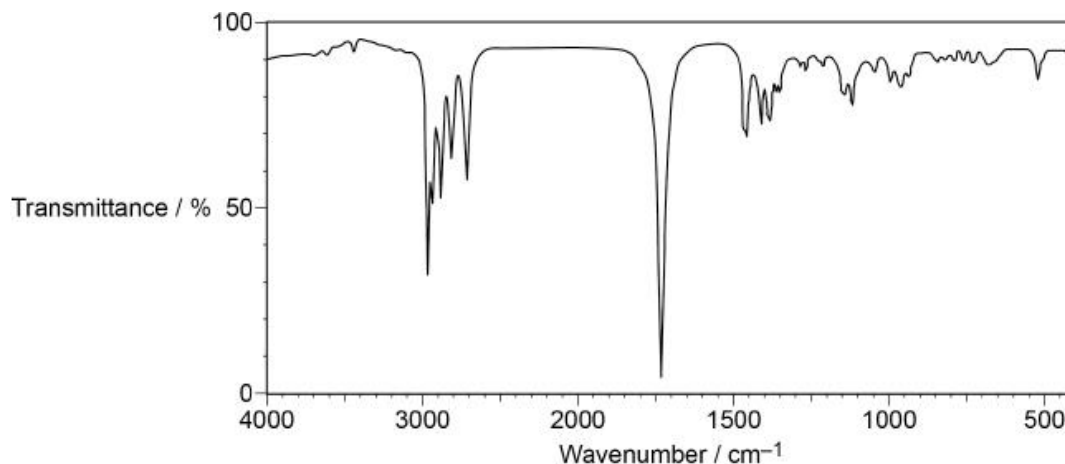


**Q18.**

Which compound gives this infrared spectrum?



- A 1-bromobutane
- B butan-1-ol
- C butanal
- D butanoic acid

(Total 1 mark)

Q19.

A student was given unlabelled samples of pentan-1-ol, pent-1-ene, pentanoic acid and pentanal.

- (a) Name the reagent(s) that the student could use to identify the sample that was pent-1-ene. Describe the observation(s) that the student would make to confirm this.

Reagent(s) _____

Observation(s) _____

(2)

- (b) Name the reagent(s) that the student could use to identify the sample that was pentanoic acid.

Describe the observation(s) that the student would make to confirm this.

Reagent(s) _____

Observation(s) _____

(2)



(c) Name the reagent(s) that the student could use to identify the sample that was pentanal.

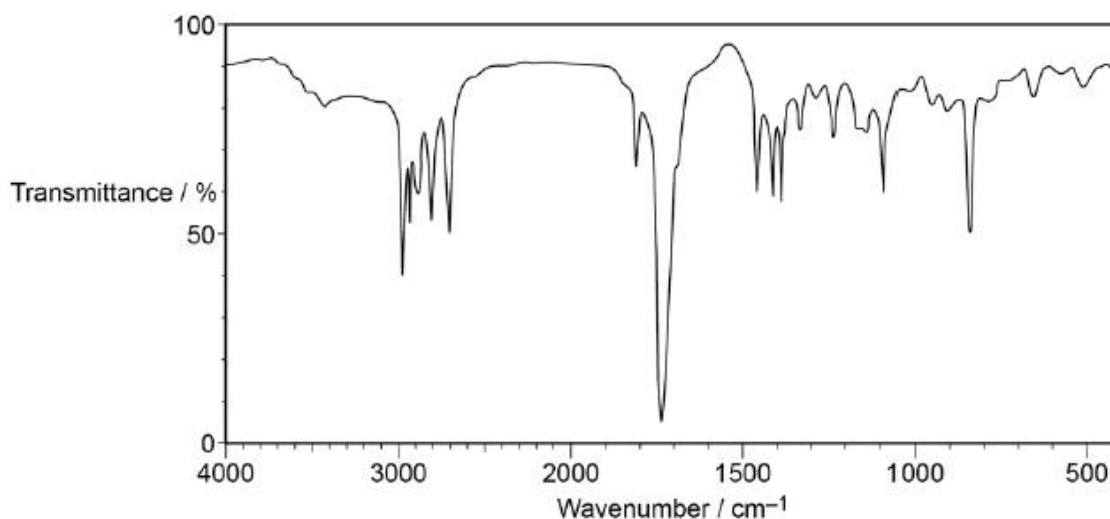
Describe the observation(s) that the student would make to confirm this.

Reagent(s) _____

Observation(s) _____

(2)

(d) The student deduced that the spectrum in the image below was that of pentanal.



