1. (a) **infrared – 1 mark only**
   shows (very broad) peak between 2500–3300 (cm\(^{-1}\))
   (due to O–H bond)
   ✓
   
   *ALLOW* (very broad) peak around 3000 (cm\(^{-1}\)) *OR* any stated
   value between 2500 and 3300 (cm\(^{-1}\)) for O–H
   *DO NOT ALLOW* peak in range 3200–3550 (cm\(^{-1}\))
   *IGNORE* any reference to C=O or C–O as both are also
   present in an ester *OR* to fingerprint region

**13C NMR – 2 marks**

(CH\(_3\))\(_2\)CHCH2COOH has 4 peaks (due to 4 different C environments) ✓
(CH\(_3\))\(_3\)CCOOH has 3 peaks (due to 3 different C environments) ✓

*ALLOW* \(^{13}\)C NMR detects the number of/different C
   environments *for 1 ✓*, suitable example for the 2nd mark 3

(b) **splitting pattern**

explains any two in terms of ‘\(n + 1\) rule’ for two marks ✓ ✓
Explain any one peak for 1 mark ✓

1 mark for correct ester

if two splitting patterns are correctly analysed *ignore* the third

- **singlet** therefore adjacent C (if any) has no Hs
  *ALLOW* singlet because next or bonded to an O

- **multiplet OR split into 7** therefore adjacent Cs have lots of/6 Hs
  *ALLOW* multiplet/heptet because next to 2 CH\(_3\)s

- **doublet** therefore adjacent C is bonded to 1H
  *ALLOW* doublet because next to a CH

must spell one of multiplet / heptet, singlet, doublet correctly

max = 2 marks
**chemical shifts**

two marks if any two absorptions are identified correctly ✓ ✓

one mark if any one absorption is identified correctly ✓

ALLOW tolerance on δ values; 3.6–3.8, 2.6–2.8 and 1.1–1.3 (ppm)

• peak ~3.7 (ppm) – bonded to an O

• peak ~2.7 (ppm) – indicates it is next to a C=O

• peak ~1.2 (ppm) – bonded to other Cs OR part of a chain

max = 2 marks

ALLOW any two gets 2 marks, any one scores 1 mark

\[\text{HC} - \text{O} \quad \text{HC} - \text{C} \quad R - \text{CH}\]

3.7 (ppm) 2.7 (ppm) 1.2 (ppm)

ALLOW peaks labelled on the spectrum

ALLOW singlet must be bonded to O, multiplet to C=O and doublet to CH or R for both chemical shift marks

if two chemical shifts are correctly identified IGNORE the third

compound identified as \( (\text{CH}_3)_2\text{CHCOOCH}_3 \) ✓ ✓

compound identified as \( \text{CH}_3\text{COOCH(CH}_3)_2 \) ✓

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2. (i) the peak is due to the \( \text{CH}_3\text{CO}^- \) group

not split, so next to a C with no protons / has no neighbouring proton / δ value is in the range 2.0 – 2.9 (1)

2

(ii) adjacent to a C with three protons / to a \( \text{CH}_3 \) (1)

1
3. IR

**Similarities**
Any 2 of the following three peaks (must give the quoted range)
- peak corresponding to OH in all three (3230 – 3550 cm⁻¹) (I)
- peak corresponding to NH in all three (3100 – 3500 cm⁻¹) (I)
- peak corresponding to CO in all three (1000 – 1300 cm⁻¹) (I) 2 max

**Differences**
only shown in the fingerprint region (I)

**Mass Spec**

**similarities**
- Mr (75)/ base peak will be the same (I)
- M + 1 peak same (I) 1

**Differences**
Fragmentation pattern may show differences between isomers
/ specific example, eg CH₃⁺ at m/e 15 (I) 1

(MAX 5)

**QWC**
Use of any two terms from: functional group / amino group /
hydroxy group / fingerprint / fragmentation / fragment ion(s) /
base peak or molecular ion / M + 1 peak / m/e 1

[6]
4. (a) propanoate and ester group (I) 2-methyl propyl (I) 2

(b) propanoic acid (I) (2-)methylpropan-1-ol (I)
heat (I) conc. H₂SO₄ (I) (allow ecf from part (a) for the equation)
CH₃CH₂COOH + CH₃)₂CHCH₂OH → CH₃CH₂COOCH₂CH(CH₃)₂ + H₂O reactants (I) products (I) 6

(c) mass spectrum / spectrometry (I)
molecular ion peak / m/e or mass of the peak furthest right (I) AW 2

