KIBABII UNIVERSITY

UNIVERSITY EXAMINATIONS

2019/2020 ACADEMIC YEAR

FOURTH YEAR FIRST SEMESTER

SUPPLEMENTARY EXAMINATIONS

FOR THE DEGREE OF BACHELOR OF SCIENCE

COURSE CODE: SCH 430

COURSE TITLE: ORGANIC SPECTROSCOPY

DURATION: 2 HOURS

DATE: 16/02/21 **TIME:** 11-1 Pm

INSTRUCTIONS TO CANDIDATES

- Answer **QUESTION ONE** (Compulsory) and any other two (2) Questions.
- Indicate **answered questions** on the front cover.
- Start every question on a new page and make sure question's number is written on each page.

This paper consists of **8** printed pages. Please Turn Over

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Question 1

a) Briefly explain the difference between the following; [4mks]

i. Ultraviolet spectroscopy (UV) and Infrared Spectroscopy (IR)

ii. **Nuclear** Magnetic Resonance (NMR) and Mass spectrometry (MS)

b) The absorbance of a 0.005M solution was reported as 0.49 at 540 nm.

i. Calculate the molar absorptivity of the solution on the assumption that a 1.00 cm cuvette was used. [2mks]

ii. Calculate percentage of light transmitted by the original solution. [3mks]

c) State three limitations of Beer Lamberts law. [3mks]

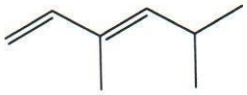
d) Explain the the following terms giving an example in each; [4mks]

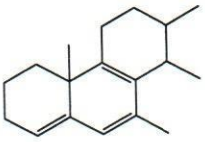
i. Bathochromic shift

ii. Hypsochromic shift

e) State four possible type of electronic transitions in excited organic molecules. [4mks]

f) Using Woodward-Fieser's rule, calculate wavelengths of maximum UV absorption for following compounds: 6mks

(i) 

(ii) 

g) Explain two structural features affecting λ max in UV absorption [4mks]

Question 2

a) Explain two types of molecular vibrations in IR: [2mks]

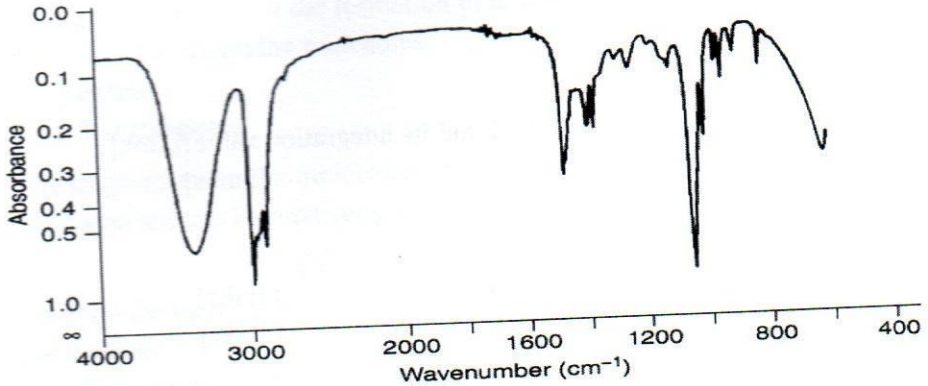
(b) Explain what is meant by the fingerprint region of an infra-red spectrum and describe how it is used to confirm the identity of organic molecules. **[2mks]**

c) Lycopene is responsible for the red colour of tomatoes. Explain. [4mks]

d) From the following list of compounds, 2-methylbutane, cyclopentane, 2-methyloctane, 3-methylpentane, butane and 1,1-dimethylcyclohexane, choose those that: [6mks]

1. absorb at 1375 cm^{-1};
2. absorb at both 720 and 1375 cm^{-1};
3. do not absorb at either 720 or 1375 cm^{-1}.

