

OCR A-LEVEL CHEMISTRY A • H432

CHEMISTRY



EXAM QUESTION PACK

6.3 ORGANIC ANALYSIS

SCORE

/276

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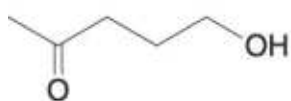
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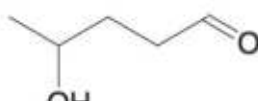
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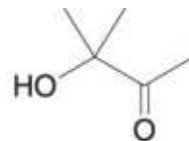
1(a) The following three carbonyl compounds are structural isomers of $C_5H_{10}O_2$.



compound C



compound D



compound E

Describe chemical tests that you could carry out in test-tubes to distinguish between compounds C, D and E.

Include appropriate reagents and any relevant observations. Also include equations showing structures for the organic compounds involved.

[4]

(b) Predict the number of peaks in the ^{13}C NMR spectra of compounds C, D and E.

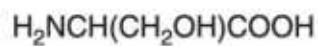
Compound	C	D	E
Number of peaks			

[1]

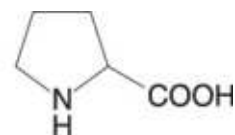
2(a) Alanine, serine and proline are α -amino acids.



alanine



serine



proline

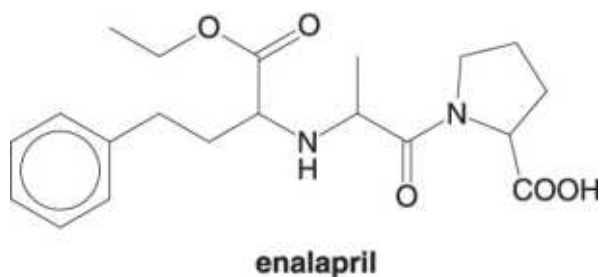
A solution of serine was shaken with a few drops of D_2O . The solution was then analysed using ^1H NMR spectroscopy.

Complete the table to predict the ^1H NMR spectrum of serine after the addition of D_2O .

^1H NMR spectrum for serine		
Chemical shift, δ / ppm	Relative peak area	Splitting pattern

[2]

(b) Enalapril is a drug used in the treatment of high blood pressure.



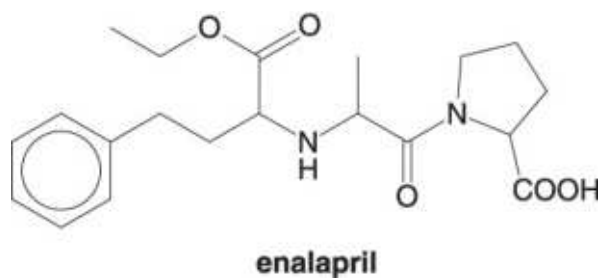
(i) On the structure above, mark each chiral centre with an asterisk (*).

[1]

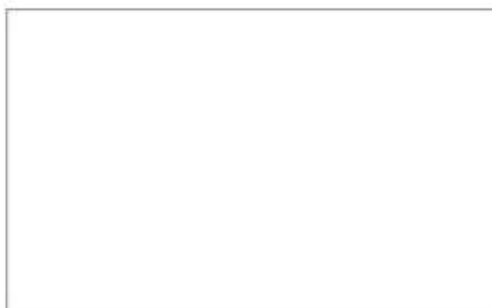
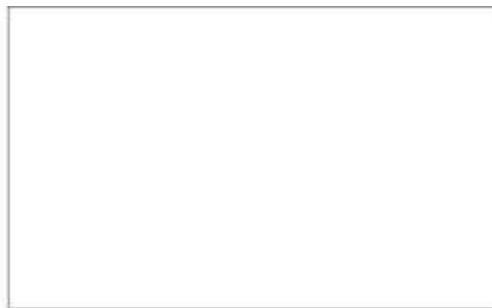
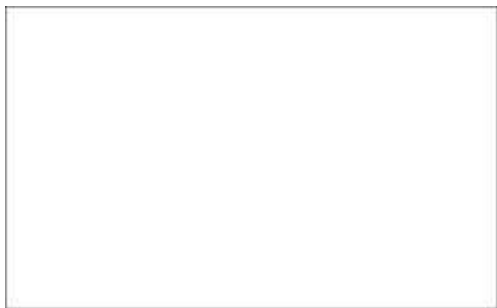
(ii) Suggest **two** benefits of using single stereoisomers in the synthesis of drugs such as enalapril.

[2]

(iii) Enalapril is broken down in the body by acid hydrolysis.



Draw the structures of the **three** organic products of the **acid hydrolysis** of enalapril.



[4]

- (iv) A scientist hydrolysed enalapril in the laboratory. The scientist then analysed the mixture of products using GC–MS.

Explain how GC–MS enables the products to be identified.

[1]

3(a) A chemist isolates compound **H** from a mixture and sends it for analysis.

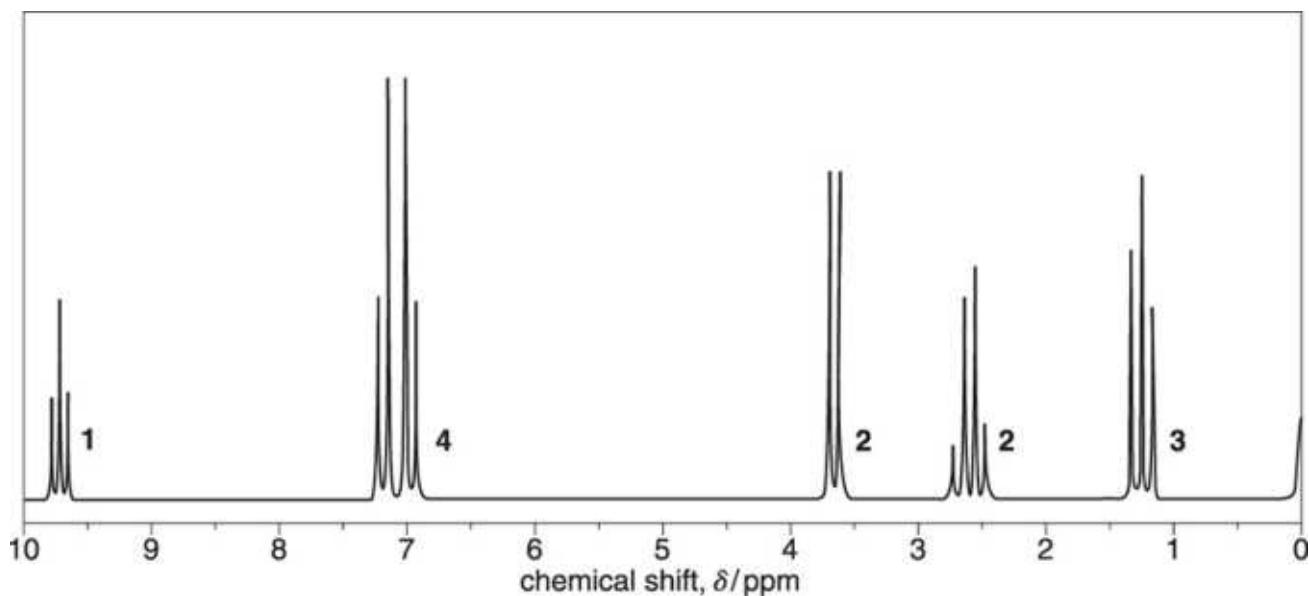
Initial analysis shows that the molecular formula of compound **H** is $\text{C}_{10}\text{H}_{12}\text{O}$.

The ^{13}C NMR spectrum of compound **H** contained eight separate peaks.

The ^1H NMR spectrum of compound **H** is shown below.

^1H NMR spectrum

The numbers by each peak are the relative peak areas.



The ^1H NMR spectrum contains a peak at $\delta = 0$ ppm resulting from a chemical added to the sample.

State the chemical responsible for the peak at $\delta = 0$ ppm, and state why this chemical was added to the sample.

----- [1]

- Use the information in this question to determine the structure of compound H.

Show all your reasoning.



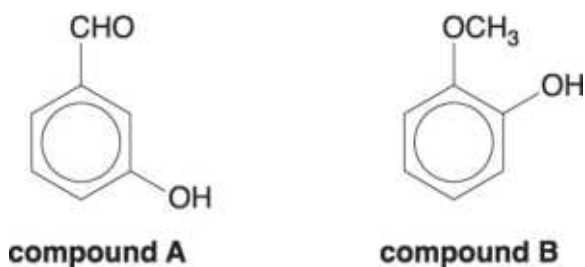
In your answer, you should use the appropriate technical terms, spelled correctly.

[illegible]

[9]

4(a) A student analysed a mixture of compounds found in red wine using gas chromatography followed by mass spectrometry (GC-MS).

Two of the compounds found to be present in the mixture are shown below.

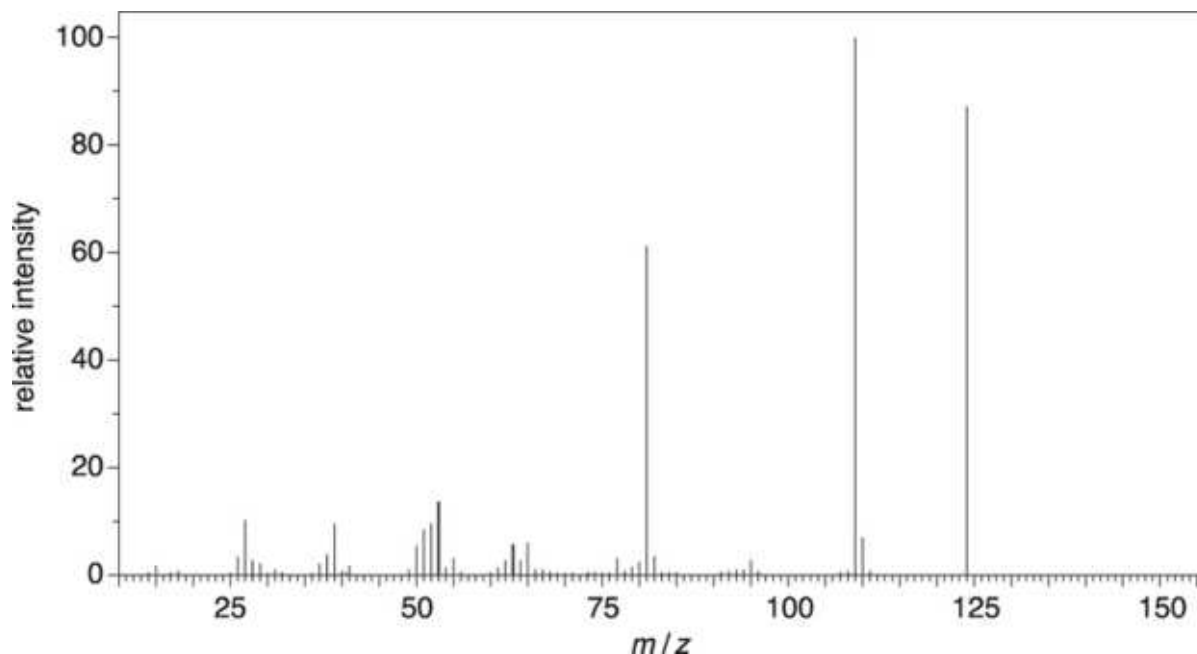


The column in the gas chromatogram is packed with solid beads coated with a liquid polymer.

How does gas chromatography (GC) separate the compounds in the mixture?

----- [1]

(b) The mass spectrum (MS) of the **first** compound to emerge from the column is shown below.



(i) Identify the compound responsible for this spectrum.

Give a reason for your answer.

----- [1]

(ii) What does your answer to (b)(i) suggest about the interaction of this compound with the phases present in the column?

----- [1]

5(a)

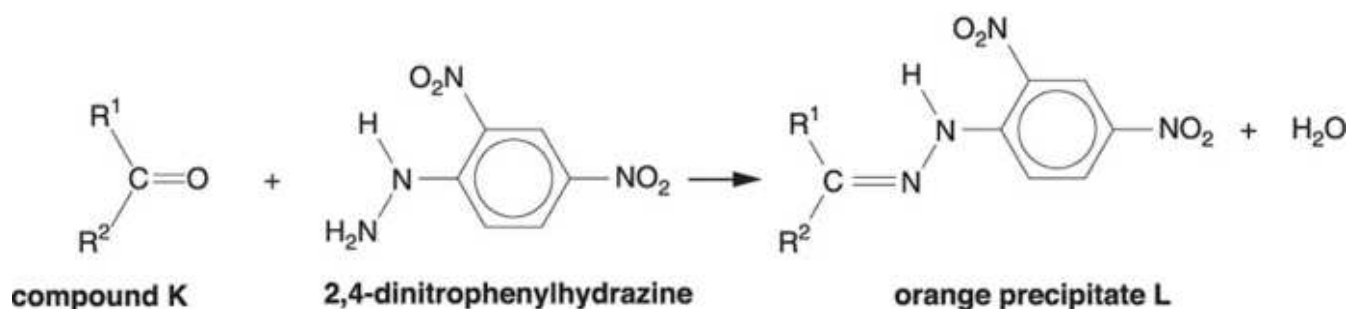
(i) State the region of the electromagnetic spectrum used in ^1H NMR spectroscopy.

-----[1]

(ii) Explain why CDCl_3 is used as a solvent in ^1H NMR spectroscopy.

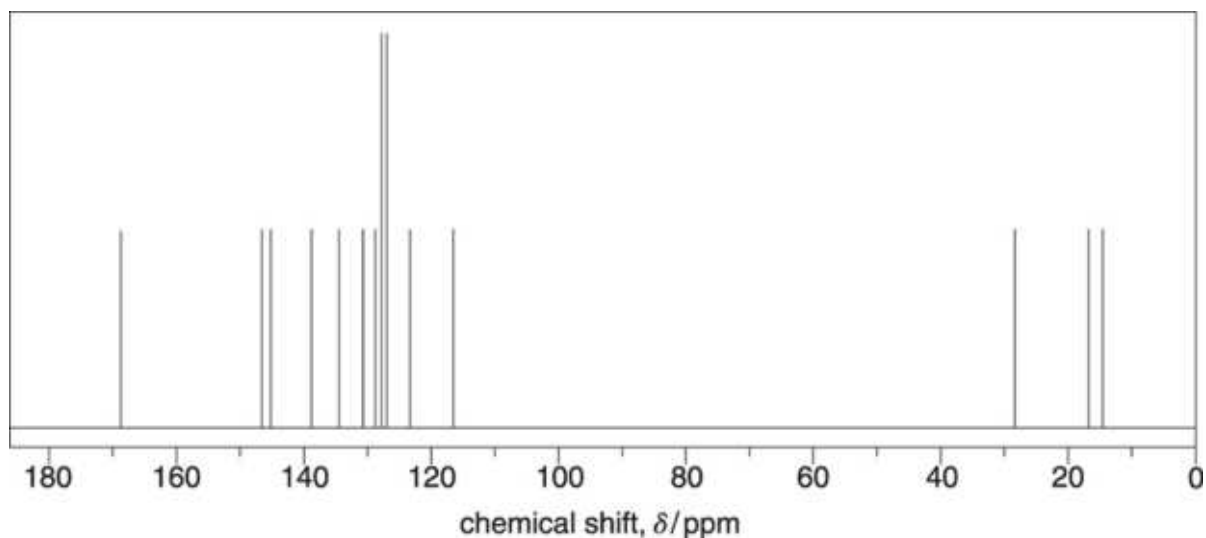
-----[1]

(b) A student reacts compound K with 2,4-dinitrophenylhydrazine. An orange precipitate, L, was formed.



The student purifies the orange precipitate, L, and sends the sample for analysis using ^1H NMR and ^{13}C NMR spectroscopy.

The ^{13}C NMR spectrum of L is shown below.



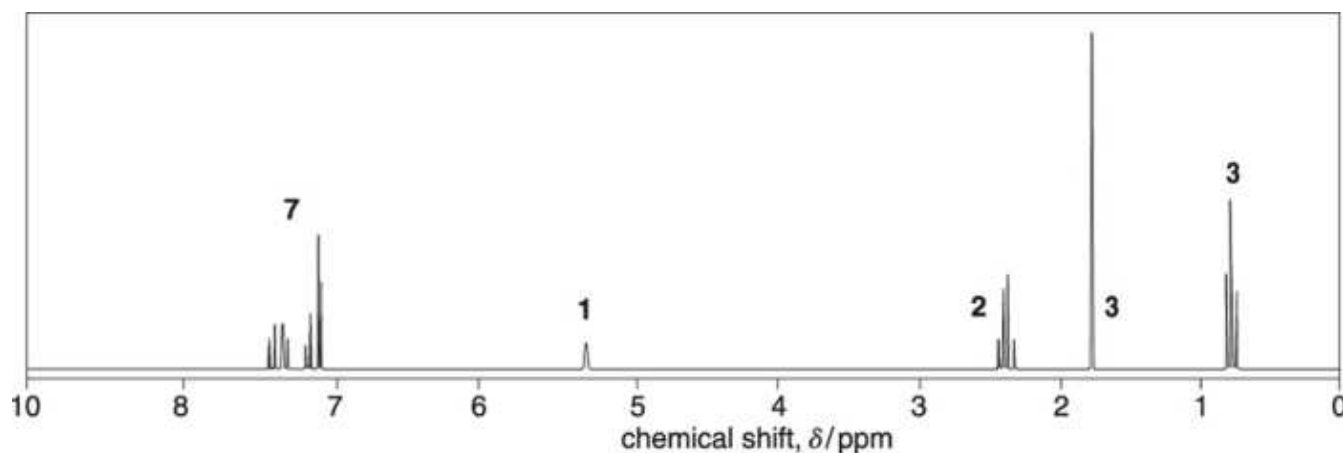
How many different carbon environments (types of carbon) are present in a molecule of compound L?

-----[1]

(c) The reaction of K to form L is repeated below.



The ^1H NMR spectrum of L is shown below.



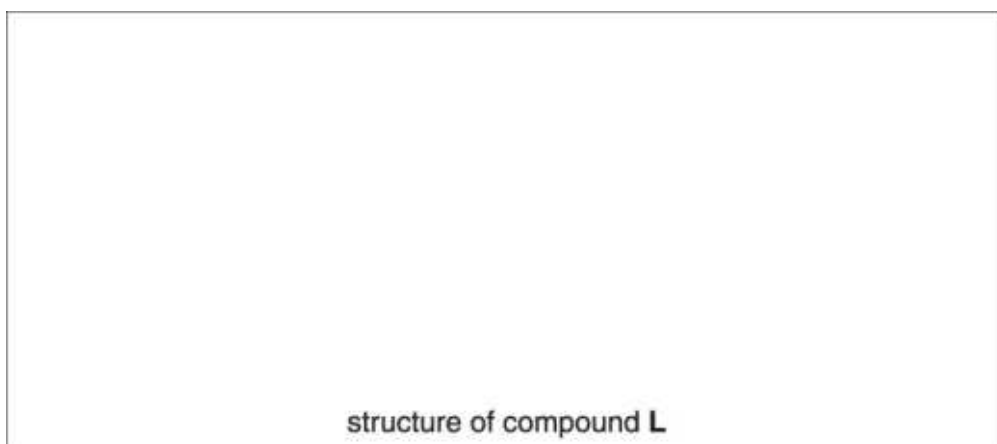
Use your answer to (c) and the data given to identify R^1 , R^2 and the structure of compound L.

Explain how you used the chemical shifts and splitting patterns in the ^1H NMR spectrum and any evidence from the ^{13}C NMR spectrum.

In the ^1H NMR spectrum, $\text{HC}=\text{C}=\text{N}-$ would have a peak in the range $\delta = 1.6\text{--}2.2$ ppm.

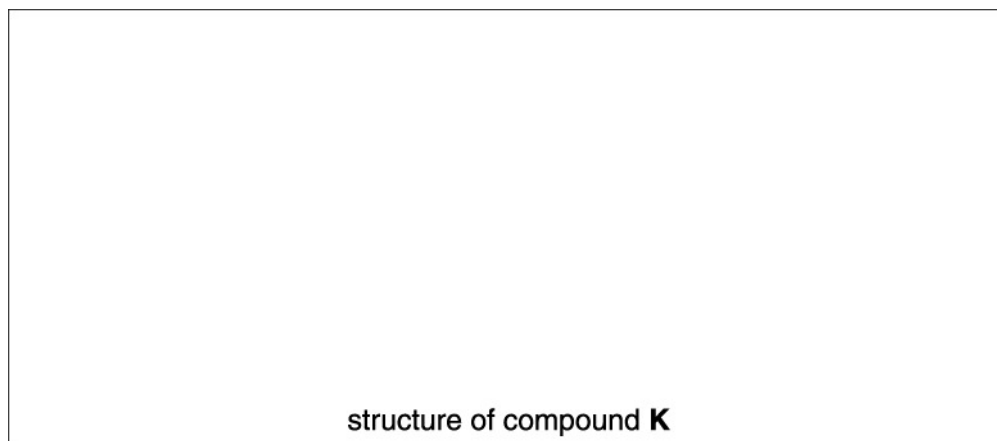


In your answer, you should use appropriate technical terms, spelled correctly.



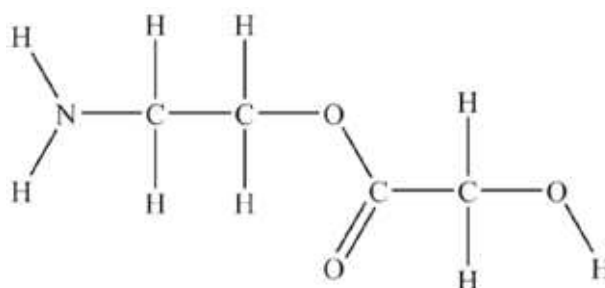
[7]

(d) Draw the structure of compound **K**.



6 The structure of molecule **Z** is shown below.

[1]



Which of the following statements is / are true?

- 1: The carbon-13 NMR spectrum of **Z** shows four peaks
- 2: The proton NMR spectrum of **Z** shows five peaks
- 3: The proton NMR spectrum of **Z** run in D₂O shows three peaks

- A 1, 2 and 3
- B Only 1 and 2
- C Only 2 and 3
- D Only 1

Your answer

[1]

7(a) Cyclohexanone can be prepared in the laboratory by reacting cyclohexanol with concentrated sulfuric acid and sodium dichromate.

Ethanedioic acid is added to the reaction mixture to react with any excess dichromate.

The mixture is then distilled. The impure distillate is a mixture of cyclohexanone and water.

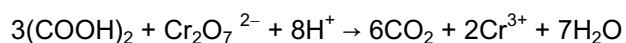
You will need to refer to some or all of the following data to answer these questions.

	Boiling point / °C	Density / g cm ⁻³	<i>M_r</i>
Cyclohexanol	161	0.962	100.0
Cyclohexanone	156	0.948	98.0

* Draw a labelled diagram to show how you would safely set up apparatus for distillation and describe a method to obtain a pure sample of cyclohexanone from the distillate.

[6]

- (b) Ethanedioic acid removes excess dichromate ions, $\text{Cr}_2\text{O}_7^{2-}$, as in the equation below.



Suggest how you could tell when the excess dichromate has completely reacted with the ethanedioic acid.

----- [1]

- (c) A student monitors the course of this reaction using thin-layer chromatography (TLC).

Outline how TLC could be used to monitor the course of the reaction.

----- [2]

- (d) Plan an experiment that would allow the student to confirm the identity of the pure organic product by means of a chemical test.

----- [3]

- 8 * A chemist isolates compound L, with empirical formula C_3H_6O , and sends a sample for analysis. The analytical laboratory sends back the following spectra.

Mass spectrum

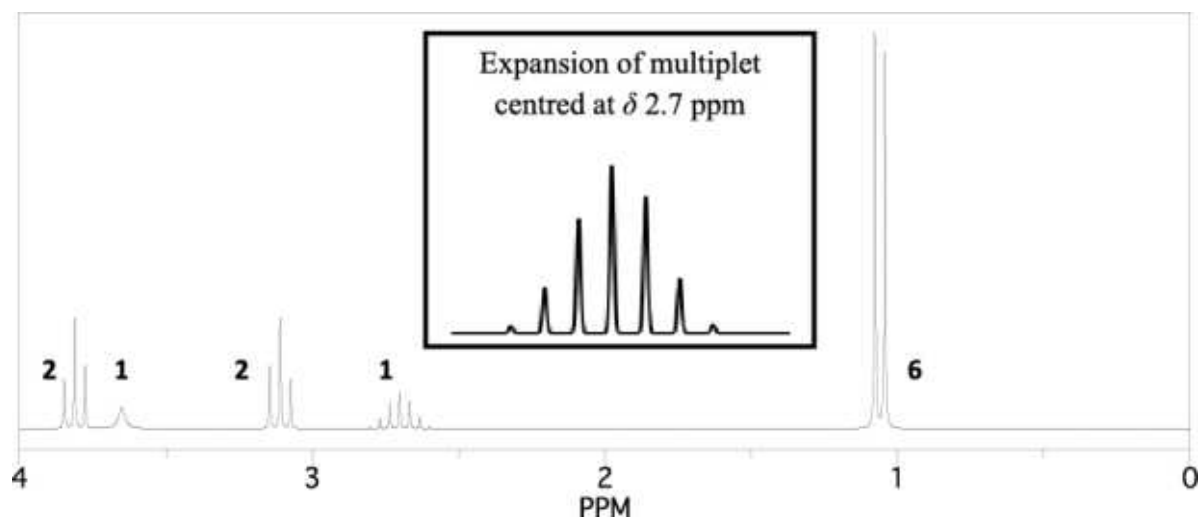
Molecular ion peak at $m/z = 116.0$.

^1H NMR spectra

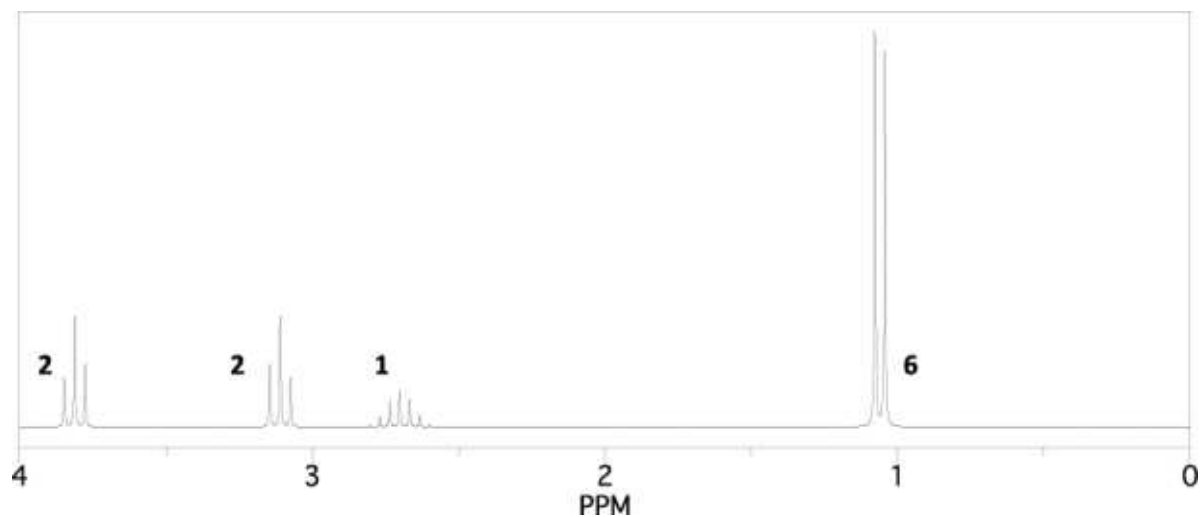
The numbers next to each signal represent the number of ^1H responsible for that signal.

Two ^1H NMR spectra were obtained: one without D_2O and one with D_2O added.

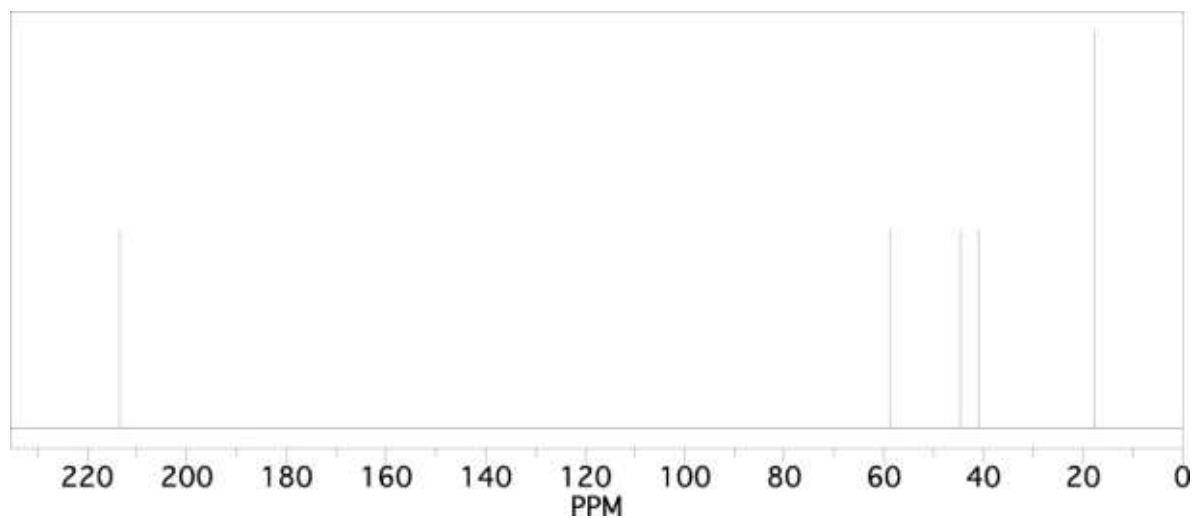
^1H NMR spectrum with no D_2O :



^1H NMR spectrum with D_2O added:



^{13}C NMR spectrum:

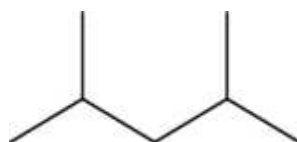


Use the information provided to suggest a structure for compound L.

