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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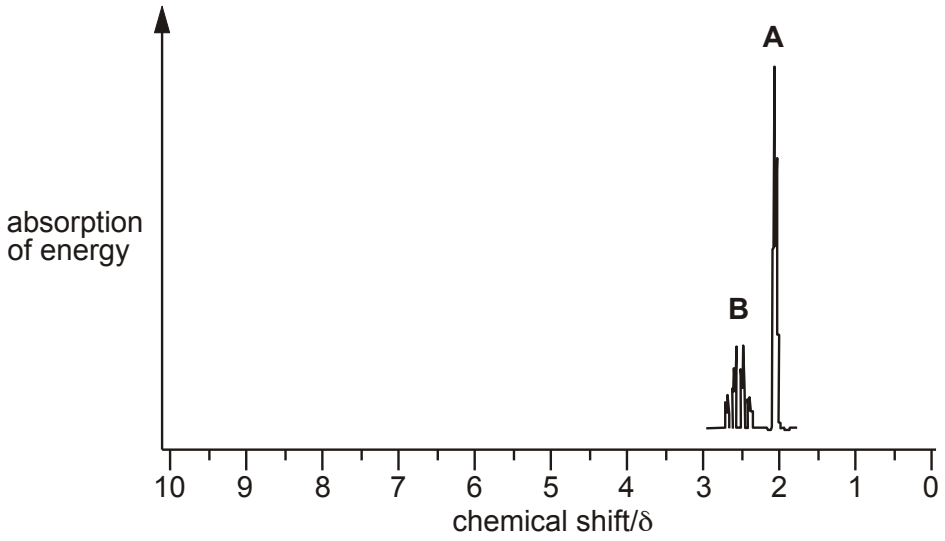
[6]

[Total 9 marks]

2. Unknown compounds are often identified by n.m.r. spectroscopy.

Part of the n.m.r. spectrum of **butanone** is shown on the axes below.



(i) State which part of the butanone molecule is responsible for peak **A** at δ = 2.1.

Explain your reasoning.

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[2]

(ii) Explain why peak **B** is split into a quadruplet.

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[1]

(iii) Predict the remainder of the n.m.r. spectrum of butanone by sketching it on the axes above.

[2]

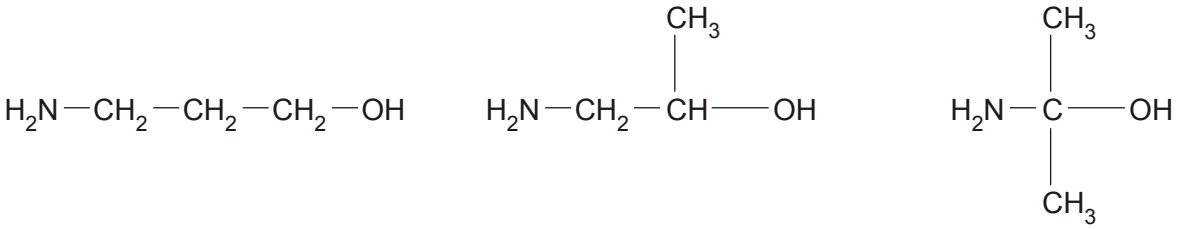
(iv) Write the relative peak area above each of the peaks on the completed spectrum of butanone.

[1]

[Total 6 marks]

3. In this question, one mark is available for the quality of use and organisation of scientific terms.

The structural formulae of three isomers of C_3H_9NO are shown below.



Describe the **similarities** and **differences** you would expect to see when comparing the

- infra-red spectrum of each isomer
- mass spectrum of each isomer.

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[5]

Quality of Written Communication [1]

[Total 6 marks]

4. An ester **D** with the formula, $CH_3CH_2COOCH_2CH(CH_3)_2$, is used in rum flavouring.

(a) Draw a displayed formula of ester **D**.

[2]

(b) Outline how you could obtain a sample of ester **D**, starting with a named carboxylic acid and a named alcohol.

Include any essential reaction conditions and write an equation for the reaction. You do not need to include any details of the separation or purification of the ester.

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[6]

(c) State a spectroscopic method that could be used to confirm that a sample of ester **D** has a molecular mass of 130.

Explain how you would obtain the molecular mass of **D** from the spectrum.

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[2]

[Total 10 marks]

5. In this question, one mark is available for the quality of the use and organisation of scientific terms.

Describe and explain the different ways that a high resolution n.m.r. spectrum can give information about a molecule.

