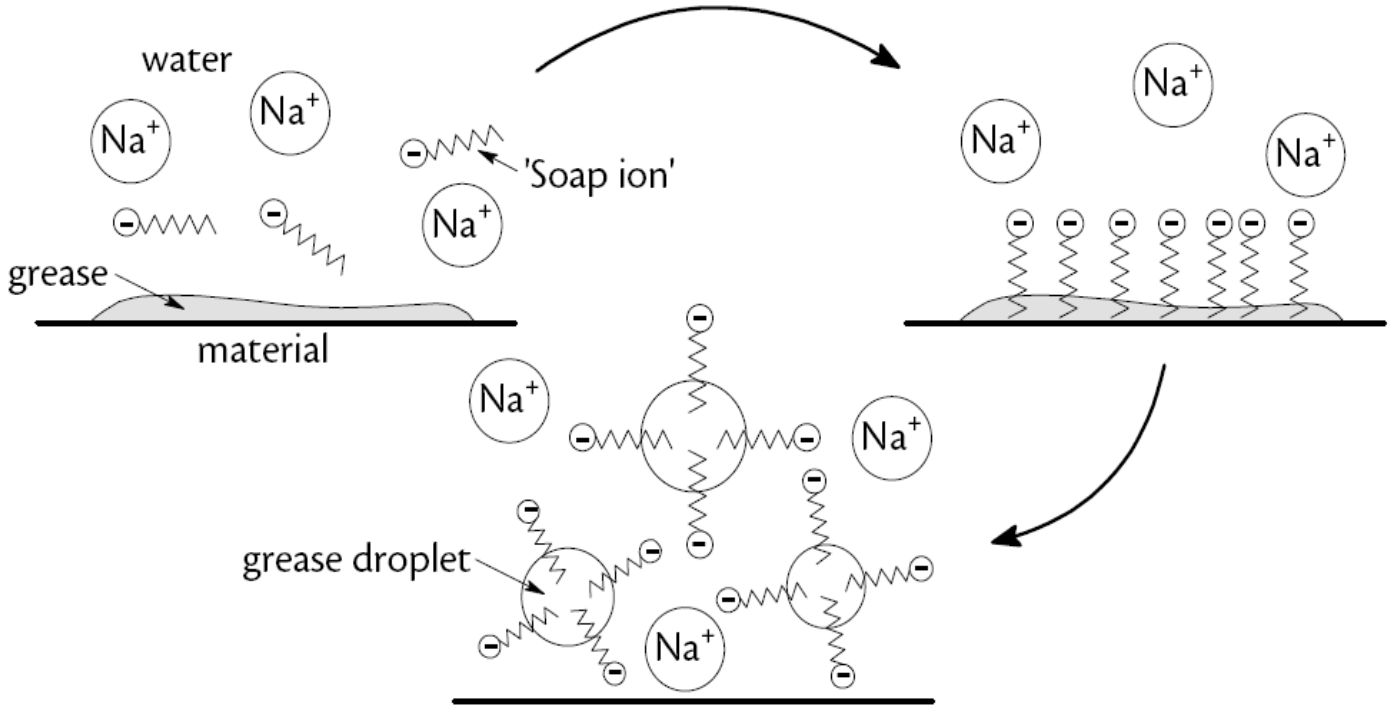
$$R^1 + R^2 = C_{11}H_{24}$$

The Cleaning Action of Soaps and Detergents

Oils and grease is insoluble in water. Soaps and detergents are 'emulsifying reagents' which make oil and water form an emulsion (a suspension of fat in water - remember margarine?). Soaps and detergents have different solubility properties because of different polarities in their structures:



The non-polar hydrophobic 'tail' attracts non-polar fat/oil molecules whilst the hydrophilic **polar** heads are attracted to polar water molecules. Large fatty 'lumps' are broken up into smaller ball-like structures called 'micelles' resulting in a suspension of fatty material in water. The following set of diagrams show how this works.

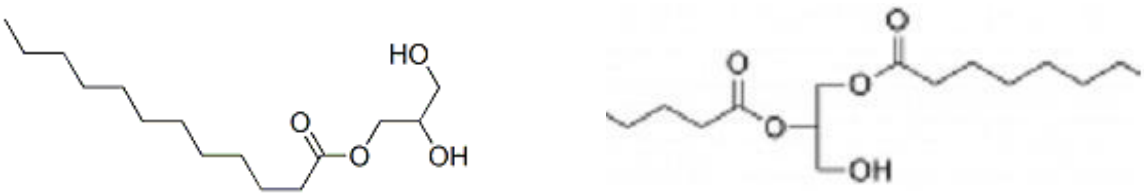


The dirt or grease is held inside the ball and suspended in the water. Repulsion between the negative charges results in a stable suspension (emulsion).

Emulsifiers in Food

Many foods, like **margarine** and mayonnaise, are **mixtures** of oil and water which could easily separate into layers. Emulsifying (re)agents, which work in exactly the same way as **soaps** and **detergents**, are added to food to maintain even suspensions of the mixture. Lecithin is used in margarine. Egg yolks or a synthetic emulsifier (xanthan gum) is used in mayonnaise. Even **dried pasta** contains an emulsifier to prevent pasta pieces sticking to each other during cooking.

Emulsifiers are usually made by reacting **edible oils** with glycerol to form molecules in which either **one** or **two** fatty acid groups are linked to a **glycerol** backbone rather than the three normally found in edible oils. The hydroxyl group(s) in these molecules are hydrophilic whilst the fatty acid chains are hydrophobic:



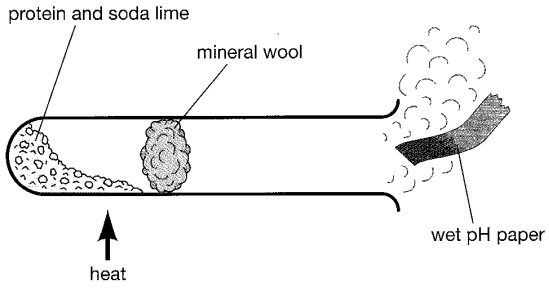
Emulsifiers have **E-numbers** which are shown on food packaging. E471 is one of the most common.

You might carry out an investigation into which foods make a good emulsifier.

(6) Proteins

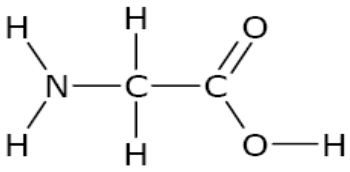
Proteins are molecules which make up the major structural materials of animal tissue such as muscle fibres, hair, nails and skin. We need protein in our diet for _____ and _____. Meat and fish are rich in protein. Proteins contain the elements carbon, hydrogen and oxygen and nitrogen.

A simple test to confirm the presence of nitrogen is shown in the diagram. The gases produced (amines or ammonia) turn moist pH paper blue so nitrogen must be present.

