ANALYTICAL TECHNIQUES

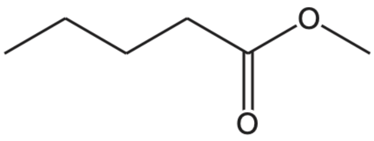
NOTE:

- TLC
    - Stationary phase: alumina/silica
    - Mobile phase: polar solvent (water/ethanol) OR non-polar (alkane)
- GLC
    - Stationary phase: High boiling point, non-polar, liquid
    - Mobile phase: helium/ nitrogen
- In NMR, to dissolve the sample: use CDCl3 (peak at 80ppm - ignore)
- In H NMR, reference point at 0ppm = TMS/ tetramethylsilane Si(CH3)4
- In H NMR D2O is used to remove OH and NH peaks.

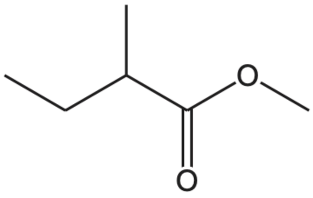
State what is meant by retention time

- Time between injection and detection.

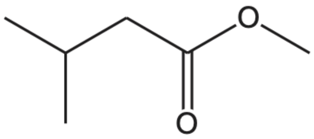
A



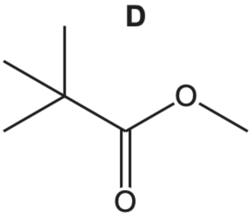
B



C



D



Separate samples of the esters, A, B, C and D, are analysed using proton (1H) NMR and carbon-13 NMR spectroscopy. State the number of peaks in each NMR spectrum for esters B and C.

Ester	**^{1}H NMR peaks**	**^{13}C NMR peaks**
B	5	6
C	4	5

Identify all of the esters from A, B, C and D that have at least one triplet peak in their proton (1H) NMR spectrum.

- A and B

NOTE: C doesn't have a triplet. You might thing the CH group adjacent to the CH_2 group shows a triplet peak. But this CH group is also adjacent to 2CH_3 groups. So the peak will not be a triplet, but more, because there are actually 8H atoms bonded to the adjacent carbons.

State the stationary phase used in TLC

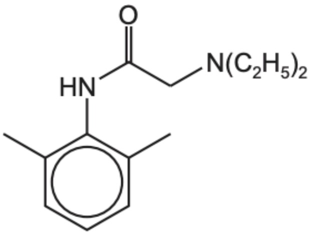
- Alumina (Al_2O_3) or silia (SiO_2)

Suggest why the Rf value for substance X is less than that of substance Y

- is more attracted / more affinity / adsorbed more to the stationary phase OR Y dissolves better in the solvent.

(f) The proton (^1H) NMR spectrum of lidocaine is shown in Fig. 6.2.

lidocaine



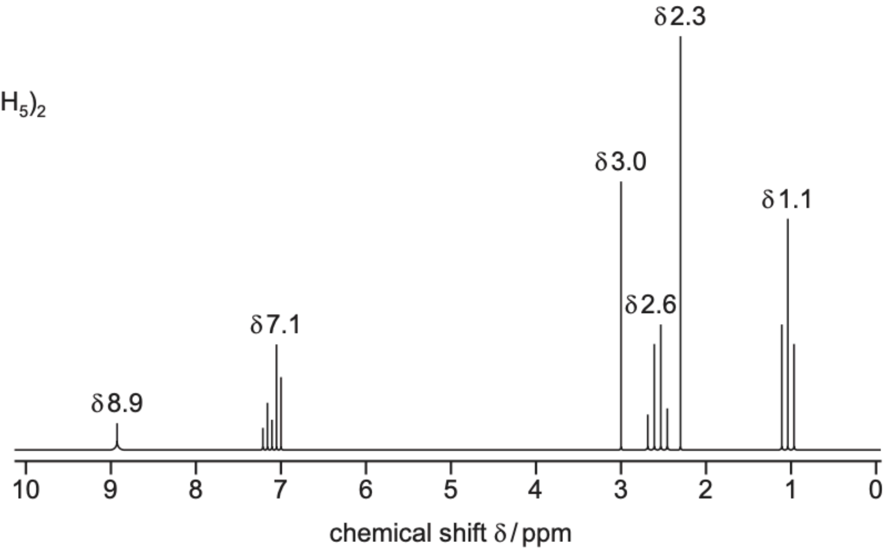
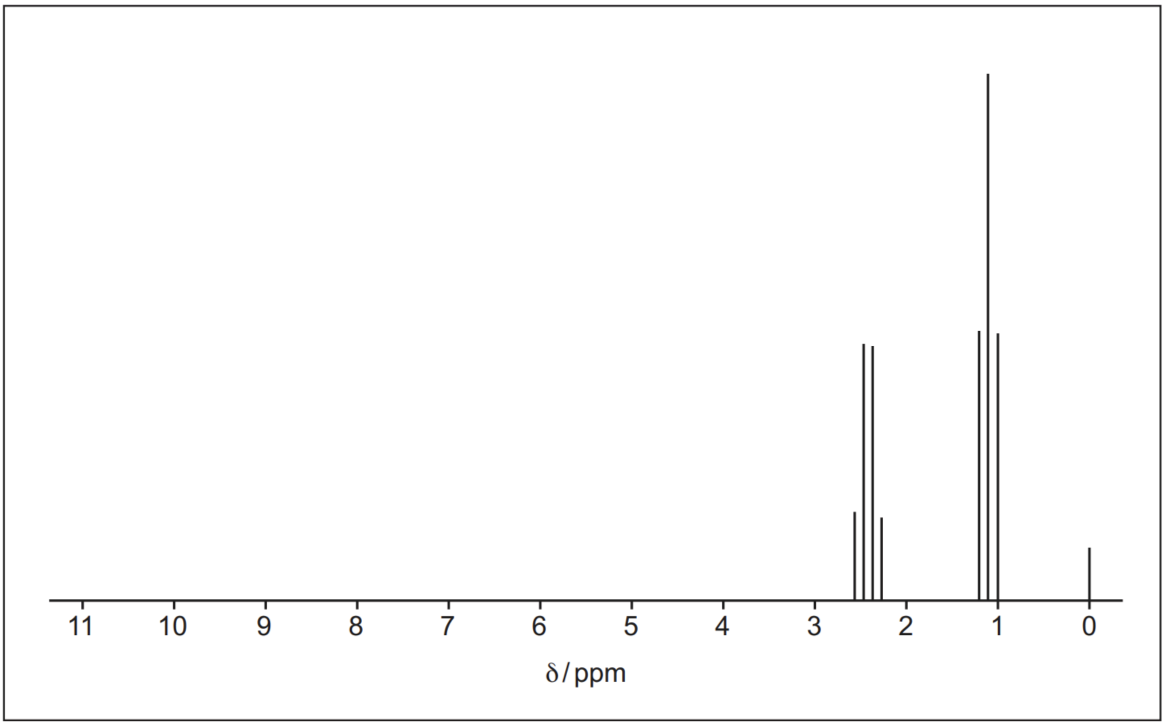