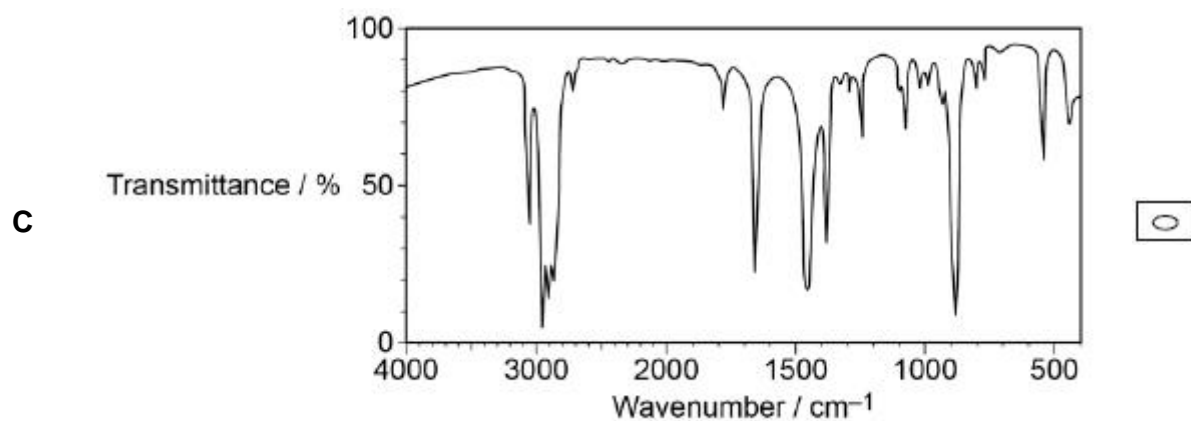
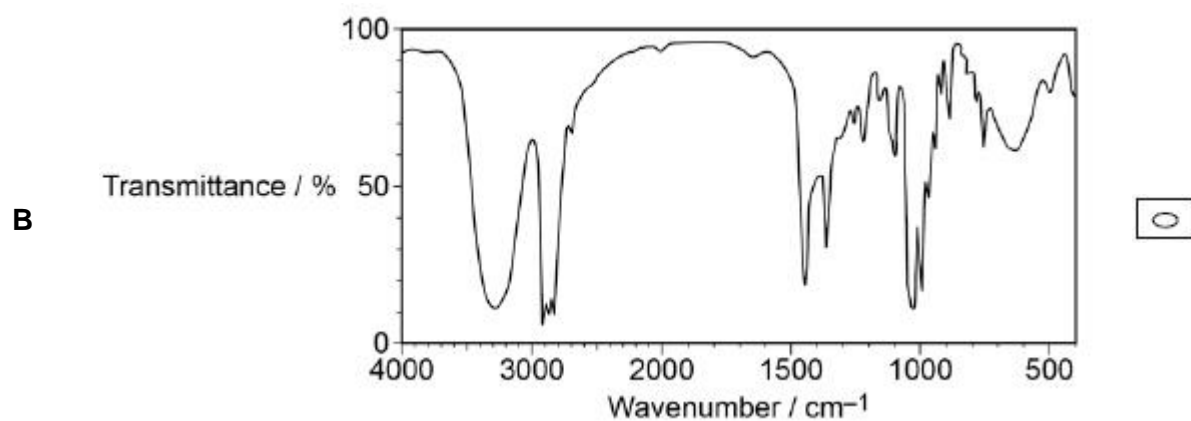
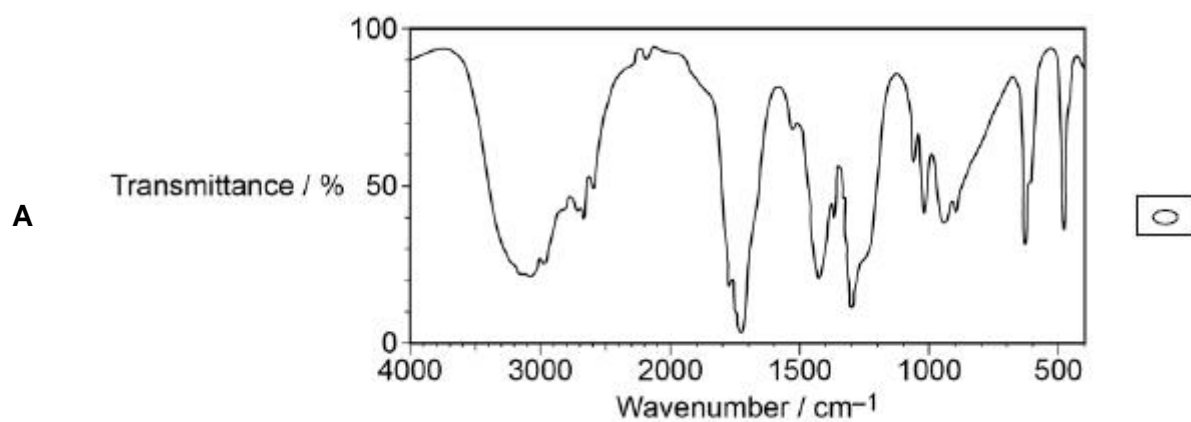
Justify this deduction and suggest why this spectrum **cannot** be that of pentan-1-ol, pentanoic acid or pent-1-ene.

(4)

(Total 10 marks)

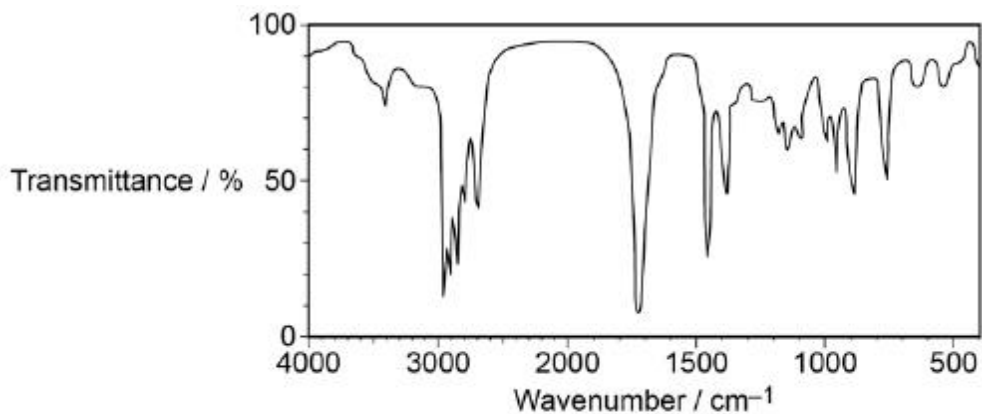
**Q20.**

Which of these infrared spectra could represent a carboxylic acid?