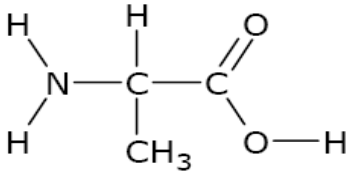


Proteins are also involved in the maintenance and regulation of life processes as haemoglobin, immunoglobulins and enzymes (biological catalysts).

Proteins are **natural polymers** made up of monomers called **amino acids**. **Amino acids** contain the **amine** functional group ($-NH_2$) and the **carboxyl** functional group ($-COOH$). Each amino acid contains **both** functional groups therefore **can react as acids and/or as bases. Natural amino acids** have the two groups bonded to the **same carbon atom** and are called alpha amino acids **(α-amino acids)**:



aminoethanoic acid
(glycine)



2-aminopropanoic acid
(alanine)

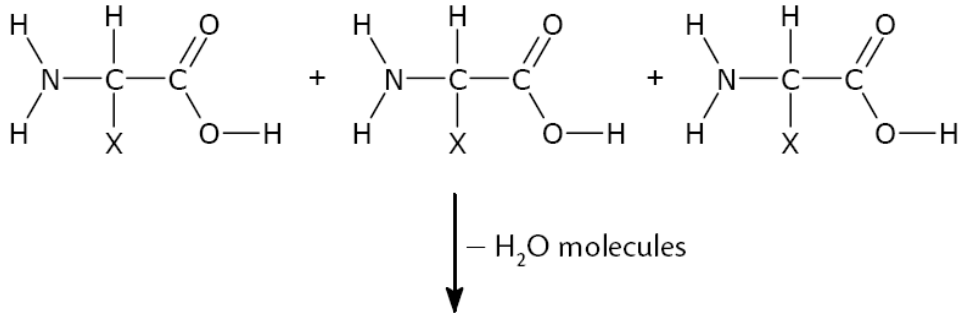
Label the acid group and the amine group in the molecules above.

20 amino acids are needed to synthesise body proteins. Since proteins can contain thousands of amino acids this means there is an enormous number of **different** proteins. 12* amino acids can be made in our body when we digest proteins. The remaining 8* **must** be obtained in our diet (**ingested)** so are known as **essential amino acids**. One **essential** amino acid missing from our diet can cause serious **deficiencies**; this could prevent the formation of an enzyme such as insulin, which controls blood sugar levels, resulting in lifelong diabetes!

* depends which text book or website you read!!

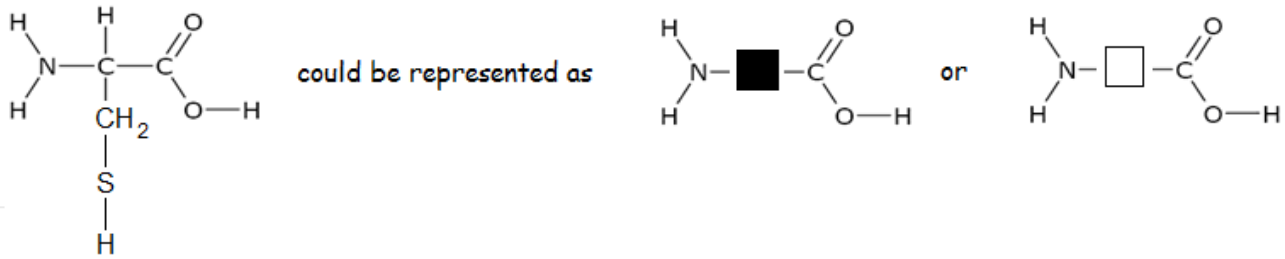
Condensation Polymerisation

An **amide link** or **peptide link** (**CONH**) is formed when the amino group of one molecule reacts with the carboxyl group of an adjacent molecule. Water is eliminated. This is condensation polymerisation. The following amino acids react to form a tripeptide:



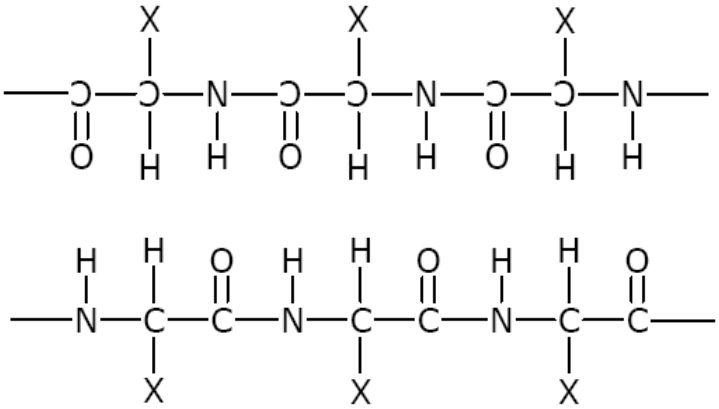
Formation of the peptide bond

X (or R) can be a Hydrogen atom, an alkyl group, or groups containing any arrangement of atoms. For example, cysteine has the structure: www.johnkyrk.com/aminoacid.html



Classification of Proteins

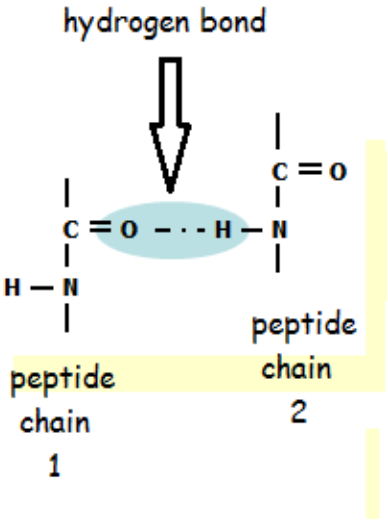
Chain of amino acids are known as a **polypeptides**. Amide (peptide links) between amino acids are polar. Hydrogen bonds can occur at these links (H atoms attracted to NOF atoms). **Show this in the diagram below:**



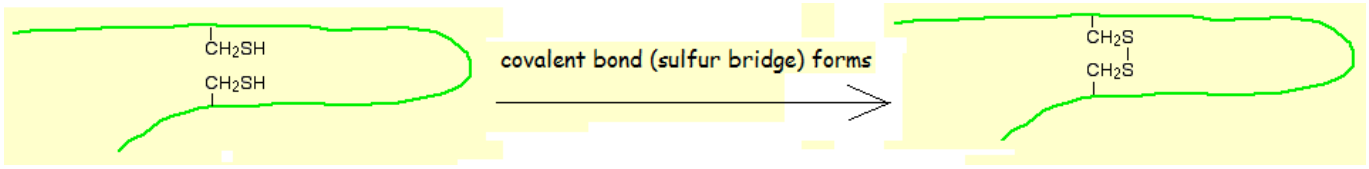
Structure of Protein

The structure of a protein depends on the amino acids present and bonding which might occur WITHIN (**intramolecular**) a single polypeptide or BETWEEN (**intermolecular**) polypeptides.