Give your reasoning.

[6]

9 The skeletal formula of a hydrocarbon is shown below.



How many peaks would be seen in a ^1H NMR spectrum of this hydrocarbon?

- A 2
- B 3
- C 5
- D 7

Your answer

[1]

10(a) Compound F has the molecular formula C_4H_8 .

Compound F is reacted with steam in the presence of an acid catalyst, to form a mixture of three alcohols, G, H and I.

Compound G is oxidised with acidified potassium dichromate(VI) to form compound J.

Compound J reacts with Tollens' reagent to form compound K.

Compounds H and I are optical isomers.

Draw the structures of the compounds F, G, H, I, J and K.

[6]

(b) Explain, with reference to a suitable chemical test, how compound J could be identified.

Your answer should not include spectroscopy.

[3]

11 A scientist analyses a compound that is present in a sample of ink.

The results are shown below:

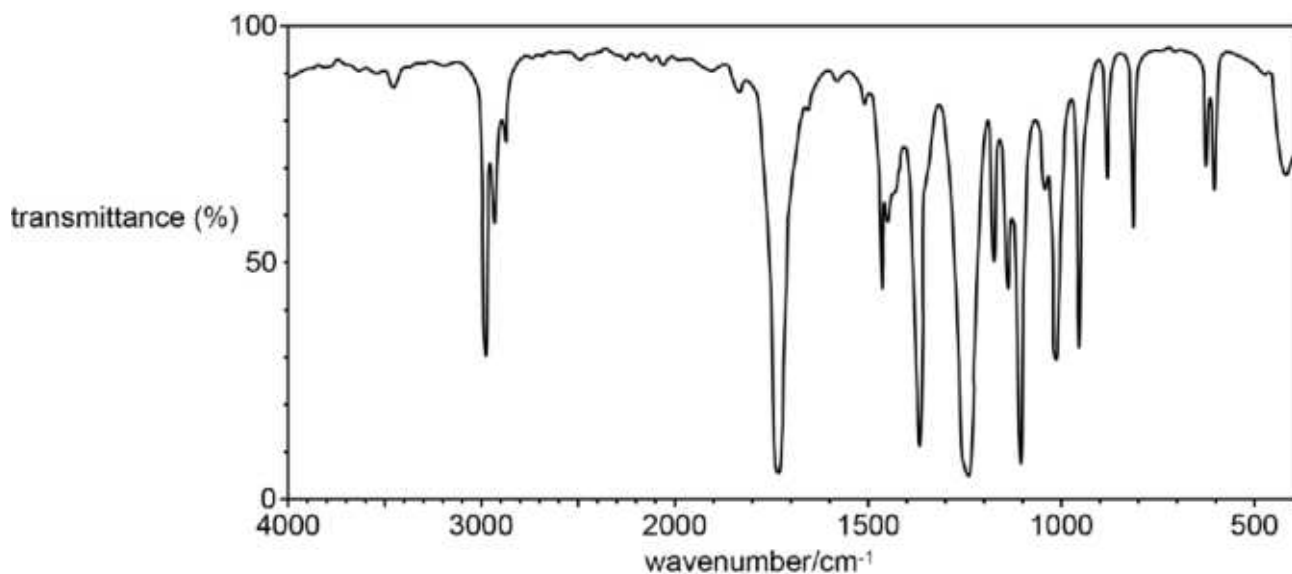
Elemental analysis by mass:

C: 58.80%; H: 9.87%; O: 31.33%

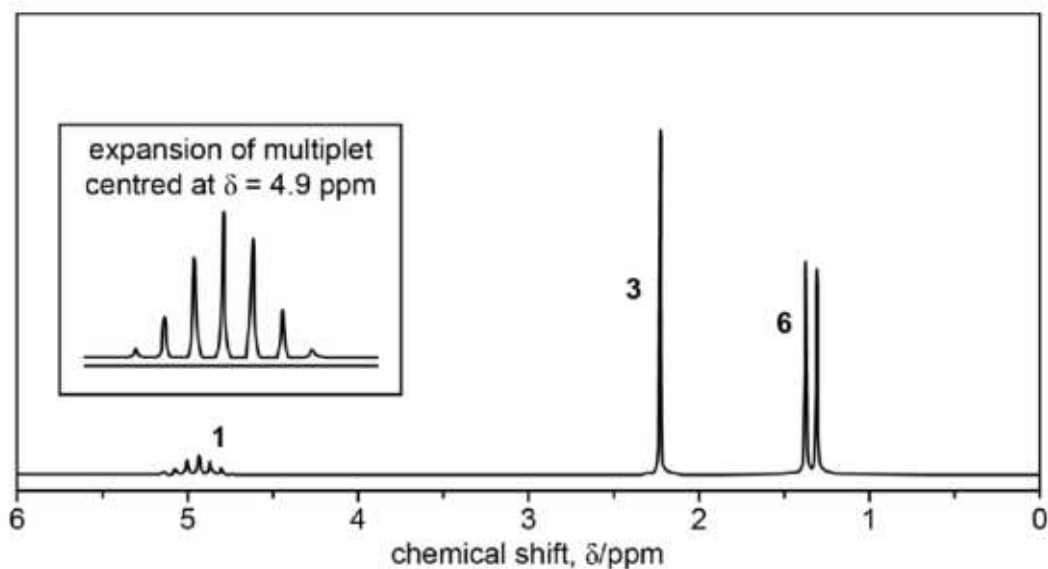
Mass spectrum

Molecular ion peak at $m/z = 102.0$

Infrared spectrum



^1H NMR spectrum



From the *Data Sheet*, the peak centred at $\delta = 4.9$ ppm would be expected at a chemical shift value about 1 ppm to the right, i.e. 3.9 ppm.

[8]

12 Information about a monobasic organic acid **D** is shown below.

- **D** reacts by both electrophilic substitution and electrophilic addition.
- The molecular formula of **D** is $C_xH_yO_2$.
- The mass spectrum of **D** has a molecular ion peak at $m/z = 148$.
- The ^{13}C NMR spectrum of **D** contains seven peaks.

Determine and draw a possible structure for **D**.

Explain your reasoning from the evidence provided.

[5]

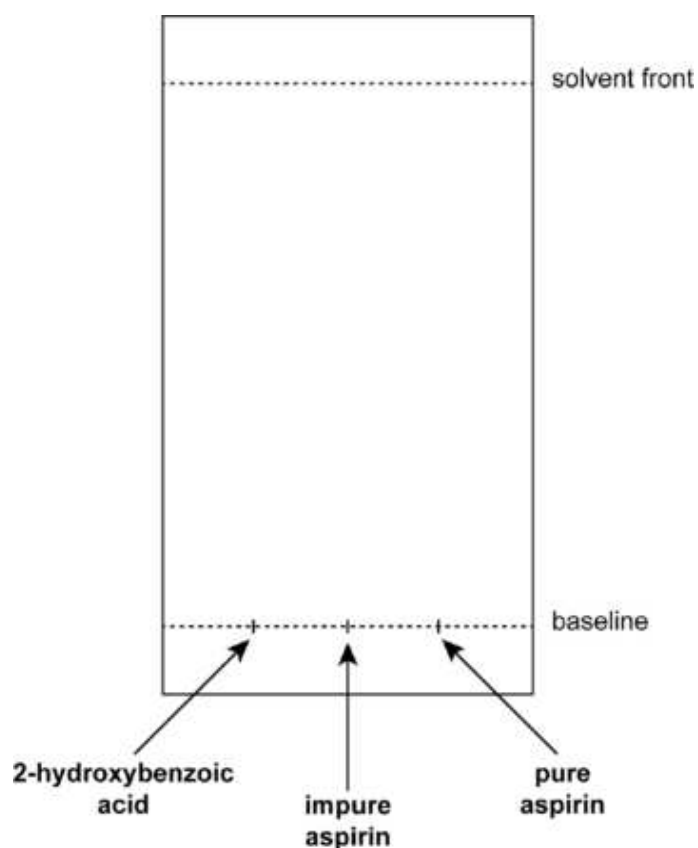
13 The R_f values and melting point ranges of 2-hydroxybenzoic acid and pure aspirin are shown in the table.

Compound	R_f	Melting point range / °C
2-Hydroxybenzoic acid	0.30	158–161
Pure aspirin	0.75	138–140

(i) A student analyses the purity of their impure aspirin by thin-layer chromatography (TLC).

From the results the student concludes that the impure aspirin is contaminated with a small amount of unreacted 2-hydroxybenzoic acid.

Draw spots on the chromatogram below to show how the student arrived at this conclusion.



[2]

(ii) Predict the melting point range of the impure aspirin.

[1]

14(a) Ethers are a homologous series of organic compounds containing the R–O–R functional group.

The structures and names of two ethers are shown in Fig. 4.1.



Fig. 4.1

Draw the **skeletal** formula of the ether, 2-ethoxy-3-methylbutane.

[1]

(b) Ethers can be prepared by nucleophilic substitution of haloalkanes with alkoxide ions, RO^- .

(i) Alkoxide ions can be prepared by reacting sodium with an alcohol. A gas is also formed.

Write an equation for the formation of methoxide ions from sodium and an alcohol.

-----[1]

(ii) Methoxyethane, shown in Fig. 4.1, can be prepared by reacting bromoethane, $\text{CH}_3\text{CH}_2\text{Br}$, with methoxide ions, CH_3O^- .

Suggest the mechanism for the nucleophilic substitution of $\text{CH}_3\text{CH}_2\text{Br}$ with CH_3O^- .

Show curly arrows, charges, relevant dipoles, and products.

[3]

(iii) In this mechanism, explain how CH_3O^- ions have acted as a nucleophile.

State the type of bond fission that takes place.

-----[1]

(c) 2-Ethoxypropane, shown in Fig. 4.1, is analysed by ^1H NMR spectroscopy.

Complete the table to predict the ^1H NMR spectrum of 2-ethoxypropane.

You may **not** need to use all the rows.

Chemical shift, δ/ppm	Relative peak area	Splitting pattern

[4]

(d) In organic reactions, alkoxide ions can also act as a base.

The diagram below shows an incomplete mechanism for the reaction of a diester with methoxide ions, CH_3O^- (**Step 1**), followed by reaction of the intermediate with bromoethane (**Step 2**).

- (i) For **Step 1**, add curly arrows to show how CH_3O^- reacts with the diester to form the intermediate.
In the box, draw the structure of the organic product formed in **Step 2**.



[3]

- (ii) Explain how CH_3O^- ions have acted as a base in this mechanism.

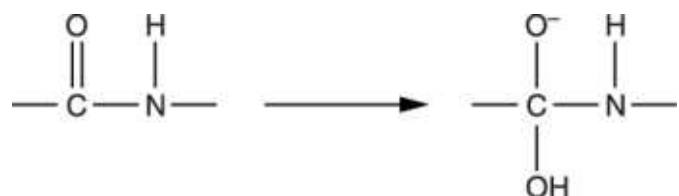
----- [1]

15(a) The building blocks of peptides and proteins are α -amino acids.

A tripeptide is hydrolysed to form a mixture of three different α -amino acids.

The first step of an incomplete mechanism for the alkaline hydrolysis of the tripeptide is shown below.

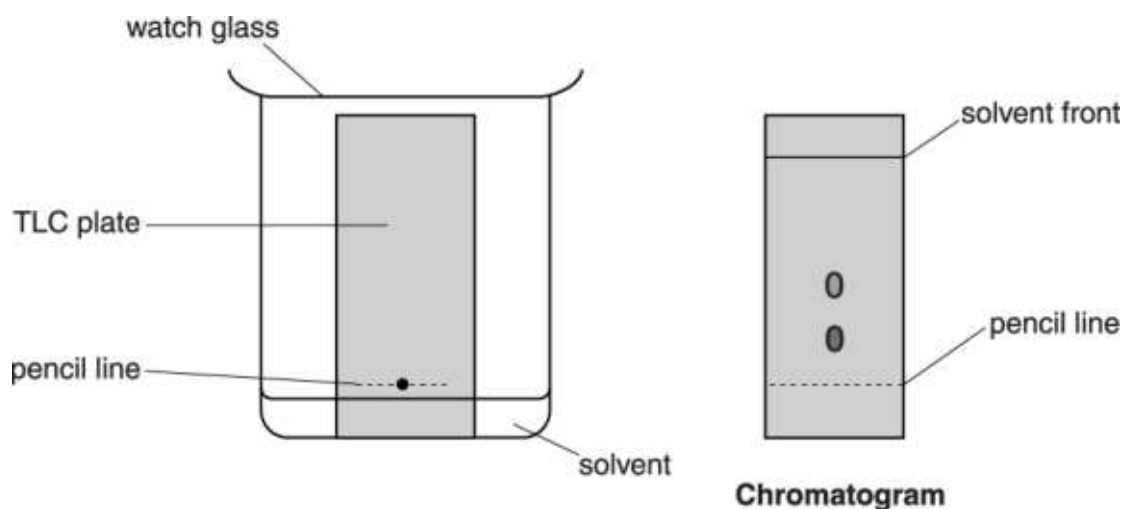
Add curly arrows and relevant dipoles to the diagram to suggest how the hydroxide ion takes part in the first step of this mechanism.



[2]

- (b) The tripeptide is hydrolysed and the resulting mixture containing the three amino acids is neutralised.

A student tries to separate and identify the three amino acids in the mixture using thin-layer chromatography (TLC). The diagram below shows the apparatus for the experiment and the chromatogram produced.



Explain how the chromatogram can be used to identify amino acids.

The student thinks that there should be three spots on the chromatogram.

Suggest why there are only two spots.

[3]

- (c) The three α -amino acids in the tripeptide are aspartic acid, glycine and isoleucine.

The general formula for an α -amino acid is $\text{RCH}(\text{NH}_2)\text{COOH}$.

α -amino acid	R-group
aspartic acid	$-\text{CH}_2\text{COOH}$
glycine	$-\text{H}$
isoleucine	$-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$

- (i) Aspartic acid has an isoelectric point of 2.77.

What is meant by the term *isoelectric point*?



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

----- [1]

- (ii) Draw the structure of aspartic acid when it is dissolved in a solution with a high pH.

[1]

- (iii) Suggest a structure for the tripeptide.

On your structure, mark each chiral centre with an asterisk (*).

[2]

16(a) A chemistry teacher carries out an experiment to synthesise 2-aminopropan-1-ol, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$.

The teacher asks a university chemistry department to test the 2-aminopropan-1-ol using proton NMR spectroscopy and mass spectrometry.

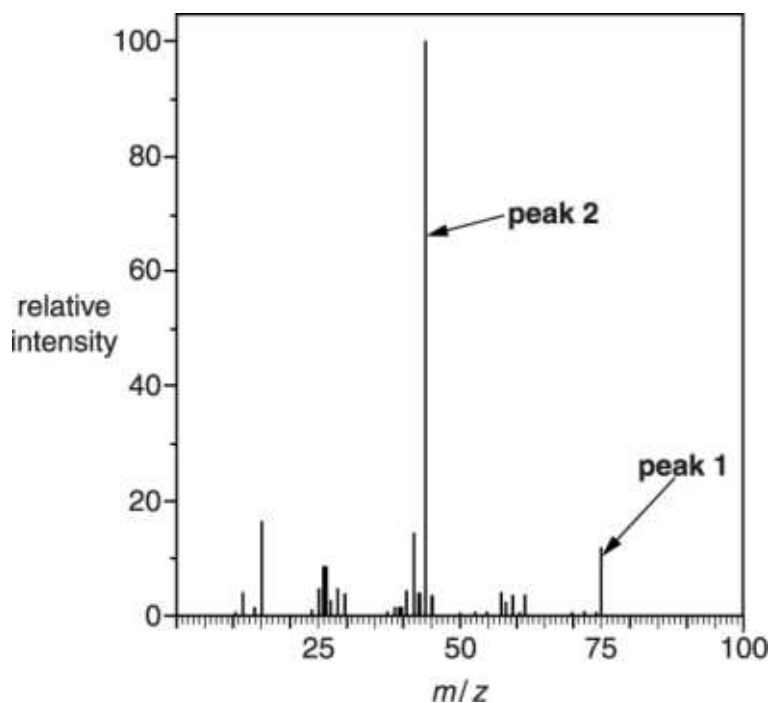
(i) For the ^1H NMR analysis, the sample was dissolved in D_2O .

Complete the table to predict the ^1H NMR spectrum of $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$ after dissolving in D_2O .

^1H NMR spectrum for $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$, dissolved in D_2O		
Chemical shift, δ / ppm	Relative peak area	Splitting pattern

[3]

(ii) The mass spectrum for $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$ is shown below.



Give the formulae for the species responsible for **peak 1** and **peak 2** in the mass spectrum.

peak 1

peak 2

[2]

(b) The teacher synthesises 2-aminopropan-1-ol, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$, from 2-chloropropan-1-ol, $\text{CH}_3\text{CHClCH}_2\text{OH}$.

(i) State the reagents and conditions required for this synthesis.

----- [1]

(ii) The sample prepared by the teacher from 2-chloropropan-1-ol is not pure. It also contains compound D.

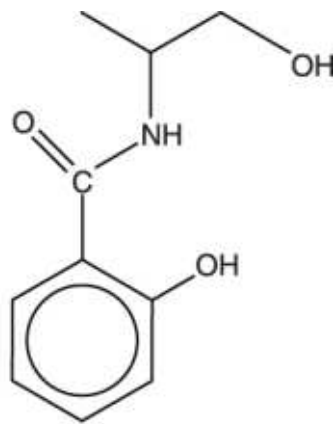
Compound D has a molecular formula of $\text{C}_6\text{H}_{15}\text{NO}_2$.

Suggest the structure of compound D.

Compound D

[1]

(c) In a separate experiment, the chemistry teacher prepares compound E from 2-aminopropan-1-ol.



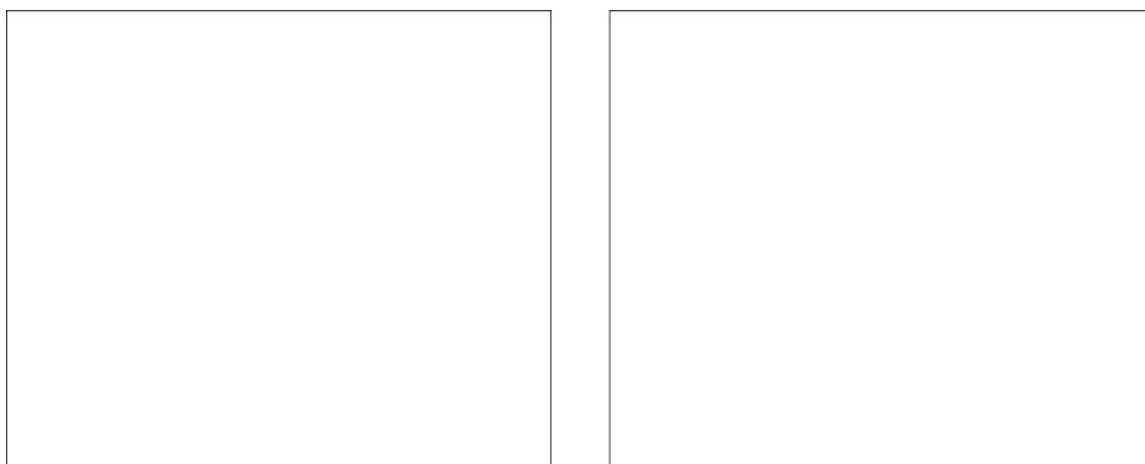
compound E

- (i) One of the functional groups in compound **E** is a phenol.

Name the other functional groups in compound **E**.

 ----- **[1]**

- (ii) Draw the structures of the **two** organic products formed when compound **E** is heated under reflux with dilute hydrochloric acid.



[2]

17(a) There are several isomeric alcohols with the formula $C_5H_{11}OH$.

Pentan-1-ol, $CH_3(CH_2)_3CH_2OH$, can be prepared in the laboratory by the reduction of an aldehyde.

State a suitable reducing agent for this reaction and write an equation to show the preparation of pentan-1-ol. Use $[H]$ to represent the reducing agent in the equation.

Reducing agent

Equation

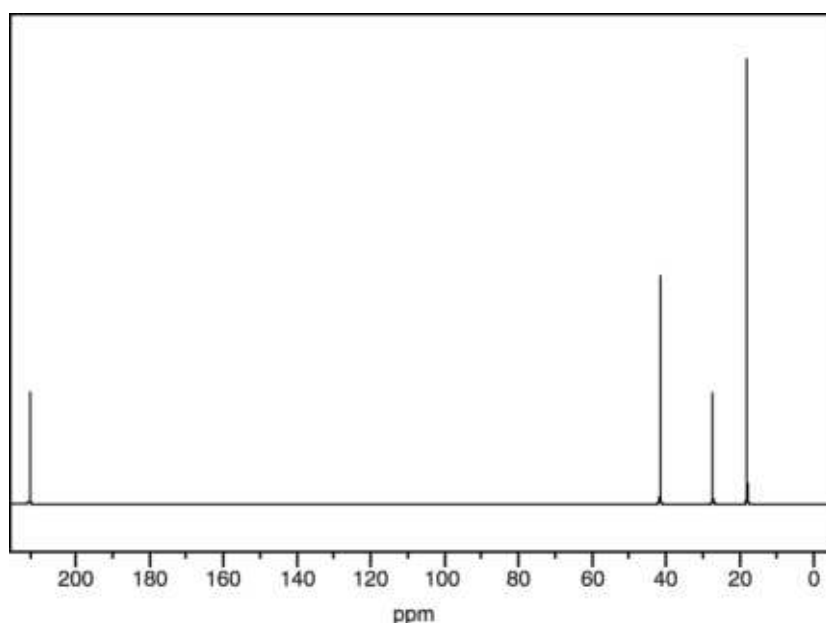
[2]

(b) Compound F is a structural isomer of $C_5H_{11}OH$.

Compound F is converted to compound G when heated under reflux with acidified potassium dichromate(VI) solution.

Compound G reacts with 2,4-dinitrophenylhydrazine to form an orange solid but compound G does not react with Tollens' reagent.

The ^{13}C NMR spectrum of compound G is shown below.

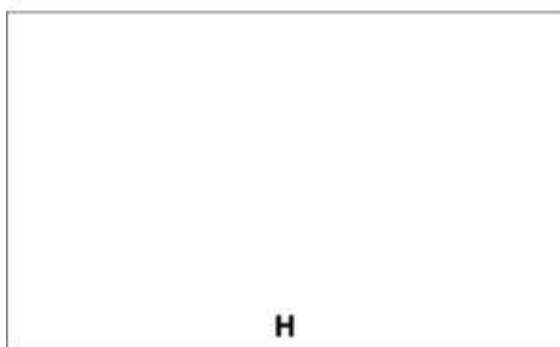
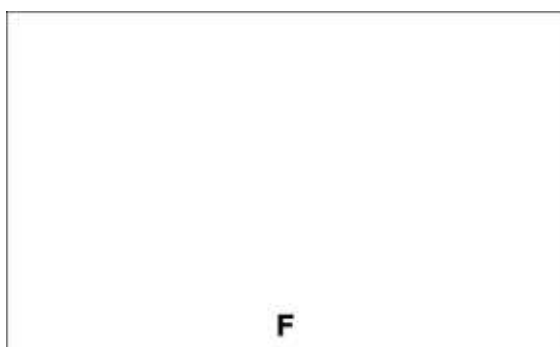


Compound H is a carboxylic acid. In a titration, 0.211 g of carboxylic acid H requires 22.8 cm^3 of 0.125 mol dm^{-3} NaOH for neutralisation.

Compound F reacts with compound H in the presence of concentrated sulfuric acid to form organic compound I.

Identify compounds F, G, H and I and draw their structures in the boxes below.

Show your working **only** for the identification of compound H.

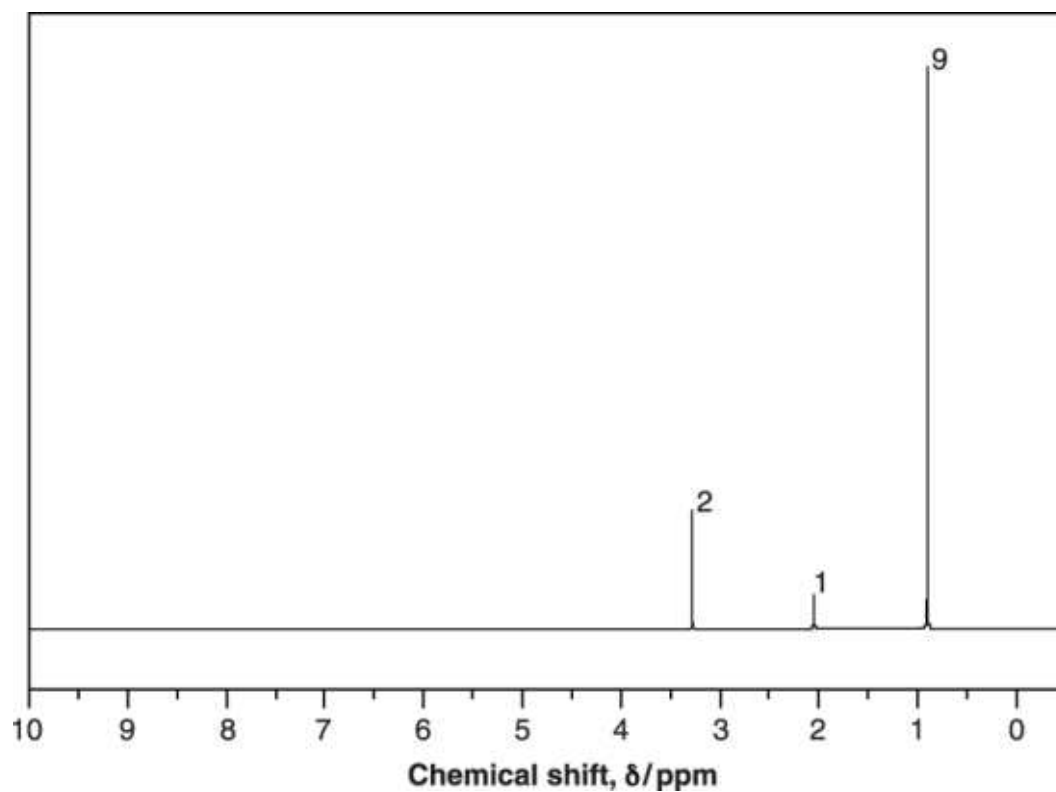


[7]

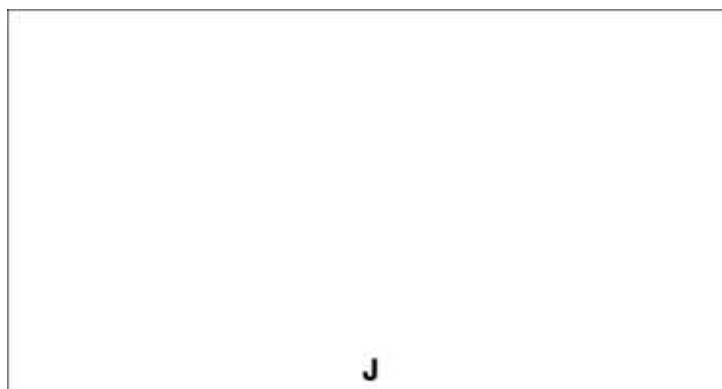
(c) Compound **J** is another structural isomer of $C_5H_{11}OH$.

The ^1H NMR spectrum of **J** is shown below.

The numbers next to each peak are the relative peak areas.



Identify compound **J** and draw its structure in the box below.



[1]

18 Which reagent could be used to distinguish between $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{C}_6\text{H}_5\text{OH}$?

- A $\text{AgNO}_3(\text{aq})$ in ethanol
- B CH_3COCl
- C $\text{Na}_2\text{CO}_3(\text{aq})$
- D Bromine water

Your answer

[1]

19 How many peaks are observed in the ^{13}C NMR spectrum of 1,3-dimethylbenzene?

- A 3
- B 4
- C 5
- D 6

Your answer

[1]

- 20 A student hydrolyses a sample of protein and uses Thin-Layer Chromatography (TLC) to analyse the mixture of amino acids produced.

The chromatogram obtained is shown in Fig. 17.1.

Table 17.1 shows the R_f values for different amino acids in the solvent used.

