THE CATHOLIC UNIVERSITY OF EASTERN AFRICA

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MAIN EXAMINATION

SEPTEMBER –DECEMBER 2021

FACULTY OF SCIENCE

DEPARTMENT OF CHEMISTRY

REGULAR PROGRAMME

CHEM 305: ORGANIC SPECTROSCOPY

Date: DECEMBER 2021	**Duration: 2 Hours**
INSTRUCTIONS: Answer Question ONE and any TWO Questions	

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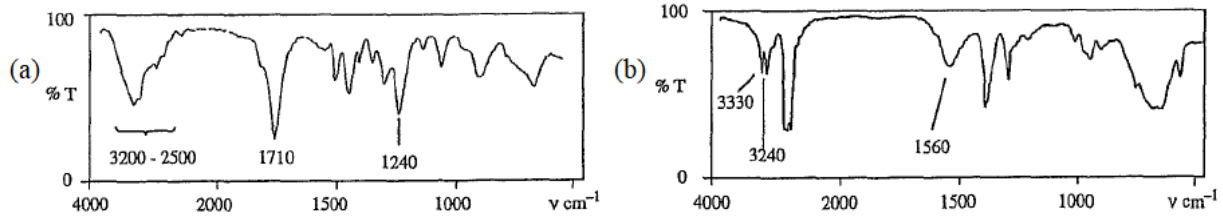
Q1.

a) The figure below shows the IR spectrum for propanoic acid(a) and hexylamine(b)



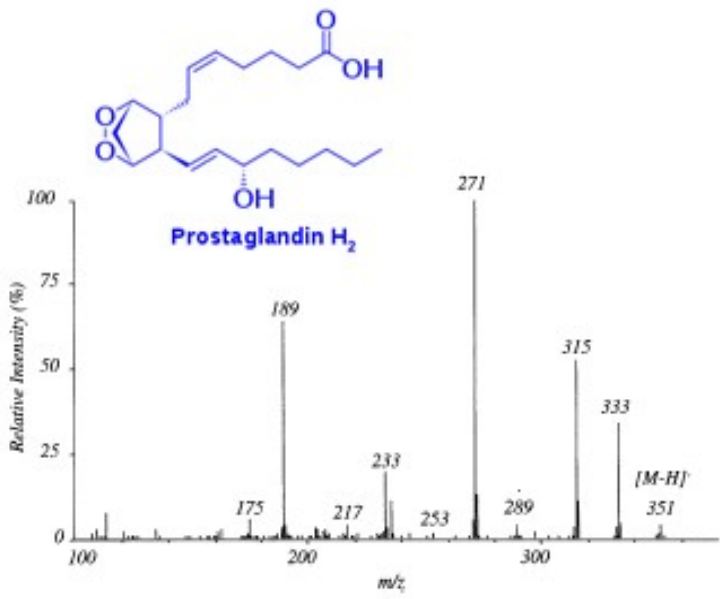
Account for the peaks at:

i. 3200 cm^{-1}, 1710 cm^{-1} and 1240 cm^{-1} in spectrum (a), and **[3marks]**

ii. 3330 cm^{-1}, 3240 cm^{-1} and 1560 cm^{-1} in spectrum (b) **[3marks]**

b) The performance of mass spectrometers depend on some of its aspects such as its sensitivity, detection limit (or limit of detection) and signal-to-noise ratio (*S/N*). Explain what you understand by these terms as used in MS. **[3marks]**

c) Assign fragmentation ions to the fragmentations pattern shown below for prostaglandin-H_2 for the labeled peaks recorded obtained by negative ion electron spray ionization. Give the corresponding formula of the respective ion fragments. **[6marks]**



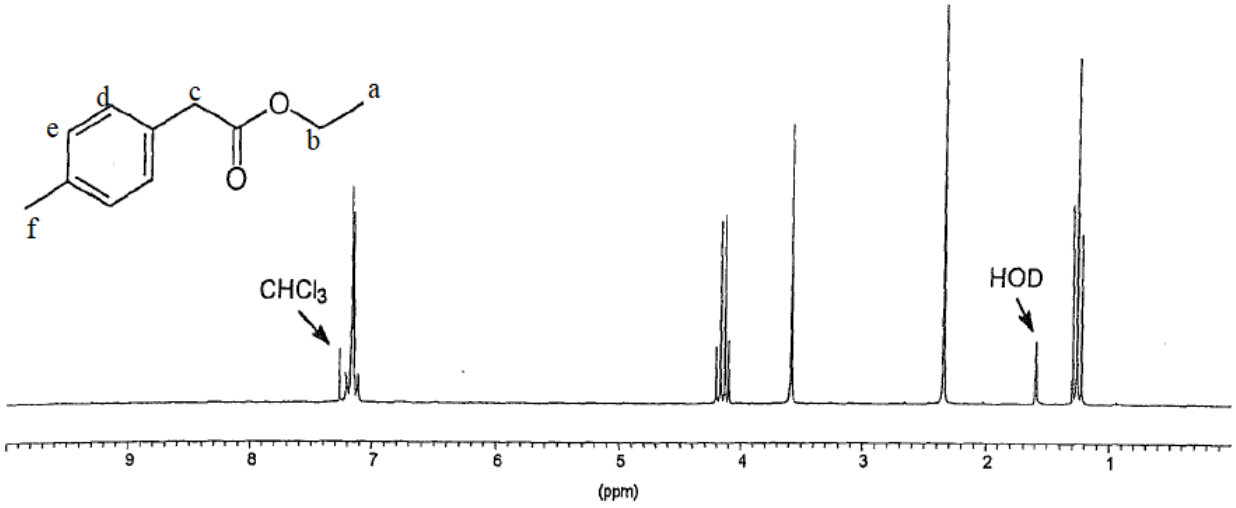
d) UV-Vis spectroscopy is an important technique in the identification of chromophores in organic molecules.