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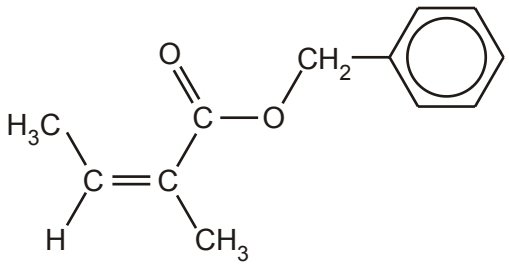
[7]

Quality of Written Communication [1]

[Total 8 marks]

6. Compound **A** is used to add the flavour of mushrooms to foods.



compound **A**

(a) (i) Apart from the benzene ring, name the two functional groups in compound **A**.

....

[2]

(ii) Draw the skeletal formula of compound **A**.

[1]

(iii) Deduce the molecular formula of compound **A**.

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[1]

(b) Compound **B** is a stereoisomer of compound **A**.

Explain what is meant by the term *stereoisomerism*. Use compounds **A** and **B** to illustrate your answer.

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[2]

(c) If the food is cooked for a long time, naturally occurring acids catalyse the hydrolysis of compound **A**.

Draw structures to show the **two** organic compounds formed by the acid hydrolysis of compound **A**.

[2]

(d) The hydrolysis of compound **A** can be monitored by sampling the mixture at regular intervals, separating the components, and recording their infra-red spectra.

(i) State **two** absorptions that would be expected in the infra-red spectrum of compound **A**, and identify the parts of the molecule responsible for each.

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[2]

(ii) Suggest a wavenumber range within the spectrum that could be used to clearly distinguish compound **A** from the products formed by the hydrolysis reaction.

Explain your answer.

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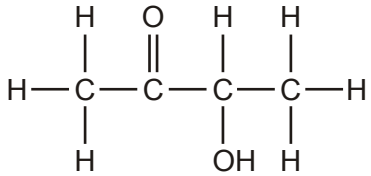
[2]

[Total 12 marks]

7. *Thua nao* is a traditional sauce made in Northern Thailand by fermenting cooked soybeans. Its unique flavour is due to a range of volatile compounds formed during the fermentation.

One of these volatile compounds is 3-hydroxybutanone.



3-hydroxybutanone

(a) State the meaning of the term *volatile*.

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[1]

(b) Several hydroxyketones with similar boiling points can be separated from the fermentation mixture.

Describe a method, which does **not** involve spectroscopy, that could be used to distinguish 3-hydroxybutanone from the other hydroxyketones.

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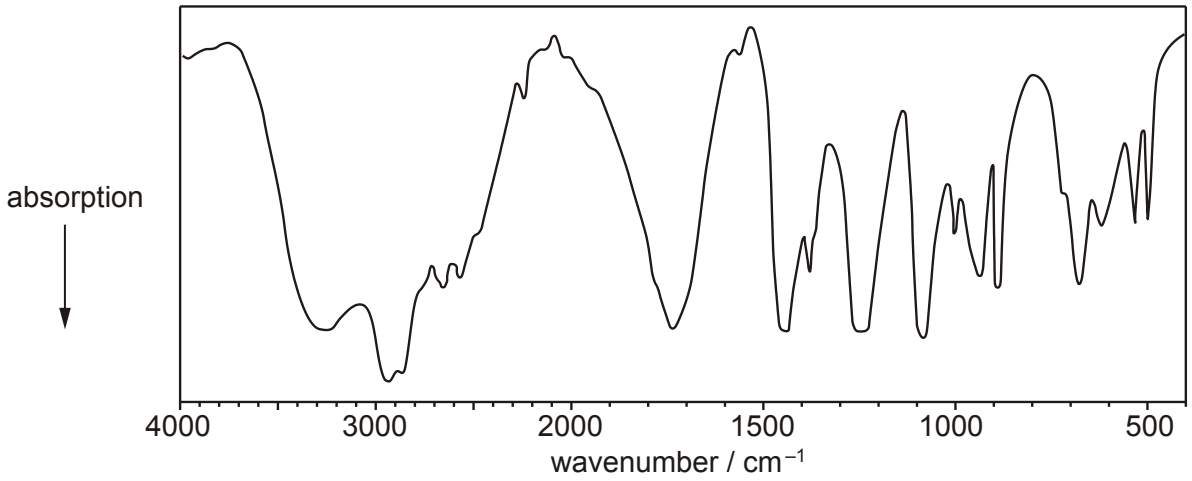
[4]

