Name	Student Code

32nd IChO • Problem 4 — 10 points

A naturally occurring compound

A naturally occurring compound **A** containing only C, H and O has the following elemental composition, percentage mass,

C: 63.2 %, H: 5.3%, O: 31.5%.

4-1 Derive the empirical formula of compound **A**.

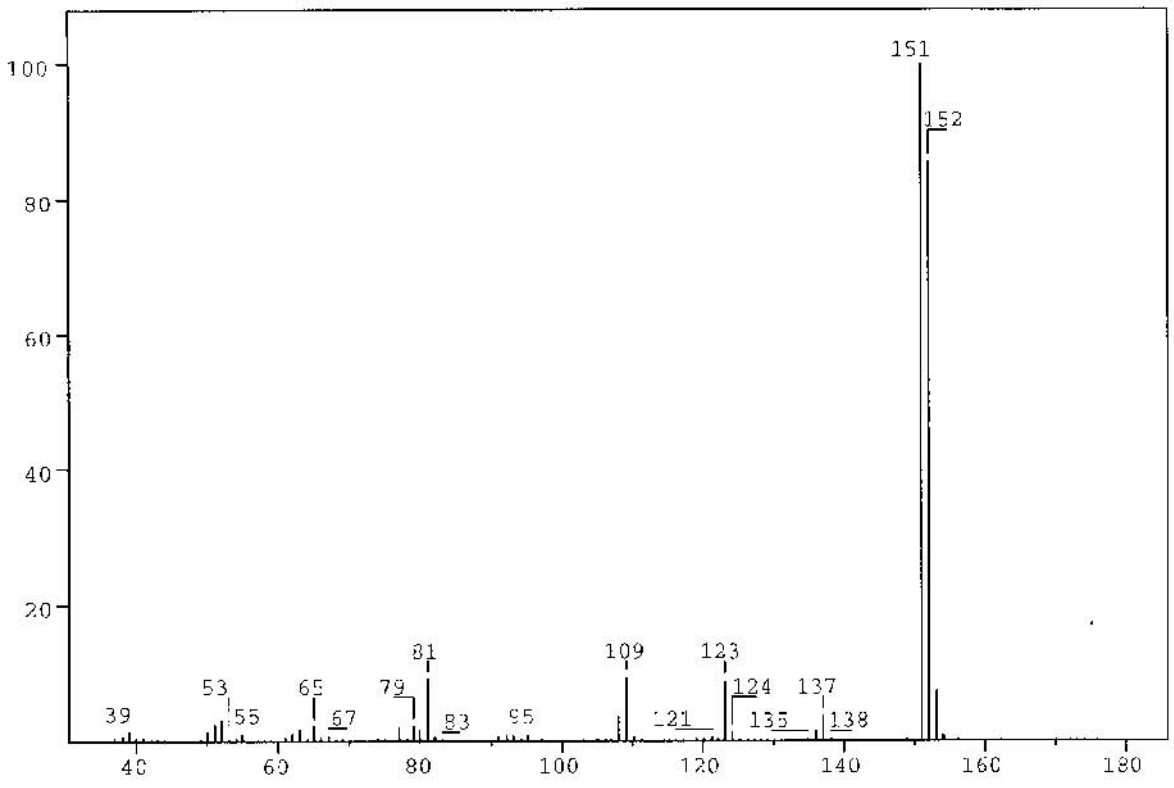


Figure 1

The mass spectrum of compound **A** is shown in Figure 1.

4-2 What is the molecular formula for compound **A**?

A solution of **A** in ether is shaken with an aqueous solution of NaOH. After this, no **A** remains in the ether phase.

Another solution of **A** in ether is shaken with an aqueous solution of $NaHCO_3$. **A** remains in the ether phase.

4-3 Which of the following classes of compounds does **A** belong to according to these experiments? Mark with an X.

alcohol ☐ phenol ☐ aldehyde ☐ ketone ☐

acid ☐ ester ☐ ether ☐

Compound **A** gave rise to formation of a silver mirror with Tollens' reagent ($Ag(NH_3)_2^+$).