Hydrogen bonding can occur **within** a peptide chain or **between** 2 peptides:

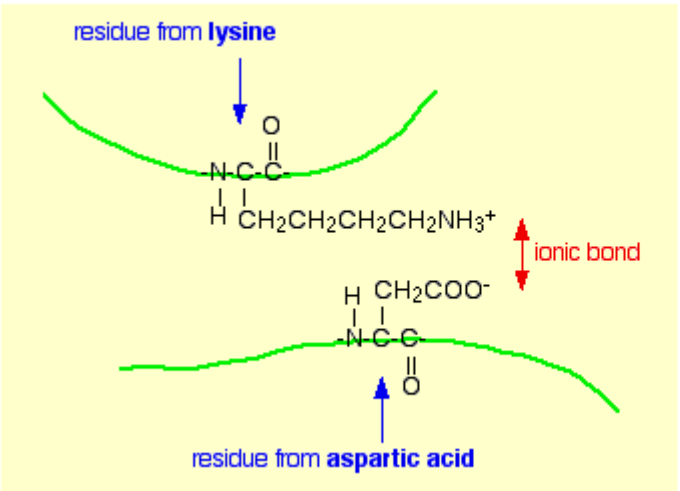


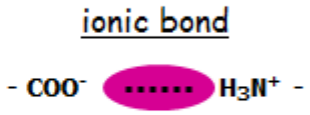
If 2 cysteine amino acids end up next to each other when a single peptide chain bends, a **covalent bond** can form between them; this is called a sulfur bridge:



Sulfur bridges can occur between peptides too.

Some amino acids have carboxylic acid or amine side groups which can react to form an ionic bond within or between peptide chains:

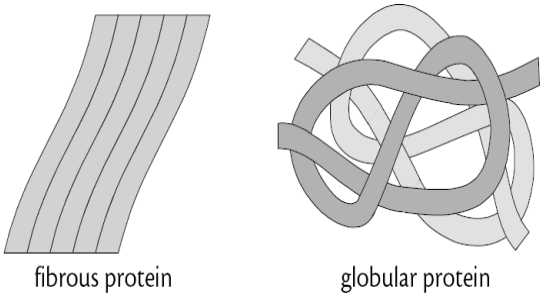




Bonding between peptide chains

Classification of Proteins

Proteins can be classified as **fibrous** or **globular.** If the H bonds occur in the same linear protein molecule, a helix structure is produced. If H bonds occur between different chains a β - pleated sheet is formed. These helices or sheets can then be folded to give fibrous or globular proteins:



Fibrous proteins are long and thin and are the major structural materials of animal tissue. For example: **skin, muscle, hair, nails**.

Globular proteins are involved in the maintenance and regulation of life processes and include **enzymes**, **hormones** such as insulin and **haemoglobin** for the transport of oxygen in the blood.

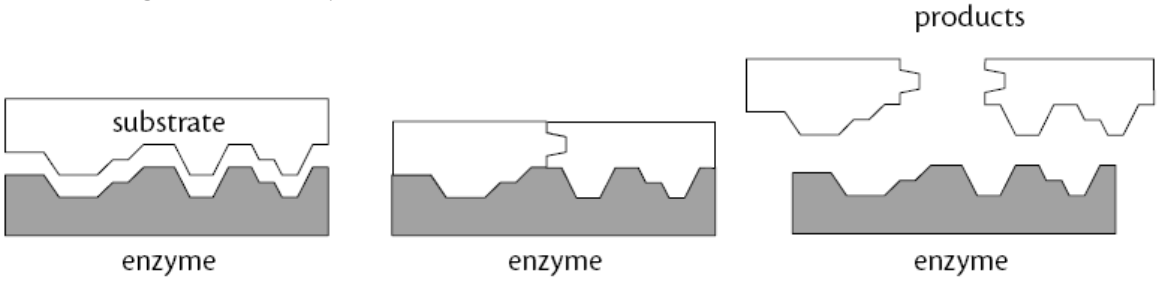
Enzymes

Enzymes are natural catalysts which lower the activation energy of biological reactions so they can take place at body temperature.

Enzymes are **specific**; amylase only catalyses the break-down of starch molecules but not the breakdown of proteins. Lipase catalyses the breakdown of fats into _____ _____ and _____ in the small intestine.

The **specificity** of enzymes is due to their molecular shapes. The 3D shapes of the molecules are the result of intramolecular and intermolecular bonds.

Enzymes are thought to work by the **'lock and key' mechanism**:



Enzymes are temperature and pH sensitive: high temperature and changes in pH can irreversibly alter the 3D structure of the enzyme. The enzyme is said to be _____. All proteins, not just enzymes, can be denatured by temperature and pH.

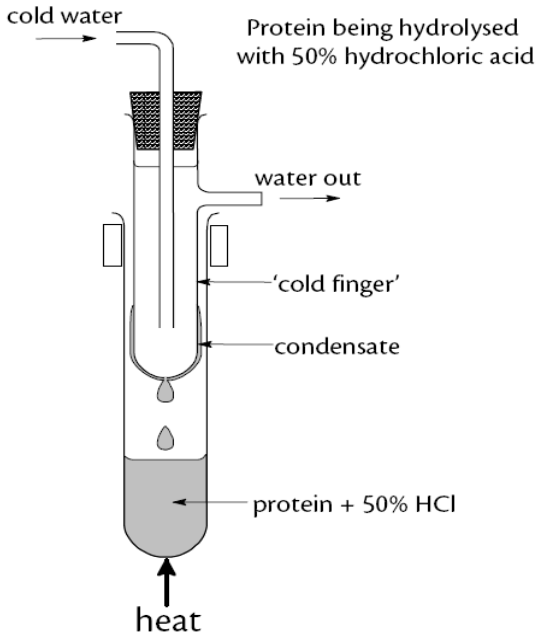
Some chemical processes involve a sequence of reactions with each stage requiring a different enzyme eg. the production of ethanol from starch in fermentation:

$$\text{starch} \xrightarrow{\text{amylase}} \text{maltose} \xrightarrow{\text{maltase}} \text{glucose} \xrightarrow{\text{zymase}} \text{ethanol} + CO_2$$

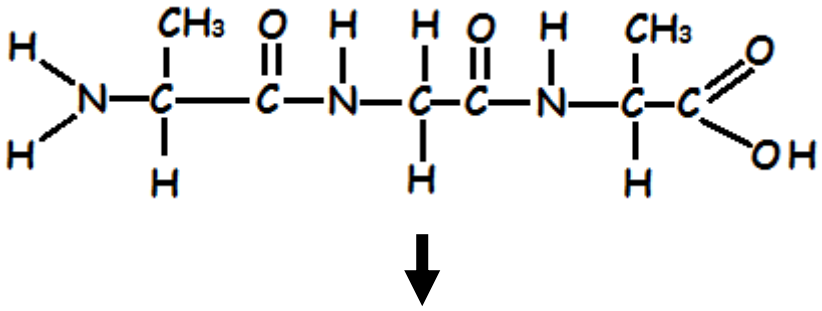
Hydrolysis (digestion) of Protein

This takes place naturally in the acid pH of the stomach with the enzyme pepsin. Large protein molecules are hydrolysed to smaller polypeptides. Further enzymes continue this hydrolysis in the gut to finally produce the constituent amino acids which can pass through the gut wall into the blood stream.