D



(Total 1 mark)

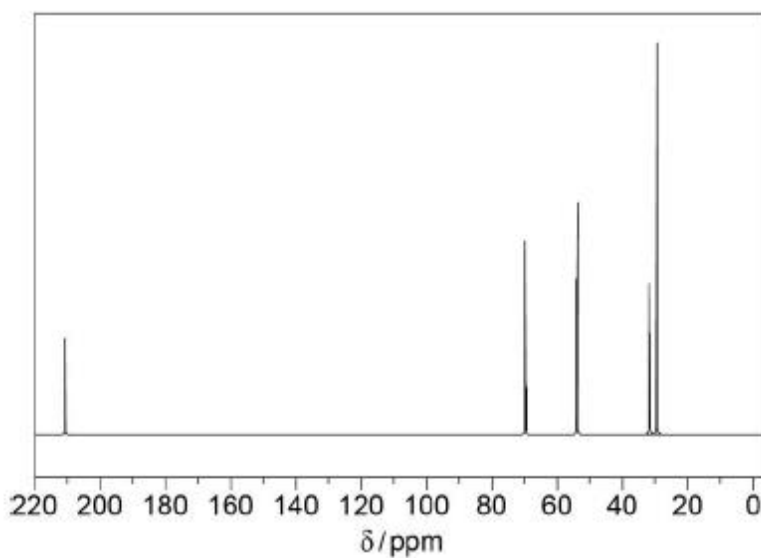
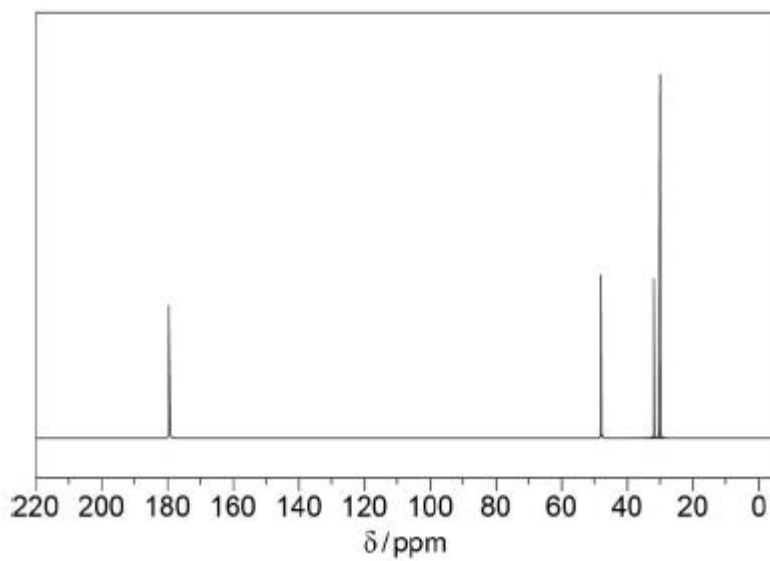
Q21.

^1H NMR, ^{13}C NMR and infrared spectroscopy are used in organic chemistry to distinguish between compounds and to identify them.

- (a) Give the skeletal formula of the compound that is used as the standard when recording a ^{13}C NMR spectrum.

(1)

- (b) Four isomers of $\text{C}_6\text{H}_{12}\text{O}_2$, **P**, **Q**, **R** and **S**, shown in **Figure 1**, were analysed by ^{13}C NMR spectrometry.

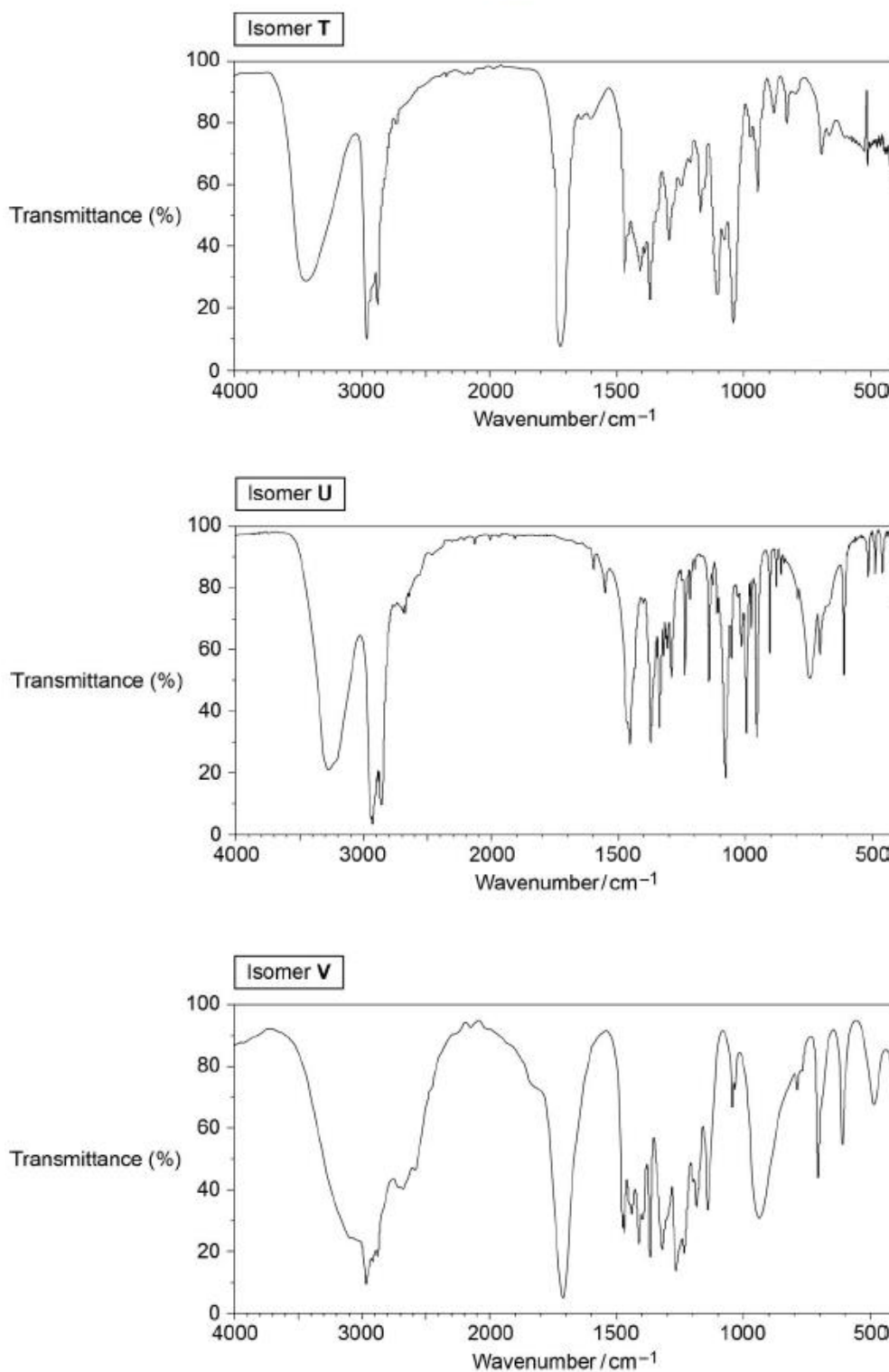


(3)



- (c) The infrared spectra shown in **Figure 3** are those of three different isomers of $C_6H_{12}O_2$, isomers **T**, **U** and **V**.