e). The infrared spectrum of an organic compound ($C_4H_{10}O$) is shown below in the Figure. Identify this compound. [6mks]



Question 3

(a) Explain four factors affecting chemical shifts in proton nmr spectra. [4mks]

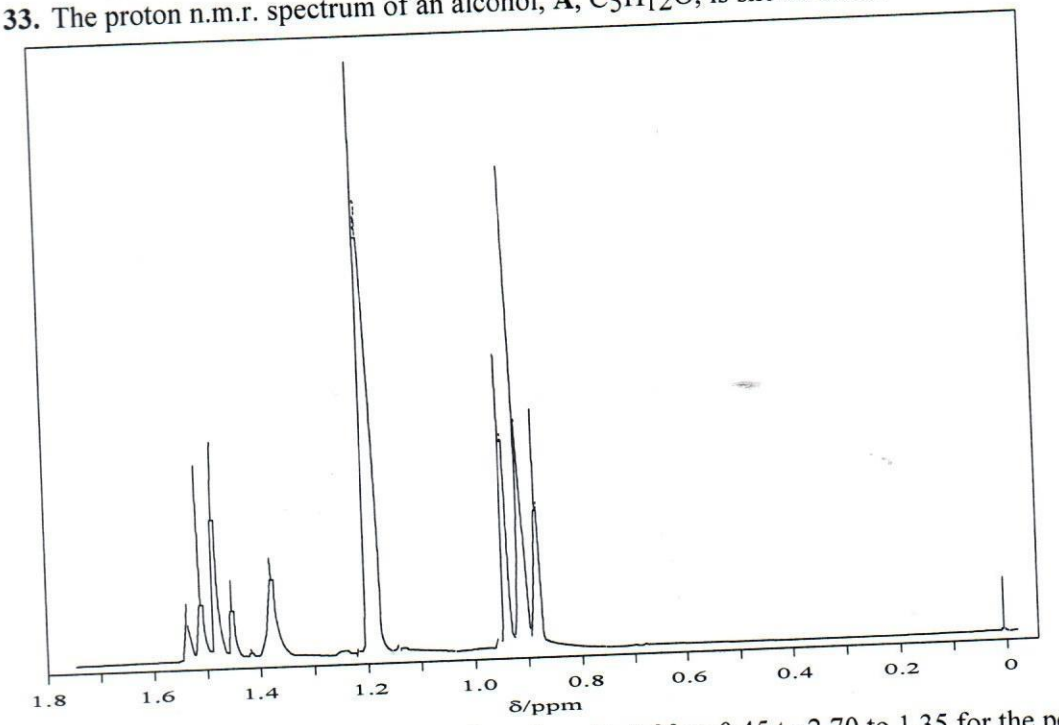
(b) The following peaks were from a 1HNMR spectra from a 400MHZ spectrometer. Convert to **δ** units. [6mks]

i. $CHCl_3$ 1415Hz

ii. CH_3OH 693HZ

iii. CH_2Cl_2 1060 HZ

33. The proton n.m.r. spectrum of an alcohol, **A**, $C_5H_{12}O$, is shown below



The measured integration trace gives the ratio 0.90 to 0.45 to 2.70 to 1.35 for the peaks at δ 1.52, 1.39, 1.21 and 0.93, respectively.

i. What compound is responsible for the signal at δ 0? Give a reason. [2mks]

ii. How many different types of proton are present in compound **A**? [1mk]

iii. What is the ratio of the numbers of each type of proton? [1mk]

iv. The peaks at δ 1.52 and δ 0.93 arise from the presence of a single alkyl group. Identify this group and explain the splitting pattern. [3mks]

v. What can be deduced from the single peak at δ 1.21 and its integration value?[1mk]

vi. Give the structure of compound A. [2mks]

Question 4

a) Explain three factors increasing the sensitivity in ^{13}C-NMR spectroscopy. [3mks]

b) Predict the number of peaks in the carbon-13 nmr spectrum of: [3mks]