Fig. 6.2

Table 6.2

environment of proton	example	chemical shift range δ / ppm
alkane	$-\mathbf{CH_3}$, $-\mathbf{CH_2}-$, $>\mathbf{CH}-$	0.9–1.7
alkyl next to C=O	$\mathbf{CH_3}$–C=O, –$\mathbf{CH_2}$–C=O, >**CH**–C=O	2.2–3.0
alkyl next to aromatic ring	$\mathbf{CH_3}$–Ar, –$\mathbf{CH_2}$–Ar, >**CH**–Ar	2.3–3.0
alkyl next to electronegative atom	$\mathbf{CH_3}$–O, –$\mathbf{CH_2}$–O, –$\mathbf{CH_2}$–C*l*	3.2–4.0
attached to alkene	=C**H**R	4.5–6.0
attached to aromatic ring	**H**–Ar	6.0–9.0
aldehyde	**H**COR	9.3–10.5
alcohol	RO**H**	0.5–6.0
phenol	Ar–O**H**	4.5–7.0
carboxylic acid	RCOO**H**	9.0–13.0
alkyl amine	R–N**H**–	1.0–5.0
aryl amine	Ar–N$\mathbf{H_2}$	3.0–6.0
amide	RCON**H**R	5.0–12.0



In a ^1H NMR spectrum, identify the substance that gives the small peak at δ = 0.

- TMS / tetramethylsilane / Si(CH3)4

(ii) The proton (^1H) NMR spectrum of **Z** in D_2O gives three peaks for the proton environments, labelled **a**, **b** and **c**, as shown on Fig. 6.2.

Z

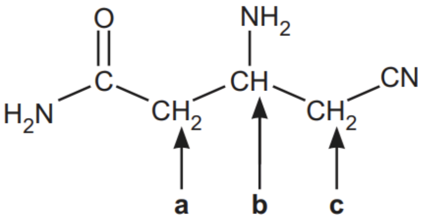
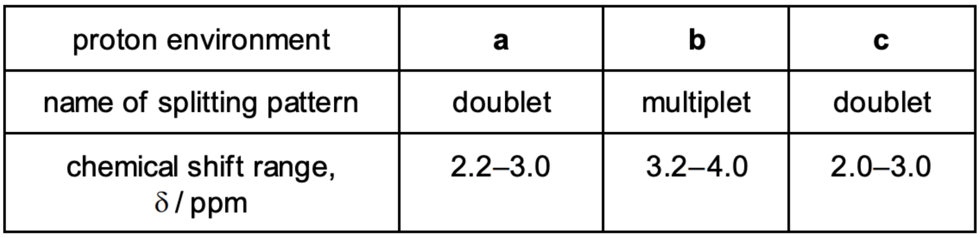


Fig. 6.2

Complete Table 6.2 for the proton (^1H) NMR spectrum of **Z** in D_2O.

Table 6.2

proton environment	**a**	**b**	**c**
name of splitting pattern			
chemical shift range, δ / ppm			



proton environment	**a**	**b**	**c**
name of splitting pattern	doublet	multiplet	doublet
chemical shift range, δ / ppm	2.2–3.0	3.2–4.0	2.0–3.0

Explain why the retention time of a particular amino acid is the longest.

- It is attracted more strongly to the stationary phase / forms stronger intermolecular forces with the stationary phase