Figure 3



Identify the functional group(s) present in each isomer **T**, **U** and **V** of $C_6H_{12}O_2$ using **Table A** in the Data Booklet.

Explain your answer.



- (e) Use the data in the table above and **Table B** in the Data Booklet to help you answer this question.

Deduce the part of the structure of **X** that causes the signal at $\delta = 3.5$ and the part of the structure at **X** that causes the signal at $\delta = 2.2$.

Explain the splitting patterns of these peaks.

Signal at $\delta = 3.5$ _____

Signal at $\delta = 2.2$ _____

(4)

- (f) Deduce the structure of compound **X**, $C_6H_{12}O_2$

Use your answer from part (e) to help you.

You are **not** required to explain how you deduced the structure.

(2)

(Total 17 marks)

**Q22.**

Glucose can decompose in the presence of microorganisms to form a range of products. One of these is a carboxylic acid ($M_r = 88.0$) containing 40.9% carbon and 4.5% hydrogen by mass.

- (a) Deduce the empirical and molecular formulas of the carboxylic acid formed.

Empirical formula = _____ Molecular formula = _____

(4)

- (b) Ethanol is formed by the fermentation of glucose.
A student carried out this fermentation reaction in a beaker using an aqueous solution of glucose at a temperature of 25 °C in the presence of yeast.

Write an equation for the reaction occurring during fermentation.

(1)

- (c) In industry, this fermentation reaction is carried out at 35 °C rather than 25 °C.

Suggest **one** advantage and **one** disadvantage for industry of carrying out the fermentation at this higher temperature.

Advantage _____

Disadvantage _____

(2)

- (d) The method used by the student in part (b) would result in the ethanol being contaminated by ethanoic acid.

How does this contamination occur?

(1)



- (e) Give **two** differences between the infrared spectrum of a carboxylic acid and that of an alcohol other than in their fingerprint regions.
Use **Table A** on the Data Sheet.

Difference 1 _____

Difference 2 _____

(2)
(Total 10 marks)

Q23.

The infrared spectrum (**Figure 1**) and the ^1H NMR spectrum (**Figure 2**) of compound **R** with molecular formula $\text{C}_6\text{H}_{14}\text{O}$ are shown.

Figure 1

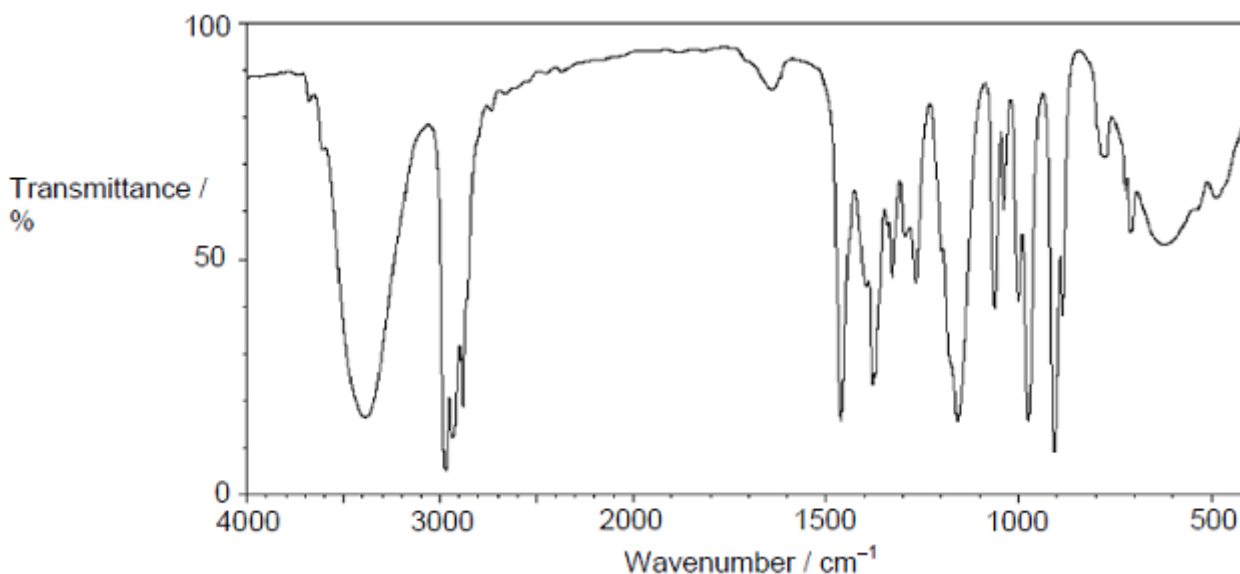


Figure 2



Q24.

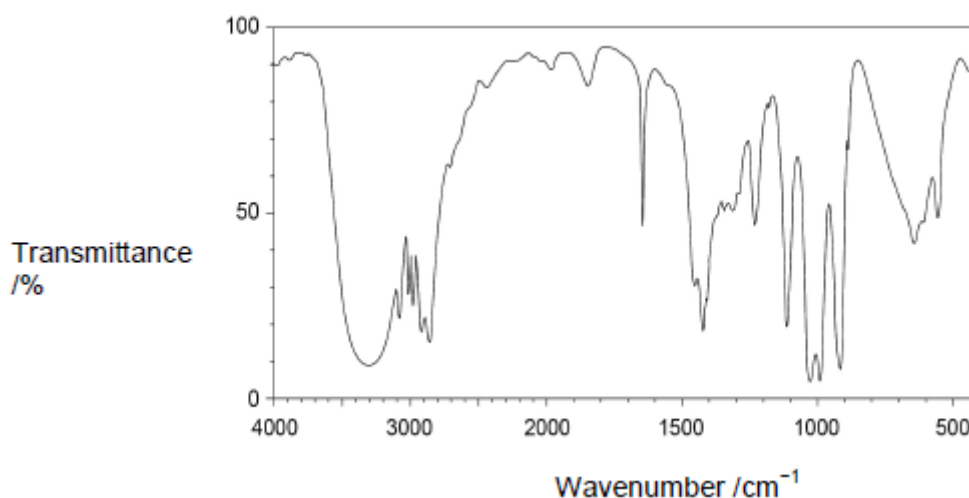
The compounds in the table all have a relative molecular mass of 58.0