i. Explain what you understand by the term chromophores. **[2marks]**

ii. Illustrate using an orbital diagram the process underwent by chromophores when they are subjected to ultra-violet light. **[3marks]**

e. Describe using a sketch diagram the working principle of a single quadrupole mass analyzer **[5marks]**

f. The figure below is a proton NMR spectrum of ethyl *p*-tolylacetate obtained in chloroform



Assign with reason the observed peaks to the protons labeled on the structure. **[3marks]**

g. Explain what you understand by the resolving power of a mass analyzer **[2marks]**

Q2.

a) Visible light spectrum of a sample can be obtained using ordinary glass while UV analysis requires quartz cuvettes. Explain **[4marks]**

b) Explain the difference between the following terms: **[6marks]**

i. Chromophore and auxochrome

ii. Bathochromic shift and hypsochromic shift

iii. Hyperchromic effect and hypochromic effect

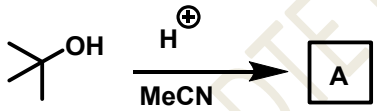
c) Explain the following terms: Larmor precession and Larmor frequency as used in nuclear magnetic resonance spectroscopy **[4marks]**

d) Ionization of an analyte for mass spectrometry can be achieved through electron impact. Explain using an appropriate example how this process occurs in Gas chromatography coupled with mass spectrometer.

[6marks]

Q3.

a) A sample of *tert*-butanol is dissolved in MeCN with an acid catalyst is left overnight, and crystals are found in the morning with the following characteristics. IR: 3435 and 1686 cm^{-1}; ^{13}C NMR: 169, 50, 29, and 25 ppm; ^{1}H NMR: 8.0, 1.8, and 1.4 ppm; Mass spectrum (%): 115 (7), 100 (10), 64 (5), 60 (21), 59 (17), 58 (100), and 56 (7).



Identify the crystals of A and account for the observed signals in IR and NMR data. Show the mechanism of the reaction **[7marks]**

b) Suggest a reasonable mechanism for the reaction in (a) above **[5marks]**

c) A Pacific sponge contains 2.8% dry weight of a sweet-smelling oil with the following spectroscopic details:

Mass spectrum gives formula: $C_9H_{16}O$. IR 1680 and 1635 cm^{-1}. ^{1}H δ_H 0.90 (6H, d, J=7 Hz), 1.00 (3H, t, J=7 Hz), 1.77 (1H, m), 2.09 (2H, t, J=7 Hz), 2.49 (2H, q, J=7 Hz), 5.99 (1H, d,

J=16 Hz), and 6.71 (1H, dt, J=16 Hz, 7 Hz). ^{13}C δ_c 8.15 (q), 22.5 (two qs), 28.3 (d), 33.1 (t), 42.0 (t), 131.8 (d), 144.9 (d), and 191.6 (s).

Identify with reason the structure and the stereochemistry of the sweet smelling oil

[8marks]

Q4.

a) i) Calculate the frequency of infrared light of wavelength $\lambda = 15$ μm. **[2marks]**

ii) It is customary to express absorption positions as wavenumbers, calculate the wavenumber of the above frequency. **[2marks]**

b) For UV light of wavelength 254 nm, ca1culate the frequency and the amount of energy absorbed by a single molecule when it absorbs a quantum of this light. Determine the corresponding energy (in J) absorbed by one mole of a molecu1e absorbing at this frequency (h = 6.6 x 10^{-34}Js, c = 3.0 x 10^8 m/s, Avogadro's number N_A= 6.02 x $10^{23}$$mol^{-1}$).

[3marks]

c) Explain the difference between electron spray ionization and chemical ionization process as used in mass spectrometry. **[6marks]**

d) Isolated double bonds in alkenes and lone pairs of electrons absorb at about 190 nm - 195 nm region of the electron magnetic spectrum whereas conjugated double bonds absorb in the visible region.

i) Suggest with reason what would likely to happen if the number of conjugated double bonds increases. **[3marks]**

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ii) State any two sources of transitions leading to the absorbed spectrum in UV-Visible spectrum of conjugated system of chromophores

[4marks]

Q5.

a) Briefly describe a typical mass spectrometry process involved in the MS analysis of a sample. Provide as sketch of the general layout of mass spectrometer

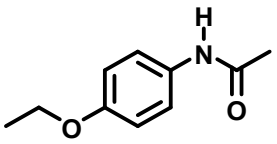
[7marks]

b) Explain the mode of operation of a photomultiplier as mass spectrometer detector.

