

**M. SC. (ORGANIC CHEMISTRY) SEM-III (CHOICE BASED
CREDIT & GRADE SYSTEM) : WINTER - 2017**
SUBJECT : SPECTROSCOPIC METHODS IN STRUCTURE DETERMINATION

Day : Monday
Date : 06/11/2017

W-2017-0779

Time: 03.00 PM TO 06.00 PM
Max. Marks : 60

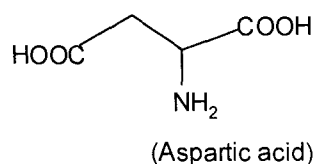
N.B.:

- 1) All questions are **COMPULSORY**.
- 2) Figures to the right indicate **FULL** marks.
- 3) Answers to both the sections should be written in **SEPARATE** answer books.

SECTION – I

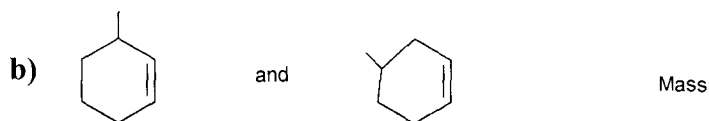
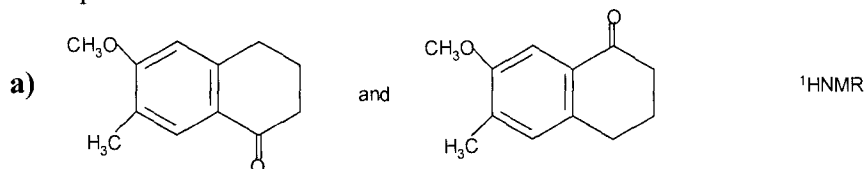
Q.1 Explain **ANY THREE** of the following: **[15]**

- a) The sodium salt of Aspartic acid in D₂O shows signals in ¹HNMR at 3.5 δ (dd, J = 10 and 4 Hz), 2.4 δ (dd, J = 15 and 4 Hz), 2.2 δ (dd, J = 15 and 10 Hz). Explain.

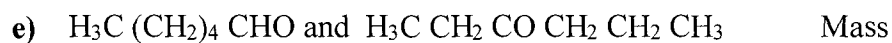
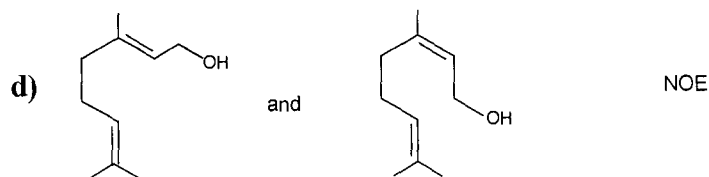
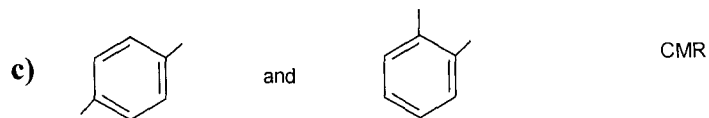


- b) ¹³C – ¹³C coupling is not seen in ¹³CMR Spectrum.
- c) Acetylenic protons are shielded than olefinic protons in ¹HNMR.
- d) CIMS is the preferred method for detection of M⁺ over EIMS in mass spectrometry.
- e) The – OH proton usually appears at a lower field in DMSO than in CDCl₃.

Q.2 Distinguish between **ANY THREE** of the following pairs using the given **[15]** spectral method:



P.T.O.



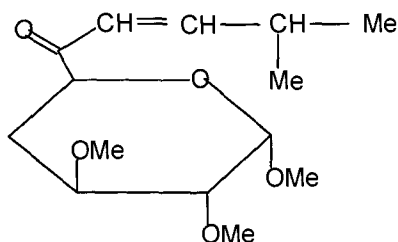
SECTION – II

Q.3 Write short notes on **ANY THREE** of the following: [15]

- AMX spin system
- COSY
- Desorption ionization technique in mass spectroscopy
- Two methods for simplification of PMR spectrum
- Mc Lafferty Rearrangement

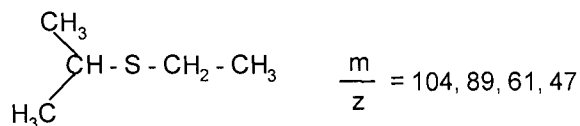
Q.4 Attempt **ANY THREE** of the following: [15]

- Assign ^{13}C NMR signals to various carbons in the following compound. Give reasons and justify your answer.

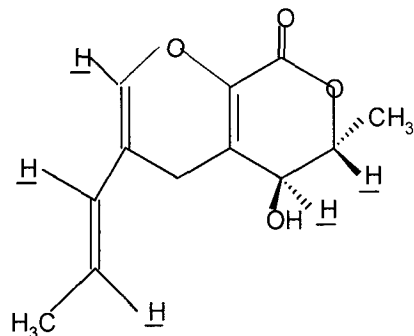


185 (s), 156 (d), 147 (d), 121 (s), 108 (d), 99 (d), 78 (d), 75 (d), 59 (q), 57 (q), 56.8 (q), 31.4 (d), 21 δ (q, strong).

- Explain the genesis of the following:



- c) Assign the signals to the underlined proton using decoupling experiments given below. Justify your answer:



- 3.92 (d, J = 5Hz, 1H)
 4.32 (dq, j = 7 and 5Hz, 1H)
 5.87 (d, J = 2Hz, 1H)
 6.06 (ddq, J = 16, 2 and 1.5 Hz, 1H)
 6.99 (dq, J = 6 and 16 Hz, 1H)

Spin decoupling experiment

Irradiate at	Change at
6.06 δ	5.87 (s); 6.99 (q, J = 6Hz)
3.92 δ	1.97 (d, J = 6Hz)
	4.32 (q, J = 7Hz)

- d) Deduce the structure based on the following data. Comment on the coupling constant, multiplicity and chemical shift.

Molecular formula	:	$C_{11}H_{14}O_2$
PMR	:	0.8 (d, J = 7Hz, 6H)
		1.84 (m, 1H)
		2.45 (d, J = 7Hz, 2H)
		7.16 (d, J = 8Hz, 2H)
		7.94 (d, J = 8Hz, 2H)
		11.5 (bs, 1H)

- e) Explain the genesis of the following:

i) Octane-4-one, $\frac{m}{z} = 128, 85, 71, 57, 43$.

ii) $BrCH_2CH_2OCH_2CH_2Br$, $\frac{m}{z} = 234, 232, 230, 139, 109, 107, 95, 93$.

* * * *