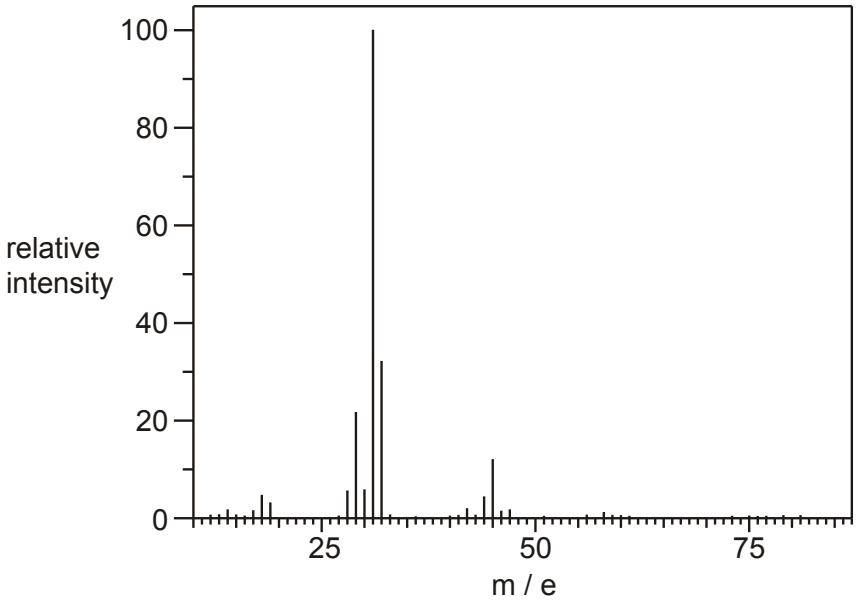
[Total 5 marks]

8. Compound **G** can be extracted from sugar-cane and is commonly used in 'rejuvenating' skin creams because it helps to remove some of the dead cells from the skin surface.

The molecular formula of **G** is $C_2O_3H_4$ and the compound contains **two different** functional groups containing oxygen atoms.

The infra-red and mass spectra of **G** are shown below.





(a) After inspection of the mass spectrum of **G**, an analyst wrote the comment:

'The molecular ion peak appears to be missing from the spectrum.
The base peak is due to a fragment ion with m / e = 31.'

(i) Explain what is meant by the following terms.

molecular ion peak .....

.....

base peak .....

.....

[2]

(ii) Suggest why the molecular ion peak is missing from the spectrum.

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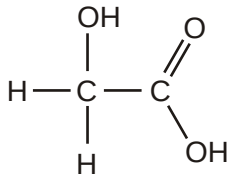
[1]

(b) The structure of compound **G** is shown below.



Show how the infra-red and mass spectra confirm this structure. In your answer, you should suggest a possible structure for the ion that gives the base peak at m / e = 31 in the mass spectrum.

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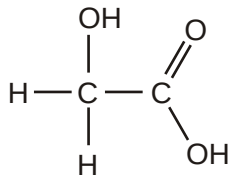
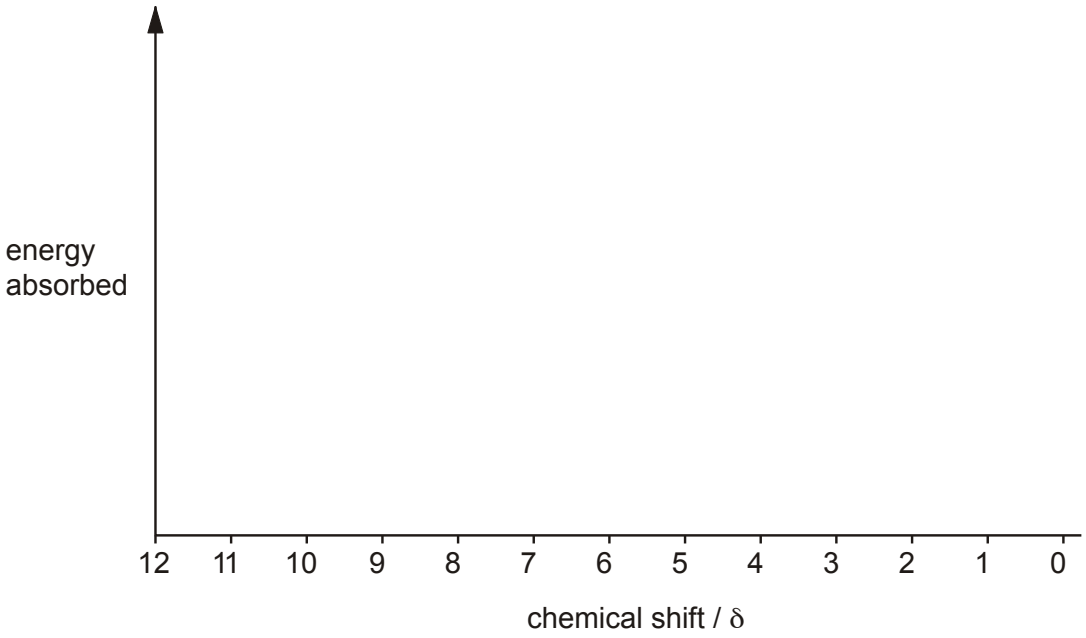
[4]