4-4 Which of the following functional groups does this indicate the presence of in **A**? Mark with an X.

hydroxy group of an alcohol ☐ hydroxy group of a phenol ☐

carbonyl group of an aldehyde ☐ carbonyl group of a ketone ☐

carboxylic group ☐ ester group ☐

alkoxy group of an ether ☐

Table of Integrals

FROM	TO	VALUE
10.00 PPM	9.69 PPM	0.94
7.56 PPM	7.32 PPM	1.91
7.15 PPM	6.92 PPM	0.93
6.41 PPM	6.20 PPM	0.94
4.02 PPM	3.89 PPM	3.10

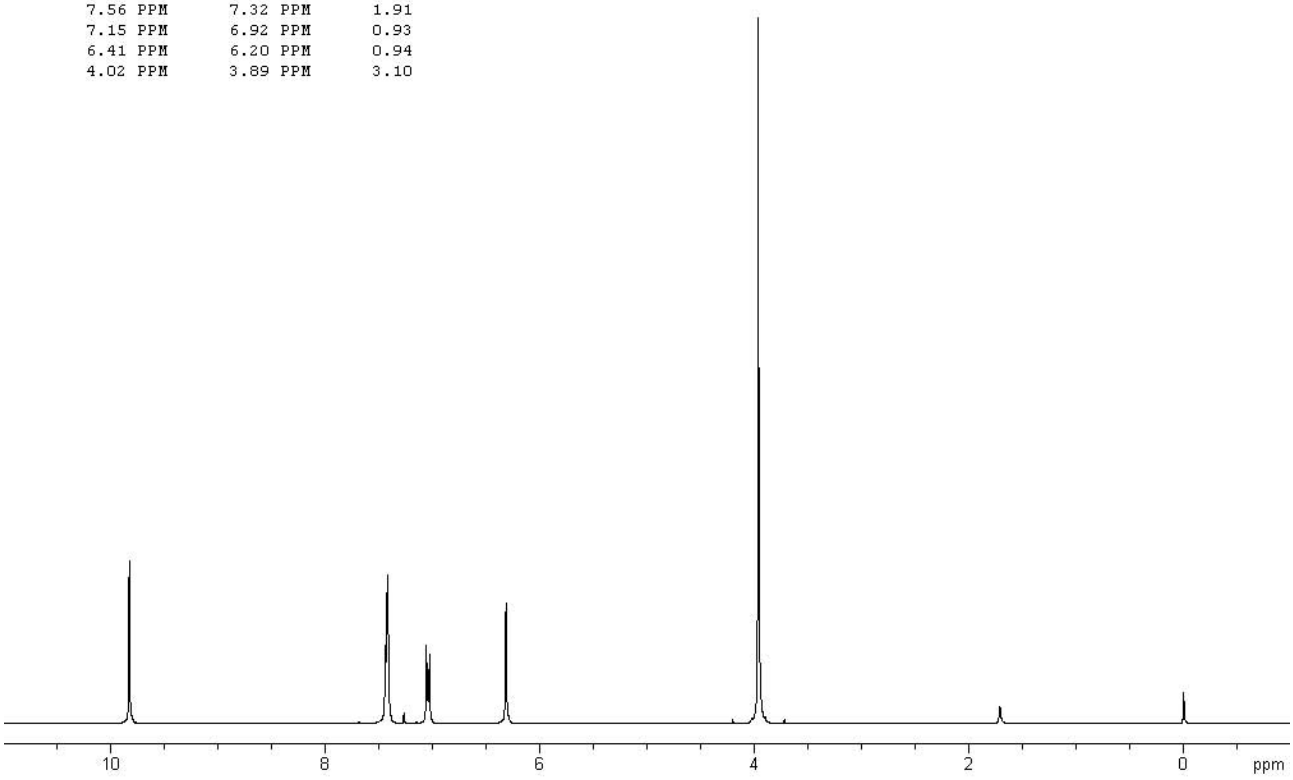


Figure 2a

The ^{1}H NMR spectrum of compound **A** recorded at 300 MHz is shown in Figure 2a (solvent $CDCl_3$ (7.27 ppm), reference tetramethylsilane). The signals at 3.9, 6.3 and 9.8 ppm are singlets. Figure 2b is an expansion of the region 6.9 –7.6 ppm.