I. butanone

II. pentan-2-one

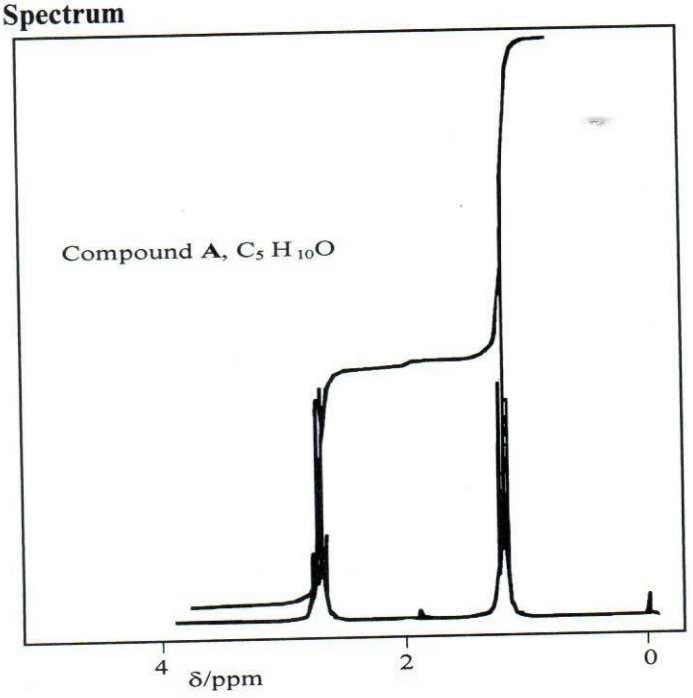
III. pentan-3-one

c) Compound **A**, $C_5H_{10}O$, reacts with $NaBH_4$ to give **B**, $C_5H_{12}O$. Treatment of **B** with concentrated sulphuric acid yields compound **C**, C_5H_{10}. Acid-catalysed hydration of **C** gives a mixture of isomers, **B** and **D**.

Fragmentation of the molecular ion of **A**, $[C_5H_{10}O]^{+\bullet}$, leads to a mass spectrum with a major peak at *m/z* 57. The infra-red spectrum of compound **A** has a strong band at 1715 cm^{-1} and the infra-red spectrum of compound **B** has a broad absorption at 3350 cm^{-1} (Table). The proton n.m.r. spectrum of **A** has two signals at δ 1.06 (triplet) and 2.42 (quartet), respectively (Spectrum).

Use the analytical and chemical information provided to deduce structures for compounds **A**, **B**, **C** and **D**, respectively. Include in your answer an equation for the fragmentation of the molecular ion of **A** and account for the appearance of the proton n.m.r. spectrum of **A**. Explain why isomers **B** and **D** are formed from compound **C**.

Spectrum



Question

a) List three essential components of a mass spectrometer. [3mks]

b) Write equations to show the formation of at least two species giving intense peaks in the mass spectra of each of the following molecules: [8mks]

i. pentane

ii. ethyl ethanoate

c). The fragmentation of a molecular ion $(M–R)^{+\bullet}$, formed in the ionisation chamber of a mass spectrometer, can be represented by the equation

$$(M–R)^{+\bullet}, = M^{+} + R^{\bullet},$$

i) Identify the three types of species shown in the equation and explain what takes place in this conversion. [3mks]

(ii) The mass spectrum of chloroethane shows two molecular ion peaks at m/z values of 64 and 66. The peak at $m/z = 64$ is approximately three times as intense as that at $m/z = 66$. Explain this observation and show, by means of an equation, how the molecular ion of chloroethane fragments to give rise to a peak at an m/z value of 29. [3mks]

(iii) Suggest why the mass spectrum of 1,2-dichloroethane shows peaks at m/z values of 98, 100 and 102. [3mks]