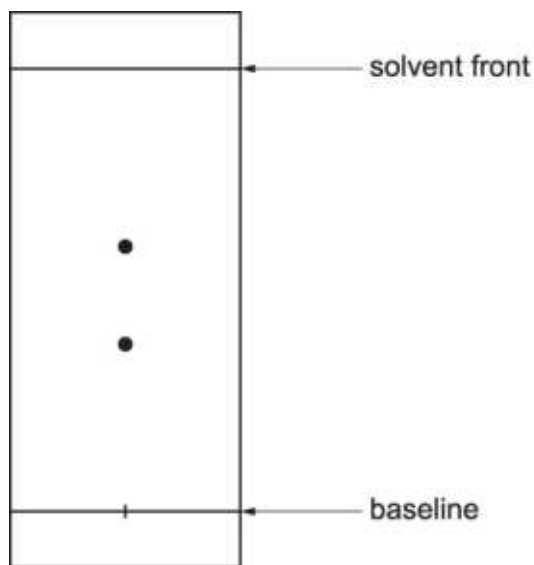


Fig. 17.1

Amino acid	R_f value
Threonine	0.65
Valine	0.60
Histidine	0.53
Serine	0.45
Leucine	0.38

Table 17.1

- (i) Analyse the chromatogram to identify the amino acids.

-----[1]

- (ii) The student runs a second chromatogram on the sample using a more polar solvent.

Predict the effect, if any, on the R_f values of the amino acids. Explain your reasoning.

-----[2]

21(a) A student was provided with five compounds: an aldehyde, a ketone, a carboxylic acid and two esters. The student decides to identify the type of compound by carrying out some chemical tests.

Suggest chemical tests to identify the carboxylic acid and aldehyde.

For each test, include essential reagent(s), observation(s) and a balanced equation.

In your equations, use 'R' for the alkyl group.

(i) Test for carboxylic acid.

Reagent(s) _____

Observation(s) _____

Equation

[2]

(ii) Test for aldehyde.

Reagent(s) _____

Observation(s) _____

Equation

[2]

- (b) Suggest a chemical test to distinguish the ketone from the two esters.

Reagent(s) _____

Observation(s) _____

-----[1]

- (c) The student wants to confirm that the other two compounds are esters. Unfortunately there is no direct test for an ester group.

The esters are $\text{CH}_3\text{COOC}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{CCOOCH}_3$.

The student plans the following:

- hydrolyse the two esters using aqueous sodium hydroxide.
- separate the hydrolysis products.
- carry out tests on the hydrolysis products.

- (i) Write an equation for the hydrolysis of one of the two esters with aqueous sodium hydroxide.

Show the structures for the organic compounds.

[2]

- (ii) Suggest a chemical test on the hydrolysis products that would allow the two esters to be identified.

Write an equation for one reaction that takes place.

Show the structures for the organic compounds.

Reagent(s) _____

Observation(s) _____

Equation

[2]

- (iii) The student thought that NMR spectroscopy could be used to identify the two esters without the need to carry out chemical tests.

The esters are $\text{CH}_3\text{COOC}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{CCOOCH}_3$.

Explain whether the student is correct for ^{13}C and ^1H NMR spectroscopy. Your answer should also clearly state any differences between the spectra of the two esters.

[3]

The ^1H NMR spectrum of the aldehyde contains two singlet peaks only: a large peak at $\delta = 1.2$ ppm and smaller peak at $\delta = 9.6$ ppm.

Show **all** your reasoning.

[5]

22 *Compound J is an organic compound containing carbon, hydrogen and nitrogen only.

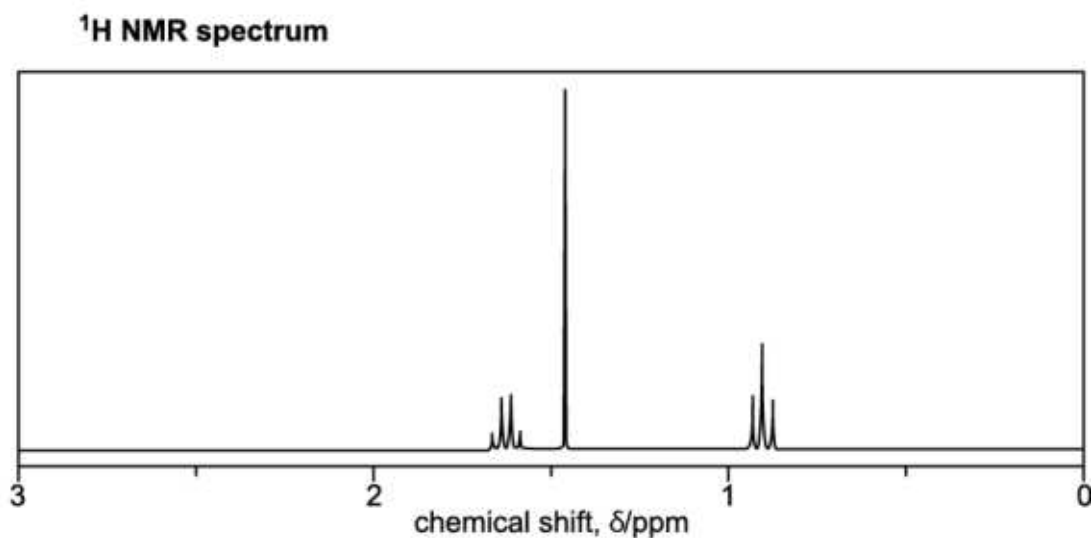
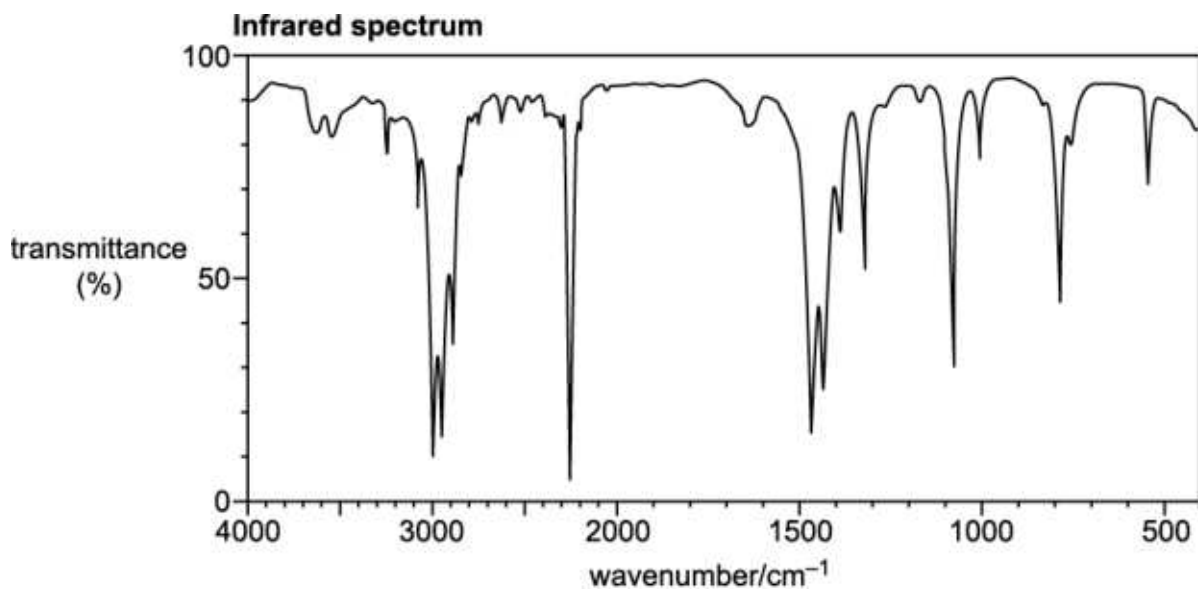
A chemist analyses compound J and the results are shown below:

Elemental analysis by mass:

C: 74.17%; H: 11.41%; N, 14.42%

Mass spectrum

Molecular ion peak at $m/z = 97.0$

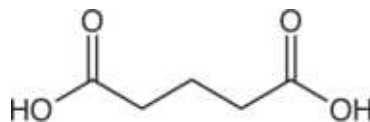


Use the information provided to suggest a structure for compound J.

Show **all** of your reasoning.

[6]

24 The compound below is analysed by ^1H NMR spectroscopy.



How many peaks are observed in the ^1H NMR spectrum?

- A 5
- B 4
- C 3
- D 2

Your answer

[1]

25 Which reagents could be used to prepare $\text{CH}_3\text{CH}_2\text{CONHCH}_3$?

- A $\text{CH}_3\text{CH}_2\text{COCl} + \text{CH}_3\text{NH}_2$
- B $\text{CH}_3\text{CH}_2\text{CONH}_2 + \text{CH}_3\text{Br}$
- C $\text{CH}_3\text{CH}_2\text{COONa} + \text{CH}_3\text{NH}_2$
- D $\text{CH}_3\text{CH}_2\text{COCH}_3 + \text{NH}_3$

Your answer

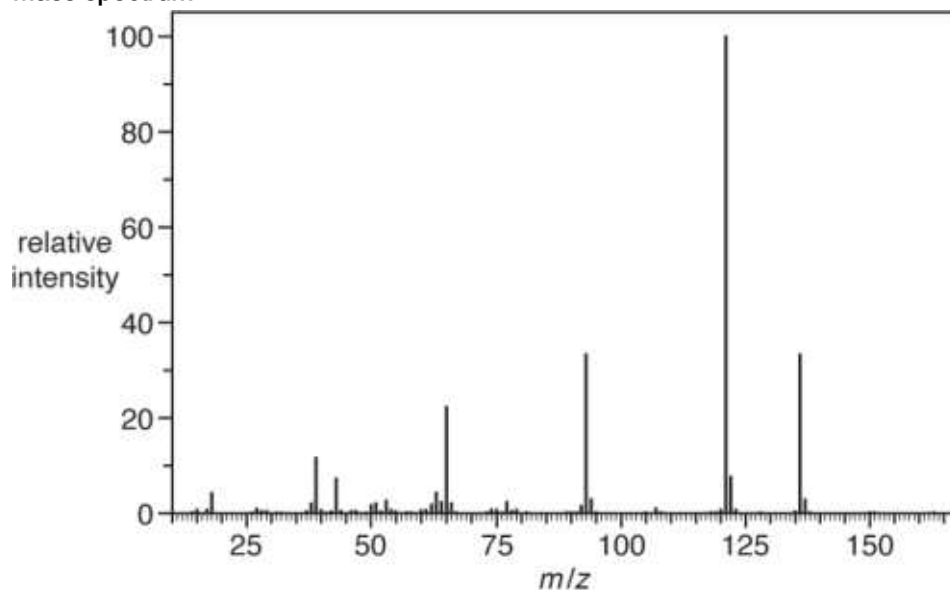
[1]

26(a) A chemist analyses a naturally occurring aromatic compound.

The percentage composition and mass spectrum of the compound are shown below.

Percentage composition by mass: C, 70.58%; H, 5.92%; O, 23.50%.

Mass spectrum



Determine the molecular formula of the compound.

Show your working.

molecular formula = _____ [3]

(b) Qualitative tests are carried out on the aromatic compound. The results are shown below.

Test	Acidity	Na ₂ CO ₃ (aq)	2,4-DNP	Tollens' reagent
Observation	pH = 5	No observable change	Orange precipitate	No observable change

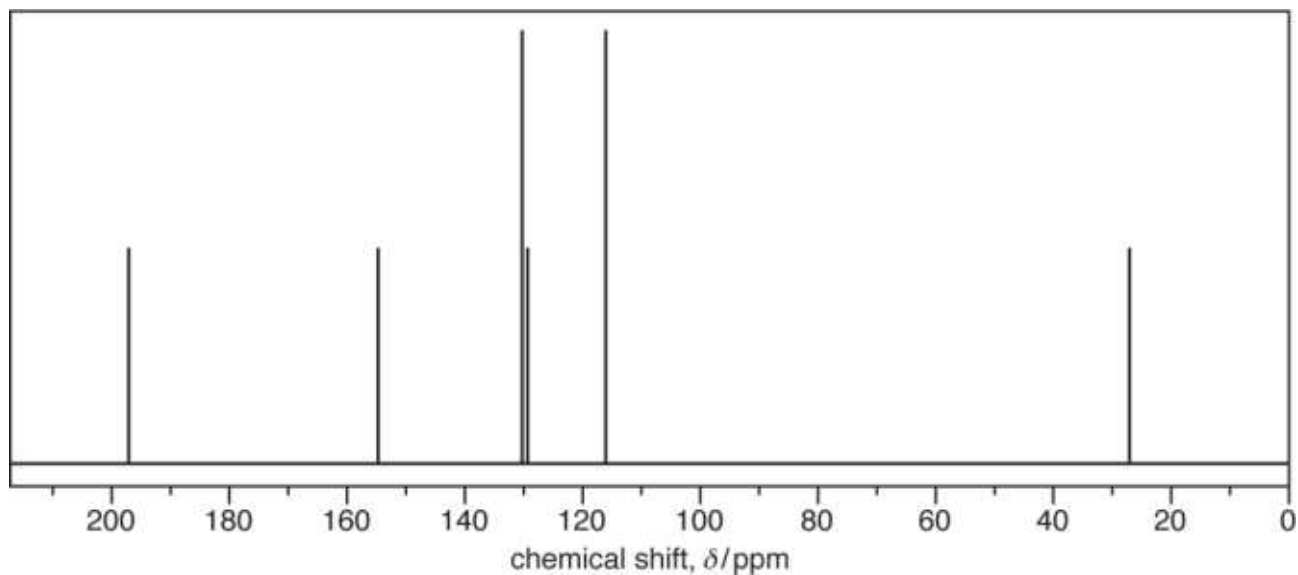
Determine the functional groups in the compound. Explain your reasoning.

Functional groups

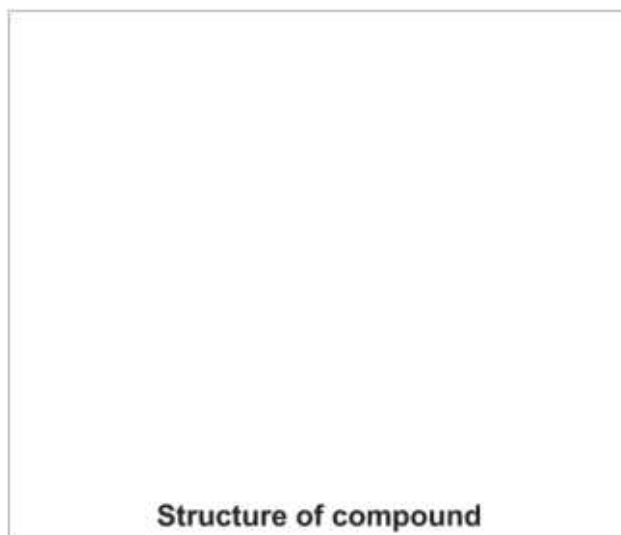
Explanation

----- [3]

(c) The carbon-13 NMR spectrum of the compound is shown below.



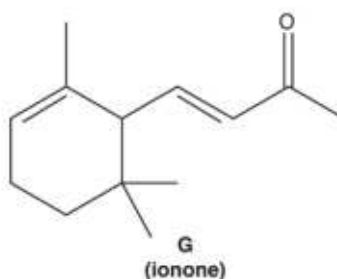
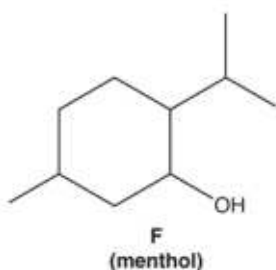
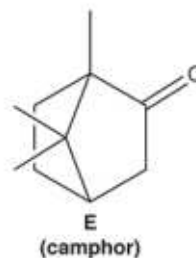
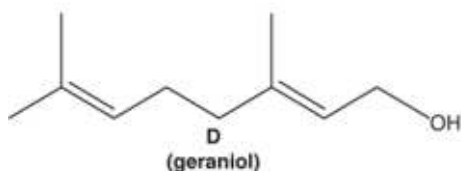
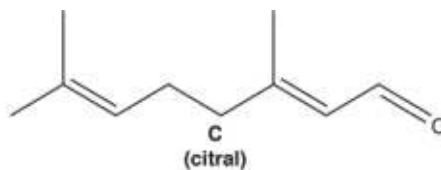
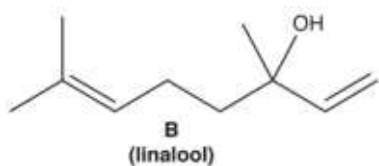
Using the spectrum and the results from (a) and (b), determine the structure of the compound. Explain your reasoning.



[3]



The structures for six naturally occurring organic compounds with pleasant smells, B–G, are shown below. The common names in brackets relate to their source and smell.



Explain how chemical tests would allow each compound to be distinguished from the other compounds.

In your answer, include essential details for all test procedures and observations.

Details of apparatus and quantities are **not** required.

[6]

28 Which compound is used as a standard for NMR chemical shift measurements?

A $\text{Si}(\text{CH}_3)_4$

B CDCl_3

C D_2O

D CCl_4

Your answer

[1]

29 What is the number of peaks in the ^1H NMR spectrum of $\text{HOOCCH}_2\text{CHOHCH}_2\text{COOH}$?

A 3

B 4

C 5

D 6

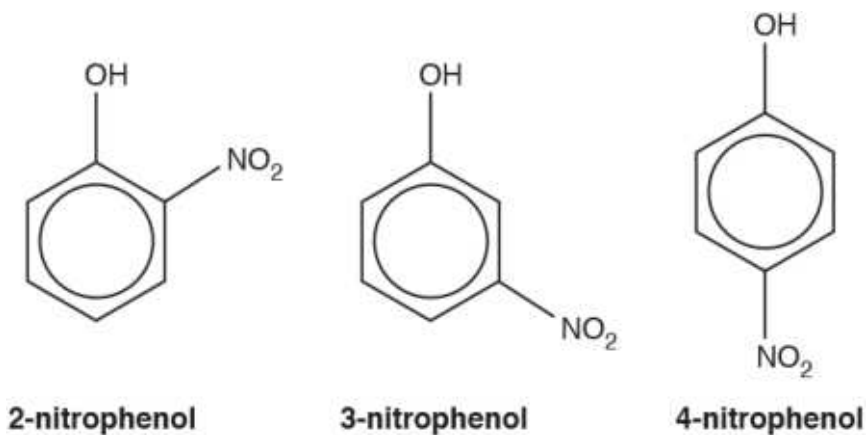
Your answer

[1]

Phenol undergoes nitration more readily than benzene.

- (i) A student carries out the nitration of phenol with dilute nitric acid to produce 2-nitrophenol and 4-nitrophenol.

A small amount of 3-nitrophenol is also produced.



The student thought that ^{13}C NMR spectroscopy could be used to distinguish between these three nitrophenols.

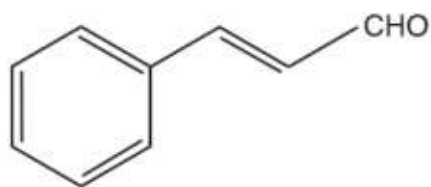
Explain whether the student is correct.

[3]

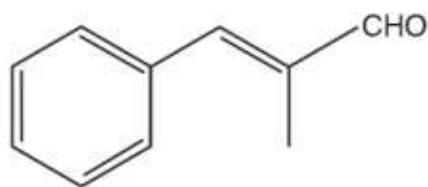
[3]

[3]

31 A student plans to carry out some chemical tests on both cinnamaldehyde and methylcinnamaldehyde.



cinnamaldehyde



methylcinnamaldehyde

- (i) Suggest a suitable chemical test to confirm that both compounds contain an unsaturated carbon chain.

Your answer should include the reagent and observations.

----- [1]

- (ii) Describe a chemical test to confirm that both compounds contain an aldehyde functional group.

Your answer should include the reagent and observations.

----- [1]

- (iii) Describe a chemical test to confirm that cinnamaldehyde and methylcinnamaldehyde contain a carbonyl group.

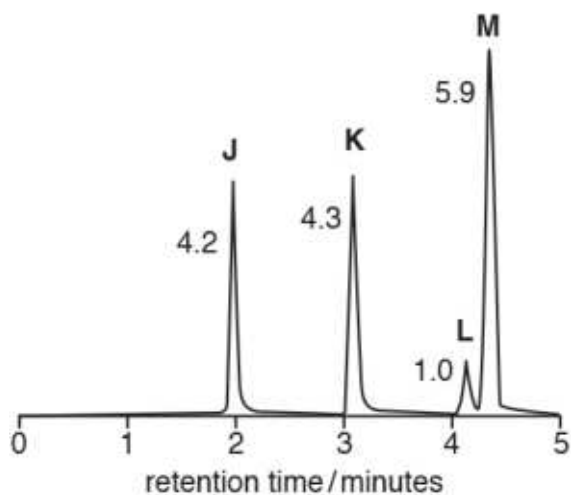
How could the products of this test be used to distinguish between the two compounds?

Your answer should **not** include spectroscopy.

----- [3]

- 32 A cosmetic product containing four esters, J, K, L and M, is analysed by gas chromatography and mass spectrometry. The results are shown below.

Gas chromatogram



The numbers by the peaks are the relative molar proportions of the compounds in the mixture.

Mass spectrometry

ester	m/z of molecular ion peak
J	152
K	166
L	180
M	180

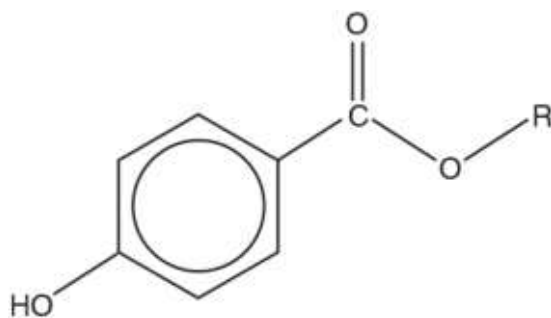
- (i) The concentration of ester K in the cosmetic product is $9.13 \times 10^{-2} \text{ g dm}^{-3}$.

Using the results, calculate the concentration, in mol dm^{-3} , of ester M in the cosmetic product.

Give your answer to **two** significant figures.

concentration of ester M = _____ mol dm^{-3} [2]

(ii) A general structure for esters **J**, **L** and **M** is shown below.



Where 'R' is an alkyl group.

Use the mass spectrometry results to deduce possible structures for esters **J**, **L** and **M**.

J	L	M

[3]

- 33 A scientist is researching compounds that might be suitable as fuel additives.
One of the compounds gives the analytical results below.

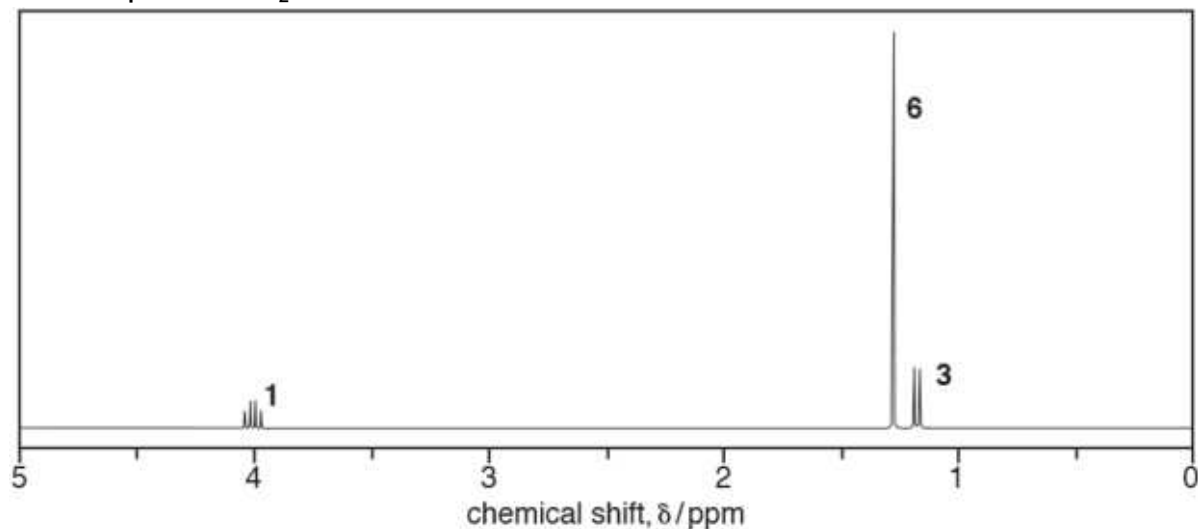
Elemental analysis by mass:

C: 54.54%; H: 9.10%; O: 36.36%

Mass spectrum:

Molecular ion peak at $m/z = 132.0$

^1H NMR spectrum in D_2O



The numbers by the peaks are the relative peak areas.

When the spectrum is run without D_2O , there are **two** additional peaks with the same relative peak areas at 11.0 ppm and 3.6 ppm.

Use the information provided to suggest a structure for the compound.

Show all your reasoning.

[6]

34 A student carried out an experiment to measure the enthalpy change of combustion of methanol.

The energy from the combustion of methanol was used to heat a beaker containing water.

The student's calculated enthalpy change of combustion was **more** exothermic than the value in data books.

Which error could have caused this difference?

- A Some methanol had evaporated from the wick before the final weighing.
- B In the calculation, the student used the molar mass of ethanol instead of methanol.
- C There was incomplete combustion.
- D The water boiled for 5 minutes before the final temperature was taken.

Your answer

[1]

35 Which one of the following reacts with ethanoic acid **and** with phenol?

- A Aqueous potassium hydroxide
- B Bromine
- C Calcium carbonate
- D Methanol and an acid catalyst

Your answer

[1]

36 Which statement(s) is/are correct for gas chromatography?

- 1 The components in a mixture can be identified from their retention time.
- 2 The relative peak areas give the proportions of components in a mixture.
- 3 Calibration curves are used to confirm the concentrations of components in a mixture.

- A 1, 2 and 3
- B Only 1 and 2
- C Only 2 and 3
- D Only 1

Your answer

[1]

37 An organic compound I is analysed, using a combination of techniques. The analytical data is shown below.

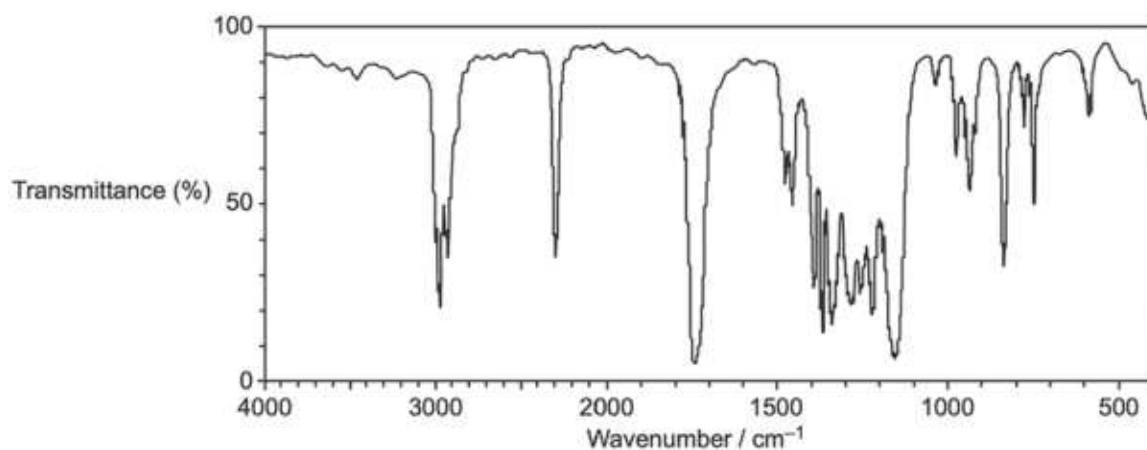
Elemental analysis by mass

C, 56.69%; H, 7.09%; N, 11.02%; O, 25.20%

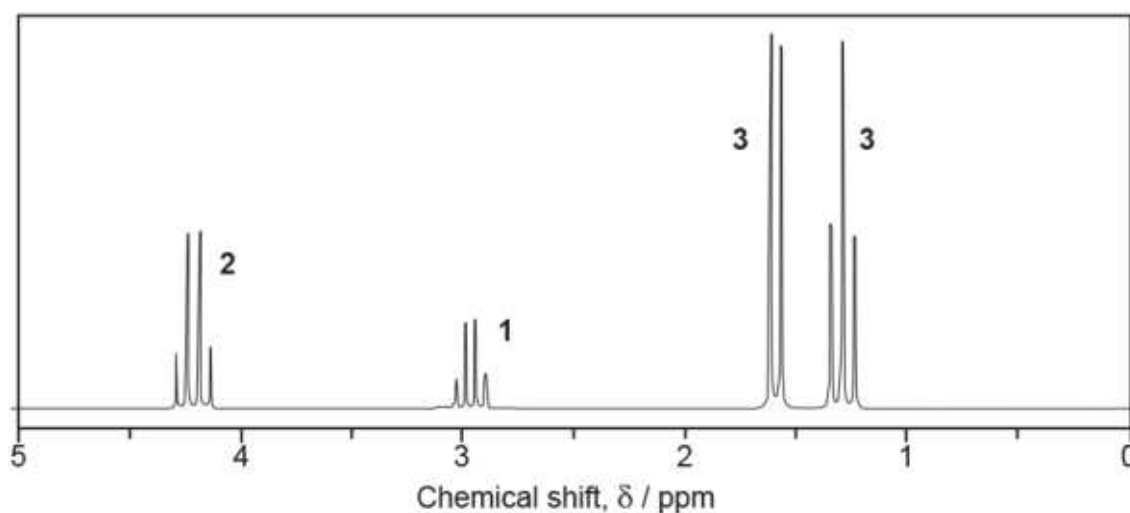
Mass spectrum

Molecular ion peak at $m/z = 127.0$

IR spectrum

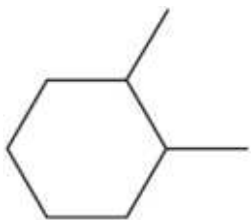
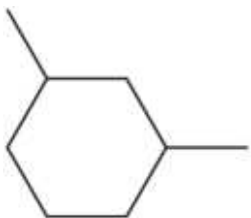


Proton NMR spectrum



Explain the use of two deuterated compounds in NMR spectroscopy.