In the lab proteins can be broken down to their amino acids by **hydrolysis** (break down using water). This can be done by 'refluxing' the protein with fairly concentrated hydrochloric acid using the apparatus below: Hydrolysis of the peptide bond

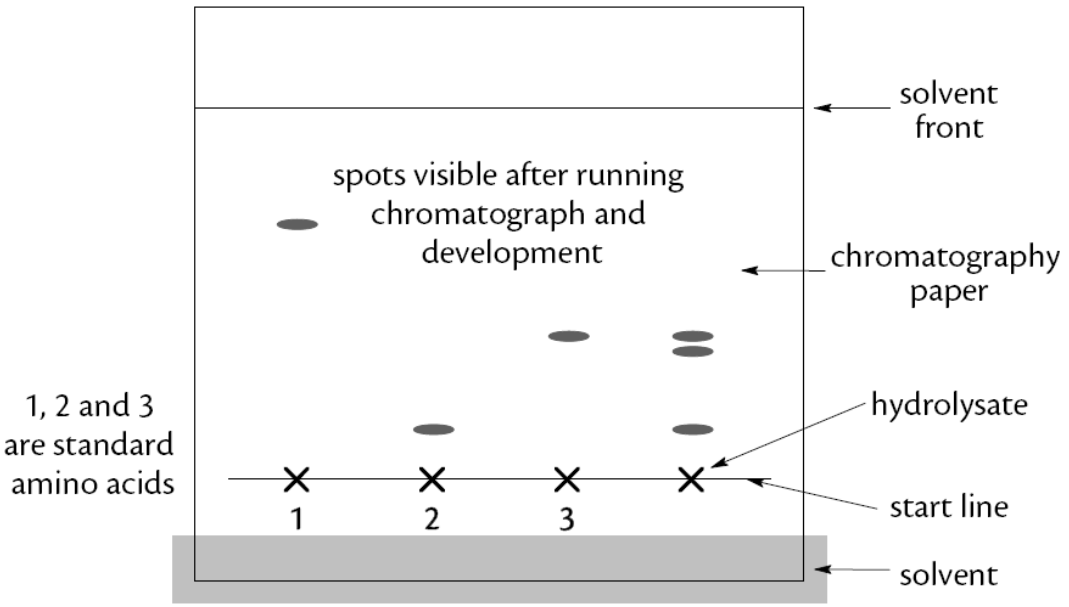


Record the results of the hydrolysis of the following tri-peptide



Chromatography

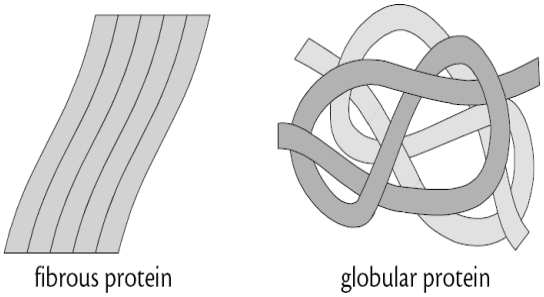
Following hydrolysis, constituent amino acids can be identified using the technique of chromatography in which the hydrolysed protein (hydrolysate) is run alongside standard amino acids (known amino acids). The individual amino acids are treated with the chemical ninhydrin to make them visible on the chromatogram:



Chromatography will be examined further in N6 : CIS: Chemical Analysis

(7) Chemistry of Cooking

Proteins are complex molecules made from long, branched amino acid chains (peptides). Intramolecular and intermolecular bonding produces spirals, sheets, or helices resulting in 3D proteins such as the fibrous or globular structures described earlier:

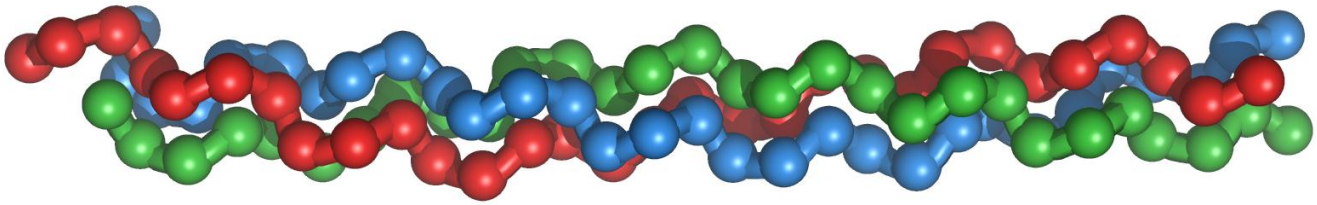


fibrous protein globular protein

When proteins are heated ('cooked') these intermolecular and intramolecular bonds are broken allowing the proteins to change shape (denature). **These changes alter the texture of foods.**

Egg whites contain **globular albumen**. Cooking causes protein chains in the albumen to unwind. Intermolecular bonds form between separated chains resulting in a 3D network - the solid egg white.

Meats contains connective tissue to hold muscle fibres together. In meat this is **mainly** the protein collagen:



Different cuts of meat contain different quantities of collagen so different temperatures are needed for cooking:

Roasting joints contain a lot of connective tissue become tender if cooked at over 60°C as the collagen denatures.

Fillet steaks have less connective tissue so need to be cooked at a lower temperature otherwise collagen molecules bunch together so the meat becomes tough.

Flavour in Food

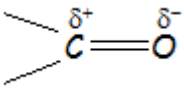
We taste food using our sense of **smell** AND **taste**. **Try chewing flavoured food without looking at it, while pinching your nose!**

Cooking causes chemical reactions which leads to **new** flavours: toasted bread tastes different from untoasted bread because there is a reaction between a carbonyl group (>C=O) in the carbohydrate and an amino group ($-NH_2$) in bread protein.

Many flavour and aroma molecules are aldehydes (alkanals) and ketones (alkanones). Both contain the **carbonyl functional group**. You **learned** about these families at the beginning of this booklet. **Revise them now!**

Boiling points of Aldehydes and Ketones

Aldehydes and ketones are classed as VOCs (volatile organic compounds). Volatility is a measure of how easy it is to evaporate a chemical. Small **non-polar** molecules have very low bps so evaporate very easily. Larger, non-polar molecules have more LDFs so have higher bps therefore are harder to evaporate.

The carbonyl group in aldehydes and ketones is **polar**: 

Draw 3 molecules of propanal in the shape above (bp 49°C) to show intermolecular bonding:

The type of intermolecular bonding is _____.

Repeat this for propanone (bp 56°C):

Why is the bp higher for propanone?

Draw diagrams to show bonding between 3 molecules of propan-1-ol (bp 97°C) then 3 molecules of propan-2-ol (bp 82°C):

What kind of bonding occurs between alcohol molecules? _____

Why is the bp of propan-1-ol higher than the bp of propan-2-ol? _____

_____

Why is the bp of the alcohol higher than that of the equivalent aldehyde or ketone? _____

_____

Which Cooking Method? (now pay attention – you will have to do this sooner than you think!!!)