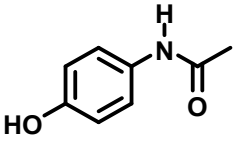
[4marks]

c) Distinguish between LUMO and HOMO as frontier orbitals. **[2marks]**

d) Acetaminophen, commonly known as paracetamol, is a medication used to treat moderate pain and fever. Its derivative has an ethyl group attached to its phenol group.



Ethyl acetominophen



Acetominophen

i) Identify with reason which one the structures below corresponds to the NMR data provided. **[4marks]**

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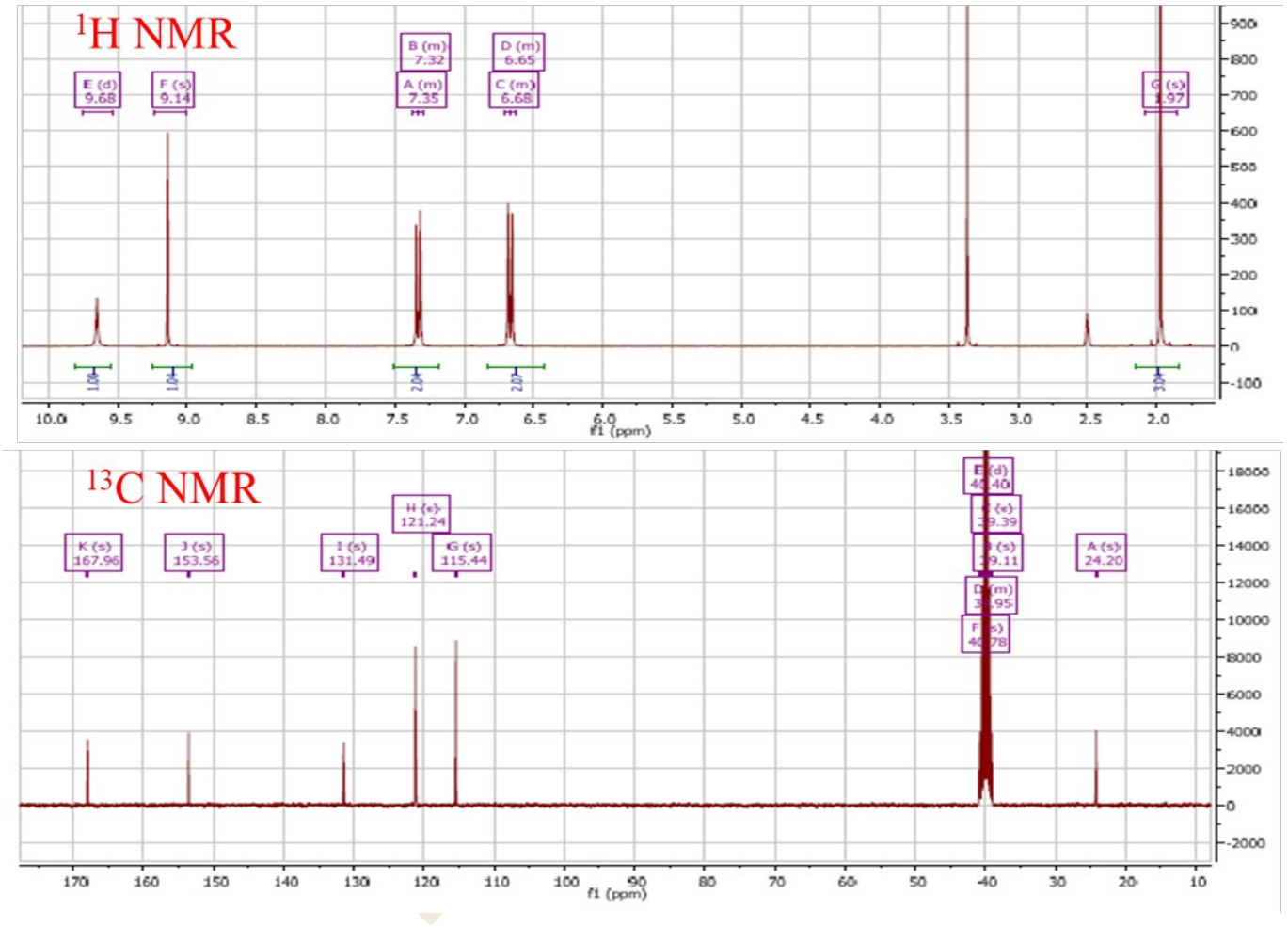
ii) Assign the observed peaks on the spectrum to the structure **[3marks]**



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