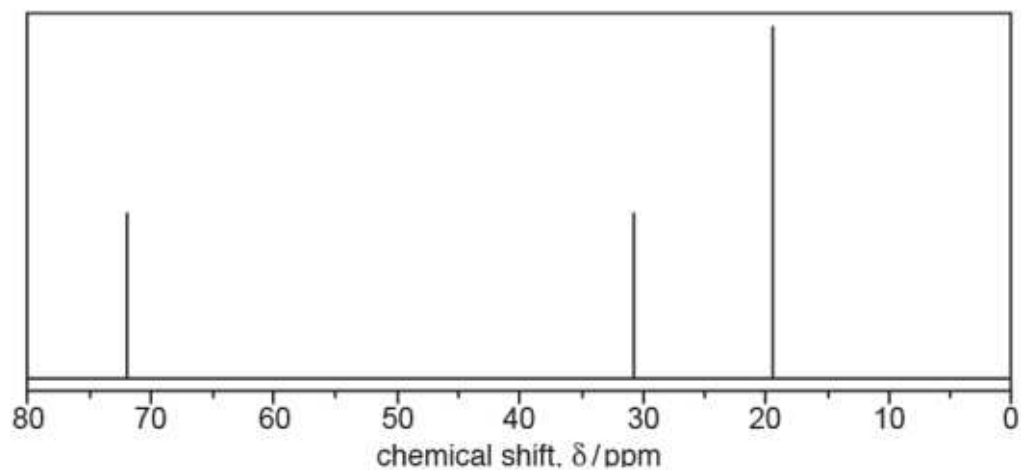
38 Which compound shows 4 peaks in its carbon-13 NMR spectrum?

A	
B	
C	
D	

Your answer

[1]

39 A compound produces the ^{13}C NMR spectrum below.



Which compound could have produced this spectrum?

- A Propane
- B 2-Methylbutane
- C 2-Methylpropan-1-ol
- D 2-Methylpropan-2-ol

Your answer

[1]

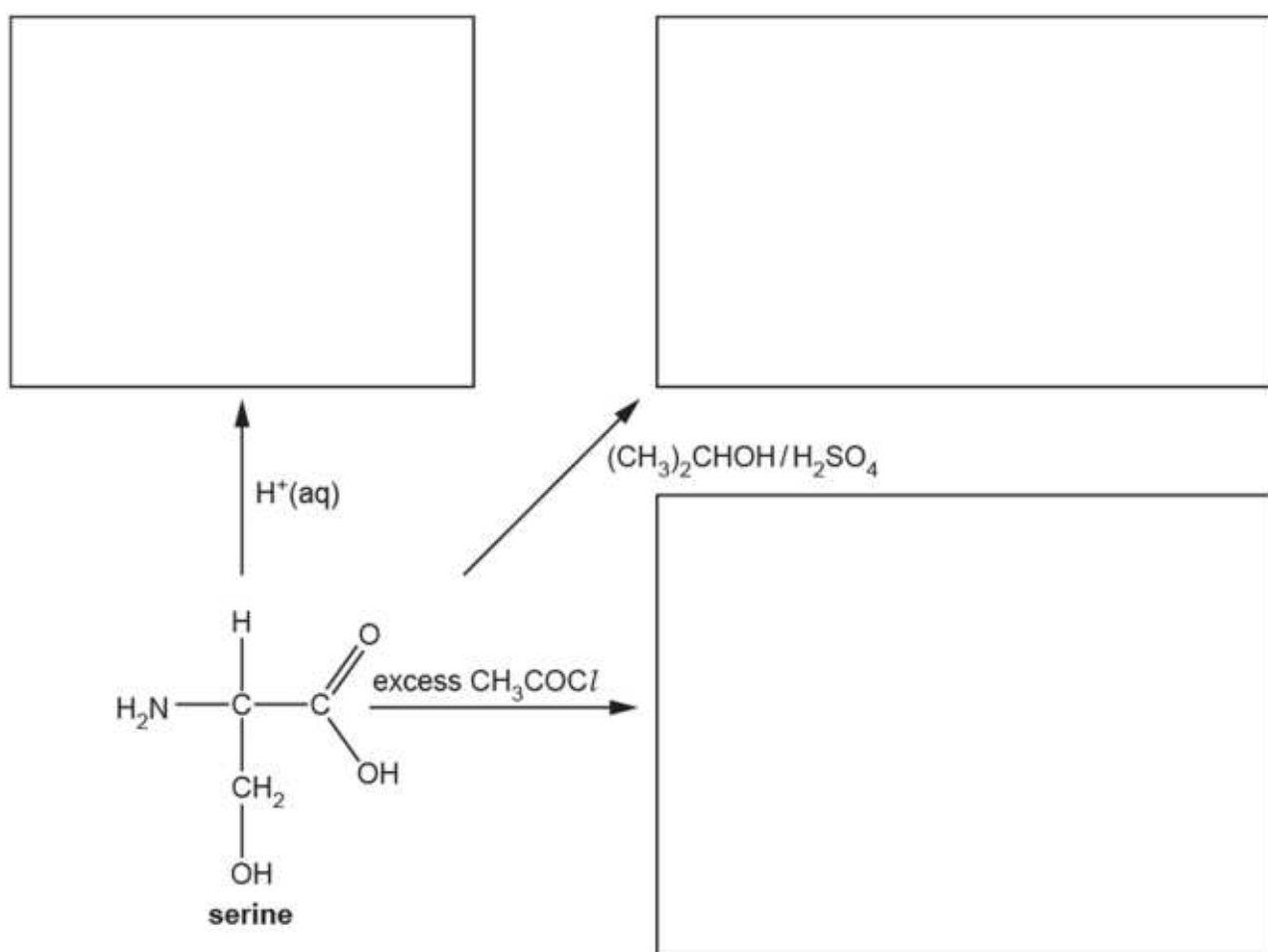
40(a) This question is about α -amino acids, $\text{RCH}(\text{NH}_2)\text{COOH}$.

Table 17.1 shows the R groups in four amino acids.

Amino acid	R group
alanine (ala)	CH_3-
serine (ser)	HOCH_2-
leucine (leu)	$(\text{CH}_3)_2\text{CHCH}_2-$
glycine (gly)	$\text{H}-$

Table 17.1

(i) In the boxes, draw the organic products for the reactions of serine shown below.



[4]

(ii) A student is provided with one of the four amino acids in **Table 17.1**.

A student carries out a titration with a standard solution of hydrochloric acid to identify the amino acid. The student's method is outlined below.

- The student dissolves 5.766 g of the amino acid in water and makes the solution up to 250.0 cm³ in a volumetric flask.
- The student titrates this solution with 25.0 cm³ of 0.150 mol dm⁻³ hydrochloric acid.
- 21.30 cm³ of the amino acid solution were required for complete neutralisation of the hydrochloric acid.

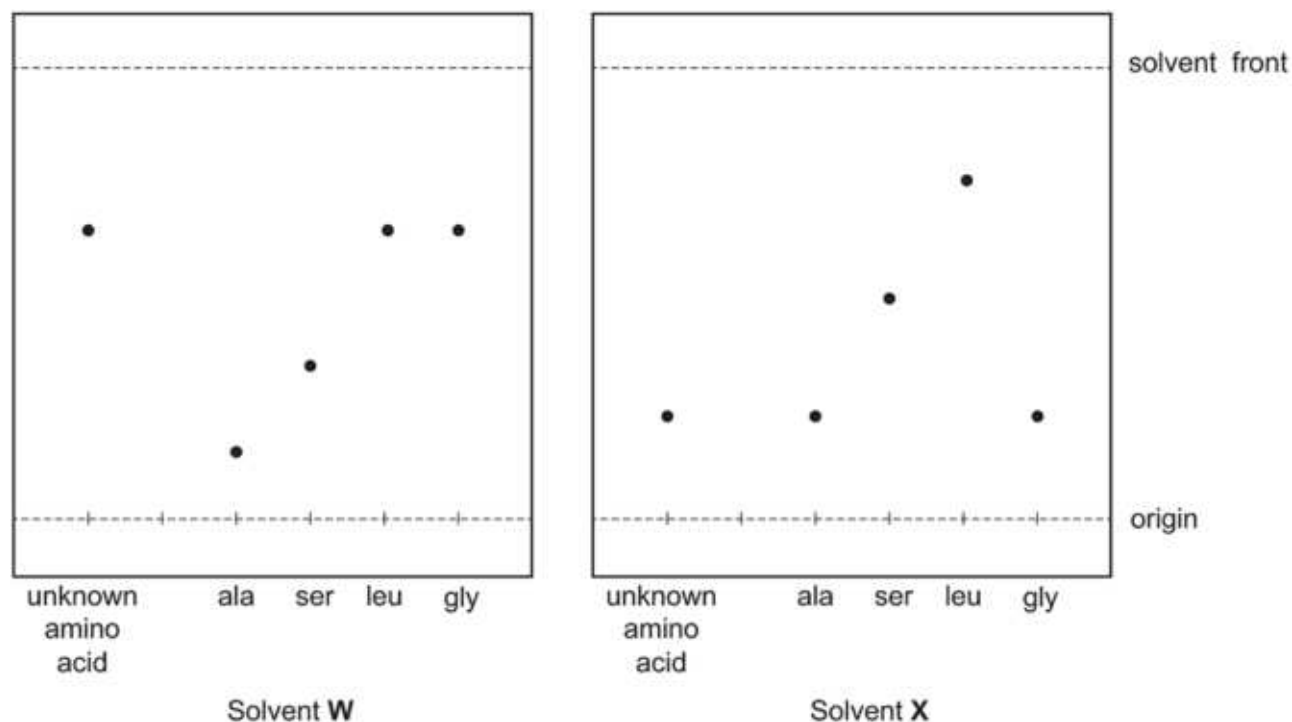
Determine which amino acid the student used.

[4]

(b) The student is provided with another amino acid.

The student attempts to identify the unknown amino acid using chromatography.

The student obtains two TLC chromatograms of the unknown amino acid and the four amino acids in Table 17.1, using two different solvents, W and X.



(i) What is the R_f value of serine (ser) in solvent W?

R_f = ... [1]

(ii) Analyse the chromatograms to identify the unknown amino acid.

Explain your reasoning.

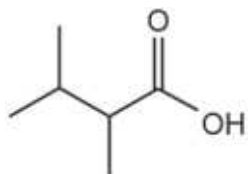
Name of unknown amino acid

Explanation

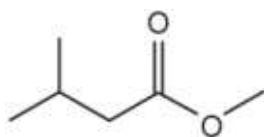
[2]

41 Which isomer of $C_6H_{12}O_2$ produces the smallest number of peaks in its ^{13}C NMR spectrum?

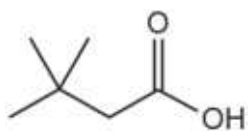
A



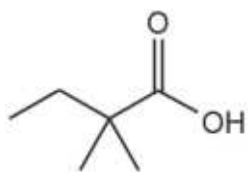
B



C



D



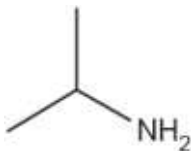
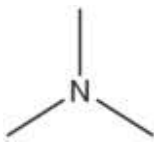
Your answer

☐

[1]

This part is about amines.

- (i) The table shows the structures and boiling points of three amines, which are structural isomers of C_3H_9N .

Amine	$CH_3CH_2CH_2NH_2$	$(CH_3)_2CHNH_2$	$(CH_3)_3N$
Skeletal formula			
Boiling point / °C	48–49 °C	33–34 °C	3–4 °C

Explain the difference in the boiling points of the three amines.

[4]

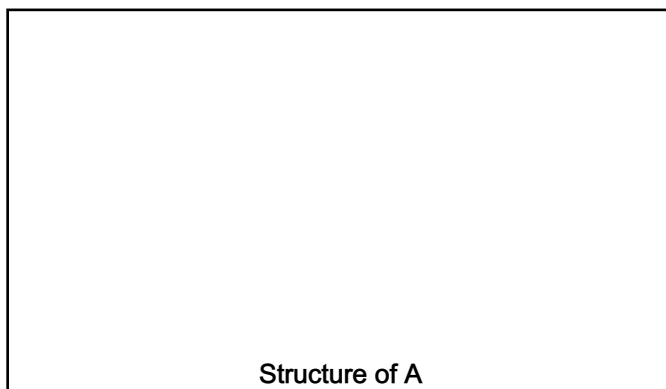
- (ii) Amine **A** is a liquid at room temperature and pressure.

When vaporised, 0.202 g of the amine produces 72.0 cm^3 of gas at $1.00 \times 10^5\text{ Pa}$ and 100 °C . The ^{13}C NMR

spectrum of amine **A** has 3 peaks.

Determine the molecular formula of **A** and suggest a possible structure for amine **A**.

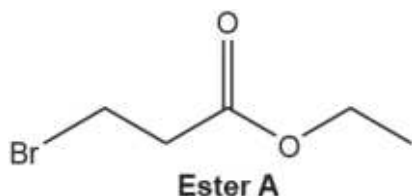
Molecular formula of **A**



[6]

43(a) This question is about esters.

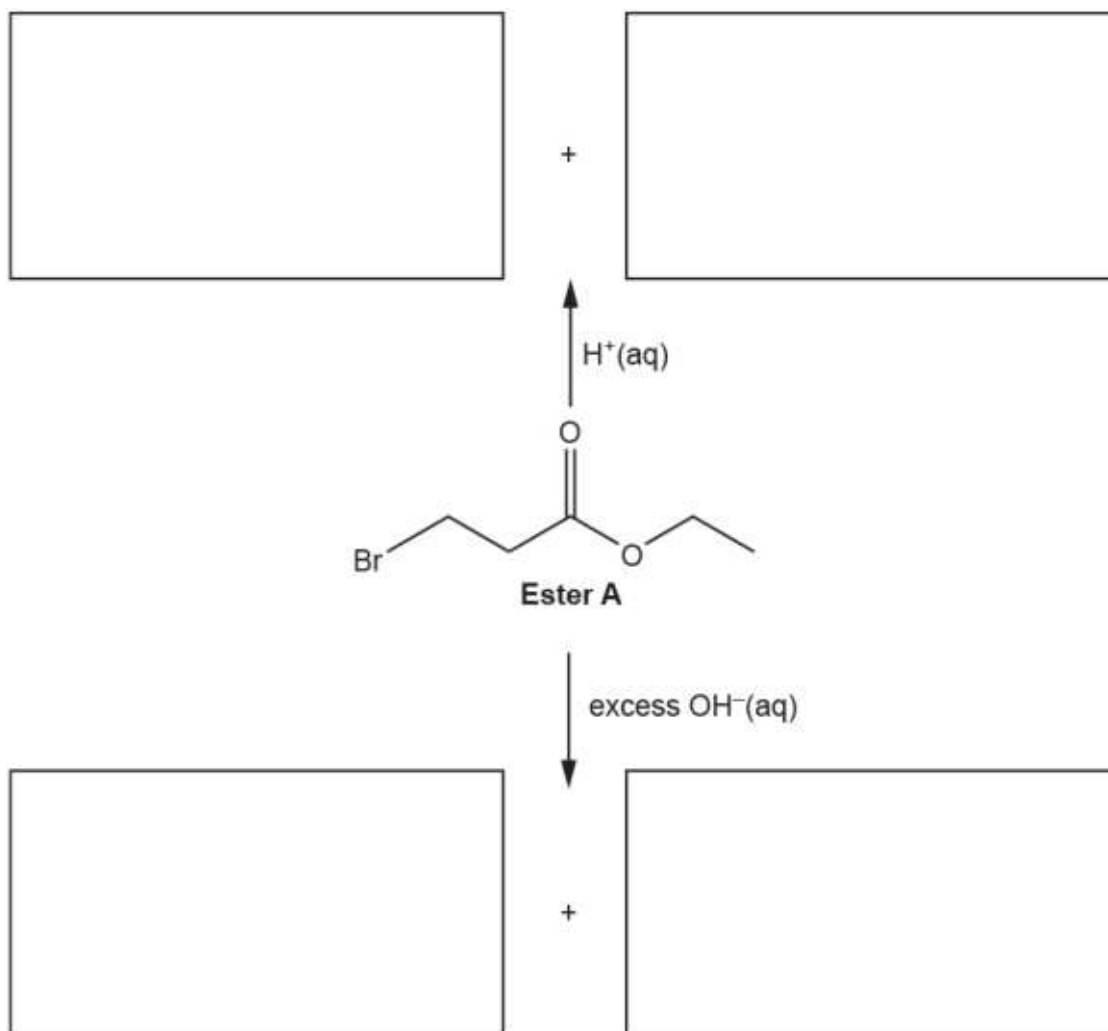
The structure of ester A is shown below.



(i) What is the systematic name of ester A?

[1]

(ii) In the boxes, draw the organic products for the reactions of the functional groups in ester A shown below. Each reaction forms two organic products.

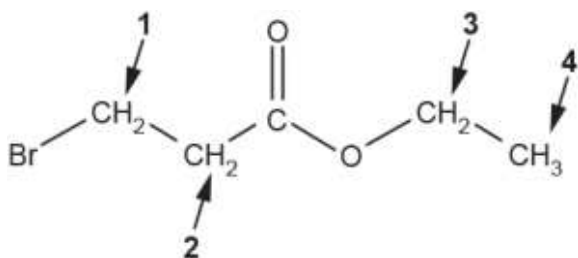


[5]

(iii) Name the type of reactions of ester **A** shown in (ii).

[1]

(b) The protons in ester **A** are in four different environments, labelled 1–4 on the structure below.



Complete the table to predict the proton NMR spectrum of ester **A**.

Proton environment	Chemical shift	Splitting pattern
1		
2		
3		
4		

[4]

(c) Compound **B** is a structural isomer of ester **A**.

- Compound **B** reacts with aqueous sodium carbonate.
- The ^{13}C NMR spectrum of **B** has 4 peaks.

Draw a possible structure for compound **B**.

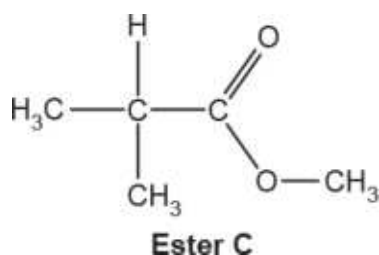
[1]

(d) A polyester is formed from 200 molecules of 4-hydroxybenzoic acid.

What is the relative molecular mass, M_r , of the polyester?

$M_r = \dots\dots\dots \text{ g mol}^{-1}$ [2]

(e) * A student intends to synthesise ester C.



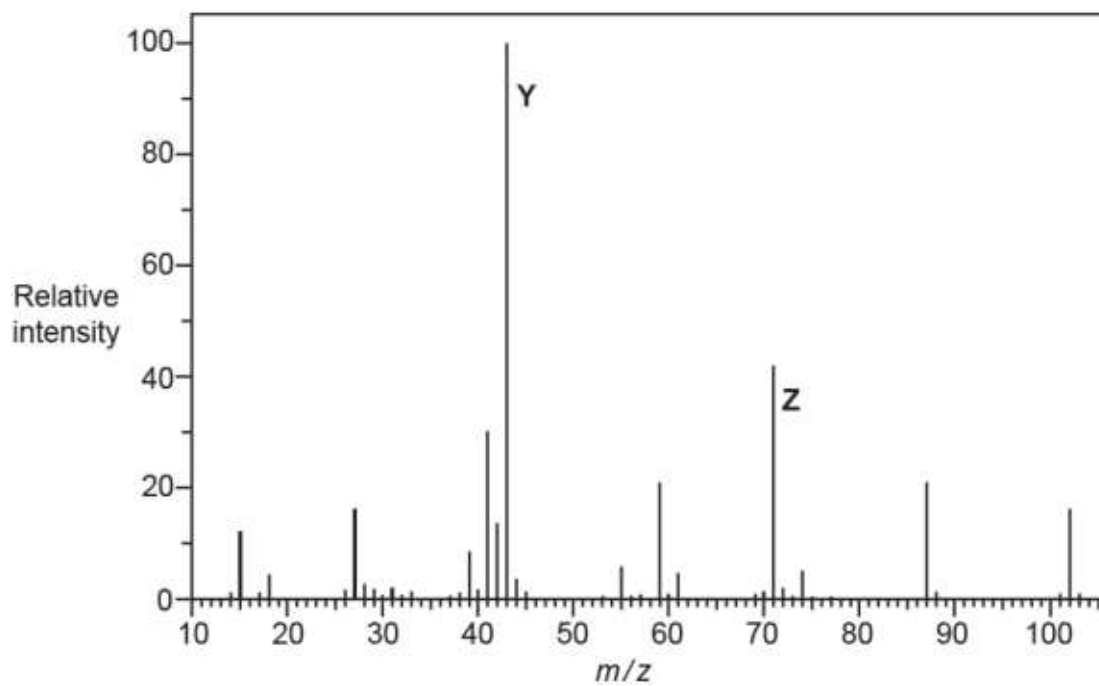
- (i) Plan a two-stage synthesis to prepare 12.75 g of ester C starting from 2-methylpropanal, $(\text{CH}_3)_2\text{CHCHO}$. Assume the overall percentage yield of ester C from 2-methylpropanal is 40%.

In your answer include the mass of 2-methylpropanal required, reagents, conditions and equations where appropriate.

Purification details are **not** required.

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(ii) The mass spectrum of ester C is shown below.



Suggest possible structures for the species responsible for peaks Y and Z in the mass spectrum.

Y	Z

[2]

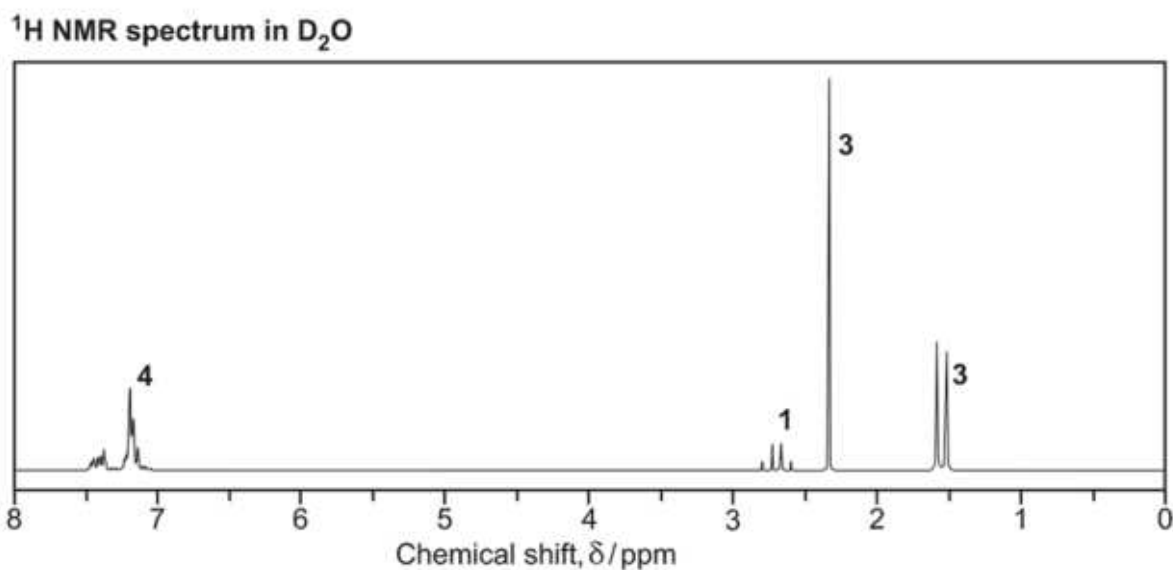
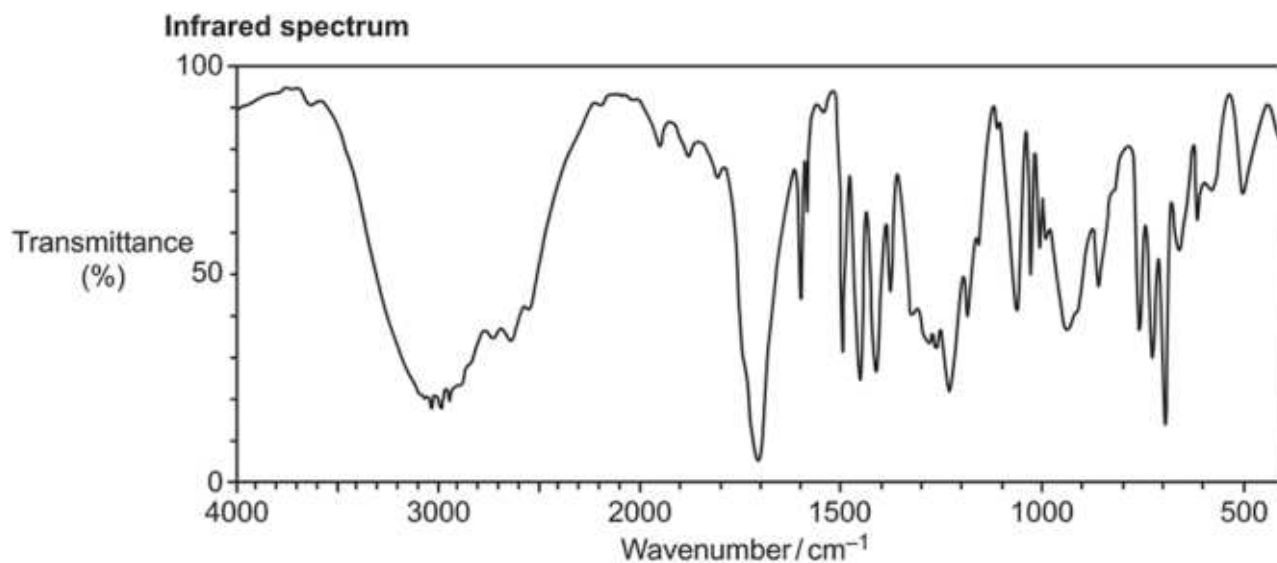
44 * Analysis of an unknown organic compound produced the following results.

Elemental analysis by mass

C: 73.17%; H: 7.32%; O: 19.51%

Mass spectrum

Molecular ion peak at $m/z = 164.0$



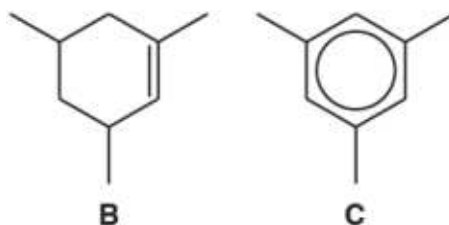
The numbers by the peaks are the relative peak areas.

Use the results to suggest **one** possible structure for the unknown compound.

Show **all** your reasoning.

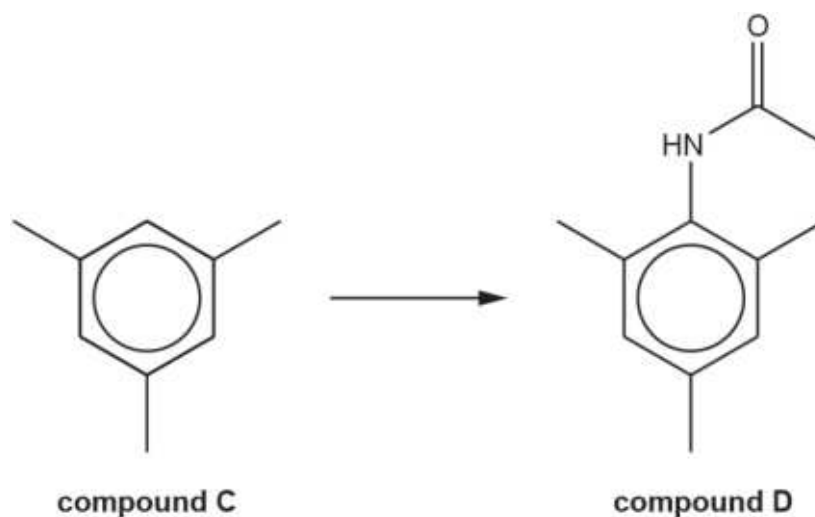
Blank lined paper for writing.

45 Compounds **B** and **C**, shown below, are unsaturated hydrocarbons containing nine carbon atoms.



An organic chemist is investigating compound **D** for possible use as a medicine.

The chemist proposes a synthesis of compound **D** from compound **C**.



(i) Predict the number of peaks in the ^{13}C NMR spectra of compounds **C** and **D**.