The **method** and **time** of cooking is very important so that flavour molecules are not lost in the cooking process.

When vegetables are boiled, water in cells evaporates and ruptures cell membranes and cell walls. This releases flavour molecules. Volatile flavour molecules enter the air if they have low bps. If they can form hydrogen bonds with water they dissolve in the cooking liquid and may be thrown away when vegetables are drained.

Structures of flavour molecules and type of intermolecular bonding are very important in determining whether they are water-soluble or oil/fat-soluble. A long hydrocarbon chain (which is non-polar) with a single polar group would be fat/oil-soluble because it would only form one hydrogen bond with a water molecule. Hydrogen bonding between flavour molecules reduces their volatility.

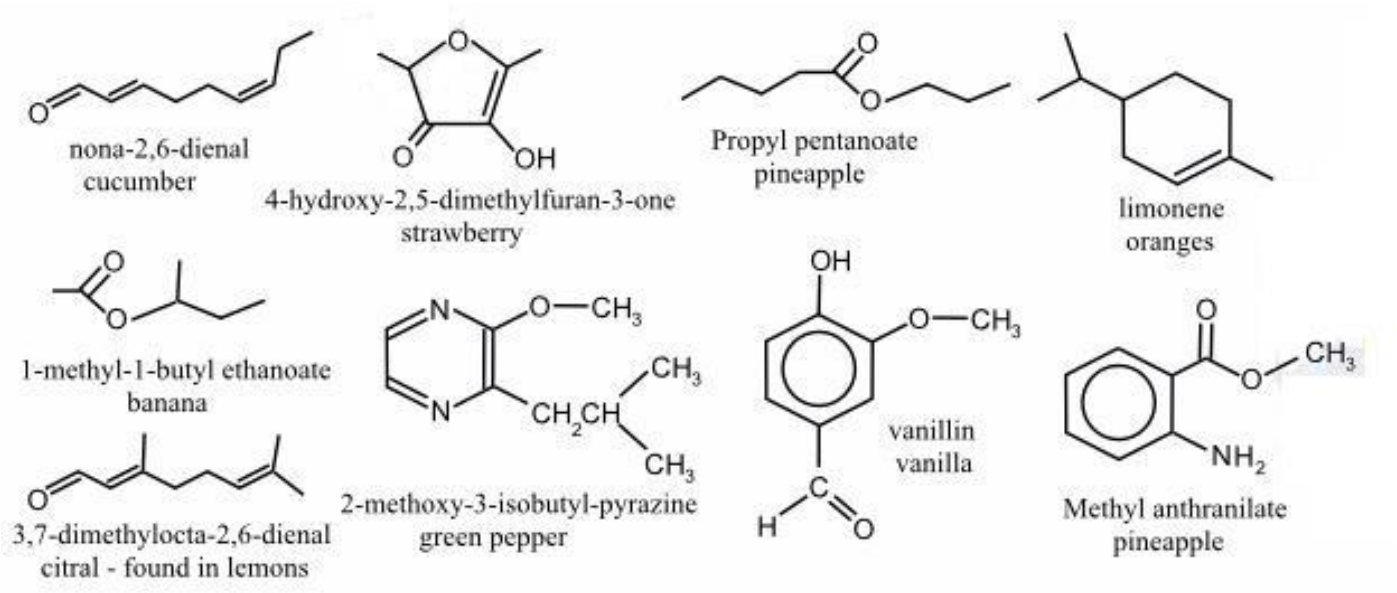
- oil/fat-soluble – cook in water e.g. green beans and broccoli.
- water soluble - cook in oil/fat e.g. asparagus.

The table below shows the impact of structure on solubility in water vs oil:

'Functional' group	**Structure**	**Hydrogen bonding?**	**Water/oil-soluble?**
Alkane	C-C	No	oil-soluble
Alkene	C=C	No	oil-soluble
Alkyne	C≡C	No	oil-soluble
Hydroxyl	-O-H	Yes	water-soluble
Carbonyl	>C=O or	Yes	water-soluble
Carboxylic acid	-COOH or	Yes	water-soluble
Aldehyde	-CHO or	Yes	water-soluble
Amino	$-NH_2$ or	Yes	water-soluble
Phenyl	C_6H_5- or	No	oil-soluble
Amide	-CONH- or	Yes	water-soluble
Ester	-COO-	Yes	water-soluble

Remember to also consider the length of the carbon backbone not just the functional group.

The molecular structures below represent the formulae of some common flavours. Examine them and try to decide if they are likely to be water- or oil soluble.



(8) Oxidation of Food

Foods contain a large variety of organic molecules like aldehydes, ketones, carboxylic acids, fats, oils and alcohols. **Some** of these can be oxidised by oxygen in the air around them. You **learned** about primary, secondary and tertiary alcohols and their oxidation reactions at the beginning of this booklet. **Revise them now!**

Oxidation increases the oxygen : hydrogen ratio in the molecules. Show this below in the oxidation of ethanol to ethanal to ethanoic acid:

Oxidation of organic molecules makes food 'go off'. Butter (a saturated fat) releases volatile, unpleasant smelling butanoic acid and other **fatty acids** which taste and smell **rancid** when oxidised.

Oils are also easily oxidised. Reaction occur at the C=C double bonds of unsaturated fatty acids in the oil releasing small volatile molecules such as aldehydes and ketones also with a **rancid** smell.

Oxidation of food is prevented/reduced by adding **antioxidants** which prolong their shelf-life. **Antioxidants are reducing agents. By undergoing oxidation, the antioxidant provides electrons to prevent the oxidation of fats/oils in food.**

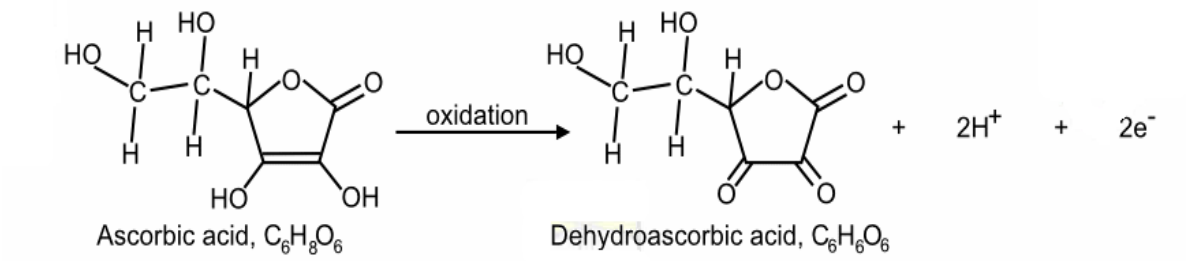
In organic chemistry **oxidation** can be:

- **gain of oxygen atoms** → an **increase** in the oxygen : hydrogen ratio
- **loss of hydrogen atoms** → an **increase** in the oxygen : hydrogen ratio
- **loss of electrons**

In organic chemistry **reduction** can be:

- **loss of oxygen atoms → decrease** in the oxygen : hydrogen ratio
- **gain of hydrogen atoms → decrease** in the oxygen : hydrogen ratio
- **gain of electrons**

Vitamin C (aka Ascorbic Acid), tocopherols and citric acid are commonly used antioxidants. Apples go brown when they are cut and oxidise in the air. A few drops of lemon juice (contains Vitamin C) prevents oxidation. Oxidation occurs at the OH groups in the 'ring' structure as shown:



O : H ratio _____ → _____

What other feature of the reaction indicates that this is an oxidation reaction? _____

Is the resulting structure an aldehyde or a ketone? _____

In crisp manufacture, potatoes are typically fried under an atmosphere of steam and packaged under **nitrogen** to help reduce oxidation.