(c) The structure of compound **G** is shown below.



Sketch the ^{1}H n.m.r. spectrum of compound **G** and label the relative peak areas. Label any peaks that would be lost from the spectrum on shaking with D_2O.



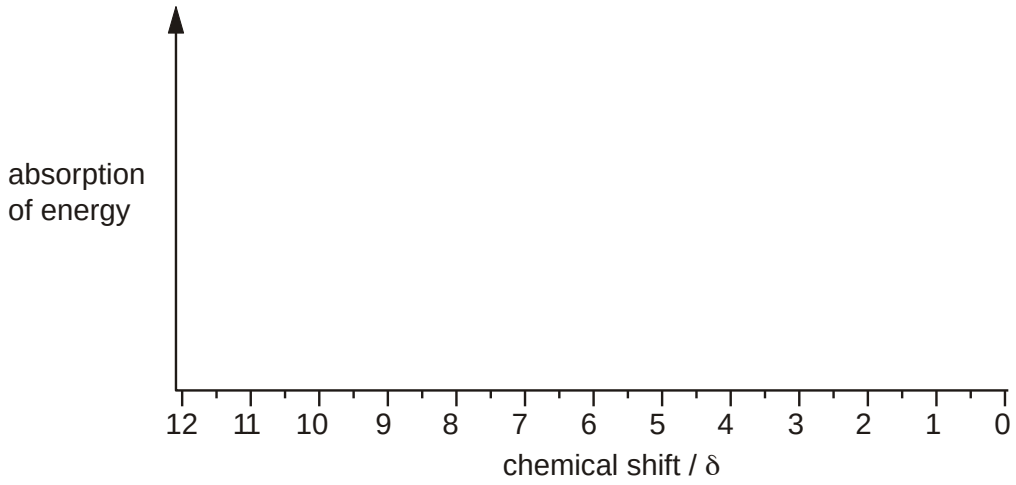
[4]

[Total 11 marks]

9. Lactic acid produces an n.m.r. spectrum in D_2O with peaks at chemical shift values of 1.4 ppm and 4.3 ppm.

(i) On the axes below, sketch the high resolution n.m.r. spectrum of lactic acid in D_2O.

Show any splitting patterns and state the relative areas of the two peaks.



[4]

(ii) How many peaks would you expect if the n.m.r. spectrum of lactic acid was run in an inert solvent rather than in D_2O? Explain your answer.

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[2]

[Total 6 marks]

10. Forest fires release a large number of organic compounds into the atmosphere. These include alcohols and carboxylic acids. An environmental chemist is trying to identify one of these compounds in a sample of air.

The unknown compound **X** is thought to be a carboxylic acid with empirical formula $C_2H_3O_2$.

(a) Mass spectrometry is used to help deduce the molecular formula of compound **X**.

(i) Describe how the mass spectrum of compound **X** is used to determine its relative molecular mass.

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[2]

(ii) The relative molecular mass of compound **X** is shown to be 118.

Explain how this relative molecular mass and the empirical formula are used to deduce that the molecular formula of compound **X** is C_4H_6O4. Show any working.

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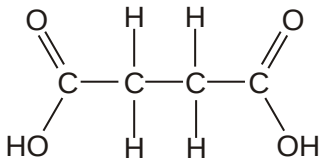
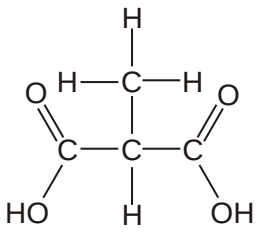
[2]

(b) The two dicarboxylic acids with molecular formula $C_4H_6O_4$ are shown below.