5. δ value / chemical shift gives the ‘type’ of proton / chemical environment (I) AW
example quoted from data sheet (I)

number of peaks gives the number of different types of proton / chemical environments (I)
relative / ratio of (I)
peak areas gives the number of protons (of each type) (I)
splitting gives number of neighbouring / adjacent protons (I)
description of n + 1 rule / example of doublet, triplet or quadruplet showing 1, 2 and 3 protons neighbouring (carbon) atom (I) AW
D₂O can be used to identify OH groups (I)

ANY 7 marks out of 8 7

Quality of written communication mark for correct use and organisation of at least two of the following technical terms: proton, environment, singlet (doublet etc.), ppm, equivalent, chemical shift, splitting, labile, integration 1
6. (a) (i) alkene (I) 
ester (I)  
allow “C=C double bond”
i.  
\[ \text{O} \]  
\[ \text{O} \]  
\[ \text{1} \]  
(ii) C_{12}H_{14}O_{2} (I)  
(b) same structural formula/order of bonds, 
different spacial arrangement AW (I)  
description or diagram showing B and how it is different from A (I)  
(c)  
\[ \text{H} \text{C} \text{==C} \text{O} \text{-OH} \]  
\[ \text{H} \text{H} \text{C} \text{-OH} \]  
\[ \text{1} \]  
(d) (i) peak at 1680-1750 (cm\(^{-1}\)) due to C=O (I)  
peak at 1000-1300 (cm\(^{-1}\)) due to C-O / (I)  
(ii) 2500-3300 / 3230-3550 (cm\(^{-1}\))  
O-H/carboxylic acid/alcohol is not present in A (I)  
allow 1 mark for ~500-1500 (cm\(^{-1}\)) which is a unique 
fingerprint region etc  
7. (a) low boiling point / easily turns to a gas AW (I)  
(b) 2,4-dinitrophenylhydrozine / 2,4-DNP(H) / Brady’s reagent (I)  
purify/recrystrallise the product/solid (derivative) (I)  
measure the melting point /mp (I)  
compare the result with data book/known values (I)
8. (a) (i) Molecular ion peak: the peak caused by the unfragmented molecule / the peak with the highest m/e value / the peak that tells you the Mr.  
Base peak: peak with the greatest (relative) intensity / peak representing most stable/abundant fragment  
NOT the tallest / biggest / most common peak

(ii) The molecular ion is too unstable / will have been completely fragmented / may not carry a positive charge  
NOT peak too small to be seen / too little ion present

(b) IR spectrum:  
C=O peak at approx 1650 cm⁻¹ (1680-1750 cm⁻¹)  
broad O-H peak at value(s) between 2500-3300 cm⁻¹  
ignore any references to C-O peak at 1000 – 1300 cm⁻¹  
mass spectrum:  
Fragment with m/e = 31 is CH₂OH⁺  
Fragment at m/e = 45 is COOH⁺  
penalise missing + sign once only

(c)  
2 proton peak at δ = 3.3-4.3 – singlet (-CH₂-)  
1 proton peak at δ = 3.5-5.5 – singlet (-OH)  
1 proton peak at δ = 11.0-11.7 – singlet (-COOH)  
(ranges of chemical shift (δ) values taken from data sheet)  
• penalise each error once only  
• ignore peak areas/heights unless incorrectly labelled

Labelled diagram of the structure of G proposed by the student may be used to provide evidence for the positioning of peaks on the sketched spectrum.  
Both OH and COOH protons disappear on shaking with D₂O
9. (i) 

**splitting:**
doublet (1)
quartet (1)

*ignore any other peaks*

**position:**
doublet peak is at ~1.4 and
quartet peak is at ~4.3 (1)

*allow ecf from one incorrect splitting pattern*

**areas:**
1 and 3 on the correct peaks
(or either way round as ecf if any errors above) (1)  

(ii) 4 (1)
OH/labile protons now visible AW (1)  

10. (a) (i) Find the m/e of … (1)
... the peak furthest to the right / with highest m/e or mass (1)  

*allow attempts to cater for the $^{13}$C peak*

C$_2$H$_3$O$_2$ /empirical formula has M$_r$ = 59 (1)
so M$_r$ of molecular formula is $^{118}$/59 = 2 /twice the empirical formula (1)  

(b) (i) OH peak disappears (with D$_2$O / on the second spectrum)  

[6]
(ii) no of peaks: one (1)
   splitting: none (1)
   all four protons equivalent / in the same environment (1) 3
   
   If the wrong structure is chosen allow ecf for:
   two peaks (1),
   splitting (1)(1) (as last 2 marks for part (ii))

11. (i) A \( \text{C}_3\text{H}_6 \) (1)  B \( \text{C}_4\text{H}_8 \) (1) 2
   (ii) A \( \text{CH}_3\text{CH}=\text{CH}_2 \) (or displayed) (‘sticks’ penalised once) 1
   (iii) \( \text{C}_3\text{H}_5^+ \) (1) for formula and (1) for charge 2 [5]