Research Unit

The concentration of vitamin C in foods can be measured by a variety of means. You may carry out investigative work to measure the quantity of vitamin C in fruit juice or vegetables. This simple method could be used to investigate the effect that cooking food has on antioxidant levels.

(9) Fragrances

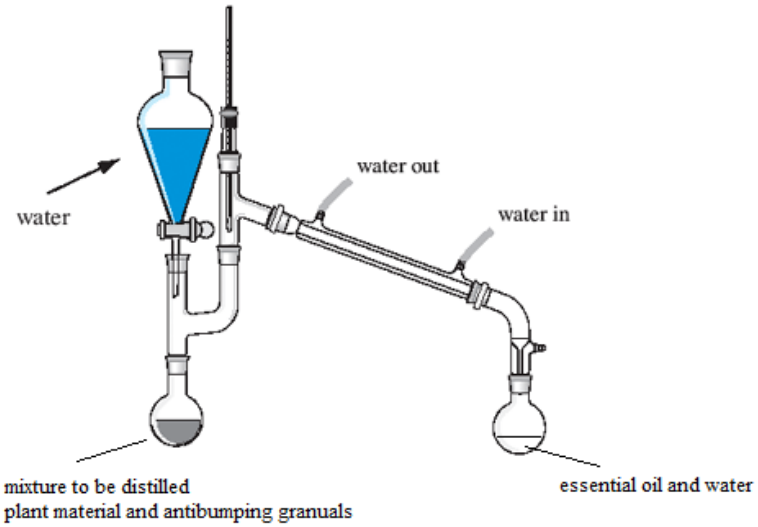
If you 'google' the word **fragrance**, you will probably find lots of sites selling perfumes. Fragrance is the old-fashioned word for perfume. Most perfumes and other 'smellies' contain **essential oils** derived from plant The term 'essential' does not refer to the 'importance' of the oil but the essence (flavour/smell/aroma). Essential oils are used in perfumes, cosmetics, soaps, candles, food and household cleaning products. So the smells are fruity, floral or spicy depending on the source.

Essential oils are mixtures of volatile (low bp) **hydrophobic** liquid aroma compounds that evaporate easily in air giving distinctive fragrances. The oils have the aroma of the plant from which they are extracted e.g. lavender, peppermint, orange, lemon, and eucalyptus oils. The difficulty is obtaining the liquid before it evaporates.

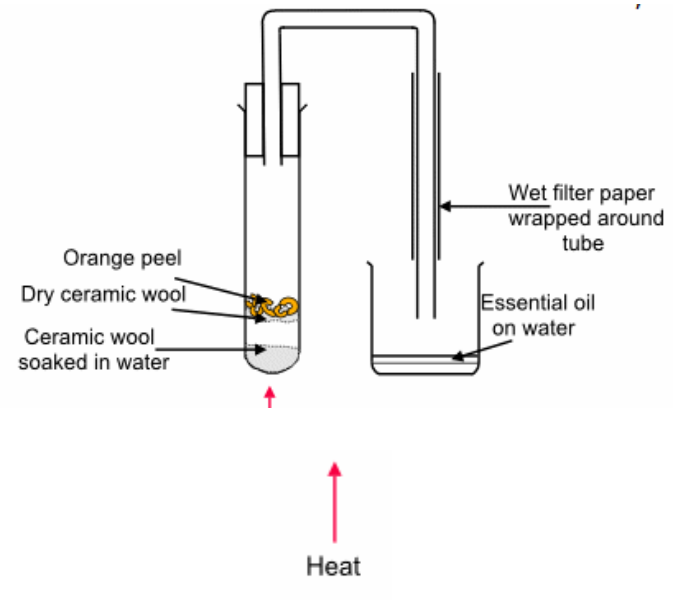
Steam Distillation

In this process the volatility of the oil is important so it is carried by the steam. More water can be added from the funnel.

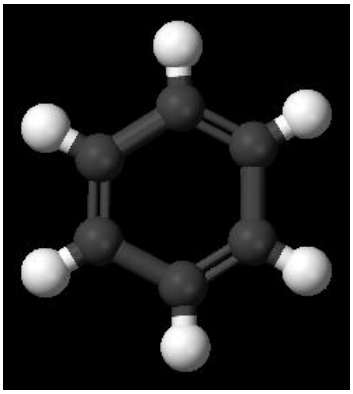
The essential oil collects as a mixture of oil and water, but as the two do not mix, they are easily separated.

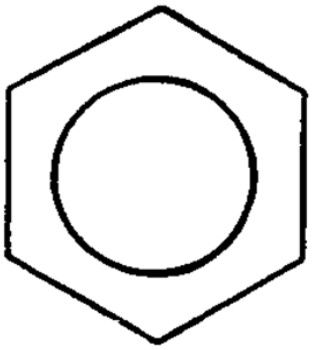


In the laboratory extraction can be achieved with the apparatus shown.



Every essential oil contains mixtures of organic compounds rather than just one pure compound, but it is often the **aromatic** molecules based on benzene C_6H_6 – no longer in the course) that provide the distinct fragrances.

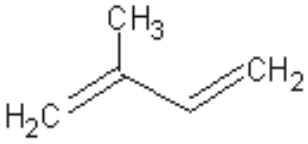




Terpenes

Terpenes are key components in most essential oils.