N.m.r. spectroscopy is used to deduce which of these is the unknown compound.

The environmental chemist obtains an n.m.r. spectrum of compound **X** and then adds some D_2O and obtains a second n.m.r. spectrum.

(i) What difference would you expect between these two n.m.r. spectra?

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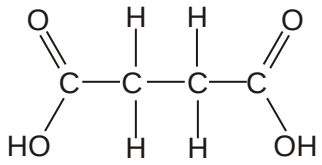
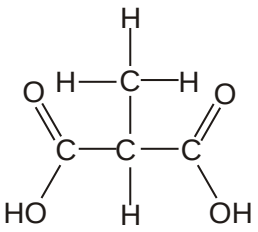
[1]

(ii) Predict the number of peaks and any spin-spin splitting expected on the n.m.r. spectrum of a solution in D_2O of the other acid with formula $C_4H_6O_4$.

Explain your reasoning.

(The two possible structures of compound **X** are shown again below.)





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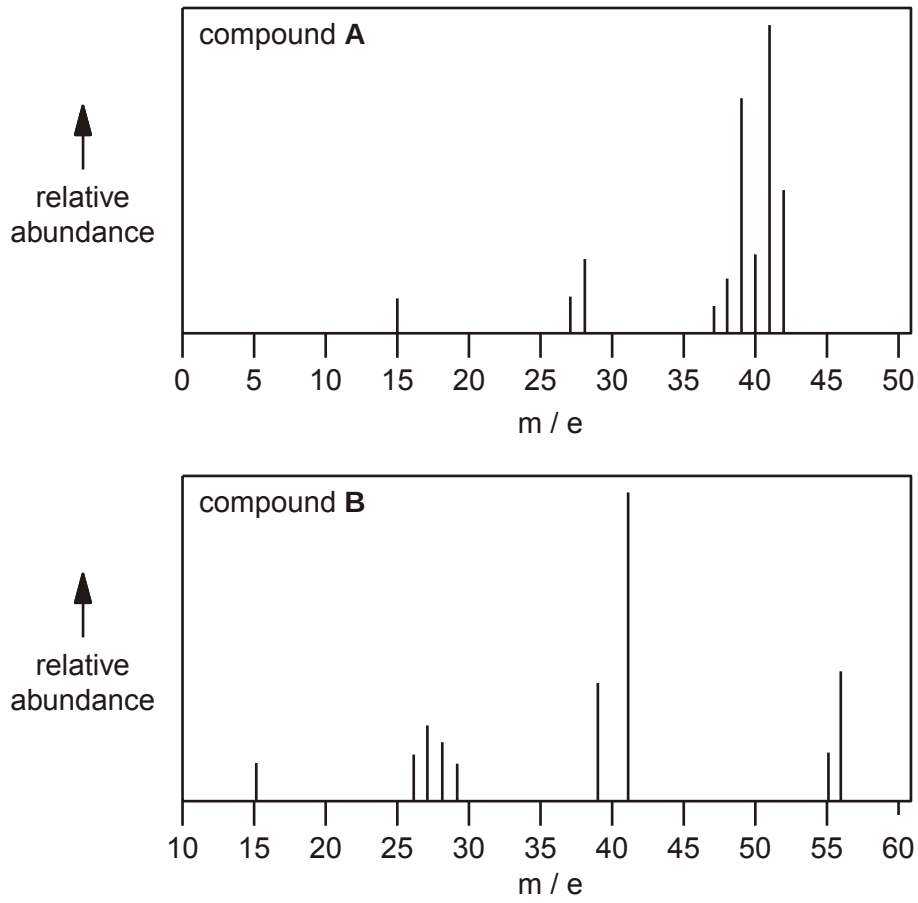
[3]

[Total: 8 marks]

11. This question is about the use of spectrometry in helping to gain information about the structure of organic molecules.

The major peaks in the mass spectra of two hydrocarbons **A** and **B** are shown below. Compounds **A** and **B** have the same empirical formula.



(i) Deduce the molecular formula of each compound.

Compound **A** .....

Compound **B** .....

[2]

(ii) Draw the structural formula of compound **A**.

[1]

(iii) Suggest the species responsible for the peak at *m/e* 41 in the spectrum of compound **B**.

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[2]

[Total 5 marks]