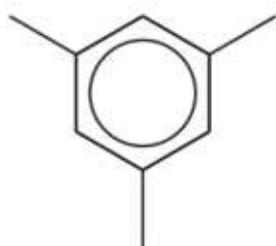
	Compound C	Compound D
Number of peaks		

[2]

(ii) The chemist develops a three-stage synthesis of compound **D** from compound **C**.

Complete the flowchart.

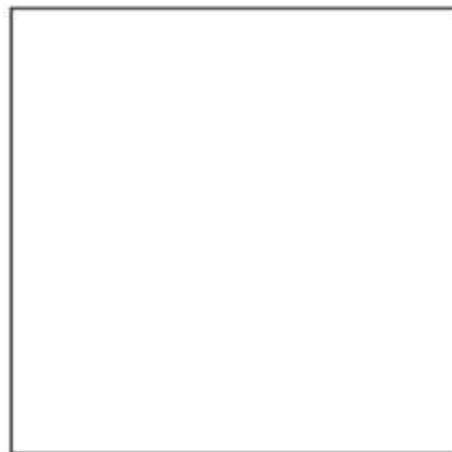
Show structures for organic compounds.



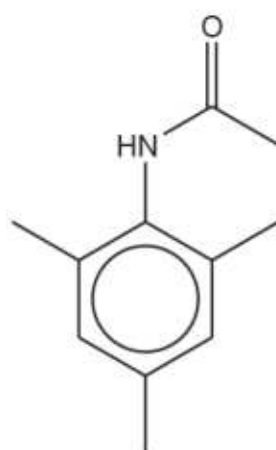
compound C

reagent:

catalyst:



1. Sn + HCl
2. Neutralise



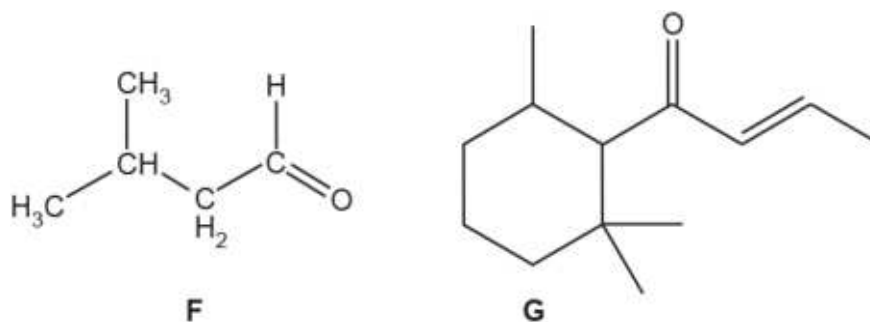
compound D

reagent:



[5]

46 The carbonyl compounds, F and G, shown below, contribute to the flavour of coffee.



Describe suitable chemical tests, with observations, that would confirm the presence of the functional groups in F and G.

[4]

47 An organic compound I is analysed, using a combination of techniques. The analytical data is shown below.

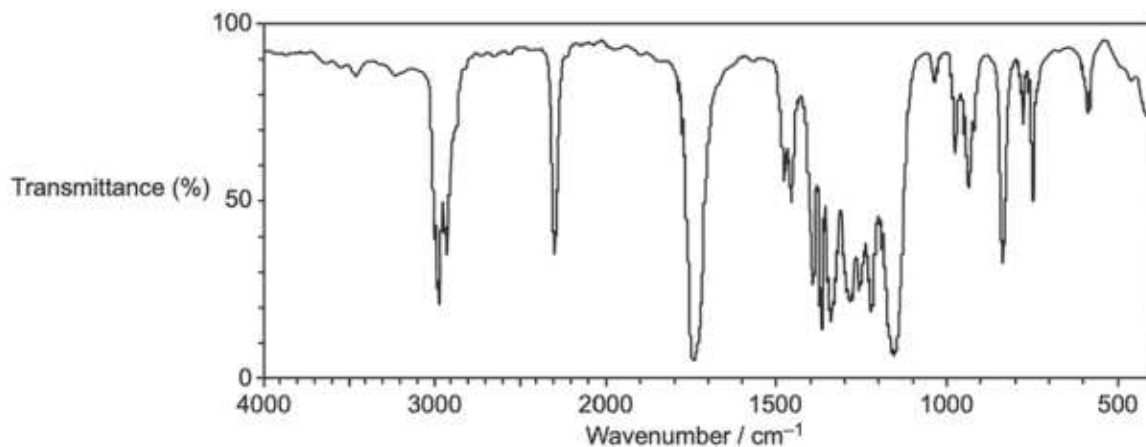
Elemental analysis by mass

C, 56.69%; H, 7.09%; N, 11.02%; O, 25.20%

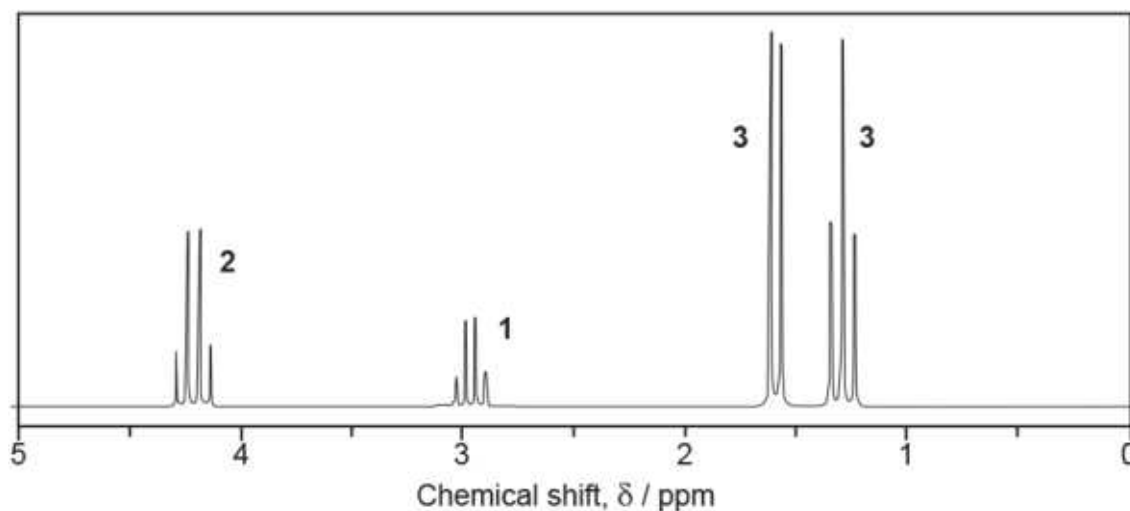
Mass spectrum

Molecular ion peak at $m/z = 127.0$

IR spectrum



Proton NMR spectrum



* Determine the structure of compound I, showing all your reasoning.

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END OF QUESTION PAPER

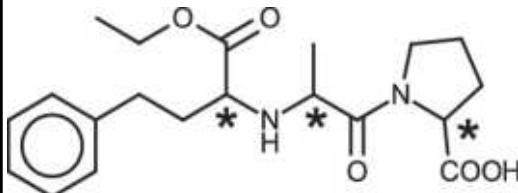
Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
1	a	FIRST react all with Tollens' reagent AND silver mirror / ppt / solid (formed) with compound D OR with Fehling's / Benedict's solutions AND (brick-red / orange) solid / precipitate (formed) with compound D ✓ NOTE: eliminates D <chem>CCCC=O.O>>CCCC(=O)O</chem> ✓ THEN react C and E with $\text{H}_2\text{SO}_4 / \text{H}^+$ AND $\text{K}_2\text{Cr}_2\text{O}_7 / \text{Cr}_2\text{O}_7^{2-} / \text{Na}_2\text{Cr}_2\text{O}_7$ AND colour change OR green colour with compound C OR no change OR no reaction OR no green colour with compound E ✓ <chem>CCCC(=O)C(=O)O.O>>CCCC(=O)C(=O)O.O</chem>	4	ALLOW ammonia + silver nitrate for reagent ALLOW black solid / ppt ALLOW 'the aldehyde gives a silver mirror' ALLOW solid OR crystals OR ppt as alternatives for precipitate ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous DO NOT ALLOW molecular formulae for organic structures IGNORE all references to 2,4-dinitrophenylhydrazine / Brady's ACCEPT acidified dichromate ALLOW blue / green blue IGNORE equation for oxidation of D ALLOW equation for partial oxidation <chem>CCCC(=O)C(=O)O.O>>CCCC(=O)C(=O)O.O</chem> ALLOW alternative sequences e.g. FIRST react all with H_2SO_4 AND $\text{K}_2\text{Cr}_2\text{O}_7$ colour change with C and D <i>eliminates E</i> At least one correct equation and structure of one product from either reaction required for the second mark. NB several possible products for the

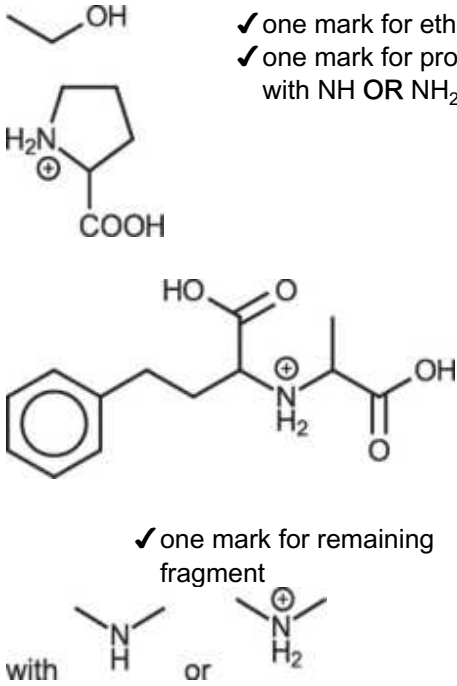
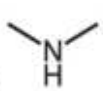
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance								
					oxidation of D THEN react C and D with Tollens'..... <i>distinguishes between C and D</i> Examiner's Comments This question discriminated well. Most candidates were able to score at least one mark for the correct use of Tollens' reagent. Answers needed to refer to test tube reactions and any reference to the use of Brady's reagent was ignored since it would give a similar observation with all three compounds. Many excellent answers described a logical sequence of tests involving the use of ammoniacal silver nitrate and acidified potassium dichromate. Some neglected to acidify the dichromate and equations were quite often missing from the answer. The best candidates included full balanced equations which clearly showed the structures of the reactants and products.								
	b		<table><tr><td>Compound</td><td>C</td><td>D</td><td>E</td></tr><tr><td>Number of peaks</td><td>5</td><td>5</td><td>4</td></tr></table> all correct ✓	Compound	C	D	E	Number of peaks	5	5	4	1	Examiner's Comments The interpretation of carbon-13 NMR spectra seems to be very well understood and the vast majority of candidates were able to correctly predict the number of peaks for all three compounds.
Compound	C	D	E										
Number of peaks	5	5	4										
			Total	5									

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance									
2	a		¹H NMR spectrum for serine <table><tr><th>chemical shift, δ /ppm</th><th>relative peak area</th><th>splitting pattern</th></tr><tr><td>2.0 to 3.0</td><td>1</td><td>triplet</td></tr><tr><td>3.3 to 4.2</td><td>2</td><td>doublet</td></tr></table> One mark for each correct row ✓✓	chemical shift, δ /ppm	relative peak area	splitting pattern	2.0 to 3.0	1	triplet	3.3 to 4.2	2	doublet	2	ALLOW δ values ± 0.2 ppm, as a range or a value within the range ALLOW a response that implies a splitting into three for a triplet / into two for a doublet Examiner's Comments Many candidates did not have the skills required to score marks on this question. Errors were made in all three columns and most often in assigning appropriate shift values from the data sheet.
chemical shift, δ /ppm	relative peak area	splitting pattern												
2.0 to 3.0	1	triplet												
3.3 to 4.2	2	doublet												
	b	i		1	ALL correct for one mark Examiner's Comments This part was answered well by many candidates. Some missed the chiral centre on the proline moiety or added an asterisk to a carbonyl carbon.									
		ii	any two from: no / fewer side effects increases the (pharmacological) activity / effectiveness Reduces / stops the need for / cost / difficulty in separating stereoisomers / optical isomers ✓✓	2	IGNORE toxic / harmful IGNORE a response that implies a reduced dose IGNORE “it takes (less) time to separate” Examiner's Comments Most candidates gained this mark by stating that the use of a single stereoisomer results in fewer side effects and increased pharmacological activity. Vague answers and comments about a reduced dose did not score marks.									

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		iii	 ✓ one mark for ethanol ✓ one mark for proline with NH OR NH₂⁺ ✓ one mark for remaining fragment with  or  ✓ Fourth mark for structure of both ions shown correctly with NH₂⁺	4	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous ALLOW + charge on H of NH₂ groups, <i>i.e.</i> NH₂⁺ IGNORE negative (counter) ions Examiner's Comments This question discriminated well. Most candidates were able to score one mark for the formula of ethanol. Only a small number of able candidates scored full marks for including the correct formulae for the protonated amine groups formed during acid hydrolysis.
		iv	idea of separating (the components / compounds) AND idea of (identifying compounds by) ✓ comparison with a (spectral) database	1	ALLOW (identifies compounds) using fragmentation (patterns) / fragment ions (but IGNORE molecular ions) IGNORE retention times Examiner's Comments To get the mark for this question candidates had to include points about the separation of the mixture and identification of the compounds. Answers based on identification using retention times or measurement of molar mass did not score the mark.
			Total	10	

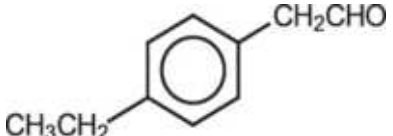
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
3	a		TMS / tetramethylsilane (which is the) standard (for chemical shift measurements) ✓	1	ALLOW $(\text{CH}_3)_4\text{Si}$ ALLOW TMS is the reference OR TMS has $\delta = 0$ (ppm) OR for calibration OR for comparison IGNORE solvent, unreactive, volatile, it gives a sharp peak Examiner's Comments This was well answered by the majority of candidates.
	b		NMR analysis = 5 marks M1: Peak(s) at (δ) 9.7 = CHO ✓ M2: Peak(s) at (δ) 7.1 = C_6H_4 ✓ M3: Triplet at (δ) 1.3 / peak at 1.3 AND quartet (at δ 2.6) / peak at 2.6 = CH_2CH_3 ✓ M4: Triplet at (δ) 9.7 / peak at 9.7 AND doublet (at δ 3.7) / peak at 3.7 = CH_2CHO ✓ M5: (n+1 rule) Any one of the following ◦ triplet at (δ) 1.3 shows (C with) 2 adjacent Hs / protons OR adjacent	9	NOTE: Each peak can be identified from: - its δ value - a range, e.g. "the peak between 0.8 and 2.0" - its relative peak area (beware two peaks with 2 protons) - its splitting (beware two triplets) - labelling on the spectrum ALLOW CH_2CHO / aldehyde IGNORE reference to phenol ALLOW (four) benzene ring proton(s) IGNORE reference to phenol M3 and M4 Look for a clear link (using words or diagrams) between the two peaks ALLOW a response that implies a splitting into three for a triplet / into two for a

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
	CH₂ (because of splitting: so triplet) ◦ quartet at (δ 2.6 shows) (C with) 3 adjacent Hs / protons OR adjacent CH₃ ◦ triplet at (δ) 9.7 shows (C with) 2 adjacent Hs / protons OR adjacent CH₂ • doublet at (δ 3.7 shows) (C with) 1 adjacent H / proton OR adjacent CH  QWC: triplet spelled correctly in the correct context once		doublet etc. ALLOW “neighbouring” Hs for “adjacent to” Hs IGNORE other comments about splitting once M5 has been awarded DO NOT ALLOW one of M3 or M4 or M5 if triplet not seen

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
	Aldehyde structure = 4 marks  ✓✓✓✓		ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous IF structure contains C₆H₄ ✓ IF structure contains C₆H₄ AND the organic structure contains CH₃CH₂ directly attached to the benzene ring OR contains CH₂CHO directly attached to the benzene ring ✓✓ IF structure has formula C₁₀H₁₂O AND structure contains C₆H₄ AND the structure contains CH₃CH₂ AND contains CH₂CHO AND 1,2 OR 1,3 substituted ✓✓✓ IF structure has formula C₁₀H₁₂O AND structure contains C₆H₄ AND the structure contains CH₃CH₂ AND contains CH₂CHO AND 1,4 substituted ✓✓✓✓ (use of ¹³C data) Examiner's Comments Good discrimination was achieved in this question. Nearly all could score at least one mark from the first two marking points by identifying the peak associated with the proton in the aldehyde group, or the peak given by benzene ring protons. Many gave a good explanation of a splitting pattern to score the fifth marking point. These marks were often achieved by the construction of a clearly labelled and well organised table. Many were able to suggest a structure for compound H. The best candidates included a 1,4 substituted benzene ring after correctly interpreting the information from the carbon-13 NMR spectrum. Candidates should avoid drawing several different structures and not indicating which one they wish to have marked.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
			Total	10	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
4	a		(Relative) solubility (in stationary phase) ✓	1	ALLOW how well the compound dissolves IGNORE retention time AND partition DO NOT ALLOW adsorption OR absorption Examiner's Comments The analysis of mixtures using gas chromatography was not well understood. The specification states that a liquid stationary phase separates by relative solubility and many incorrect answers focussed on the adsorption of molecules onto the solid beads rather the relative solubility of molecules in the liquid polymer that coated the beads. No credit was given to answers that stated that the separation produced different retention times.
	b	i	Compound B AND M^+ / molecular ion peak (at m/z) = 124 ✓	1	ALLOW M_r = 124 IGNORE compound B because m/z = 124 ALLOW $C_7H_8O_2^+$ = 124 OR $C_7H_8O_2$ = 124 ALLOW peak at (m/z =) 109 due to $HOC_6H_4O^+$ ALLOW peak at (m/z =) 109 due to loss of CH_3 IGNORE reference to other peaks in the spectrum Examiner's Comments This question was well answered. The majority of candidates focussed on the different molar masses of the compounds and many referred to the M^+ peak or molecular ion peak of compound B.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii	Compound (B) is less soluble in the stationary phase / liquid	1	ORA Answer refers to the first compound to emerge from the column ALLOW compound (B) is more soluble in mobile phase / gas ALLOW compound interacts less with stationary phase / liquid OR compound interacts more with mobile phase / gas IGNORE compound adsorbs less IGNORE compound is not very soluble (comparison needed) IGNORE volatility OR reactivity Examiner's Comments Relatively few creditworthy responses were seen here. The specification describes chromatography as an analytical technique that separates components in a mixture between a mobile phase and a stationary phase. Many candidates referred to differences in solubility or the strength of interactions without linking this to a particular phase in the column.
			Total	3	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
5	a	i	Radio (waves) ✓	1	ALLOW a value in the range 60 – 900 MHz Examiner's Comments The interaction of materials with the low-energy radio wave region of the electromagnetic spectrum is described in the specification but this question was surprisingly poorly answered. Infrared, ultraviolet, X-rays and gamma rays were all commonly seen answers in addition to ranges of chemical shift quoted from the data sheet.
		ii	The solvent does not have any hydrogen / H / protons ✓	1	ALLOW to prevent (^1H nuclei from) the solvent from interfering with the NMR spectrum ALLOW does not show on the spectrum ALLOW no peak / signal (from solvent) IGNORE volatility Examiner's Comments The need for deuterated solvents was well known but some candidates confused the use of this solvent with the use of TMS as the standard for chemical shift measurements or the identification of O—H and N—H protons by proton exchange using D₂O.
	b		14 ✓	1	Examiner's Comments Almost all candidates scored this mark for counting the peaks in the ^{13}C NMR spectrum.
	c		NMR analysis (5 marks) M1 Peaks between (δ) 7.1 and 7.5 (ppm) OR Relative peak area of 7 OR Multiplet =	7	ANNOTATE ANSWER WITH TICKS AND CROSSES ETC IGNORE analysis of ^{13}C spectrum Each peak can be identified from its δ value ± 0.2 ppm ALLOW (seven) benzene ring protons OR

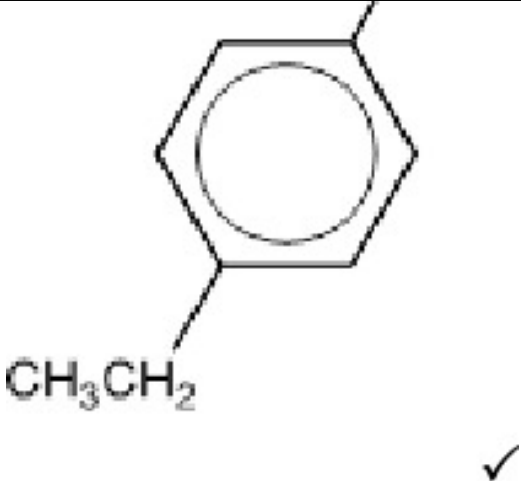
Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
	✓ M2 Peak at 5.2/5.3 OR Relative peak area of 1 = N-H ✓ M3 Peak at 2.3/2.4 OR Relative peak area of 2 OR Quartet = OR C₆H₅CH₂ ✓ M4 Peak at 0.7/0.8 OR Triplet = R-CH OR R-CH₃ ✓ M5 Triplet (at δ 0.7) AND quartet (at δ 2.3) = CH₂CH₃ OR triplet at (δ) 0.7 shows (C with) 2 adjacent Hs / protons = CH₂CH₃ OR quartet (at δ 2.3) shows (C with) 3 adjacent Hs / protons = CH₂CH₃ ✓		aromatic protons DO NOT ALLOW benzene ring without reference to protons ALLOW C₆H₆ IGNORE IGNORE O-H , CONH AND C=CH ALLOW quadruplet IGNORE CHC=O AND HC-N DO NOT ALLOW triplet = CH₃ OR CH₂CH₃ This also scores M4 if triplet is linked to R-CH₃ ALLOW CH₃CH₂ described as R-CH₃ and 2 adjacent H OR —CH₂— and 3 adjacent H The information can be presented on the spectrum or in a table.

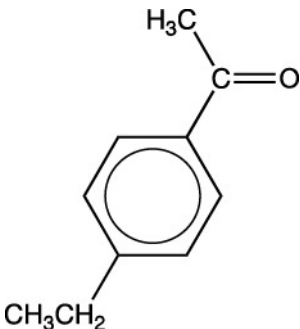
Mark Scheme

Question	Answer/Indicative content	Marks	Guidance																								
	 QWC: triplet or quartet spelled correctly in the correct context for M5 Identification of R¹ and R² (2 marks) Orange precipitate L Correct structure scores 2 marks R¹ or R² = -CH₃ ✓ R₁ or R₂ =		<table border="1" data-bbox="991 443 1501 757"> <thead> <tr> <th>Chemical shift/ppm</th><th>Relative peak area</th><th>Splitting pattern</th><th>Type of proton</th></tr> </thead> <tbody> <tr> <td>7.1 – 7.5</td><td>7</td><td>Multiplet</td><td></td></tr> <tr> <td>5.3</td><td>1</td><td>Singlet</td><td>N-H</td></tr> <tr> <td>2.3/2.4</td><td>2</td><td>Quartet</td><td></td></tr> <tr> <td>1.7/1.8</td><td>3</td><td>Singlet</td><td>HC-C=N-</td></tr> <tr> <td>0.7/0.8</td><td>3</td><td>triplet</td><td>R-CH(R)-CH₃</td></tr> </tbody> </table> IGNORE peak in the range 1.6–2.2 = HC-C=N- because this information is given in the question. H₃C-C=N- scores one mark for the identification of R¹ or R² (see below) ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous Marks are for structure of R¹ and R² IGNORE errors in the rest of the structure ALLOW 1 mark for CH₃ and CH₃CH₂ swapped, i.e. the following structure ALLOW H₃C-C=N-	Chemical shift/ppm	Relative peak area	Splitting pattern	Type of proton	7.1 – 7.5	7	Multiplet		5.3	1	Singlet	N-H	2.3/2.4	2	Quartet		1.7/1.8	3	Singlet	HC-C=N-	0.7/0.8	3	triplet	R-CH(R)-CH ₃
Chemical shift/ppm	Relative peak area	Splitting pattern	Type of proton																								
7.1 – 7.5	7	Multiplet																									
5.3	1	Singlet	N-H																								
2.3/2.4	2	Quartet																									
1.7/1.8	3	Singlet	HC-C=N-																								
0.7/0.8	3	triplet	R-CH(R)-CH ₃																								

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
	 The structure shows a benzene ring with an ethyl group (CH₃CH₂) at the bottom position and a methyl group (represented by a single line) at the top position, indicating a 1,4-disubstitution pattern. A checkmark is placed to the right of the structure.		MUST BE 1,4-disubstituted (14 carbon environments in the ¹³C NMR spectrum) Examiner's Comments Although the use of 2,4-dinitrophenylhydrazine to detect the presence of a carbonyl group in an organic compound and to identify a carbonyl compound from the melting point of the derivative is required in the specification, the equation for this reaction and the structure of the derivative was not required in the question. The equation for the reaction and the structure of the derivative, with R¹ and R² groups from the original carbonyl compound, was given in the question. The structure of carbonyl K was similar in complexity to structures featured in previous papers. The mark scheme was constructed so that at least two of the first five marks awarded for the analysis were easily accessible by comparing the chemical shifts in the ¹H NMR spectrum with those displayed in the data sheet. These marks were often achieved by the construction of a clearly labelled and well organised table or by annotating the spectrum. Splitting patterns were well understood but one problem for candidates was the difficulty in associating the peak at δ = 2.3/2.4 ppm with a benzylic hydrogen; many candidates focused more on coupling than on chemical shifts and missed a chance to solve the structure. Of the two marks available for identifying R¹ and R², one could be derived quickly by linking information given in the question with one of the peaks in the ¹H NMR spectrum. The second identification mark required careful analysis of both the ¹H NMR and ¹³C NMR data. Overall, most candidates were able to score marks on this question and completely correct answers were achieved by the most able candidates.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	d		Carbonyl compound K  ✓	1	ALLOW ECF from incorrect compound L Must be a correct carbonyl structure Examiner's Comments It was not possible to score a mark for this question unless a structure had been drawn for compound L. However, many candidates were able to score this mark as error carried forward from structures that had failed to gain any credit in the previous question were allowable.
			Total	11	
6			A	1	
			Total	1	

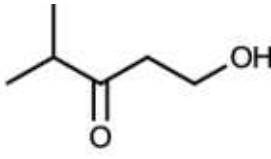
Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
7	a	<i>* Please refer to the marking instruction point 10 for guidance on how to mark this question.</i> Level 3 (5–6 marks) Correctly labelled diagram of apparatus that works, with no safety problems AND Full appreciation of further two steps required to gain pure sample <i>There is a well-developed diagram which is clear and structured. The information on further purification is detailed and relevant.</i> Level 2 (3–4 marks) Labelled diagram of apparatus but with safety / procedural problems OR clear diagram of functional apparatus without labelling AND Some details of further purification steps <i>The diagram presents apparatus that is in the most-part relevant with some correct labelling, and supported by some details of further purification steps.</i> Level 1 (1–2 marks) Diagram of apparatus drawn with no labelling OR labelled diagram with significant safety / procedural problems AND Few or imprecise details about further purification stages <i>The diagram is basic and unstructured. Any mention of purification steps is limited to generic term, e.g. 'drying', without relevant detail.</i> 0 marks No response or no response worthy of credit.	6	Indicative scientific points may include: Diagram Includes following components: distillation flask heat source thermometer at outlet (bulb level with outlet) still-head water condenser (correct direction of water flow) receiving vessel open system. Further purification Shake and leave to settle in a separating funnel Separate layers by tapping off Add (a small amount of) anhydrous magnesium sulfate / anhydrous calcium chloride to organic layer (in a dry conical flask) (Re)distil the organic layer Collect fraction distilling at (between 150 °C and) 156 °C.
	b	Lack of (further) effervescence	1	ALLOW fizzing / bubbling stops

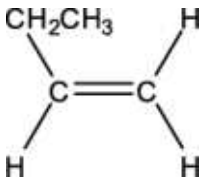
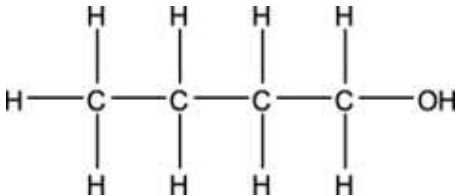
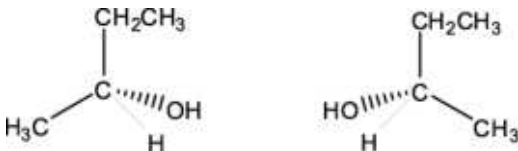
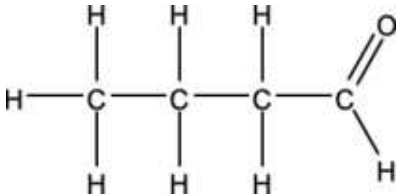
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	c		Take samples from reaction mixture at regular intervals Spot / run on a TLC plate, alongside cyclohexanol (and cyclohexanone) controls	2	ALLOW "frequent" for "regular" ALLOW measure / compare R_f value to cyclohexanol IGNORE reference to solvent or visualising chemicals / UV
	d		React (sample of distillate) with 2,4-dinitrophenylhydrazine recrystallise AND determine the melting point Compare melting point to known / library value for cyclohexanone (derivative)	3	ALLOW (2,4-)DNPH / Brady's reagent
			Total	12	