Name	Propanal	Prop-2-en-1-ol	Butane
Structure	$ \begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array} $	$ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{C}=\text{C}-\text{C}-\text{O}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array} $	$ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array} $

- (a) Explain why determining the precise relative molecular mass of propanal and prop-2-en-1-ol by mass spectrometry could not be used to distinguish between samples of these two compounds.

(2)

- (b) The infrared spectrum of one of these three compounds is shown below.



Use the spectrum to identify the compound.
 State the bond that you used to identify the compound and give its wavenumber range.
 You should only consider absorptions with wavenumbers greater than 1500 cm⁻¹.

Compound _____

Bond used to identify compound _____

Wavenumber range of bond used to identify compound _____ cm⁻¹

(2)



- (c) Predict the relative boiling points of these three compounds from the highest to the lowest boiling points.

Justify this order in terms of intermolecular forces.

(6)

(Total 10 marks)

Q25.

Compounds **A**, **B**, **C** and **D** are isomers with the molecular formula $C_4H_{10}O$
They all have a broad absorption in their infrared spectra in the range $3230\text{--}3550\text{ cm}^{-1}$.

- (a) Use **Table A on the data sheet** to identify the bond and the functional group present responsible for this absorption.

(1)



- (b) Compounds **A** and **B** are both straight-chain compounds.
A can be oxidised to form **P**.
B can be oxidised to form **Q**.
P and **Q** are isomers with molecular formula C_4H_8O

Tollens' reagent and Fehling's solution can be used to distinguish between isomers **P** and **Q**. The results shown in the table are obtained.

Compound	Observation with Tollens' reagent	Observation with Fehling's solution
P	No visible change	No visible change
Q	Silver mirror formed	Brick-red precipitate formed

Use the information about compounds **P** and **Q** to identify compounds **A** and **B**.
Explain your answer with reference to the functional groups in **P** and **Q**.

Identity of **A** _____

Identity of **B** _____

Explanation _____

(3)

- (c) Isomer **C** is resistant to oxidation.
Isomer **C** reacts to form compound **R** that has an absorption in its infrared spectrum in the range $1620-1680\text{ cm}^{-1}$.

State the bond that causes the absorption in the range $1620-1680\text{ cm}^{-1}$.

Give the displayed formula of isomer **C**.

Identify the reagent and give **one** reaction condition needed to convert **C** into **R**.

Bond _____

Displayed formula of **C**

Reagent _____

Condition _____

(4)



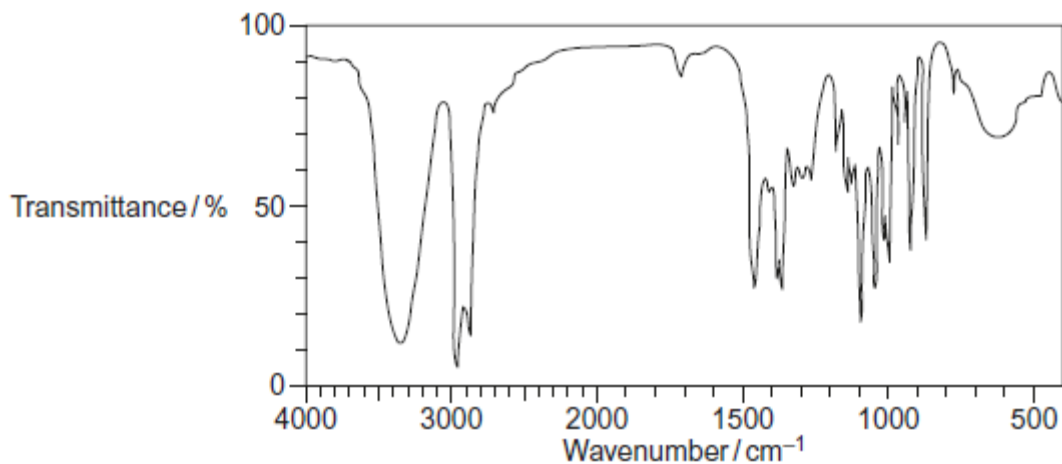
- (d) Compound **D** is a branched-chain isomer that can be oxidised to form compounds **S** and **T**.
- (i) Compound **S** is obtained by distilling it off as it forms during the oxidation. Compound **T** is formed when the oxidation takes place under reflux.

Identify the functional groups in **S** and **T**.

Explain, with reference to intermolecular forces, why it is possible to obtain compound **S** but not **T** from the reaction mixture by distilling off **S** as soon as it forms.

(3)

- (ii) A student claims to have oxidised compound **D**. The infrared spectrum of the product obtained by the student is shown.



Suggest two ways in which the spectrum shows that compound **D** has **not** been oxidised.