Terpenes are unsaturated compounds formed by joining together isoprene (2-methylbuta-1,3-diene) units. **LEARN THIS!!**



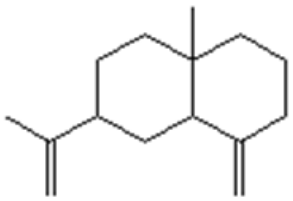
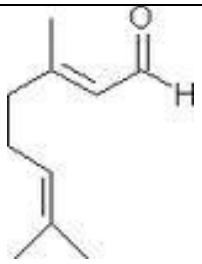
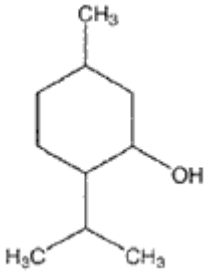
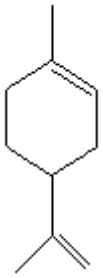
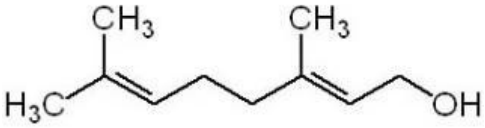
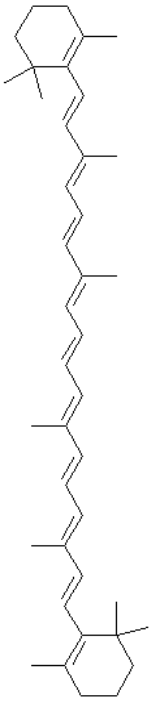
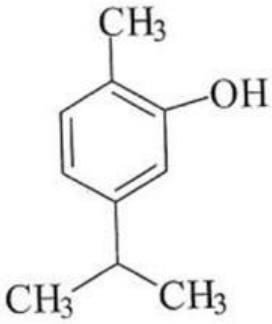
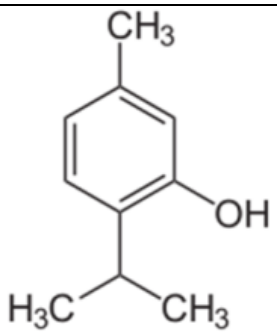
Isoprene

Isoprene units link together to form terpenes with the basic molecular formulae $\mathbf{(C_5H_8)_n}$ where **n** is the number of linked isoprene units. This is called the **isoprene rule**.

Isoprene units may link together **"head to tail"** to form **linear chains** or join to **form rings**. Isoprene units can be thought of as one of nature's common building blocks.

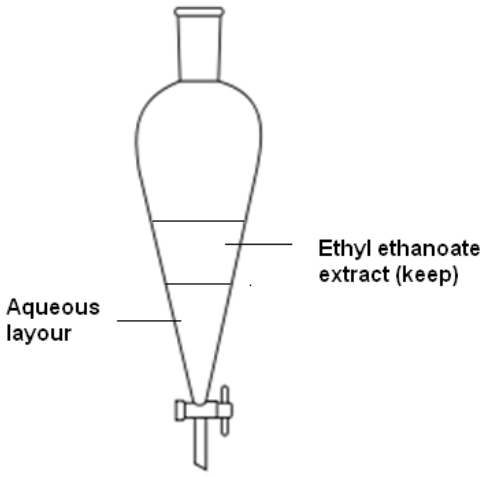
Terpenes can be oxidised within plants to produce some of the compounds responsible for the distinctive aroma of spices. These derivatives, such as alcohols, aldehydes ketones etc. may still be referred to as **terpenes** or **terpenoids**. The names of the molecules usually indicate the predominant functional group. Some examples of terpenes and derivatives are show on the table on the next page. Complete the tasks below by studying the molecules in the table:

- Highlight and count the number of **isoprene** units in the carbon structures.
- Identify any **functional** groups.
- Comment on their **solubility**.

<table>
<tr>
<td> 
Selinene
(celery)</td>
<td> 
Citral
(lemon grass)</td>
<td> 
Menthol
(peppermint)</td>
</tr>
<tr>
<td> 
Limonene
(oranges/lemons)</td>
<td> 
Geraniol
(rose oil)</td>
<td rowspan="2"> 
β Carotene
(carrots)</td>
</tr>
<tr>
<td> 
Carvacrol
(oregano/thyme)</td>
<td> 
Thymol
(thyme plant)</td>
</tr>
</table>

Solvent extraction

Limonene can be extracted from oranges using ethyl ethanoate as a solvent. This process separates organic chemicals from water soluble substances. Some substances are more soluble in the organic solvent than in aqueous solvents.

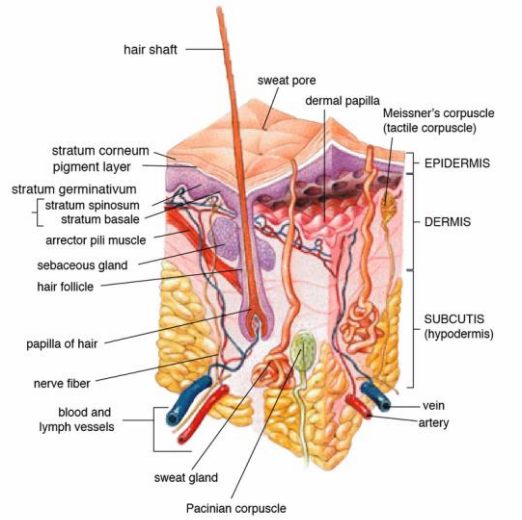


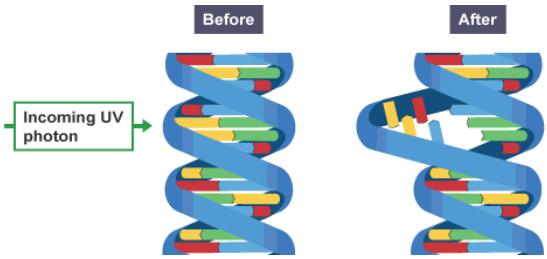
Non-polar terpenes dissolve well in ethyl ethanoate and dissolve poorly in water. If an impure terpene in an aqueous extract is shaken with ethyl ethanoate, most of the terpene will 'move' into the ethyl ethanoate layer (see diagram) and very little will remain in the lower aqueous layer.

Water soluble impurities move into the water layer which is removed using a separating funnel then further purified by another shake with ethyl ethanoate to dissolve more of the terpene. All the terpene/ethyl ethanoate fractions can be added together and distilled to separate the 2 components.

(9) Skin Care

Huge sums of money are spent on cosmetics every year (men and women!!) to **prevent wrinkles** or to **protect** against **sun damage**. In the seventies, cheap package holidays became readily available and many tourists used a variety of **oils** to promote sun tans. Many of these people have, at best, prematurely 'aged' their skin or, at worst, developed skin cancer (malignant melanoma). About 11000 new cases are diagnosed here every year.





Both "photo-aging" and skin cancer are caused by harmful, **high energy** ultraviolet (UV) radiation. UV radiations are found beyond the visible part of the electromagnetic spectrum. There are 3 main types of UV radiation:

- UVA: most penetrating → damages collagen in the dermis → loss of elasticity → wrinkles
- UVB: high energy breaks bonds in DNA of epidermal cells → sun burn and/or skin cancer
- UVC: higher energy than UVA and UVC – way beyond visible - very little reaches Earth

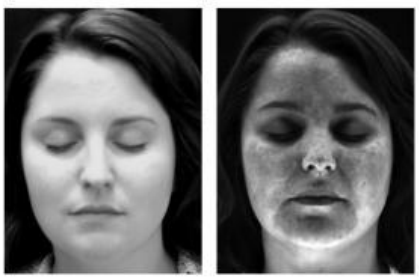
Continued exposure to UV radiation results in the production of melanin from cells in the dermis. Melanin protects the skin but makes it appear tanned. So, although tans look healthy, they are not!