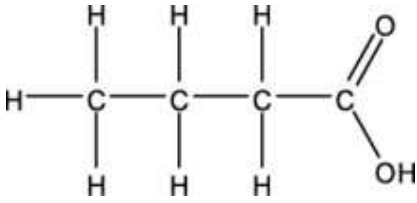
Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
8	<i>* Please refer to the marking instruction point 10 for guidance on how to mark this question.</i> Level 3 (5–6 marks) Structure correct AND Analysed all ^1H NMR signals with at least two supporting statements made. <i>The analysis is clear and logically structured. The supporting statements are relevant to the correct structure drawn.</i> Level 2 (3–4 marks) Structure has correct molecular formula AND C=O AND OH but in incorrect positions AND Analysed at least three ^1H NMR signals with one or two supporting statements made. <i>The analysis is presented with some structure. The supporting statements are in the most-part relevant to the structure drawn.</i> Level 1 (1–2 marks) Structure has correct molecular formula AND C=O OR OH but in incorrect positions. AND Analysed at least two ^1H NMR signals with no or one supporting statements made. <i>The analysis is basic and communicated in an unstructured way. The relationship of the supporting evidence to the structure may not be clear.</i> 0 marks No response or no response worthy of credit.	6	Indicative scientific points may be included: Structure  $\text{L} =$ ^1H NMR spectrum $\delta = 3.8$ ppm, triplet, 2H $\text{CH}_2\text{—CH}_2\text{—O}$ $\delta = 3.7$ ppm, singlet, 1H O—H $\delta = 3.1$ ppm, triplet, 2H $\text{CH}_2\text{—CH}_2\text{C=O}$ $\delta = 2.7$ ppm, septet, 1H $(\text{CH}_3)_2\text{CHC=O}$ $\delta = 1.0$ ppm, doublet, 6H $(\text{CH}_3)_2\text{CH}$ Supporting statements $\delta = 3.7$ ppm lost after D_2O, indicating —OH $\delta = 213$ ppm in ^{13}C NMR but no $\delta = 9\text{--}10$ ppm in ^1H NMR so ketone, not aldehyde $M_r(\text{C}_3\text{H}_6\text{O}) = 58 \quad 116/58 = 2 \rightarrow \text{C}_6\text{H}_{12}\text{O}_2$
	Total	6	
9	B	1	
	Total	1	

Mark Scheme

Question		Answer/Indicative content	Marks	Guidance
10	a	F–K clearly identified Compound F:  Compound G:  Compounds H and I:  Compound J:  Compound K:	6	ANNOTATE ANSWER WITH TICKS AND CROSSES ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous IGNORE names H and I can be identified either way round

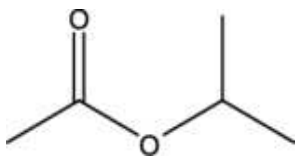
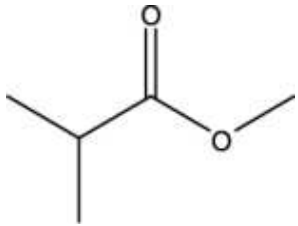
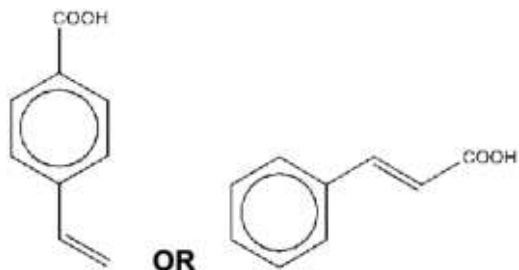
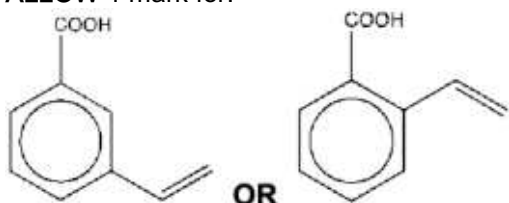
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					
	b		(Add) 2,4-dinitrophenylhydrazine AND orange/yellow/red precipitate Take melting point of crystals Compare to known values	3	NOTE: (b) ☐ is marked completely independently of (a) ALLOW errors in spelling ALLOW 2,4(-)DNP OR 2,4(-)DNPH ALLOW Brady's reagent or Brady's Test ALLOW solid OR crystals OR ppt as alternatives for precipitate Mark second and third points independently of response for first marking point DO NOT ALLOW 2nd and 3rd marks for taking and comparing boiling points OR chromatograms
			Total	9	

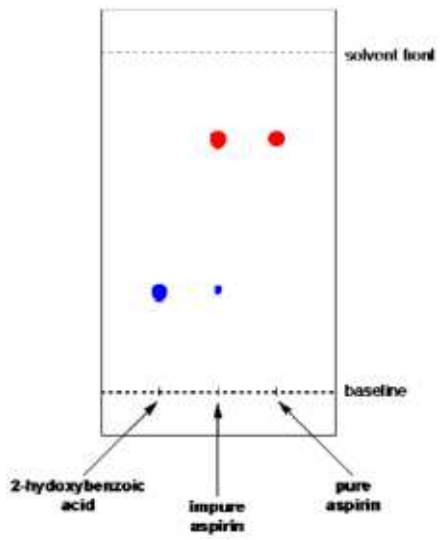
Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
11	Elemental analysis and molecular formula Use of percentages to give empirical formula $C_5H_{10}O_2$ Evidence of using empirical formula AND 102 to give molecular formula = $C_5H_{10}O_2$ IR Spectrum Peak at ~1750 OR 1630–1820 (cm^{-1}) AND C=O NMR analysis Peak(s) at (δ) 4.9 shows HC–O AND 1 H in environment (peak area) OR 6H on adjacent C as peak is multiplet / heptet / septet Peak at (δ) 2.2 shows HC–C=O AND 3 H in environment (peak area) OR No H on adjacent C as peak is singlet Peak(s) at (δ) 1.3 shows HC–R AND 6 H (or $2 \times CH_3$) in environment (peak area) OR 1H on adjacent C as peak is doublet	8	ANNOTATE ANSWER WITH TICKS AND CROSSES C : H = 58.8 : 9.87 : 31.3 : O 0 / / 1 3 / 12 16 4.90 : 9.87 : 1.96 2.5 : 5.04 : 1 5 : 10 : 2 Alternative method: carbon: $(102 \times 58.80 / 100) / 12 = 5$ hydrogen: $(102 \times 9.87 / 100) / 1 = 10$ oxygen: $(102 \times 31.33 / 100) / 16 = 2$ ALLOW C=O peak labelled on spectrum IGNORE reference to C–O peak NOTE each peak can be identified from: - its δ value - a range <i>e.g.</i> 'the peak between 1.3–1.4' - its relative peak area - its splitting - labelling on spectrum

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
			Structure Correct structure:  Allow one mark for 		ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous DO NOT ALLOW ECF from incorrect molecular formula
			Total	8	
12			Electrophilic substitution means benzene ring Electrophilic addition means alkene / C=C Isomer of C₉H₈O₂ containing C=C, benzene ring AND COOH Correct isomer:  justification in terms of number of carbon environments	5	Concluded using data provided and conclusions from 1st two marks. ALLOW 1 mark for:  (does not gain final justification mark)
			Total	5	

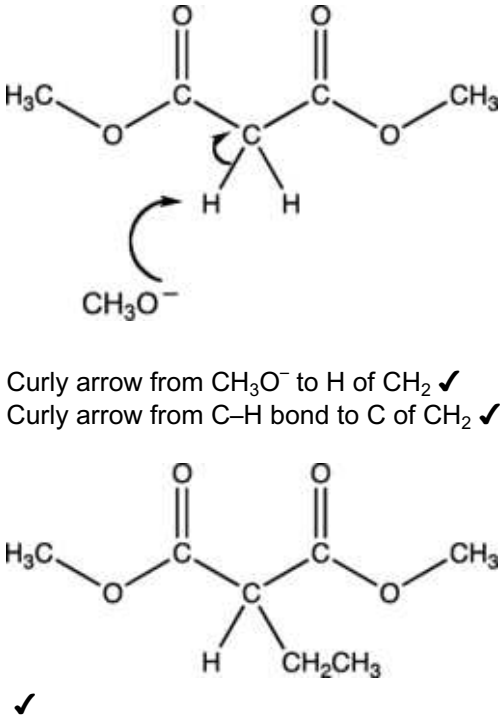
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
13		i	 2-hydroxybenzoic acid impure aspirin pure aspirin solvent front baseline Pure aspirin and 2-hydroxybenzoic acid correct Impure aspirin with 2 spots in line with aspirin and 2-hydroxybenzoic acid spots AND 2-hydroxybenzoic acid spot fainter than aspirin spot	2	Check measurements on diagram using online measuring tool. Distance from baseline to top of spot for aspirin = 70–80% of baseline → solvent front Distance from baseline to top of spot for aspirin = 25–35% of baseline → solvent front
		ii	Melting point range between 130–140°C AND Range $\geq 2^{\circ}\text{C}$	1	Range that starts <138 and finishes ≤ 140
			Total	3	

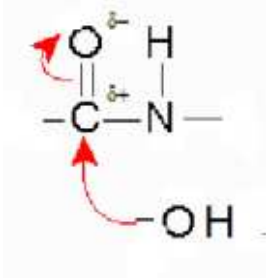
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance																				
14	a		✓	1																					
	b	i	$2\text{Na} + 2\text{CH}_3\text{OH} \rightarrow 2\text{Na}^+ + 2\text{CH}_3\text{O}^- + \text{H}_2$ ✓	1	ALLOW $2\text{Na} + 2\text{CH}_3\text{OH} \rightarrow 2\text{CH}_3\text{ONa} + \text{H}_2$																				
		ii	 Curly arrow from CH_3O^- to carbon atom of C-Br bond ✓ Dipole shown on C-Br bond, $\text{C}^{\delta+}$ and $\text{Br}^{\delta-}$ AND curly arrow from C-Br bond to the Br atom ✓ Products of reaction (must not be ambiguous) ✓	3	ALLOW correct structural OR skeletal OR displayed formula OR mixture of the above as long as non-ambiguous. The curly arrow must start from O atom of CH_3O^- AND must start either from a lone pair or from the negative charge. No need to show lone pair if curly arrow comes from negative charge. ALLOW $\text{S}_{\text{N}}1$ Dipole shown on C-Br bond, $\text{C}^{\delta+}$ and $\text{Br}^{\delta-}$, and curly arrow from C-Br bond to the Br atom. Correct carbocation drawn. AND curly arrow from CH_3O^- to carbocation. The curly arrow must start from the oxygen atom of the CH_3O^-, and must start either from a lone pair or from the negative charge.																				
		iii	CH_3O^- donates an electron pair AND heterolytic fission ✓	1	ASSUME 'it' refers to CH_3O^-																				
	c		<table><tr><th>Chemical shift, δ/ppm</th><th>Relative peak area</th><th>Splitting pattern</th><th></th></tr><tr><td>0.5–1.9</td><td>3</td><td>Triplet</td><td>✓</td></tr><tr><td>3.0–4.3</td><td>2</td><td>Quartet</td><td>✓</td></tr><tr><td>0.5–1.9</td><td>6</td><td>Doublet</td><td>✓</td></tr><tr><td>3.0–4.3</td><td>1</td><td>Heptet</td><td>✓</td></tr></table>	Chemical shift, δ/ppm	Relative peak area	Splitting pattern		0.5–1.9	3	Triplet	✓	3.0–4.3	2	Quartet	✓	0.5–1.9	6	Doublet	✓	3.0–4.3	1	Heptet	✓	4	ALLOW δ values ± 0.2 ppm, as a range or a value within the range ALLOW multiplet for heptet
Chemical shift, δ/ppm	Relative peak area	Splitting pattern																							
0.5–1.9	3	Triplet	✓																						
3.0–4.3	2	Quartet	✓																						
0.5–1.9	6	Doublet	✓																						
3.0–4.3	1	Heptet	✓																						

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	d	i	 Curly arrow from CH_3O^- to H of CH_2 ✓ Curly arrow from C-H bond to C of CH_2 ✓	3	The curly arrow must start from O atom of CH_3O^- AND must start either from a lone pair or from the negative charge. No need to show lone pair if curly arrow comes from negative charge. ALLOW any unambiguous structure, skeletal, displayed, structural or combination.
		ii	CH_3O^- accepted a proton ✓	1	ASSUME 'it' refers to CH_3O^-
			Total	14	

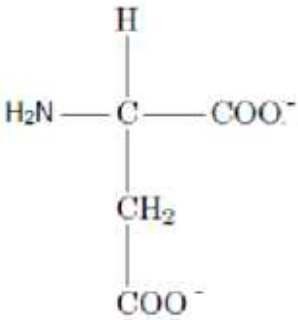
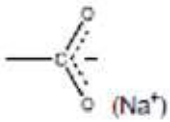
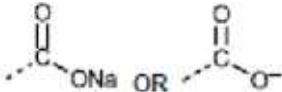
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
15	a		 Curly arrow from OH⁻ to C(δ^+) ✓ Dipole correct AND curly arrow from C=O bond to O(δ^-) ✓	2	First curly arrow must come from either a lone pair on O or negative charge on O Examiner's Comments Some candidates lost a mark for the incorrect positioning of the curly arrow from the hydroxide ion. The mark scheme specifies that it should start at either the lone pair on the oxygen atom or the negative charge on the oxygen atom.
	b		Measure distance moved by spot/distance moved by solvent ✓	2	ALLOW attempt at calculation of R_f value using distances measured on the chromatogram IGNORE explanation of how chromatography works

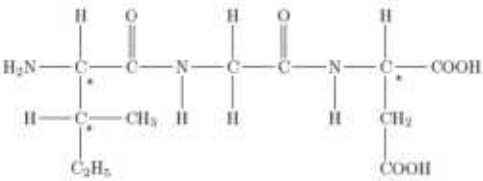
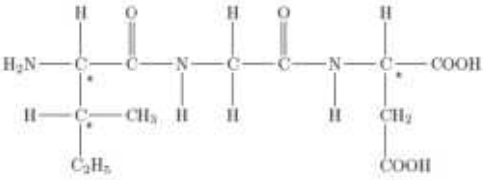
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
			Compare (R_f) value with data book values/known values ✓ Two amino acids have the same/similar R_f value OR similar adsorption OR move the same/similar distance ✓	1	ALLOW One spot contains two amino acids ALLOW Two amino acids have not separated IGNORE relative solubility ALLOW two of the amino acids have similar structures Examiner's Comments This question discriminated well with relatively few candidates able to score all three marks. Some candidates attempted to explain how the technique separates components between a mobile phase and a stationary phase which was not required by the question. There was some confusion with gas chromatography and retention times. Vague answers about all amino acids having similar structures did not score the final marking point to explain why only two spots appeared on the chromatogram.
	c	i	The pH at which the amino acid exists as a <u>zwitterion</u> ✓  QWC: zwitterion spelled correctly in the correct context	1	DO NOT ALLOW PH/ph ALLOW zwitter ion Examiner's Comments This definition had been learned by the majority of candidates.

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
ii		1	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous Two COO⁻ groups are required in the structure ALLOW –COO⁻Na⁺ OR –COONa  ALLOW delocalised carboxylate ALLOW  DO NOT ALLOW -COO-Na OR -O-Na (covalent bond) Examiner's Comments Generally well answered but structures with only one carboxylate group were quite common and some candidates showed aspartic acid being protonated at high pH.

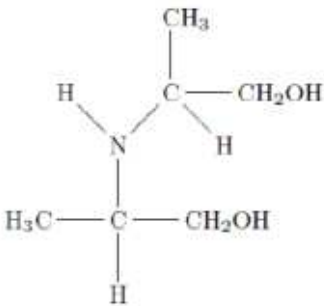
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		iii	M1 structure  ✓ M2 correct structure has three chiral centres  ✓	2	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous ALLOW tripeptide with the 3 amino acids in any order ALLOW cyclic tripeptide Isoleucine has two chiral centres, aspartic acid has one chiral centre and glycine has none. ALL three correct for one mark ALLOW chiral centres correctly identified if the three amino acids are part of a polypeptide chain Examiner's Comments A more challenging question with relatively few candidates able to show the position of all three chiral centres on a correct tripeptide structure. Most candidates identified the chiral centres in the amino acid backbone of aspartic acid and isoleucine and realised that glycine was not chiral, but many missed the second chiral centre in isoleucine.
			Total	9	

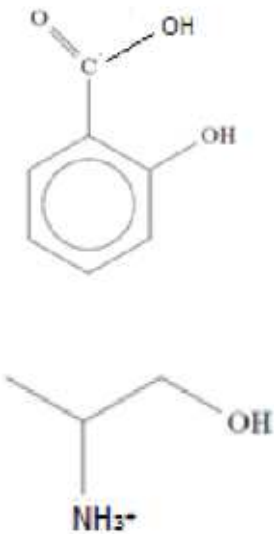
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance															
16	a	i	<table><tr><th colspan="3">¹H NMR spectrum for 2-aminopropan-1-ol</th></tr><tr><th>Chemical shift, δ/ppm</th><th>Relative peak area</th><th>Splitting pattern</th></tr><tr><td>0.8 – 2.0</td><td>3</td><td>doublet</td></tr><tr><td>2.3 – 3.0</td><td>1</td><td>multiplet</td></tr><tr><td>3.3 – 4.2</td><td>2</td><td>doublet</td></tr></table> ✓✓✓	¹ H NMR spectrum for 2-aminopropan-1-ol			Chemical shift, δ/ppm	Relative peak area	Splitting pattern	0.8 – 2.0	3	doublet	2.3 – 3.0	1	multiplet	3.3 – 4.2	2	doublet	3	One mark for each correct row ALLOW δ values as a range or a value within the specified range. ALLOW δ values +/- 0.2 ppm. ALLOW a response that implies a splitting into two for a doublet etc. ALLOW sextet/hextet/six (or more than 5) as alternative to multiplet Relative peak area = CH /3H etc. penalise once Examiner's Comments Although it could be argued that this question tested the same skill three times, the full range of marks was awarded and errors were seen in the chemical shift, relative peak area and splitting pattern. Fully correct responses included either a chemical shift value within the range specified on the data sheet or a range that matched the one given on the data sheet.
¹ H NMR spectrum for 2-aminopropan-1-ol																				
Chemical shift, δ/ppm	Relative peak area	Splitting pattern																		
0.8 – 2.0	3	doublet																		
2.3 – 3.0	1	multiplet																		
3.3 – 4.2	2	doublet																		
		ii	M⁺ peak at 75 (peak 1) CH₃CH(NH₂)CH₂OH⁺/C₃H₉NO⁺ ✓ Fragment peak at 44 (peak 2) CH₃CH(NH₂)⁺/C₂H₆N⁺ ✓	2	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous Positive charge is essential but ALLOW maximum of one mark if both formulae are correct AND neither species has a positive charge Examiner's Comments Although peak 2 was often correct, the species responsible for the M⁺ peak was often missing a positive charge. Possibly students have learned that the particles become charged as part of the fragmentation process and don't realise that only charged particles can be detected by a mass spectrometer.															

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	b	i	Ethanolic ammonia OR ammonia/NH ₃ AND ethanol ✓	1	ALLOW ammonia in a sealed tube ALLOW dilute ethanolic ammonia/NH₃ IGNORE heat ALLOW alcohol for ethanol DO NOT ALLOW any reference to water or hydroxide ions Examiner's Comments A well answered question. Some candidates forgot to use a solvent or suggested the use of aqueous ammonia.
		ii	(compound D)  ✓	1	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous Examiner's Comments This question discriminated well. Although there were very few blank pages, many incorrect structures were seen.
	c	i	Alcohol AND Amide/peptide ✓	1	IGNORE phenol IGNORE hydroxyl/hydroxy IGNORE attempts to classify alcohol or amide as primary, secondary or tertiary DO NOT ALLOW hydroxide Examiner's Comments Generally well answered but incorrect functional groups included carbonyl and amine.

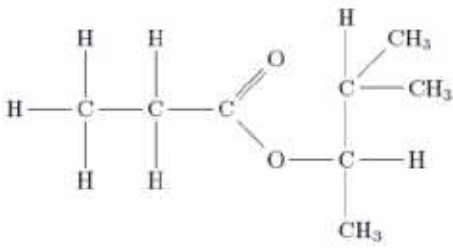
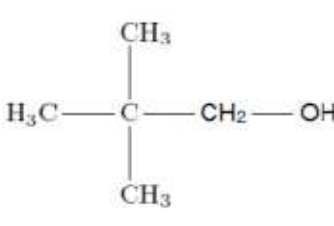
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii		2	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous ALLOW + on N or H i.e. NH_3^+ or NH_3^+ ALLOW NH_3^+Cl^- Examiner's Comments Many candidates were able to score one mark for this question but the amine group was often not protonated and it was surprisingly common to see the amine group as NH_2^+.
			Total	10	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
17	a		<u>Reducing agent</u> NaBH_4 / sodium tetrahydridoborate(III) / sodium borohydride ✓ <u>Equation</u> $\text{CH}_3(\text{CH}_2)_3\text{CHO} + 2[\text{H}] \rightarrow \text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$ ✓	1	ALLOW LiAlH_4/lithium tetrahydridoaluminate(III)/lithium aluminium hydride ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above ALLOW $\text{C}_4\text{H}_9\text{CHO} + 2[\text{H}] \rightarrow \text{C}_5\text{H}_{11}\text{OH}$ ALLOW molecular formulae: $\text{C}_5\text{H}_{10}\text{O} + 2[\text{H}] \rightarrow \text{C}_5\text{H}_{12}\text{O}$ DO NOT ALLOW $-\text{COH}$ for aldehyde Examiner's Comments Very well answered. The most common error was an incorrect formula for the aldehyde.
	b		M1 Compound F structure is a secondary alcohol with the formula $\text{C}_5\text{H}_{11}\text{OH}$ ✓ M2 Compound F $= \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{CH}_3)\text{CH}_3$ ✓ M3 Compound G = $\text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}_3$ ✓ M4 $n(\text{NaOH}) = (0.125 \times 22.8/1000) =$	7	ANNOTATE WITH TICKS AND CROSSES ETC ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous IGNORE names if structures are given ALLOW 3-methylbutan-2-ol if structure not given ALLOW ECF from an incorrect secondary alcohol for M3 e.g. pentan-2-ol → pentan-2-one e.g. pentan-3-ol → pentan-3-one ALLOW (3-)methylbutanone if structure not given IGNORE any discussion of the reactions of compound G with 2,4-dinitrophenylhydrazine and/or Tollens' reagent. ALLOW 3 SF up to calculator value correctly rounded

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
			0.00285 (mol) ✓ M5 M(compound H) = (0.211/0.00285 =) 74(.0) (g mol⁻¹) ✓ M6 Compound H = / CH₃CH₂COOH ✓ M7 Compound I =  ✓		IF M(compound H) = 74 award 2 marks (M4 + M5) ALLOW ECF from incorrect calculation of amount of NaOH ALLOW propanoic acid if structure not given ALLOW ECF from incorrect compound F (alcohol) and/or incorrect compound H (carboxylic acid) to form compound I (ester). Compounds F, G, H and I must be placed in the correct box or correctly labelled for M2. M3, M6 and M7 Examiner's Comments A high scoring question with many candidates gaining full marks. Although most realised that Compound F was a secondary alcohol, fewer candidates combined this knowledge with the information provided by carbon-13 NMR to deduce the correct structure of the secondary alcohol.
	c		The structural isomer is:  ✓	1	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous ALLOW 2,2-dimethylpropan-1-ol Examiner's Comments A good discriminator but many correct structures were seen.
			Total	10	
18			D	1	
			Total	1	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
19			C	1	
			Total	1	
20		i	Leucine AND valine ✓	1	
		ii	R _f values would be larger ✓ (amino acids) are more soluble (in more polar solvent so would travel further up the plate) ✓	2	
			Total	3	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
21	a	i	Reagent and observation sodium carbonate AND Fizzing/effervescence/bubbling ✓ Equation Correctly balanced equation ✓ e.g. $2\text{RCOOH} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{RCOONa} + \text{CO}_2 + \text{H}_2\text{O}$	2	Note: both reagent and observation are required for first mark ALLOW name or formula for any suitable carbonate e.g. NaHCO_3, potassium carbonate etc. ALLOW reagent from equation if not stated elsewhere
		ii	Reagent and observation Tollens' (reagent) AND Silver (mirror) ✓ Equation $\text{RCHO} + [\text{O}] \rightarrow \text{RCOOH}$ ✓	2	Note: both reagent and observation are required for first mark ALLOW ammoniacal silver nitrate OR Ag^+/NH_3 ALLOW $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$ OR acidified (potassium/sodium) dichromate AND Orange to green (<i>this would identify the aldehyde from the carboxylic acid, ketone and esters</i>)
	b		2,4-dinitrophenylhydrazine AND Orange/yellow/red precipitate ✓	1	ALLOW errors in spelling ALLOW 2,4(-)DNP OR 2,4(-)DNPH ALLOW Brady's reagent or Brady's Test ALLOW solid OR crystals OR ppt as alternatives for precipitate
	c	i	$\text{CH}_3\text{COOC}(\text{CH}_3)_3 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + (\text{CH}_3)_3\text{COH}$ CH_3COONa ✓ Rest of equation correct ✓ OR $(\text{CH}_3)_3\text{CCOOCH}_3 + \text{NaOH} \rightarrow (\text{CH}_3)_3\text{CCOONa} + \text{CH}_3\text{OH}$ $(\text{CH}_3)_3\text{CCOONa}$ ✓ Rest of equation correct ✓	2	Note: the hydrolysis of either ester may be given ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous DO NOT ALLOW molecular formulae of products (<i>question requires structures of products to be shown</i>)

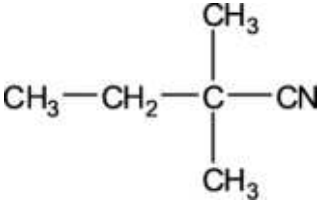
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii	Reagent and observation $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$ OR acidified (potassium/sodium) dichromate AND Orange to green (with CH_3OH) ✓ Equation $\text{CH}_3\text{OH} + [\text{O}] \rightarrow \text{HCHO} + \text{H}_2\text{O}$ OR $\text{CH}_3\text{OH} + 2[\text{O}] \rightarrow \text{HCOOH} + \text{H}_2\text{O}$ ✓	2	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous DO NOT ALLOW molecular formulae <i>(question requires structures of organic compounds to be shown)</i>
		iii	^{13}C NMR (1 mark) (It is) not possible to identify (the esters) with ^{13}C NMR AND (both) spectra would contain four peaks (with similar chemical shifts) ✓ ^1H NMR (2 marks) (It is) possible to identify (the esters) with ^1H NMR (^1H NMR spectrum of) $\text{CH}_3\text{COOC}(\text{CH}_3)_3$ has a singlet/peak between 2.0–3.0 (ppm) (^1H NMR spectrum of) $(\text{CH}_3)_3\text{CCOOCH}_3$ has a singlet/peak between 3.0–4.3 (ppm) All three correct statements ✓✓ Any two correct statements ✓	3	ALLOW 'same number of peaks' in place of 'four peaks' ALLOW any value or range of values within 2.0–3.0 ALLOW any value or range of values within 3.0–4.3

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	d		<u>Possible structures for ketone (2 marks)</u> $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$ $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2 - \text{C} - \text{CH}_2\text{CH}_3 \end{array}$ $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{CH} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ All three correct ✓✓ Any two correct ✓ <u>Aldehyde (3 marks)</u> Peak at (δ) 1.2 shows HC–R AND No H on adjacent C atom as peak is singlet ✓ Peak at (δ) 9.6 shows H–C=O AND No H on adjacent C atom as peak is singlet ✓ $\begin{array}{c} \text{CH}_3 \quad \text{O} \\ \quad \parallel \\ \text{H}_3\text{C} - \text{C} - \text{C} - \text{H} \\ \\ \text{CH}_3 \end{array}$ OR (2,2-)dimethylpropanal ✓	5	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous IGNORE names of ketones
			Total	17	

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
22	<i>*Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.</i> Level 3 (5–6 marks) Structure of J identified as $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CN}$ AND/OR A comprehensive analysis with most of the spectral data analysed and few omissions. <i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i> Level 2 (3–4 marks) Analysis may be incomplete and structure of J identified. OR Thorough analysis of one aspect of the information given in question and structure of J may be incorrectly identified. <i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i> Level 1 (1–2 marks) An attempt at a simple analysis. OR Explains one scientific point thoroughly with a few omissions. <i>The information is basic and communicated in an unstructured way. The information is supported by limited evidence and the relationship to the evidence may not be clear.</i> 0 marks No response or no response worthy of credit.	6	LOOK ON THE SPECTRA for labelled peaks. Indicative scientific points may include: Empirical and Molecular Formula of J $\begin{array}{rcccl} \text{C} : \text{H} : \text{N} = & 74.17/12 & : & 11.41/1 & : & 14.42/14 \\ & 6.18 & : & 11.41 & : & 1.03 \\ & 6 & : & 11 & : & 1 \end{array}$ - Empirical formula of J = $\text{C}_6\text{H}_{11}\text{N}$ - uses $m/z = 97.0$ and empirical formula to determine molecular formula of J as $\text{C}_6\text{H}_{11}\text{N}$ <u>^1H NMR spectrum</u> $\delta = 0.9$ ppm, triplet, $\text{CH}_3-\text{CH}_2-(\text{C}-)$ $\delta = 1.4$ ppm, singlet, $(\text{CH}_3)_2\text{C}^-$ $\delta = 1.6$ ppm, quartet, $\text{CH}_3-\text{CH}_2^-(\text{C}_-)$ <u>IR Spectrum and Structure of J</u> - peak at $2220-2260\text{ cm}^{-1}$ is $\text{C}\equiv\text{N}$ - Correct structure of J  ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous
	Total	6	