(2)

(Total 13 marks)

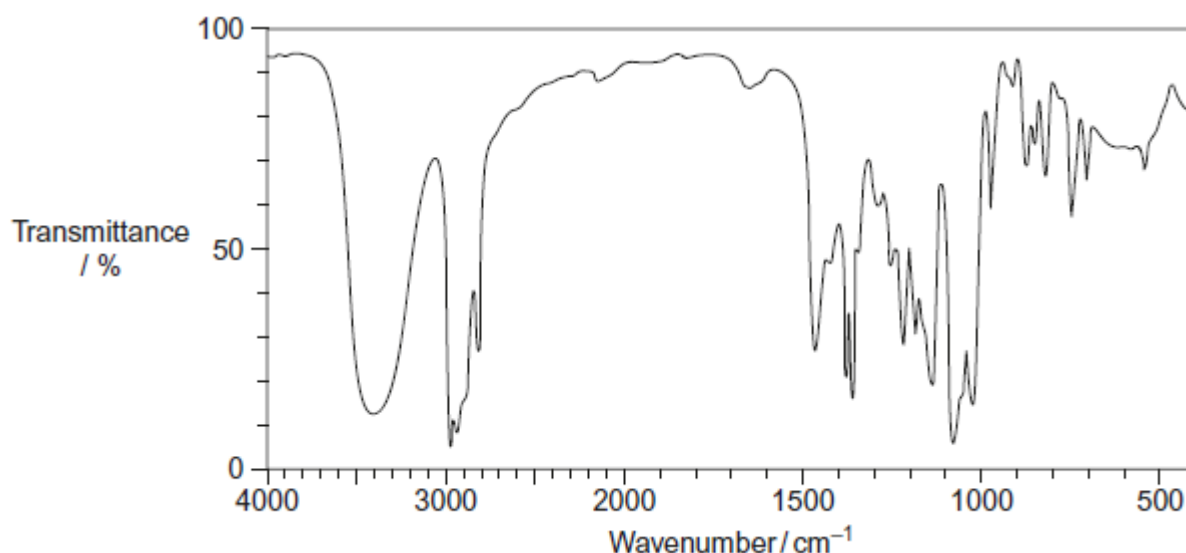
**Q26.**

Compound **R** contains 61.0% carbon and 11.9% hydrogen by mass. The remainder is oxygen. The mass spectrum of **R** contains a molecular ion peak at $m/z = 118$.

- (a) Use these data to show that the molecular formula of **R** is $C_6H_{14}O_2$.

(3)

- (b) The infrared spectrum of **R** ($C_6H_{14}O_2$) is shown below.



The proton n.m.r. spectrum of **R** contains five peaks. The chemical shift values, integration ratios and splitting patterns of these peaks are given in the table.

Chemical shift/ppm	3.8	3.2	3.1	1.4	1.1
Integration ratio	2	3	1	2	6
Splitting patterns	triplet	singlet	singlet	triplet	singlet

When **R** is warmed with acidified potassium dichromate(VI) a green solution is formed.

Use **Table A** and **Table B** on the data sheet and all of the data provided in the question to deduce the structure of **R**.

In your answer, explain how you have used the data provided in the question.



Mark Scheme

Q18.
C

[1]

Q19.

(a) Bromine (water)

1

Colour change from orange to colourless

1

(b) Add sodium hydrogencarbonate (or alternative named carbonate)

Allow suitable correct alternative test e.g.

Test the pH with named indicator (e.g. Universal Indicator)

1

Propanoic acid will produce effervescence / bubbles

Propanoic acid would turn Universal Indicator red

1

(c) Tollen's reagent

1

(Colourless solution to) silver mirror

1

OR

Fehling's solution

(Blue solution to) brick red precipitate

(d) Absorption at $1680\text{--}1750\text{ cm}^{-1}$ caused by C=O

1

No absorption at $1620\text{--}1680\text{ cm}^{-1}$ caused by C=C

1

No absorption at $3230\text{--}3550\text{ cm}^{-1}$ due to -OH (alcohol)

1

No absorption at $2500\text{--}3000\text{ cm}^{-1}$ due to -OH (acid)

1

[10]

Q20.
A

[1]

Q21.



(a)



1xAO1

1

(b) **S**

1

R

1

Q

1

(c) (Isomer T)

signals due to OH (alcohol) at 3230–3350 and C=O at 1680–1750

1

OH and C=O (functional groups) separated in molecule.

Allow not a carboxylic acid.

1

(Isomer U)

(only) signal for OH (alcohol) at 3230–3350

1

2 x OH groups present / diol / OH & cyclo(ether) structure.

Allow OH but not C=O.

1

(Isomer V)

signals due to OH (acid) at 2500–3000 (and C=O at 1680–1750)

carboxylic acid group / –COOH present.

1

1

(d) 2:2:2:3:3

Any order.

1

(e) (The quartet at $\delta=3.5$ is for a CH₂ group) next to –O–CH₂ **OR** shifted significantly downfield by electronegative O

1

(is a quartet) because of an adjacent CH₃ group / couple with 3 adjacent protons

1

(singlet at $\delta=2.2$ is for a CH₃ group) attached to $\begin{array}{c} \text{O} \\ || \\ \text{— C —} \end{array}$ CH₃ **OR** shifted downfield by



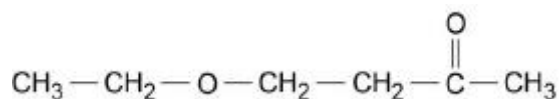
electronegative C=O

1

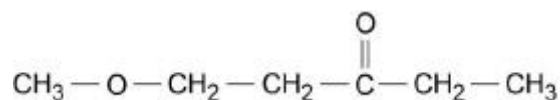
(is a singlet) because there are no adjacent protons / no coupling.

1

(f)



Allow 1 mark for:



2

[17]

Q22.

(a) Percentage of oxygen by mass = $100 - 40.9 - 4.5 = 54.6$

1

	C	H	O
%	<u>40.9</u>	<u>4.5</u>	<u>54.6</u>
Divide by A_r	<u>12</u>	<u>1</u>	<u>16</u>
	= 3.41	= 4.5	= 3.41

1

Divide by smallest = $\frac{3.41}{3.41} = 1$ $\frac{4.5}{3.41} = 1.32$ $\frac{3.41}{3.41} = 1$

Nearest whole number ratio = 1×3 1.32×3 1×3
 = 3 : 3.96 : 3

Nearest integer ratio = 3 : 4 : 3

1

Empirical formula $\text{C}_3\text{H}_4\text{O}_3$

Empirical formula mass = 88 = molecular formula mass

Therefore, molecular formula is same as the empirical formula - $\text{C}_3\text{H}_4\text{O}_3$

1

(b) $\text{C}_6\text{H}_{12}\text{O}_6 \longrightarrow 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2$

1

(c) Advantage – ethanol is produced at a faster rate

1

Disadvantage – more energy is used / required in the reaction

1

(d) Air gets in / oxidation occurs



- (e) Alcohol OH absorption in different place ($3230\text{--}3550\text{ cm}^{-1}$) from acid OH absorption ($2500\text{--}3000\text{ cm}^{-1}$)

1

1

The C=O in acids has an absorption at $1680\text{--}1750\text{ cm}^{-1}$

1

[10]**Q23.**

IR

Extended response

Absorption at 3360 cm^{-1} shows OH alcohol present

Deduction of correct structure without explanation scores maximum of 4 marks as this does not show a clear, coherent line of reasoning.

