1 A chemist prepares and analyses some esters.

(a) The chemist prepares an ester of propan-2-ol, $CH_3CH(OH)CH_3$, by reacting $CH_3CH(OH)CH_3$ with ethanoic anhydride, $(CH_3CO)_2O$.

Using structural formulae, write an equation for the reaction of propan-2-ol and ethanoic anhydride.

[2]

(b) A sample contains a mixture of two esters contaminated with an alkane and an alcohol.

The chemist attempts to separate the four organic compounds in the mixture using gas chromatography, GC.

The column in the gas chromatograph contains a liquid alkane which acts as the stationary phase.

(i) How does a liquid stationary phase separate the organic compounds in a mixture?

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..... **[1]**

(ii) Suggest how well these four compounds would be separated using the alkane stationary phase. In your answer, include some indication of the length of the retention times.

Explain your answer.

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..... **[2]**

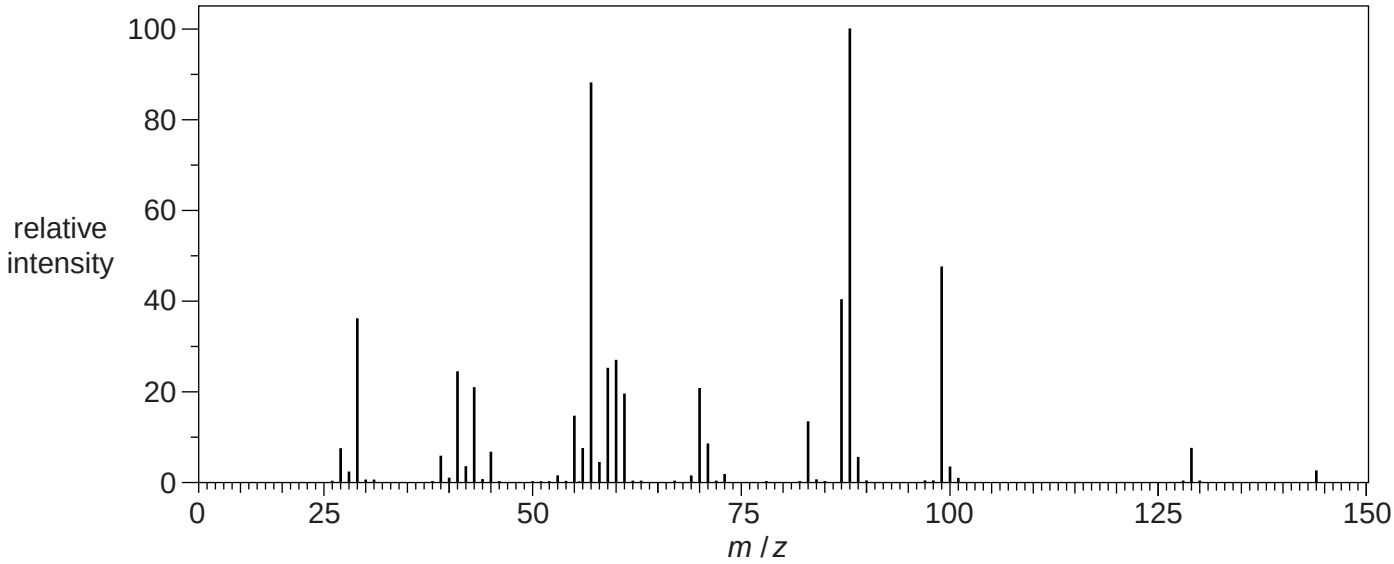
(c) GC is often used together with other techniques, such as mass spectrometry, MS, and NMR spectroscopy, to provide a far more powerful analytical tool than GC alone.

One of the esters in a perfume is separated by GC and then analysed.