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
23	<i>Please refer to marking instructions on page 4 of mark scheme for guidance on how to mark this question.</i> Level 3 (5–6 marks) A comprehensive analysis of the information available with through explanations linked to the evidence. Acid C identified as a tricarboxylic acid with a tertiary –OH group and the correct molecular formula of C₆H₈O₇. <i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated</i> Level 2 (3–4 marks) Analysis of the information available but explanations may be incomplete or there may be mistakes in calculations, although the method may be sound. <i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i> Level 1 (1–2 marks) A simple analysis of the information available and limited explanations which may or may not be explicitly linked to the evidence. <i>The information is basic and communicated in an unstructured way. The information is supported by limited evidence and the relationship to the evidence may not be clear.</i> 0 marks – No response worthy of credit.	6	Indicative scientific points may include Identification of functional groups • Tribasic acid → three –COOH groups <i>From 1 mol C requires 3 mol NaOH</i> • Tertiary alcohol <i>From no colour change with hot acidified dichromate(VI)</i> Determination of molecular formula of C $\frac{2.323}{1.21 \times 10^{-2}} = 192 \text{ (g mol}^{-1}\text{)}$ From 1.21 × 10^{–2} mol C has a mass of 2.323 g. • 192 – 3 × 45 (3 × COOH) – 16 (O) = 41 41 → C₃H₅ (<i>or evidence of working</i>) • Molecular formula = C₆H₈O₇ Structure of citric acid • 4 peaks in ¹³C NMR → 4 types of carbon • Correct structure of C matching evidence. $\begin{array}{c} \text{COOH} \\ \\ \text{HOOC}-\text{CH}_2-\text{C}-\text{CH}_2-\text{COOH} \\ \\ \text{OH} \end{array}$ NOTE: Structure below match all evidence except for ¹³C NMR. See Level 3 criteria. $\begin{array}{cc} \begin{array}{c} \text{COOH} \\ \\ \text{HO}-\text{C}-\text{CH}_2-\text{CH}_2-\text{COOH} \\ \\ \text{COOH} \end{array} & \begin{array}{c} \text{COOH} \\ \\ \text{HOOC}-\text{C}-\text{CH}-\text{COOH} \\ \quad \\ \text{OH} \quad \text{CH}_3 \end{array} \end{array}$
	Total	6	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
24			C	1	ALLOW 3 (This is the number of peaks in the NMR spectrum) Examiner Comments This was well answered on the whole, with some candidates failing to include the peak associated with the –COOH part of the molecule. The common incorrect answer was D.
			Total	1	
25			A	1	Examiner Comments Many Candidates scored well on this question having clearly learned that an acyl chloride will react with an amine to produce an amide. Where candidates failed to score this mark answers provided showed no pattern, with all distractors being seen equally.
			Total	1	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
26	a		Empirical formula Mole Ratio C : H : O = 5.88 : 5.92 : 1.47 ✓ Empirical formula = C₄H₄O ✓ Molecular formula Molecular formula = C₈H₈O₂ AND Evidence of 136 in working or from labelled peak in spectrum ✓	3	ANNOTATE ANSWER WITH TICKS AND CROSSES ALLOW $\frac{70.58}{12.0} : \frac{5.92}{1.0} : \frac{23.50}{16.0}$ ALLOW 4:4:1 if linked to C:H:O Alternative method for 3 marks: C: $\frac{136 \times 70.58/100}{12.0} = 8$ H: $\frac{136 \times 5.92/100}{1.0} = 8$ O: $\frac{136 \times 23.50/100}{16.0} = 2$ Examiner Comments The empirical formula was correctly calculated by all but the weakest candidates. The final mark was more difficult to obtain as it required evidence that the molar mass had been determined from the mass spectrum and used in establishing the molecular formula.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	b		Functional groups Phenol AND ketone ✓ Explanation Links phenol to (weak) acidity AND no reaction with Na₂CO₃ (so not carboxylic acid) ✓ Links 2,4-DNP(H) or Brady's reagent observation to carbonyl AND Tollens' reagent observation (so not an aldehyde) ✓	3	DO NOT ALLOW any other functional groups for first marking point. ALLOW identity of functional groups in the explanation if not stated on functional group prompt line. ALLOW "aldehyde or ketone" in place of carbonyl Examiner Comments Many candidates were able to suggest that the compound contained a ketone but found it more difficult to indicate the presence of phenol. Approximately 20% of the entry obtained all three marks. When explaining the presence of the ketone some failed to indicate that the 2,4-DNP test indicated that the compound must contain a carbonyl and just focused on the lack of reactivity with Tollens'. Answers suggesting the molecule contained a ketone as no reaction was observed with Tollens' did not gain credit when no reference to carbonyl was seen. Those who recognised the presence of a phenol explained that the only acidic functional group that does not react with sodium carbonate is a phenol.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	c		Carbon NMR analysis Peaks between 110–160 ppm are the (four) aromatic (carbon environments) ✓ Compound contains a C=O between 190 – 200 ppm AND Compound contains a C-C at 20 – 30 ppm ✓ Structure 	3	ALLOW peaks to be identified by: • Peaks labelled on spectrum • Peaks indicated on a chemical structure • Peaks indicated from within text Note: If identifying aromatic peaks from the spectrum all four peaks should be indicated. ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous Examiner Comments When interpreting a carbon-13 NMR spectrum, candidates should be advised to fully label any peaks. Many candidates failed to indicate the presence of four aromatic peaks yet produced a structure containing a benzene ring. In some cases candidates did not link their answer to part (a) of the question giving structures that did not match their molecular formula.
			Total	9	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance																																			
27			Refer to the marking instructions on page 5 of the mark scheme for guidance on marking this question. Level 3 (5–6 marks) Develops a plan that identifies all compounds by a process of elimination AND includes essential detail for all required tests and observations <i>There is a well-developed line of reasoning which is clear and logically structured</i> Level 2 (3–4 marks) Develops a plan that identifies at least half of the compounds OR identifies the functional groups in most of the compounds AND includes detail of the required tests and observations <i>There is a line of reasoning with some structure. The information is mostly relevant and supported by some evidence.</i> Level 1 (1–2 marks) Develops a plan that attempts to identify the compounds OR functional groups AND includes detail of the required tests and observations <i>There is a line of reasoning using information that is mostly relevant.</i> 0 marks – No response or no response worthy of credit with no compounds identified	6	Indicative scientific points may include: <u>Functional groups</u> • B alkene and tertiary alcohol • C alkene and aldehyde • D alkene and primary alcohol • E ketone • F secondary alcohol • G alkene and ketone <u>Tests</u> • B, C, D and G → Bromine decolourises • C, D and F → $(\text{H}^+)/\text{Cr}_2\text{O}_7^{2-}$ green • C, E and G → 2,4-DNP orange precipitate • C → Tollens silver mirror For Tollens' ALLOW alternative: Fehling's solution produces a 'brown / brick red / orange' precipitate For 2,4- DNP, ALLOW 2,4-DNPH and Brady's <table><tr><td></td><td>B</td><td>C</td><td>D</td><td>E</td><td>F</td><td>G</td></tr><tr><td>Bromine</td><td>✓</td><td>✓</td><td>✓</td><td></td><td></td><td>✓</td></tr><tr><td>$(\text{H}^+)/\text{Cr}_2\text{O}_7^{2-}$</td><td></td><td>✓</td><td>✓</td><td></td><td>✓</td><td></td></tr><tr><td>2,4-DNP</td><td></td><td>✓</td><td></td><td>✓</td><td></td><td>✓</td></tr><tr><td>Tollens'</td><td></td><td>✓</td><td></td><td></td><td></td><td></td></tr></table> No credit for tests on products of tests, melting points, spectra, etc. <i>For other tests seen, contact TL for advice</i> Examiner's Comment: This question required candidates to apply their knowledge of functional group tests for several naturally occurring organic compounds. Candidates were free to plan a series of chemical tests and there were many different solutions. The best responses planned to identify compounds by using tests that eliminated compounds one by one for further tests.		B	C	D	E	F	G	Bromine	✓	✓	✓			✓	$(\text{H}^+)/\text{Cr}_2\text{O}_7^{2-}$		✓	✓		✓		2,4-DNP		✓		✓		✓	Tollens'		✓				
	B	C	D	E	F	G																																		
Bromine	✓	✓	✓			✓																																		
$(\text{H}^+)/\text{Cr}_2\text{O}_7^{2-}$		✓	✓		✓																																			
2,4-DNP		✓		✓		✓																																		
Tollens'		✓																																						

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					These were often concise and very clear. Unfortunately, many responses were excessive in length with confusing plans that sometimes broke down partway through. Some candidates gave chemical tests for the functional groups in each compound in turn. They then didn't link the tests together to show how the compounds could be distinguished. Weaker candidates sometimes wrote down chemical tests for the different functional groups without linking these to the compounds. Poorly prepared candidates sometimes had the wrong observations for the tests. A significant number of candidates thought that the cyclic alcohol F was a phenol. Despite these difficulties, there were many candidates who scored all six marks by a variety of methods.
			Total	6	
28			A	1	<u>Examiner's Comments</u> Candidates found this question more challenging than anticipated. While many correctly chose A, a significant proportion of candidates selected C.
			Total	1	
29			B	1	ALLOW 4 (This is the number of peaks in the NMR spectrum) <u>Examiner's Comments</u> Many candidates correctly identified that the ^1H NMR spectrum would contain 4 peaks and selected B. In most cases candidates arrived at this answer by drawing out the structure and labelling the environments. A common distractor was A (3 peaks) which presumably arose from candidates assuming that the C–H and O–H protons in the centre of the structure were equivalent.
			Total	1	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
30		i	Number of peaks 2 marks 2-nitrophenol AND 3-nitrophenol have six peaks/environments/types of carbon ✓ 4-nitrophenol has four peaks/environments/types of carbon ✓ Statement 1 mark 4-nitrophenol can be distinguished OR 2-nitrophenol and 3-nitrophenol cannot be distinguished ✓	3	IGNORE any numbers shown on structures ALLOW 1 mark only IF a response identifies that all the compounds have 6 peaks/environments/types of C OR all the compounds have 4 peaks/environments/types of carbon IGNORE chemical shifts DO NOT ALLOW ECF from an incorrect number of peaks/environments/types of carbon <u>Examiner's Comments</u> This question required candidates to apply their knowledge of ^{13}C NMR spectroscopy to deduce the number of different carbon environments in each of the nitrophenols shown. The best responses were succinct, stating that it is possible to distinguish 4-nitrophenol from the other two after deducing the correct number of carbon environments for each compound. Lower ability candidates' responses did not identify the symmetry in 4-nitrophenol and suggested all three compounds would produce six peaks, therefore making it impossible to distinguish between them.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii	(In phenol) a (lone) pair of electrons on O is (partially) delocalised/donated into the π-system / ring ✓ Electron density increases/is higher (than benzene) ✓ ORA (phenol) is more susceptible to electrophilic attack OR (phenol) attracts/accepts electrophile/HNO_3 more OR (phenol) polarises electrophile/HNO_3 more ✓ ORA	3	ALLOW the electron pair in the p-orbitals of the O atom becomes part of the π-system / ring ALLOW diagram to show movement of lone pair into ring ALLOW lone pair of electrons on O is (partially) drawn/attracted/pulled/ into π-system / ring IGNORE activating IGNORE charge density IGNORE electronegativity IGNORE phenol reacts more readily (<i>no reference to electrophile</i>) ALLOW NO_2^+ for electrophile <u>Examiner's Comments</u> The relative reactivity of phenol is well known by candidates at this level and the majority scored two or three marks. Candidates who did not score full marks gave imprecise or vague explanations. This included reference to 'higher charge density' or 'higher electronegativity' of the phenol ring, rather than 'higher electron density'.
			Total	6	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
31		i	Bromine/ Br ₂ AND goes colourless/decolourised ✓	1	Note: both reagent and observation are required ALLOW bromine water/ Br₂(aq) <u>Examiner's Comments</u> Almost all candidates were able to correctly describe the use of bromine as a test for an unsaturated chain.
		ii	Tollens' (reagent) AND Silver (mirror/precipitate/ppt/solid) ✓	1	Note: both reagent and observation are required for the mark. ALLOW ammoniacal silver nitrate OR Ag⁺/NH₃ ALLOW black ppt OR grey ppt <u>Examiner's Comments</u> Almost all candidates were able to correctly describe the use of Tollens' reagent as a test for an aldehyde functional group.

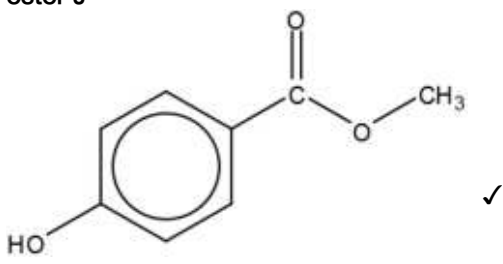
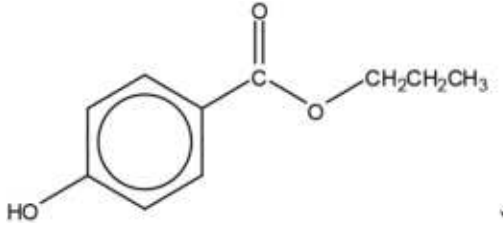
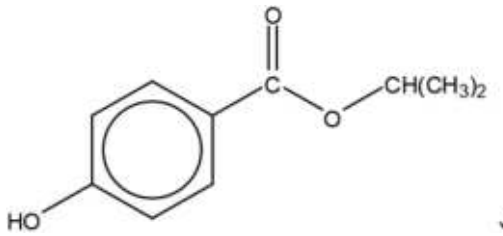
Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		iii	(Add) 2,4-dinitrophenylhydrazine AND orange/yellow/red precipitate ✓ Take melting point (of crystals) ✓ Compare to known values/database ✓	3	ALLOW errors in spelling ALLOW 2,4(-)DNP OR 2,4(-)DNPH ALLOW Brady's reagent or Brady's Test ALLOW solid OR crystals OR ppt as alternatives for precipitate Mark second and third points independently of response for first marking point DO NOT ALLOW 2nd and 3rd marks for taking and comparing boiling points OR chromatograms <u>Examiner's Comments</u> The use of 2,4-dinitrophenylhydrazine as a test for the carbonyl group is well known by candidates at this level. The majority of the cohort correctly identified this test and the subsequent analysis of the melting point of the products as a method of identifying each compound. Lower ability candidate responses made reference to analysis of the boiling points of the cinnamaldehyde and methylcinnamaldehyde as a means of identification.
			Total	5	

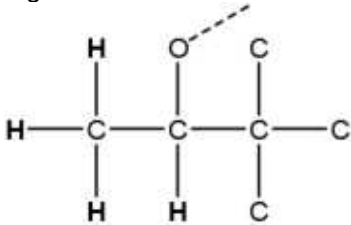
Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
32	i FIRST CHECK ANSWER ON ANSWER LINE IF answer = 7.5×10^{-4} award 2 marks ----- [K] in mol dm⁻³ $\frac{9.13 \times 10^{-2}}{166} = 5.50 \times 10^{-4} \text{ (mol dm}^{-3}\text{)} \checkmark$ [L] from peak areas $5.50 \times 10^{-4} \times \frac{5.9}{4.3}$ OR $5.50 \times 10^{-4} \times 1.37 \dots$ $= 7.5 \times 10^{-4} \text{ (mol dm}^{-3}\text{)} \checkmark$ <i>2 SF Required</i>	2	If there is an alternative answer, Apply ECF Alternative method [K] in g dm⁻³ with peak area of 5.9 $9.13 \times 10^{-2} \times \frac{5.9}{4.3}$ OR $9.13 \times 10^{-2} \times 1.37$ $= 0.125$ OR $0.13 \text{ (g dm}^{-3}\text{)} \checkmark$ Calculator: 0.125272093 [L] in mol dm⁻³ $\frac{0.125}{166} = 7.5 \times 10^{-4}$ OR $\frac{0.13}{166} = 7.8 \times 10^{-4} \text{ (mol dm}^{-3}\text{)} \checkmark$ ----- Common errors: Common errors: Award 1 mark for: • 0.099 (from $\frac{9.13 \times 10^{-2}}{166} \times 180$) • 6.9×10^{-4} (from $\frac{0.125}{180}$) • 7.2×10^{-4} (from $\frac{0.13}{180}$) • 7.0×10^{-4} (from $\frac{0.25272093}{180}$) <u>Examiner's Comments</u> This question required candidates to apply their knowledge of gas chromatography and the mole to solve this problem. Most candidates recognised the need to use the relative peak areas to determine the relative proportion of M. Many also realised that division by the molar mass was required to ensure the final answer was given in mol dm⁻³. However, some used molar mass of M rather than K in this step, leading to an answer of $7.0 \times 10^{-4} \text{ mol dm}^{-3}$. Answer = $7.5 \times 10^{-4} \text{ mol dm}^{-3}$

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii	ester J  esters L and M  	3	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous L and M can be identified either way round IGNORE 'C₃H₇' in L and/or M as ambiguous (<i>question requires structures</i>) IGNORE connectivity of phenol OH group (<i>masks are for structures of alkyl groups</i>) <u>Examiner's Comments</u> Examiners were encouraged by the number of good responses to this problem solving question. Most candidates achieved at least one mark in this part, often from a correct structure of J. Although many candidates deduced that the R group for both L and M consisted of 3 C atoms and 7 H atoms, only the highest ability candidates were able to join these correctly. A small but significant number of responses showed R groups that involved O atoms, despite the prompt that the R represented an alkyl group. Candidates are advised to read questions carefully.
			Total	5	

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
33	<i>Please refer to the marking instructions on page 5 of this mark scheme for guidance on how to mark this question.</i> Level 3 (5–6 marks) Compound is a structure of $C_6H_{12}O_3$ that is consistent with splitting pattern and chemical shifts in NMR spectrum. AND Comprehensive reasoning with most of the data analysed. <i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i> Level 2 (3–4 marks) Compound has a feasible chemical structure that is consistent with the splitting pattern in NMR spectrum but may have incorrect molecular formula. AND Reasoning provided with some of the data analysed. <i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i> Level 1 (1–2 marks) Correct determination of empirical formula and/or molecular formula. OR Analyses most of the NMR data. OR Attempts to determine empirical and/or molecular formula AND analyses some of the NMR data. <i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.</i> 0 marks No response or no response worthy of credit.	6	Indicative scientific points: Empirical and Molecular Formula • C : H : O = 54.54/12 : 9.10/1 : 36.36/16 4.545 : 9.10 : 2.273 2 : 4 : 1 • Empirical formula = C_2H_4O • uses $m/z = 132.0$ to determine molecular formula as $C_6H_{12}O_3$ <u>^1H NMR analysis</u> Spectrum: • $\delta = 4.0$ ppm, quartet, 1H, CH_3-CH-O • $\delta = 1.3$ ppm, singlet, 6H, $(CH_3)_2-C$ • $\delta = 1.2$ ppm, doublet, 3H, CH_3-CH- Without D_2O: • Peak at 11.0 ppm $COOH$ or OH • peak at 3.6 ppm OH Note: Data Sheet shows O-H chemical shift can occur around 11.0 ppm Structure ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous Contains • region that gives doublet and quartet e.g.  • region that gives singlet e.g.

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
			Examples of structures consistent with splitting and chemical shift in NMR Note: there may be other possible structures that are consistent with the splitting pattern and chemical shifts in NMR – if an alternative structure is seen, please contact your team leader <u>Examiner's Comments</u> Most candidates were able to determine the empirical and molecular formula of the unknown compound. A number of excellent

Mark Scheme

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			and clear response were seen, where the NMR data was explained, including interpretation of the additional peaks observed without D₂O. However many candidates were unable to suggest a structure that matched their NMR interpretation. Some candidates used the quartet, doublet and singlet to suggest a structure that would give rise to this splitting pattern, but which was not consistent with the chemical shifts, see Exemplar 12. Such responses received a level 2 mark (3-4). Stronger responses were able to use all the data to suggest a correct structure. The most common was CH₃CH(OH)C(CH₃)₂COOH although other viable structures, including CH₃CH(OH)COC(CH₃)₂OH, were also seen. Examiners were impressed with the problem solving ability shown by candidates and a significant proportion of responses were credited six marks. Exemplar 12 <table><tr><th>C</th><th>H</th><th>O</th></tr><tr><td>54.54</td><td>9.10</td><td>36.36</td></tr><tr><td>12</td><td>1</td><td>16</td></tr><tr><td>4.545</td><td>9.10</td><td>2.2725</td></tr><tr><td>2</td><td>4</td><td>1</td></tr></table> empirical formula = C₆H₁₂O₅ Mr = 144 132 = 3 44 molecular formula = C₆H₁₂O₅ x 3 = C₆H₁₂O₅ peak at 1.2 ppm = 1H, H-C-R, 1H, a doublet so adjacent carbon has 1 H. peak integral of 3 → CH₃ peak at 1.3 ppm = H-C-R, singlet so adjacent C has no protons. Integral of 6 = (CH₃)₂ Peak at 4 ppm indicative of H-C-O. Quartet so adjacent C has 3 protons. Integral of 1 = CH Additional answer space if required. D₂O at 11 ppm = -C=O and 3.6 ppm indicative of H-C-O. M.F. = C₆H₁₂O₅ <chem>CC(C)(C)C(O)C(=O)O</chem> CH₃CH(OH)C(CH₃)₂COOH <chem>CC(C)(C)C(O)C(=O)O</chem> CH₃CH(OH)COC(CH₃)₂OH	C	H	O	54.54	9.10	36.36	12	1	16	4.545	9.10	2.2725	2	4	1
C	H	O																
54.54	9.10	36.36																
12	1	16																
4.545	9.10	2.2725																
2	4	1																

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					This logically presented Level 2 response uses the elemental analysis and mass spectrum data to determine the correct empirical and molecular formula of the unknown compound. The peaks in the NMR spectrum are analysed in detail, with a clear explanation of the splitting patterns. A comment about the two additional peaks observed when the spectrum is run without D₂O is also provided. The response concludes with a structure of C₆H₁₂O₃ that would show a singlet, doublet and quartet in its ¹H NMR spectrum. However, this structure is not consistent with the chemical shift values shown in the spectrum provided. In particular this structure would produce a quartet between 2.0–2.9 ppm, rather than at 4.0 as in the spectrum shown. Consequentially this response does not achieve Level 3. When tackling questions of this type candidates are advised to check that a proposed structure would produce peaks in the correct region of the NMR spectrum to ensure it is totally consistent with the data analysed.
			Total	6	
34			B	1	<u>Examiner's Comments</u> Candidates find questions based on practical procedures difficult and this question proved to be no exception. A similar number of candidates selected each option, suggesting that most guessed. The correct option is B.
			Total	1	
35			A	1 (AO1.1)	
			Total	1	
36			A	1 (AO1.1)	
			Total	1	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
37			CDCl ₃ used as a solvent ✓ D ₂ O used to identify OH OR NH protons ✓	2 (AO1.1×2)	Example and use required for each mark ALLOW for 1 mark, D₂O as a solvent <u>Examiner's Comments</u>  Misconception The use of deuterated compounds in NMR analysis was often explained the use in terms of lack of spin but did not give examples (e.g. CDCl₃ as a solvent or D₂O as for identifying OH/NH protons)
			Total	2	
38			B	1 (AO 2.5)	<u>Examiner's Comments</u> Most candidates correctly selected B as the compound that would show four peaks in the ¹³C NMR spectrum. Many candidates annotated the structures, indicating the different carbon environments with a circle. This proved a good strategy. Common incorrect responses included C and D which were seen in roughly equal proportions.
			Total	1	
39			C	1 (AO 2.5)	<u>Examiner's Comments</u> Many candidates identified that 2-methylpropan-1-ol (C) produced the ¹³C NMR spectrum show. The majority of successful responses included diagrams showing the structures of the compounds to choose from. The most frequently seen incorrect response was D.
			Total	1	

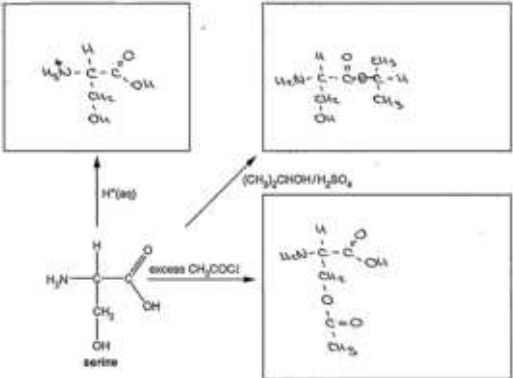
Mark Scheme

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40 a i		4(AO 2.5 ×4)	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW protonation of NH₂ group in reaction with (CH₃)₂CHOH i.e. ALL structures must be based on serine For reaction with excess CH₃COCl, IGNORE reaction of COOH to form an acid anhydride ----- ALLOW 1 mark for (both NH and OH groups reacted but acyl chloride instead of COOH) OR (both NH and OH groups reacted but H missing from a C atom) OR

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Question	Answer/Indicative content	Marks	Guidance
			<i>(NH group reacted correctly but rest of serine unchanged)</i> OR <i>(OH group reacted correctly but rest of serine unchanged)</i> <u>Examiner's Comments</u> This question focused on the reactions of the different functional groups in serine. Candidates are familiar with these reactions and most candidates scored at least two marks. These were achieved by the formation of the ammonium ion by reaction with H^+ and the formation of the ester from $(\text{CH}_3)_2\text{CHOH}$. Determining the organic product from the reaction of serine with excess CH_3COCl proved more difficult. Some candidates realised that the OH of serine's R group would react and others drew the amide formed from the reaction of the NH_2 group. The best responses showed both conversions and scored full marks. Lower ability responses often showed organic products containing the Cl atom from the ethanoyl chloride rather than the CH_3CO group.

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
			Exemplar 2  This response scored three marks. The candidate has drawn correct organic products for the reaction of serine with H^+ and $(\text{CH}_3)_2\text{CHOH}$. The product from the reaction of excess CH_3COCl shows the formation of an ester but not the formation of the amide. This product was seen often by examiners and scored one mark. If an amide group had been shown this response would have received full marks. Notice the candidate has presented their organic products clearly with the structures drawn in a similar manner to serine shown in the question. This is a good strategy to avoid errors and omissions when drawing organic structures.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii	IF $M_r(\text{amino acid}) = 131$ from titration analysis AWARD first 3 marks ALLOW 3SF or more throughout IGNORE trailing zeroes, e.g. ALLOW 0.044 for 0.0440 ----- $n(\text{HCl}) = 0.150 \times \frac{25.0}{1000}$ OR $3.75 \times 10^{-3} \text{ (mol)}$ ✓ $n(\text{amino acid})$ in 250 cm^3 $= 3.75 \times 10^{-3} \times \frac{250.0}{21.30}$ OR 0.0440 (mol) ✓ $M(\text{amino acid}) = \frac{5.766}{0.0440} = 131 \text{ (g mol}^{-1}\text{)}$ ✓ Amino acid = $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_2)\text{COOH}$/leucine AND working to show $R = 57$ to justify choice OR evidence to show M_r leucine = 131 to justify choice ✓	4 (AO 2.8) (AO 2.8) (AO 2.8) (AO 3.2)	ALLOW alternative approaches Calculator: 0.04401408451 ALLOW ECF from incorrect $n(\text{HCl})$ ALLOW ECF from incorrect $n(\text{amino acid})$ ALLOW ECF from incorrect $M(\text{amino acid})$ i.e. ECF for alkyl group closest to calculated $M(\text{alkyl group})$, e.g. for $M(\text{alkyl group}) = 15$, ALLOW $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ Note: evidence may be shown with table <u>Examiner's Comments</u> Candidates are confident in tackling titration analysis and the majority of responses were well structured. Most candidates used the results to determine the M_r of the unknown amino acid and hence identify it as leucine. However, other approaches were also seen and these were given full credit if correct. A common error was incorrect scaling to determine the amount of amino acid used to make the 250 cm^3 solution. A significant number of responses simply multiplied the number of moles of acid by ten rather than using a factor of $250/21.30$. Error carried forward marks were available and so the majority of candidates scored 3 or 4 marks.