M1

1

NMR

There are 4 peaks which indicates 4 different environments of hydrogen

Maximum of 6 marks if no structure given OR if coherent logic not displayed in the explanations of how two of OH, CH₃ and CH₂CH₃ are identified.

M2

1

The integration ratio = $1.6 : 0.4 : 1.2 : 2.4$

The simplest whole number ratio is $4 : 1 : 3 : 6$

M3

1

The singlet (integ 1) must be caused by H in OH alcohol

M4

1

The singlet (integ 3) must be due to a CH₃ group with no adjacent H

M5

1

Quartet + triplet suggest CH₂CH₃ group

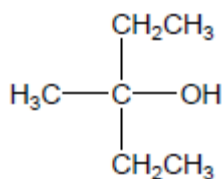
M6

1

Integration 4 and integration 6 indicates two equivalent CH₂CH₃ groups

M7

1



M8

1

[8]

Q24.

- (a) M1 have the same molecular formula
or are $\text{C}_3\text{H}_6\text{O}$
or both have the same number/amount of each type of atom or same amount of
each element
or are isomers
Not just the same atoms;
- 1
- M2 identical / exactly the same / same precise (relative) molecular
mass / formula mass / M_r
*Same (relative) molecular mass / formula mass / M_r is NOT
enough got score M2*
Allow same accurate (relative) molecular mass / formula mass / M_r
Ignore reference to number of decimal places
- 1
- (b) M1 prop-2-en-1-ol
*Must refer to this compound clearly by name or structure (not to
alcohol alone); ignore minor slips in name/structure*
- 1
- M2 O(-)H (alcohol) and 3230–3550 (cm^{-1}), or
C=C and 1620–1680 (cm^{-1})
Marked independently from M1
Could score from bond labelled on correct signal on spectrum
Allow any value within these ranges
If additional incorrect signals given penalise M2
Ignore signals below 1500 cm^{-1} and C-H signals
- 1
- (c) (i) Determine the level by looking at the chemical content. (**NB** - If there is clear
breakage of covalent bonds then max level 2 (max 3 marks).
- (ii) The mark within that level is then determined by looking at how coherent and
logical the answer is and by use of terminology; start at the higher mark and
penalise poor terminology/explanation; examples of terminology that would
reduce the mark to the lower one:
- reference to van der Waals 'bonds' or dipole-dipole 'bonds in relevant
compounds that are being credited
 - uncertainty about whether hydrogen bonds are the O-H bonds within or
are forces/bonds between molecules (if the alcohol is being credited)



- use of 'vdw' or 'dip-dip' unless these terms 'van der Waals' for 'dipole-dipole' have been used elsewhere in answer (note that IMF and H-bond would not be penalised)
- (iii) If the answer does not achieve level 1, then 1 mark maximum could be scored for any correct point from the list of indicative content

Level 3

- **Relative order** of boiling points of **all three** compounds
- Strongest intermolecular force of **all three** compounds identified
- Answer explains this coherently and logically and uses correct terminology for all **three** compounds

5-6 marks

Level 2

- **Relative** boiling points of **two** compounds correctly compared
- Strongest intermolecular force for these **two** compounds correctly identified
- Answer explains this coherently and logically and uses correct terminology for **these two** compounds

3-4 marks

Level 1

- **One** compound with the **highest** or **lowest** boiling point is correctly identified
- Strongest intermolecular force for that **one** compound identified
- Answer explains this coherently and logically and uses correct terminology for **this one** compound
- Allow 1 mark for individual correct point from indicative content on the right if no other mark scored

1-2 marks

Level 0

None of the indicative chemistry content given.

0 marks

Indicative chemistry content:

- *Correct order (highest to lowest) = prop-2-en-1-ol > propanal > butane*
 - *Prop-2-en-1-ol has hydrogen bonds*
 - *Propanal has (permanent) dipole-dipole forces*
 - *Butane has van der Waals' forces*
 - *Strength of intermolecular forces: hydrogen bonds > dipole-dipole > van der Waals*
- (Note - actual values for reference are prop-2-en-1-ol 97°C, propanal 46°C and butane -1°C)*

[10]

Q25.(a) OH AND alcohol**IGNORE** hydroxy(l)

1

(b) **A** = butan-2-ol / CH₃CH(OH)CH₂CH₃*If formulae given then must be unambiguous**If both formula and name given then formula must match name for*



mark to be awarded

- B** = butan-1-ol / $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ 1
- Product from **A / P** is a ketone 1
- AND**
- Product from **B / Q** is an aldehyde
- Penalise reference to incorrect class of alcohol* 1
- (c) Type of Bond: C=C 1
-
- Must show all bonds in Isomer C including O-H bond* 1
- Reagent: conc. H_2SO_4 / conc. H_3PO_4
- If incorrect attempt at correct reagent, mark on*
- Apply list principle for reagents and conditions marks*
- Conc required - may appear on conditions line*
- NOT (aq) For M3 even if seen on conditions line*
- ALLOW*
- Reagent = Al_2O_3*
- Condition = 'passing vapour over hot solid' owtte* 1
- Conditions: 180 °C / High temp / Hot / Reflux /
- ALLOW stated temp in range 100-300 °C/373-573 K*
- IGNORE 'heat'*
- M4 dependent on correct reagent in M3* 1
- (d) (i) **S** = aldehyde/CHO **AND** **T** = carboxylic/COOH/CO₂H 1
- T** forms hydrogen bonds 1
- (Which are) stronger than / need more energy to break than forces between molecules/IMFs in **S** ora (or reverse argument) 1
- If implication of breaking covalent bonds max M1 only* 1
- (ii) (No oxidation has occurred as..)
- (Still) contains peak at 3230–3550 cm^{-1} due to O–H/alcohol
- Does not contain peak at 2500–3000 cm^{-1} due to O–H/carboxylic acid
- Does not contain peak at 1680–1750 cm^{-1} due to C=O



Must have wavenumber range (or value within range) and bond or functional group to score each mark.