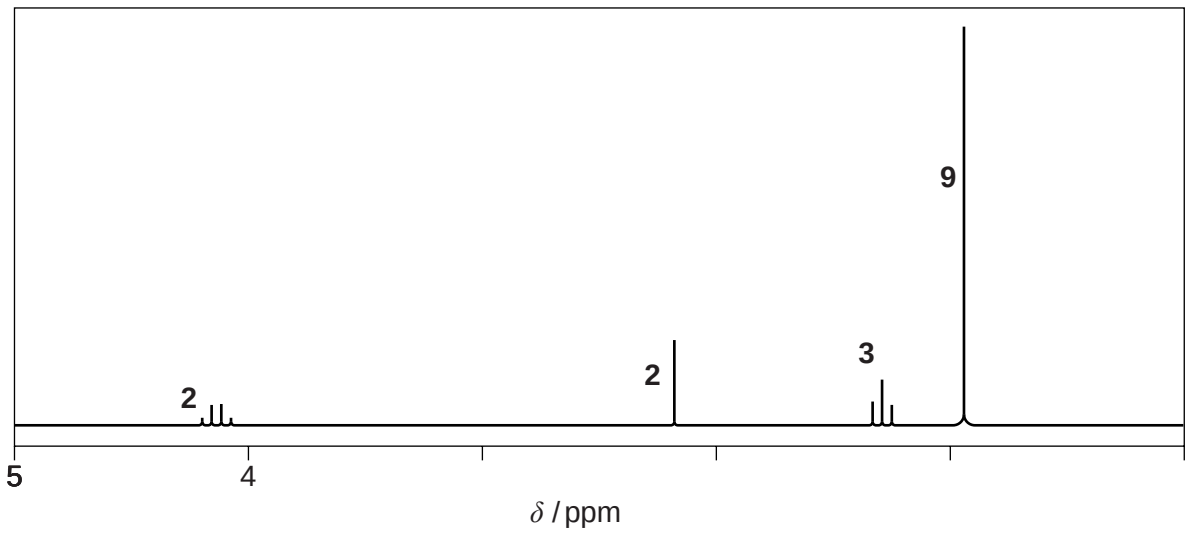
The results are shown below.

Elemental analysis by mass
C, 66.63%; H, 11.18%; O, 22.19%

Mass spectrum



Proton NMR spectrum
The numbers by each peak are the relative peak areas.



Use the results to identify the ester. Show **all** your reasoning.

In your answer, you should use appropriate technical terms, spelled correctly.

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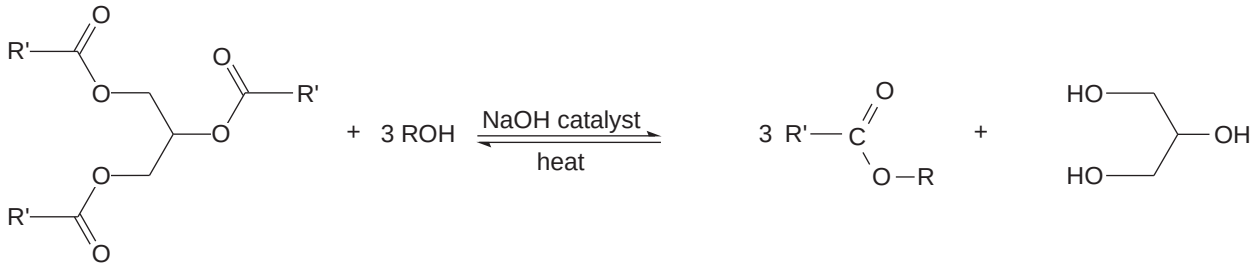
.... **[10]**

[Total: 15]

2 Esters of fatty acids are used as biodiesels. These esters can be produced from triglycerides by the transesterification process below.



triglyceride **biodiesel** **glycerol**

(a) Give the systematic name of glycerol.

..... **[1]**

(b) **(i)** Suggest a suitable alcohol, ROH, that could be used industrially to make biodiesel.

Justify your answer.

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..... **[1]**

(ii) The alcohol, ROH, is added in excess.

Suggest why the alcohol has to be in excess.

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..... **[1]**

(c) Esters can also be made by reacting an alcohol with either a carboxylic acid or with an acid anhydride.

Write equations for the formation of ethyl propanoate, $CH_3CH_2COOCH_2CH_3$, starting from:

- a carboxylic acid and an alcohol,

- an acid anhydride and an alcohol.

[2]

(d) Compound **A**, $C_4H_8O_3$, can lose water to form either:

compound **B**, a cyclic ester
OR
compound **C**, a polyester.

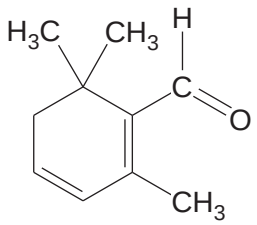
Identify compounds **A**, **B** and **C**.

compound **A**	compound **B**
compound **C**	

[3]

[Total: 8]

3 Safranal, shown below, is an aldehyde which contributes to the aroma of saffron.



safranal

An undergraduate chemist investigated some reactions of safranal.