Selected chemical shift and coupling constant values are given in Table 1.

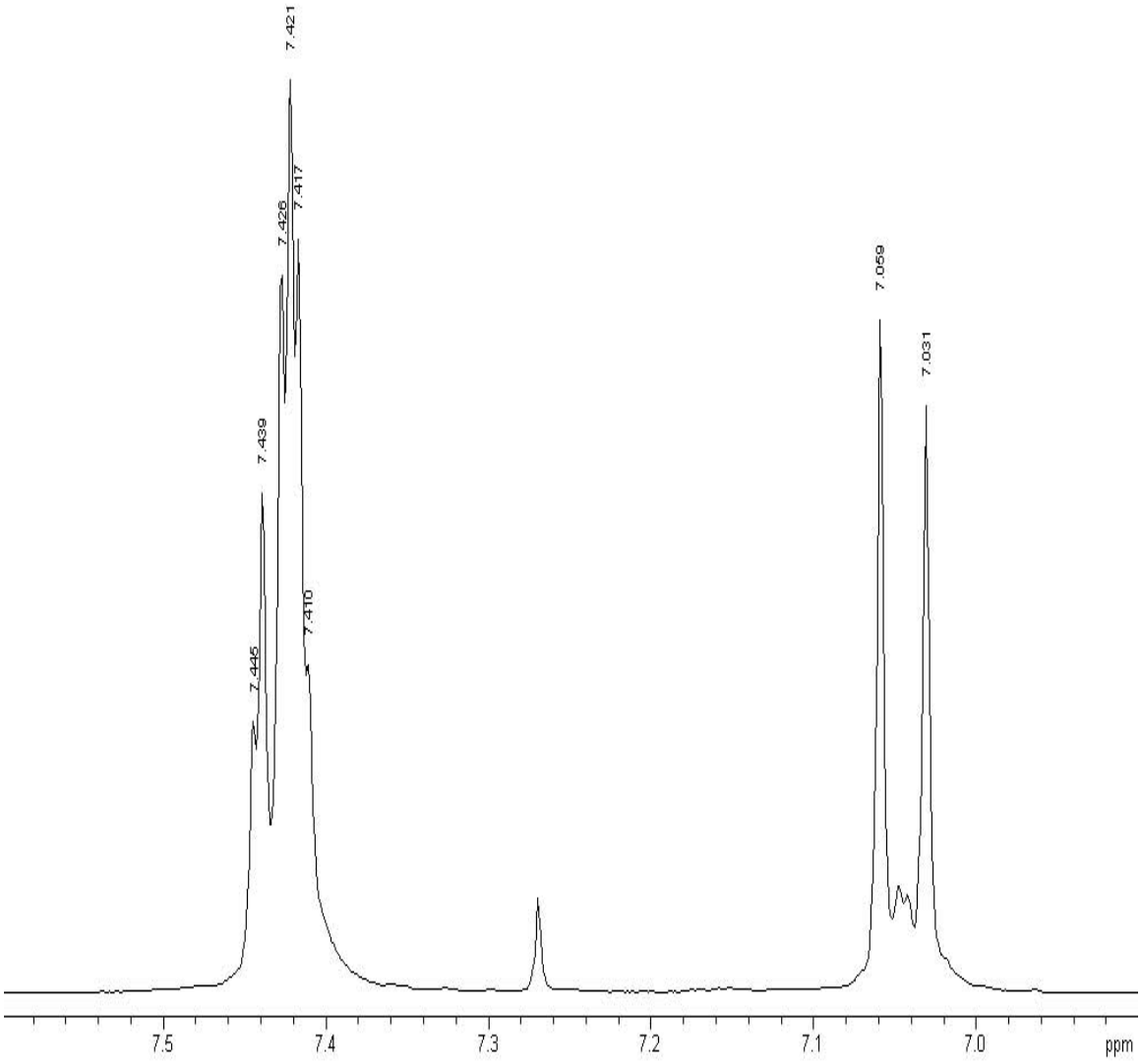


Figure 2b

The signal at 6.3 ppm disappears when a drop of D_2O is added.