Any 2

[13]

Q26.

(a) Method 1

$$\text{M1 } \%O = 27.1$$

$$\begin{array}{ccc} \frac{61.0}{12.0} & \frac{11.9}{1.0} & \frac{27.1}{16.0} \\ = 5.08 & = 11.9 & = 1.69 \end{array}$$

$$\text{M2 } 3 \quad 7 \quad 1$$

$$\text{M3 } \text{C}_3\text{H}_7\text{O} = 59 \text{ which is half of } M_r \text{ so MF} = 2\text{EF}$$

OR

Method 2

$$\text{M1 } 61\% \text{ of } 118 = 72.0 \text{ and } 11.9\% \text{ of } 118 = 14.0$$

$$\text{M2 } 72 + 14 = 86 \text{ so oxygen} = 32 \text{ out of } 118$$

$$\text{OR } 27.1\% \text{ of } 118 = 32.0$$

$$\text{M3 } \begin{array}{ccc} \frac{72.0}{12.0} & \frac{14.0}{1.0} & \frac{32.0}{16.0} \\ = 6 & = 14 & = 2 \end{array}$$

Method 3

Alternative using given molecular formula

$$\text{M1 } \text{C} = \frac{12 \times 6}{118} \times 100 = 61.0\%$$

$$\text{M2 } \text{H} = \frac{14 \times 1}{118} \times 100 = 11.9\%$$

$$\text{M3 } \text{O} = \frac{16 \times 2}{118} \times 100 = 27.1\%$$

3

- (b) For this question, marks can be awarded either for a description of how the structure is derived or from the given structure itself. The maximum mark to be awarded is nine from the ten marks listed.

Marks fall into three sections:

- Infrared evidence : two marks are available for use of the infrared evidence, (M1 and M10)



- Chemical evidence: one mark is available for use of the chemical evidence (M2)
- N.m.r. evidence: six marks are available for use of the n.m.r. evidence (M3 – M8 inclusive)

plus one mark (M9) for a completely correct structure.

Suggested procedure for marking

First look at the infrared spectrum: marks M1 and M10 may be scored there or in the written answer.

Then look for use of the acidified potassium dichromate(VI) evidence, (M2).

Then look at the final structure: this may lead to the award of marks M3 to M9 as shown on the structures below.

Beware contradictions, e.g. using the chemical evidence they may state that **R** is a primary or secondary alcohol but then draw a tertiary alcohol. This will lose M2 but may score M3.

The written 'evidence' frequently simply contains extracts from the Table **B** on the Data Sheet and, if only this is given, is unlikely to score many marks.

Described

Or drawn

- M1 Infrared peak/absorbance at 3400 (cm⁻¹) = O-H alcohol
(reference to ir spectrum needed)
Note: please check the spectrum
If peak at 3000 (cm⁻¹) is identified as acid then cannot score M1 (contradiction)
- M10 **Either** no peak between 1680-1750 (cm⁻¹) so no C=O or not aldehyde/acid
OR peak at 1000-1300 (cm⁻¹) so C–O present
Apply list principle to IR analysis for M10
- M2 (Acidified potassium dichromate(VI) turns green) so primary alcohol or secondary alcohol or not tertiary alcohol
Ignore aldehyde here
Lose M2 if just tertiary alcohol in structure
- M3 $\delta = 3.1$ singlet or integration = 1 is O-H
Award M3 if structure has 1 O-H group only (can be primary, secondary or tertiary)
Lose M3 if more than one OH group shown
- M4 two triplets at 1.4 & 3.8 = –CH₂–CH₂–
Allow –CH₂–CH₂–CH₂–
- M5 $\delta = 3.8$ means CH₂ attached to O (in ether NOT ester)
Allow O–CH₂–CH₂–CH₂–C
- $\delta = 1.4$ means CH₂ attached to C (but not to C=O)



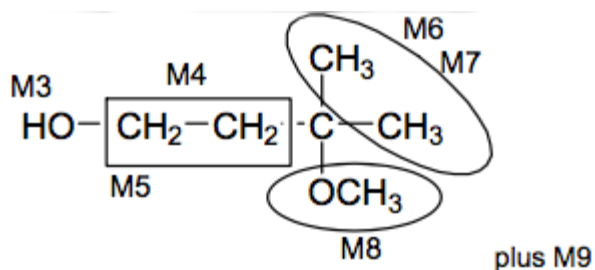
M6 $\delta = 1.1$ (singlet) integration 6 = 2 \times equivalent CH_3 on same C
 $-\text{C}(\text{CH}_3)_2-$

M7 $\delta = 1.1$ singlet so no H attached to $-\text{C}(\text{CH}_3)_2-$
 $\text{R}-\text{C}(\text{CH}_3)_2-\text{R}$

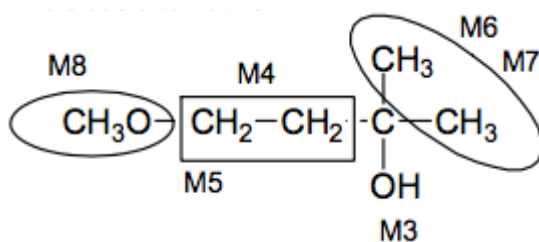
M8 $\delta = 3.2$ singlet integration 3 = $-\text{OCH}_3$
 $-\text{OCH}_3$

M9 For completely correct
If no structure given then Max 8

R is



This close alternative



would not score M9, but could score up to 8 marks

[12]