(a) She prepared a solution of Tollens' reagent and added a few drops of safranal. She then warmed the mixture for about 5 minutes in a water bath.

Describe what you would expect the chemist to see.

State the type of reaction that the safranal undergoes.

Draw the structure of the organic product formed in this reaction.

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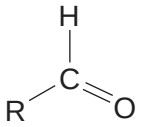
[3]

(b) The chemist then reduced safranal using an aqueous solution of $NaBH_4$.

Outline the mechanism for this reaction.

Use curly arrows and show any relevant dipoles.



can be used to represent safranal.

[4]

(c) Suggest one reaction of safranal that does **not** involve the aldehyde group.

State the reagent, observation (if any) and draw the organic product.

reagent .....

observation .....

organic product

[3]

[Total: 10]

4 Hydroxyethanal, $HOCH_2CHO$, is sometimes referred to as the 'first sugar' as it is the simplest possible molecule that contains both an aldehyde group and an alcohol group.

A biochemist investigated some redox reactions of hydroxyethanal and found that several different products were produced.

(a) The biochemist reacted hydroxyethanal with Tollens' reagent.

(i) State what the biochemist would see when hydroxyethanal reacts with Tollens' reagent.

..... **[1]**

(ii) Write the structural formula of the organic product formed when hydroxyethanal reacts with Tollens' reagent.

[1]

(b) The biochemist also reacted hydroxyethanal with acidified dichromate by heating under reflux.

Write an equation for this oxidation.

Use **[O]** to represent the oxidising agent.

[2]

(c) The biochemist then reduced hydroxyethanal using aqueous $NaBH_4$.

(i) Write the structural formula of the organic product.

..... **[1]**

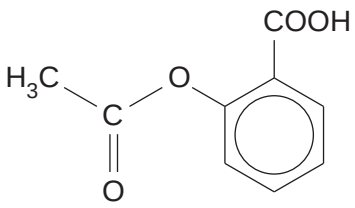
(ii) Outline the mechanism for this reduction.

Use curly arrows and show any relevant dipoles.

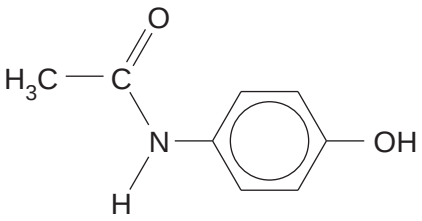
[4]

[Total: 9]

5 Aspirin and paracetamol are commonly available painkillers.



aspirin



paracetamol

Aspirin and paracetamol can be prepared using ethanoic anhydride, $(CH_3CO)_2O$.

Some examples of the reactions of ethanoic anhydride are shown below.

reaction 1 $(CH_3CO)_2O + CH_3OH \rightarrow CH_3COOCH_3 + CH_3COOH$

reaction 2 $(CH_3CO)_2O + CH_3NH_2 \rightarrow CH_3CONHCH_3 + CH_3COOH$

reaction 3 $(CH_3CO)_2O + C_6H_5OH \rightarrow CH_3COOC_6H_5 + CH_3COOH$

(a) Draw the structure of a compound that could react with ethanoic anhydride to form aspirin.

[1]

(b) Ethanoic anhydride can react with 4-aminophenol to produce paracetamol.

(i) Write an equation, showing structural formulae, for this formation of paracetamol.

[2]

(ii) An impurity with molecular formula $C_{10}H_{11}NO_3$ is also formed.

Draw the structure of this impurity.

[1]

(iii) Explain why it is necessary for pharmaceutical companies to ensure that drugs and medicines are pure.

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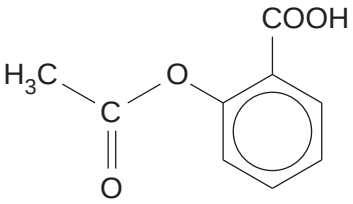
..... **[1]**

(c) Name the functional groups in aspirin and in paracetamol.

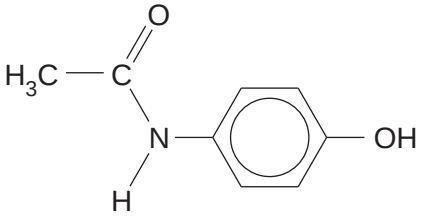
aspirin .....

paracetamol ..... **[2]**

(d) A student carried out some reactions with samples of aspirin and paracetamol in the laboratory. Their structures are repeated below.



aspirin



paracetamol

The student tried to react each of the reagents **A**, **B** and **C** with aspirin and paracetamol.