4-5 Which of the following does this indicate? Mark with an X.

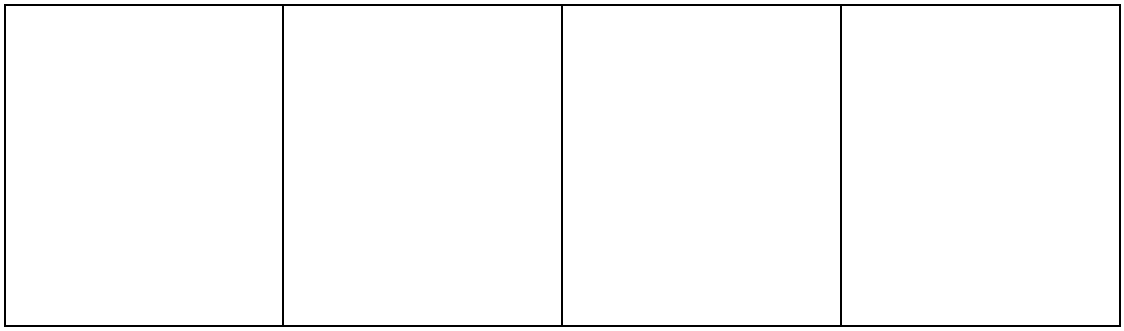
Exchange of carbon-bonded hydrogen	☐
Exchange of oxygen-bonded hydrogen	☐
Dilution effect	☐
Hydrolysis	☐

The same signal moves to a lower ppm value upon dilution with $CDCl_3$.

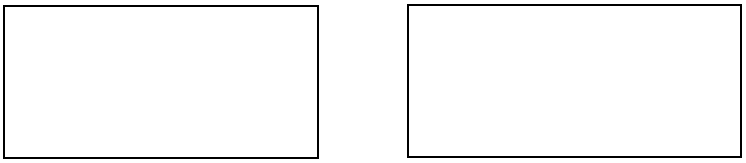
4-6 Which of the following does this indicate?
Indicate the true statements (more than one).

Increased hydrogen bonding	☐
Decrease in hydrogen bonding	☐
Intermolecular hydrogen bonding	☐
Intramolecular hydrogen bonding	☐
No hydrogen bonding	☐

4-7 Draw the four possible structural formulas for compound **A** based on the information given above



4-8 Give structural formulas for the fragments lost corresponding to the peaks at 137 and 123 mass units in the mass spectrum.



4-9 Two of the isomers have a lower pK_a value than the others. Write the formulas for those.

Table 1

^{1}H Chemical Shift d

Hydrogens attached to carbon		
Methyl	CH_3–C– CH_3–C=O– CH_3–O–R CH_3–OCOR	0.9 – 1.6 ppm 2.0 – 2.4 ppm 3.3 – 3.8 ppm 3.7 – 4.0 ppm
Methylene	CH_2–C– CH_2–C=O– CH_2–OR CH_2–OCOR	1.4 – 2.7 ppm 2.2 – 2.9 ppm 3.4 – 4.1 ppm 4.3 – 4.4 ppm
Methine	CH–	1.5 – 5.0 ppm depending on the substituents. Generally higher than for methyl and methylene
Alkene		4.0 - 7.3 ppm depending on the substituent
Aldehyde	R–CHO	9.0 – 10.0 ppm
Hydrogens attached to oxygen		
Alcohols	ROH	0.5 -5.0 ppm
Phenols	ArOH	4.0 - 7.0 ppm
Carboxylic acids	RCOOH	10.0 - 13.0 ppm
Selected spin-spin coupling constants		
Alkanes (free notation)	H-C-C-H vicinal	6 - 8 Hz
Alkenes	trans cis geminal	11 - 18 Hz 6 - 12 Hz 0 - 3 Hz
Aromates	ortho meta para	6 - 10 Hz 1 – 4 Hz 0 – 2 Hz