<u>Sunblocks</u>

Currently 2 types of sunblock exist - ZnO and TiO_2 sunblocks reflects UV away from the skin
- chemical sunblocks absorbs UV radiation

UV Photography reveals the effects of or aging of skin caused by UV radiation light.

Some skin-care products claim to contain chemicals which prevent wrinkling. Manufacturers claim that these products are 'anti-aging'. You need to examine adverts for anti-aging products carefully to **verify** the scientific basis of the claims.



Free Radical Reactions

UV light provides enough energy to break bonds in molecules in the skin. This **photochemical** reaction produces **free radicals**. Free radicals are atoms or molecules which have **unpaired electrons**; this makes them **extremely reactive** with the potential to harm cells.

Free radicals are formed naturally in the body and are important in many normal cellular processes but, at high concentrations, can be very dangerous. Free radicals can damage major cell components e.g. DNA, cell proteins and cell membranes. Damage to DNA may result in skin cancer.

The chemistry is complicated so simple examples of free radical formation and chain reactions are given here.

Free radical chain reactions include the following steps: **initiation**, **propagation** and **termination**. For example in the **explosive** reaction between **hydrogen** and **chlorine the overall reaction is:**

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

The presence of acidic HCl(g) in the product can be shown using moist pH paper.

Initiation

U.V. light provides the energy for the **homolytic fission** of the halogen into **free radicals** with an **unpaired electron**:

$$Cl_2(g) \rightarrow Cl^{\bullet}(g) + {}^{\bullet}Cl(g)$$

Propagation

Free radicals collide with other molecules to produce stable atoms/molecules as well as more free radicals to continue the **chain reaction**:

$$H_2(g) + {}^{\bullet}Cl \rightarrow H^{\bullet}(g) + HCl(g)$$

$$H^{\bullet}(g) + Cl_2(g) \rightarrow HCl(g) + Cl^{\bullet}(g)$$

Termination

Free radicals are used up by collision with each other.

$$H^{\bullet}(g) + {}^{\bullet}Cl(g) \rightarrow HCl(g)$$

$$H^{\bullet}(g) + {}^{\bullet}H(g) \rightarrow H_2(g)$$

$$Cl^{\bullet}(g) + {}^{\bullet}Cl(g) \rightarrow Cl_2(g)$$

The following reaction is very useful in chemistry to produce substituted alkanes from unreactive parent molecules.

Substitution Reactions

Alkanes are unreactive because they contain only single carbon to carbon covalent bonds. Hydrogen atoms in an alkane can be **substituted** for a halogen atom in the presence of UV light. This reaction is slow and the bromine solution is slowly **decolourised**. The overall reaction is:

$$CH_4(g) + Br_2(g) \rightarrow CH_3Br(g) + HBr(g)$$

The presence of acidic HBr(g) in the product can be shown using moist pH paper.

Initiation

U.V. light provides the energy for the **homolytic fission** of the halogen into **free radicals:**

$$Br_2(g) \rightarrow Br\bullet\ (g) + \bullet Br(g)$$

Propagation

Free radicals collide with alkane molecules to produce stable molecules as well as more free radicals to continue the **chain reaction**:

$$CH_3\text{-}H(g) + \bullet Br \rightarrow CH_3\bullet\ (g) + HBr(g)$$

$$CH_3\bullet\ (g) + Br_2(g) \rightarrow CH_3\text{ - }Br(g) + Br\bullet\ (g)$$

Termination

In this stage, free radicals are used up by collision with each other.

$$Br\bullet\ (g) + \bullet Br(g) \rightarrow Br_2(g)$$

$$CH_3\bullet\ (g) + \bullet Br(g) \rightarrow CH_3\text{ - }Br(g)$$

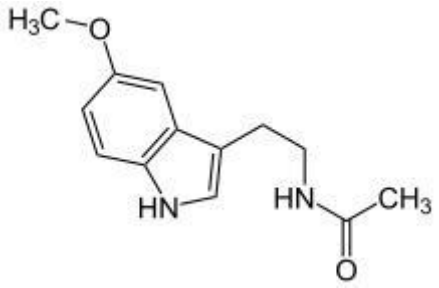
$$CH_3\bullet\ (g) + \bullet CH_3(g) \rightarrow CH_3\text{ - }CH_3(g)$$

The product of the last equation is ethane. However, to minimise the range of possible products, an excess of the original alkane is used and the products separated from the excess alkane by distillation. **Further substitution can occur with hydrogen atoms progressively replaced by halogen atoms.**

Free Radical Scavengers

Antioxidants are chemicals which react with and remove free radicals. Antioxidants are also known as **free radical scavengers**. Many cosmetic products contain free radical scavengers. These are molecules which can react with free radicals to form stable molecules and **prevent chain reactions**.

Most of the antioxidants which protect us from free radical are ingested in our food including beta-carotene, lycopene and vitamins A, C and E. Melatonin, a hormone, is also a free radical scavenger:



Melatonin

Free radical scavengers are added to food products and to plastics e.g. food wrapping to prevent both degradation of the food and the wrapper itself.

Some skin-care products claim to contain chemicals which prevent wrinkling. Manufacturers claim that these products are 'anti-aging'. You need to examine adverts for anti-aging products carefully to **verify** the scientific basis of the claims.

Vitamin D

Vitamin D has many different forms e.g. cholecalciferol and ergocalciferol. These can be ingested in food but very few foods contain vitamin D. Many of us have to take food supplements. Cholecalciferol is needed for intestinal absorption of calcium, iron, magnesium, phosphate and zinc.

Vitamin D is mainly synthesised in the skin from cholesterol – this process is dependent on exposure to the sun's UVB radiation.

Ozone Layer

Ozone is pale blue, pungent and highly toxic form of oxygen made up of unstable molecules with the formula O_3.

A layer of ozone about 12 – 50km about the Earth's surface protects us from harmful UV radiation. The ozone absorbs UV radiation.

The ozone layer is gradually being damaged by the over use of propellants in aerosols and cooling agents in fridges which contain chlorofluorocarbons (CFCs) e.g. $CClF_3$ and CCl_2F_2.

Aldehydes, but not ketones, can be oxidised to carboxylic acids.

Fehling's solution, Tollens' reagent and acidified dichromate solution can be used to differentiate between an aldehyde and a ketone.
Positive test results:

- Fehling's — blue solution to a brick red precipitate
- Tollens' — formation of a silver mirror
- Acidified dichromate test — colour change from orange to green

Essential oils are concentrated extracts from plants, and are mixtures of organic compounds.

Terpenes are key components in most essential oils.
Terpenes are unsaturated compounds formed by joining together isoprene (2methylbuta-1,3-diene) units.

Essential oils are concentrated extracts of the volatile, non-water soluble aroma compounds from plants. They are widely used in perfumes, cosmetic products, cleaning products and as flavourings in foods.

Terpenes are components in a wide variety of fruit and floral flavours and aromas.

Terpenes can be oxidised within plants to produce some of the compounds responsible for the distinctive aroma of spices.