- Reagent **A** reacted with aspirin **and** with paracetamol.
- Reagent **B** reacted **only** with aspirin.
- Reagent **C** reacted **only** with paracetamol.

Suggest possible identities of reagents **A**, **B** and **C** and the organic products that would be formed.

(i) Reagent **A**: .....

Organic product with aspirin:

Organic product with paracetamol:

[3]

(ii) Reagent **B**: .....

Organic product with aspirin:

[2]

(iii) Reagent **C**: .....

Organic product with paracetamol:

[2]

[Total: 14]

6 An industrial chemist discovered five bottles of different chemicals (three esters and two carboxylic acids) that were all labelled $C_5H_{10}O_2$.

The different chemicals had the structural formulae below.

$CH_3CH_2COOCH_2CH_3$ $(CH_3)_3CCOOH$ $CH_3COOCH(CH_3)_2$

$(CH_3)_2CHCH_2COOH$ $(CH_3)_2CHCOOCH_3$

(a) The chemist used both infrared and ^{13}C NMR spectroscopy to identify the two carboxylic acids and to distinguish between them.

How do both types of spectra allow the carboxylic acids to be identified and distinguished?

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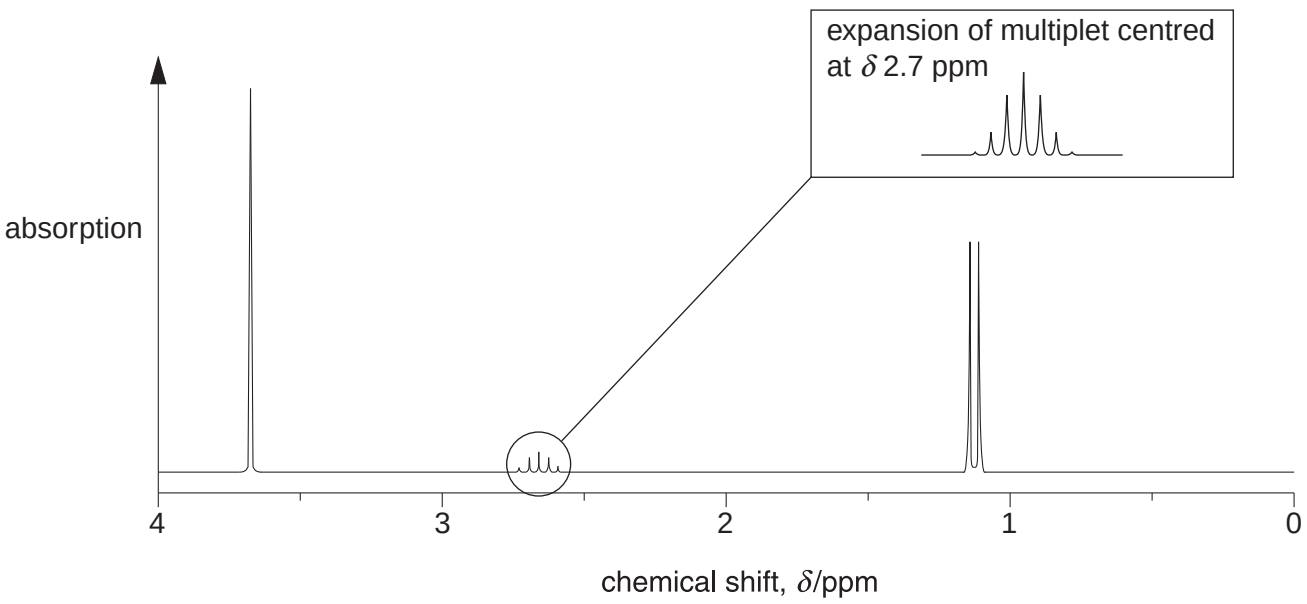
..... **[3]**

(b) The chemist analysed one of the esters by ^1H NMR spectroscopy. The spectrum is shown below.



Analyse the splitting patterns and the chemical shift values to identify the ester.

Give your reasoning.

In your answer, you should use appropriate technical terms, spelt correctly.

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..... **[6]**

[Total: 9]