Mark Scheme

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	b	i	R _f value in range 0.33 – 0.35 ✓	1(AO 1.1)	ALLOW 2 SF or more. But ignore digits after second sig fig ALLOW 0.3 for 0.33..... <u>Examiner's Comments</u> Candidates are familiar with the calculation of R_f values and this question was answered very well. Although almost all candidates showed appropriate working as part of their response some candidates gave the final answer to only one significant figure and did not receive credit. Candidates were expected to give their answer to a number of significant figures appropriate to the measurements they had made, so a minimum of two significant figures was expected. The mark scheme allowed a response within a range, rather than a specific value, and most candidates scored in this part.
		ii	gly(cine) ✓ Amino acid matches (leu(cine) and) glycine in Solvent W AND Amino acid matches (ala(nine) and) glycine in Solvent X ✓	2(AO 2.3 ×2)	ALLOW glycine has the same/similar R_f as the unknown in both solvents/chromatograms ALLOW suitable alternatives for R_f e.g. moves same distance
			Total	11	
41			C	1 (AO2.2)	
			Total	1	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
42		i	Comparison of branching and points of contact e.g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ has longer chain / straight chain / no branches AND e.g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ has more points of contact / more surface interaction (between molecules) ✓ Relative strength of force e.g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ has stronger/more induced dipole(–dipole) interactions OR London forces ✓ ----- Hydrogen bonds $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ OR $(\text{CH}_3)_2\text{CHNH}_2$ have hydrogen/H bonds OR $(\text{CH}_3)_3\text{N}$ has no hydrogen/H bonds ✓ Relative strength of force Hydrogen bonds are stronger than London forces /permanent dipole interactions ✓ ----- Comparison of energy required to break force e.g. More energy to break/overcome London forces/intermolecular forces in $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ OR More energy is needed to break H bonds (than London forces) ✓	5 → 4 max (AO 1.2) (AO 2.1) (AO 1.2) (AO 2.1)	ANNOTATE WITH TICKS AND CROSSES, etc. ----- ALLOW ORA throughout ALLOW 'The straighter the chain, the more points of contact' IGNORE comparison using 'primary', 'secondary' and 'tertiary'. <i>Comparison of branching is required.</i> For London forces, • ALLOW induced dipole(–dipole) interactions • IGNORE IDID OR van der Waals' forces/VDW DO NOT ALLOW $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ has more electrons <i>(number of electrons are the same)</i> DO NOT ALLOW 'more energy to break covalent bonds ALLOW little energy is required to break London forces (compared with H bonds) <u>Examiner's Comments</u> Candidates were expected to explain the different boiling points of three amines. Most candidates linked increased branching with less surface contact between molecules, leading to weaker induced dipole interactions (London forces). Fewer candidates linked the decreasing boiling points to less energy being required to break the intermolecular bonds. The highest performing candidates recognised the large difference between

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					the boiling points of the primary and tertiary amines. They then identified the cause: primary amines form hydrogen bonds but tertiary amines do not. This question was answered reasonably well with fewer candidates than in the past describing relative strengths of covalent bonds, a common misconception.
		ii	FIRST CHECK MOLECULAR FORMULA and STRUCTURE IF molecular formula = C₅H₁₃N AND correct structure AND evidence of ideal gas equation → 6 marks Correct up to 87 AND C₅H₁₃N → 5 marks Correct up to 87 → 4 marks <i>Rearranging ideal gas equation</i> $n = \frac{pV}{RT} \checkmark$ <i>Unit conversion AND substitution into</i> $n = \frac{pV}{RT} :$ • $R = 8.314$ OR 8.31 • $V = 72(.0) \times 10^{-6}$ • T in K: 373 K e.g. $\frac{1.00 \times 10^5 \times 72.0 \times 10^{-6}}{8.314 \times 373} \checkmark$ <i>Calculation of n</i> $n = 2.32 \times 10^{-3}$ (mol) $\checkmark$ <i>Calculation of M</i> $M = \frac{0.202}{2.32 \times 10^{-3}} = 87 \checkmark$ <i>Molecular formula</i> C₅H₁₃N $\checkmark$ Molecular formula required	6 (AO 2.2×4) (AO 3.2)	IF $n = \frac{pV}{RT}$ is omitted, ALLOW when values are substituted into rearranged ideal gas equation. Calculator: $n = 2.321740325 \times 10^{-3}$ from 8.314 From 8.31, $n = 2.322857889 \times 10^{-3}$ ALLOW elements in any order ALLOW molecular formula = C₃H₉N₃ ALLOW other molecular formulae of an amine that has $M = 87$, e.g. C₄H₉NO

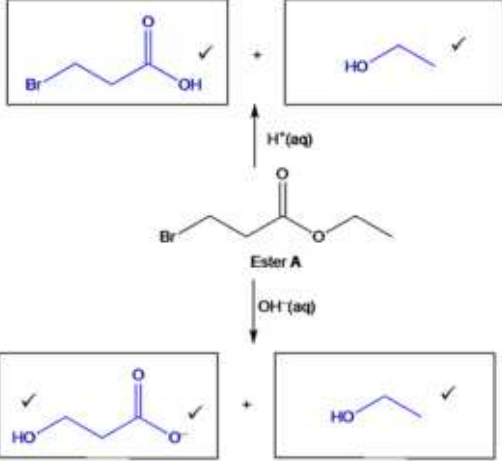
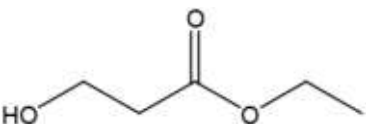
Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
	Structure of amine A from $C_5H_{13}N$ ✓ Use of 24000 3 marks max possible for use of 72.0 cm^3 OR 0.720 dm^3 by ECF Calculation e.g. $n = \frac{72.0}{24000} = 3.00 \times 10^{-3}$ No mark <i>(calculation much simpler)</i> $M = \frac{0.202}{3.00 \times 10^{-3}} = 67.3$ OR 67 ✓ ECF Molecular formula = ✓ ECF C_4H_9N Structure ✓ ECF	(AO 3.2)	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW structures below from molecular formula = $C_3H_9N_3$ ALLOW ECF but only if structure has calculated M_r AND has 3 peaks in ^{13}C NMR spectrum. Examiner's Comments Most candidates rearranged the ideal gas equation correctly to make n the subject. They then substituted correct values for p, V, R and T into the equation, with correct unit conversions. Most candidates then calculated n correctly as 2.32×10^{-3} and combined this value with the mass of 0.202 g to derive the molecular formula as 87. Lower-attaining candidates often made an error in their conversion of cm^3 into m^3, by multiplying by 10^{-3} rather than 10^{-6}. This error resulted in a value of n as 2.32 and the unrealistic molecular mass of 8.7×10^{-3}, from which a molecular formula is impossible. Candidates in this position are advised to check back at the unit conversions in the working. Very few candidates did not convert 100°C into 373 K. Candidates with the correct molecular formula of 87 usually suggested $C_5H_{13}N$ as the molecular formula. A significant number quoted $C_5H_{11}NH_2$. This response was not credited as it is not a 'molecular' formula. There are several possible structures of $C_5H_{13}N$ with three ^{13}C NMR peaks and any were credited. Error carried forward was applied from a

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					different molecular mass for both the molecular formula and a structure. This emphasises the importance of working within calculation; credit will always be given for a correct method. Instead of using the ideal gas equation, some candidates used the molar gas constant at room temperature and pressure, 24.0 dm³, which gives a molecular mass of 67. This simplified approach could only gain the final 2 marks for this question: a molecular formula (with an error carried forward value of 67, e.g. C₄H₅N) and a structure of an amine with this molecular formula and 3 peaks in the ¹³C NMR spectrum.
			Total	10	

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
43 a i	ethyl 3-bromopropanoate ✓	1(AO 1.2)	ALLOW one word: ethyl3-bromopropanoate OR more words, e.g. ethyl 3-bromo propanoate IGNORE lack of hyphens, or addition of commas <u>Examiner's Comments</u> This demanding question discriminated well. The most able candidates were able to apply the nomenclature rules to name ester A correctly as ethyl 3-bromopropanoate. Common incorrect responses included ethyl 1-bromopropanote and ethyl 4-bromopropanoate.
	ii 	5(AO 2.5 ×5)	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW in either order ALLOW any vertical bond to the OH group e.g. ALLOW $\begin{array}{c} \\ \text{OH} \end{array}$ OR $\begin{array}{c} \\ \text{HO} \end{array}$ DO NOT ALLOW OH- ALLOW in either order For reaction with OH⁻, ALLOW one mark for $\text{Br}-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})\text{O}^-$ OR $\text{HO}-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})\text{OH}$ OR 

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					<u>Examiner's Comments</u> This question required candidates to apply their knowledge of hydrolysis reactions to ester A. The majority of candidates were able to show 3-bromopropanoic acid and ethanol in the top two boxes to secure two marks. The organic products from the alkaline hydrolysis proved more difficult. Many candidates identified ethanol as a product in one of the lower boxes but lower ability responses showed the ethoxide ion. Some candidates drew the 3-bromopropanoate ion as the other product. Higher ability candidates realised that the Br atom would be replaced by an OH group and the best responses showed the correct carboxylate ion. Examiners were encouraged by the number of excellent responses seen and the majority of candidates scored 4 or 5 marks.
		iii	hydrolysis ✓	1(AO 1.1)	IGNORE 'acid' and 'alkaline' IGNORE nucleophilic substitution

Mark Scheme

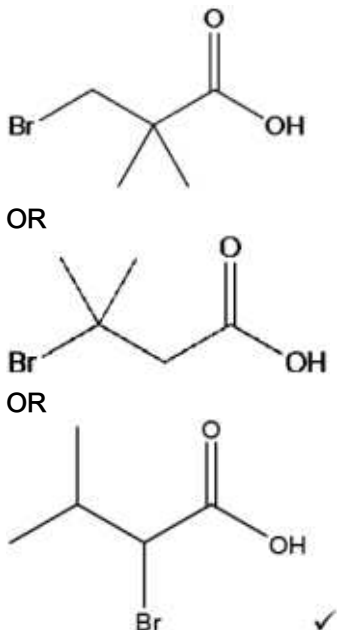
Question		Answer/Indicative content			Marks	Guidance														
b			<table><tr><th>Proton environment</th><th>Chemical shift</th><th>Splitting pattern</th></tr><tr><td>1</td><td>3.0–4.3</td><td>Triplet</td></tr><tr><td>2</td><td>2.0–3.0</td><td>Triplet</td></tr><tr><td>3</td><td>3.0–4.3</td><td>Quartet</td></tr><tr><td>4</td><td>0.5–1.9</td><td>Triplet</td></tr></table>	Proton environment	Chemical shift	Splitting pattern	1	3.0–4.3	Triplet	2	2.0–3.0	Triplet	3	3.0–4.3	Quartet	4	0.5–1.9	Triplet	4(AO 3.1 × 4)	ALLOW δ values ± 0.2 ppm, as a range or a value within the range ALLOW integers for δ values e.g. 2 is equivalent to 2.0 ALLOW quadruplet for quartet ALLOW diagrams to show splitting pattern e.g.  for triplet  for quartet ALLOW splitting patterns shown as numbers i.e. '3' for triplet, '4' for quartet <u>Examiner's Comments</u> This question was answered well and most candidates scored full marks. A common error was the chemical shift of environment 2, which was sometimes shown as 9.0-10.0. Some candidates gave incorrect splitting patterns for environment 2, stating it would give a singlet, rather than a triplet. This is presumably the result of focusing on the carbon atom to the right of the environment with no H atoms. Candidates should be reminded to consider adjacent carbon atoms on both sides of a particular environment, rather than just looking in one direction.
	Proton environment	Chemical shift	Splitting pattern																	
	1	3.0–4.3	Triplet																	
	2	2.0–3.0	Triplet																	
	3	3.0–4.3	Quartet																	
4	0.5–1.9	Triplet																		

Mark by column

Chemical shift: all 4 correct ✓✓
3 correct ✓

Splitting pattern: all 4 correct ✓✓
3 correct ✓

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	c		 OR OR ✓	1(AO 3.1)	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous <u>Examiner's Comments</u> This question required candidates to use both pieces of information to deduce that B was a carboxylic acid with two equivalent carbon atoms. Many candidates were able to suggest a suitable structure. However some candidates did not use all the information and it was common to see responses that showed an ester or a straight chain carboxylic acid.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
	d		IF answer on answer line = 24018, AWARD 2 marks IF answer on answer line = 27600, AWARD 1 mark ----- Relative mass of 200 molecules = $200 \times 138 = 27600$ ✓ M_r of polyester = $27600 - 199 \times 18 = 24018$ ✓	2(AO 2.2 ×2)	ALLOW ECF from incorrect M_r Alternative method based on repeat unit: M_r of 200 repeat units = $200 \times 120 = 24000$ ✓ M_r of polymer = $24000 + 1 + 17 = 24018$ ✓ <u>Examiner's Comments</u> A variety of responses was seen in this demanding question. In general candidates adopted one of two approaches. The most common was to multiply the M_r of 2-hydroxybenzoic acid by 200 and then subtract the mass of the 199 water molecules removed during polymerisation. The other approach used the M_r of the repeat unit. This was multiplied by 200 and the mass of H and OH at each end of the polymer was added to give the final answer. Many candidates were successful with the first step of their approach, but the best responses included the second step taking into account the M_r of water. A significant number of candidates used an incorrect value for the M_r in their first step. Candidates are advised to draw out the structure of a compound before determining the M_r. This is particularly important when only a name is given in the question.

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
e i	<i>* Refer to marking instructions on page 4 of mark scheme for guidance on marking this question.</i> Level 3 (5-6 marks) Correct calculation of the mass of (CH₃)₂CHCHO. AND Planned synthesis includes oxidation of aldehyde and formation of ester C with most of the reagents and conditions identified and equations are mostly correct. <i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i> Level 2 (3-4 marks) Calculation of the mass of (CH₃)₂CHCHO is partly correct AND Planned synthesis includes oxidation of aldehyde and formation of ester C with some of the reagents and conditions identified OR Attempts to calculate mass of (CH₃)₂CHCHO but makes little progress AND Planned synthesis includes oxidation of aldehyde and formation of ester C with most of the reagents and conditions identified and equations for each step are mostly correct <i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i> Level 1 (1-2 marks) Calculation of the mass of (CH₃)₂CHCHO is partly correct OR Planned synthesis includes both steps with some of the reagents and conditions identified OR	6 (AO 3.3 ×6)	Indicative scientific points may include: <u>Calculation of mass of (CH₃)₂CHCHO</u> Using moles $n(\text{ester}) = \frac{12.75}{102.0}$ = 0.125 (mol) • $n((\text{CH}_3)_2\text{CHCHO}) = 0.125 \times \frac{100}{40}$ = 0.3125 (mol) • Mass of (CH₃)₂CHCHO = 72.0 × 0.3125 = 22.5 g Using mass • Theoretical mass of ester $= 12.75 \times \frac{100}{40}$ = 31.875 (g) • Theoretical $n((\text{CH}_3)_2\text{CHCHO})$ $= \frac{31.875}{102}$ = 0.3125 (mol) • Mass of (CH₃)₂CHCHO = 72.0 × 0.3125 = 22.5 g ALLOW small slip/rounding errors such as errors in <i>Mr</i> e.g. use of 71 instead of 72 for (CH₃)₂CHCHO ----- Examples of partly correct calculations Mass = 3.60 g from $0.125 \times \frac{40}{100} \times 72$ (% yield inverted) Mass = 9.00 g from 0.125×72 (% yield omitted) <u>Synthesis: reagents and conditions</u> Step 1: Oxidation of aldehyde (CH₃)₂CHCHO

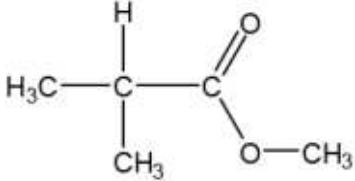
Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
	Attempts equations for both steps but these may contain errors OR Describes one step of the synthesis with reagents, conditions and equation mostly correct <i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.</i> 0 marks No response or no response worthy of credit.		• Reagents: $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ • Conditions: reflux • Equation: $(\text{CH}_3)_2\text{CHCHO} + [\text{O}] \rightarrow (\text{CH}_3)_2\text{CHCOOH}$ Step 2: Formation of ester C • Reagents: methylpropanoic acid/$(\text{CH}_3)_2\text{CHCOOH}$ and methanol/CH_3OH • Conditions: acid (catalyst) reflux/heat • Equation: $(\text{CH}_3)_2\text{CHCOOH} + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3)_2\text{CHCOOCH}_3 + \text{H}_2\text{O}$ IGNORE attempts to form methanol in synthesis <u>Examiner's Comments</u> This question was marked using a level of response mark scheme. Most candidates gave a response worthy of at least Level 2 (3-4 marks) by either providing the synthetic steps with reagents and/or equations for the synthesis of ester C as well as calculating the mass of 2-methylpropanal required. Exemplar 3, below, shows a frequently seen Level 2 response. The best performing candidates determined the mass correctly and showed the synthesis efficiently, using equations to communicate the preparation of ester C and received Level 3 (5-6 marks). Some responses focused solely on the 2-methylpropanal and suggested it would be both oxidised and reduced with each of the products being used to form an ester. Others omitted the mass calculation or gave only a partial synthesis. Such responses received Level 1 (1-2 marks).

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
			Exemplar 3 ① Oxidation of 2-methylpropanal to form 2-methylpropanoic acid using $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ under reflux. $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}}}-\text{H} + [\text{O}] \rightarrow \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}}}-\text{OH}$ ② Esterification of 2-methylpropanoic acid with methanol to form ester C. $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}}}-\text{OH} + \text{CH}_3-\text{OH} \rightarrow \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}}}-\text{O}-\text{CH}_3 + \text{H}_2\text{O}$ Ester C: 2-methylpropanal 0.4: 1 $\therefore$ 2-methylpropanal mass = $\frac{12.75}{0.4} = 31.875 \text{ g}$ required $= 31.88 \text{ g}$ (to 2 d.p.) This response includes an excellent description of the synthesis of ester C. Each step is labelled clearly with the most of the reagents and conditions stated and correct equations. The candidate makes little progress with the calculation of the mass of 2-methylpropanal required, completing only the first step. This response satisfies the Level 2 criteria. The information is provided is relevant and presented with a clear logical structure and was therefore given the upper mark within the level and achieved four marks. The presentation of the synthesis by equations rather than words is an excellent strategy. Candidates are advised to adopt such an approach in questions like this as it allows them develop and clear line of reasoning without the need to write lots of unnecessary text.

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
		ii	Y (43) = $(\text{CH}_3)_2\text{CH}^+$ ✓ Z (71) $(\text{CH}_3)_2\text{CHCO}^+$ ✓ <i>If '+' charge is missing/incorrect but the structures of both fragments are correct, award one mark</i>	2(AO 2.7 × 2)	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW positive charge to be anywhere on the structure For Y and Z, ALLOW structure of a feasible fragment ion formed from ester C  Ester C e.g. Y (43) = CH_3OC^+ Z (71) = $^+\text{CCOOCH}_3$ ALLOW 1 mark if both correct ions are shown but in the incorrect columns ALLOW 1 mark for both correct ions if one or both have an 'end bond' ALLOW 1 mark if both ions are shown using correct molecular formulae <u>Examiner's Comments</u> Most candidates were able to provide a correct structure for each of the ions responsible for the peaks labelled Y and Z. Some candidates omitted the charge, or included 'end bonds'. These responses were able to achieve one mark if both fragments were correct. So the majority of candidates scored one or two marks in this part.
			Total	22	

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
44	<i>* Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.</i> Level 3 (5–6 marks) Structure is $\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{COOH}$ AND Most of the data analysed. <i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i> Level 2 (3–4 marks) A viable aromatic structure of $\text{C}_{10}\text{H}_{12}\text{O}_2$ that contains $\text{C}=\text{O}$ AND most key features consistent with spectral data AND Some of the spectral data analysed <i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i> Level 1 (1–2 marks) Correct determination of empirical formula and/or molecular formula. OR Analyses some of the IR and NMR data. OR Analyses most of the NMR data. <i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.</i> 0 marks No response or no response worthy of credit.	6(AO 1.2 × 2)(AO 3.1 × 2)(AO 3.2 × 2)	Indicative scientific points: Empirical and Molecular Formulae $\text{C} : \text{H} : \text{O} = \frac{73.17}{12.0} : \frac{7.32}{1.0} : \frac{19.51}{16.0}$ $= 6.10 : 7.32 : 1.22$ $= 5 : 6 : 1$ - Empirical formula = $\text{C}_5\text{H}_6\text{O}$ - uses $m/z = 164.0$ to determine molecular formula as $\text{C}_{10}\text{H}_{12}\text{O}_2$ Structure ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous Key features of an aromatic structure consistent with spectral data COOH group 4 aromatic H atoms - single H atom that would give a quartet CH_3 group that would give a doublet CH_3 group that would give a singlet Correct Structure $\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{COOH}$ ALLOW 2-, 3- OR 4- substitution of ring i.e. Spectral analysis ^1H NMR $\delta = 1.6$ ppm, doublet, 3H $\text{CH}_3\text{--CH--}$ $\delta = 2.3$ ppm, singlet, 3H Ar--CH_3 $\delta = 2.7$ ppm, quartet, 1H CO--CH--CH_3 OR Ar--CH--CH_3 / $\text{C}_6\text{H}_5\text{--CH--CH}_3$ $\delta = 7.1\text{--}7.5$ ppm, multiplet, 4H $\text{C}_6\text{H}_4\text{--}$

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					ALLOW approximate values for chemical shifts. IR: • peak at 2300–3700 (cm^{-1}) is O–H • peak at ~ 1720 (cm^{-1}) is C=O • unknown is a carboxylic acid ALLOW ranges from <i>Data Sheet</i> IGNORE references to C–O peaks <u>Examiner's Comments</u> Candidates are confident in tackling questions requiring spectral analysis. Most candidates were able to determine the empirical and molecular formula of the unknown compound and analyse the IR and NMR data. A number of excellent responses were seen which included interpretation of the peak splitting in the NMR spectrum. However, many candidates were unable to suggest a structure that matched their spectral analysis. The majority of structures seen were aromatic but not all contained the carboxylic acid group. Some candidates focused on the NMR data and suggested a structure that was consistent with some of these peaks and included a two substituents of the ring or a degree of chain branching. Lower ability responses often showed a simpler structure of a monosubstituted ring with a straight chain. Stronger responses were able to use all the data to suggest a correct structure as demonstrated in Exemplar 9. Examiners were impressed with the problem solving ability shown by candidates and a significant proportion of responses were given six marks.

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
			Exemplar 8  The student's work includes the following: - Calculations for empirical formula: $\begin{array}{r} \text{C: } 73.17 \\ \text{H: } 7.32 \\ \text{O: } 19.51 \\ \hline \text{C: } 6.0925 \\ \text{H: } 7.32 \\ \text{O: } 1.219375 \\ \hline \text{C: } 5 \\ \text{H: } 6 \\ \text{O: } 1 \end{array}$ Empirical formula: $\text{C}_5\text{H}_6\text{O}$. The molecular mass is 166. The molecular formula is $\text{C}_{10}\text{H}_{12}\text{O}_2$. - IR analysis: - Sharp peak at 1700 cm^{-1} is due to a C=O group. - Broad peak at 2500 cm^{-1} is due to a O-H. This suggests a carboxylic acid is present. - NMR analysis (Additional answer space required): - Peak at 1.5 ppm is due to a CH_3 group. It is a doublet due to being adjacent to 1 proton. Peak at 2.4 ppm is due to a CH_2 group. It is a quartet due to being adjacent to 3 protons. Peak at 7.2 ppm is due to a benzene ring. The peak at 12.2 ppm is due to a carboxylic acid O-H group. It is a broad singlet due to being adjacent to 3 protons. - Chemical structure: The student has crossed out an incorrect structure and drawn the correct one: 2-phenylpropanoic acid. <chem>CC(C)(O=O)c1ccccc1</chem> This candidate starts their analysis by determining the empirical and molecular formula of the unknown compound. Next the IR and NMR data is analysed in a clear, logical fashion. Although not shown in this report, the candidate had annotated the spectra, a good strategy. At the end of the response the candidate has determined a possible structure. Notice how the candidate has crossed out the first attempt at a structure. This is much better than rubbing out a pencil diagram and re-drawing over the space as this often leads to unclear images that are difficult for examiners to read. This candidate received full marks in this question.
	Total	6	

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance						
45		i	<table><tr><td></td><td>Compound C</td><td>Compound D</td></tr><tr><td>Number of peaks</td><td>3 ✓</td><td>8 ✓</td></tr></table>		Compound C	Compound D	Number of peaks	3 ✓	8 ✓	2 (AO3.2)	
	Compound C	Compound D									
Number of peaks	3 ✓	8 ✓									
		ii		5 (AO3.2×5)	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous IGNORE names for organic intermediates (question asks for structures) ALLOW names of reagents and catalyst Around top arrow, ALLOW 1 of 2 marks if HNO₃ and H₂SO₄ swapped. i.e. reagent: <u>H₂SO₄</u> catalyst: <u>HNO₃</u> IGNORE references to concentration ALLOW (CH₃CO)₂O for left arrow IGNORE CH₃COOH IGNORE acyl chloride DO NOT ALLOW AlCl₃/FeCl₃/Fe4						
		Total		7							

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
46			F/aldehyde AND Tollens' (reagent) AND Silver (mirror/precipitate/ppt/solid) ✓ G/alkene/C=C AND Bromine/Br₂ AND goes colourless/decolourised ✓ G/ketone AND 2,4-dinitrophenylhydrazine AND orange/yellow/red precipitate ✓ G/ketone AND Tollens' (reagent) AND no silver mirror/no change/no reaction ✓	4 (AO2.3) (AO3.3) (AO3.3) (AO3.3)	IGNORE use of 2,4-DNP with F ALLOW ammoniacal silver nitrate OR Ag⁺/NH₃ ALLOW black ppt OR grey ppt ALLOW bromine water/ Br₂(aq) ALLOW errors in spelling for 2,4-DNP ALLOW 2,4(-)DNP OR 2,4(-)DNPH ALLOW Brady's reagent or Brady's Test ALLOW solid OR crystals OR ppt as alternatives for precipitate ALLOW ammoniacal silver nitrate OR Ag⁺/NH₃ ALLOW black ppt OR grey ppt ALLOW alternative approach using acidified potassium dichromate for tests with F and/or G, with correct observations, alongside use of 2,4-DNP <u>Examiner's Comments</u> Candidates who found this question difficult often did not give a response that would identify all three of the functional groups (aldehyde, ketone and alkene). The use of Tollens' in identifying aldehydes was well demonstrated, however no reaction with Tollens' was less well demonstrated as a result for ketones.
			Total	4	

Mark Scheme

Question	Answer/Indicative content	Marks	Guidance
47	Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question. Level 3 (5–6 marks) Structure I has a viable chemical structure of $C_6H_9NO_2$ which has the key features consistent with spectral data AND Most of the data analysed <i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i> Level 2 (3–4 marks) Compound I has a viable chemical structure of $C_6H_9NO_2$ with most of the key features consistent with spectral data AND Some of the spectral data analysed. <i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i> Level 1 (1–2 marks) Correct determination of empirical formula and/or molecular formula. OR Analyses some of the IR and NMR data. OR Analyses most of the NMR data. <i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.</i> 0 marks No response or no response worthy of credit.	6 (AO3.1×4) (AO3.2×2)	Indicative scientific points: <u>Empirical and Molecular Formulae</u> $ \begin{array}{cccc} \text{C} & : & \text{H} & : & \text{N} & : & \text{O} \\ = & \frac{56.69}{12.0} & : & \frac{7.09}{1.0} & : & \frac{11.02}{14.0} & : & \frac{25.20}{16.0} \\ \text{OR} & 4.72 & : & 7.09 & : & 0.787 & : & 1.575 \\ = & 6 & : & 9 & : & 1 & : & 2 \end{array} $ - Empirical formula = $C_6H_9NO_2$ $m/z = 127.0$ and empirical formula mass (127) used to determine molecular formula as $C_6H_9NO_2$ <u>Structures of compound I</u> OR OR OR ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous <u>Key features</u> $C \equiv N$ $C=O$ in aldehyde, ketone, ester, amide, acid anhydride CH_3 group that would give a doublet CH_3 group that would give a triplet CH_2 group that would give a quartet <u>^1H NMR and IR analysis</u> ^1H NMR spectrum $\delta = 4.2$ ppm, quartet, 2H CH_3-CH_2-O $\delta = 2.9$ ppm, quartet, 1H $CO-CH-CH_3$ $\delta = 1.7$ ppm, doublet, 3H $CO-CH-CH_3$ $\delta = 1.3$ ppm, triplet, 3H CH_3-CH_2 IR spectrum - peak at 1750 cm^{-1} is $C=O$ - peak at 2280 cm^{-1} is $C \equiv N$

Mark Scheme

Question			Answer/Indicative content	Marks	Guidance
					ALLOW ranges from <i>Data Sheet</i> IGNORE references to C–O peaks <u>Examiner's Comments</u> Candidates achieving Level 2 had most of the key features, e.g. CN, C=O bond and a methyl group but did not consider the splitting patterns seen in the NMR. Most candidates could correctly work out the empirical and molecular formula but then did not use their analysis of the NMR and IR data to suggest a structure. This limited their response to Level 1. The IR spectrum had no O–H peak from an alcohol or carboxylic acid, but candidates often included these groups in their suggested structures.
			Total	6	