(2 ½ hours) Total Marks:60

**N.B.** (1) All questions are **compulsory.** 

(2) Figures to the right indicate full marks.

Q.1 A Attempt **any two** of the following:

8

- a. Explain structural features and applications of Starch and Cellulose.
- b. Give evidence for
  - i) reducing sugar in Lactose is Glucose
  - ii) Glucose and Galactose are linked through  $\beta$ -glycosidic linkage in Lactose.
- c. Give the synthesis of Ubiquinone from 3,4,5-trimethyl acetophenone.
- d. Give structural features and biological importance of carotenoids and anthocyanins.
- Q.1 B Attempt **any one** of the following:

4

- a. Give the Synthesis of Bombykol from acetylene.
- b. Give the synthesis of Atropine.
- Q.2 A Answer **any two** of the following:

8

a. How is reserpine synthesized from the following compounds?

b. Outline the steps involved in the following conversion as a part of Longifoline synthesis.

- c. Give Gilbert-stork synthesis of Griseofulvin from phloroglucinol.
- d. Give analytical evidence for structural elucidation of PGE1.

31198 Page 1 of 7

Q.2 B Answer **any one** of the following:

- 4
- a. Write structural features and give the applications of Gibberelic acid.
- b. Give analytical evidence for the structure determination of PGE1 $\alpha$ .
- Q.3 A Answer **any two** of the following:

8

a. Using spin system notation, designate the type of spin system in the following compounds.

- b. Explain the terms chemical and magnetic equivalence of protons with suitable examples.
- c. Calculate <sup>13</sup>CNMR shift for all aromatic carbons using incremental shifts of all the aromatic carbon atoms from the table given below for the following compounds.
  - i) Salicylaldehyde ii) p-Hydroxyacetophenone

Substituents	Increments in ppm			
	Ipso	Ortho	Meta	Para
-ОН	+27.0	-13.0	+1.0	-7.0
-СНО	+9.0	+1.0	+1.0	+6.0
-COCH <sub>3</sub>	+9.0	+1.0	+1.0	+6.0

- d. Explain long range coupling in aromatic and allylic compounds.
- Q.3 B Answer **any one** of the following:

4

a. The proton NMR spectrum for a compound with formula  $C_8H_{18}$  shows only one peak at 0.86 ppm. The  $^{13}$ CNMR spectrum has two peaks, a large at 26 ppm and a small one at 35 ppm. Predict the structure of this compound.

31198

Page 2 of 7

b. A compound having molecular formula C<sub>8</sub>H<sub>8</sub>O<sub>2</sub> shows following data:

UV: 250,265 nm

IR (cm<sup>-1</sup>): 2700-3500 (very broad), 1700, 1600 (w), 1500, 920

<sup>1</sup>HNMR (δppm): 3.5 (12mm, s), 7.2 (30mm, s) ,12.3 (6mm, s)

Assign suitable structure to the compound and state the number of signals obtained in its proton decoupled <sup>13</sup>CNMR spectrum.

Q.4 A Answer **any two** of the following:

8

- a. Explain COSY technique with suitable example.
- b. A compound shows following spectral data:

Mass spectrum(m/e):M+=102

IR(cm<sup>-1</sup>): 1735(s),1250(s)

<sup>1</sup>HNMR(δppm): 4.023(t,2H),2.050(s, 3H),1.65(m,2H),0.95(t,3H)

<sup>13</sup>CNMR(δppm): 171.09,66.10,22.14,20.91,10,41

What is the structure of the compound?

- c. What is NOE? What is its significance? Explain with suitable example.
- d. The following chemical shifts are obtained in the <sup>13</sup>CNMR spectrum of the compound

(δppm) 17.3,20.9,31.0,33.2,41.5,79.2

Match the chemical shifts with the appropriate carbons and draw its proton decoupled <sup>13</sup>CNMR, DEPT-90 and DEPT-135 spectra.

- Q.4 B Answer **any one** of the following:
  - a. Explain NOESY technique with suitable example.
  - b. The following chemical shifts are obtained in the <sup>1</sup>HNMR and <sup>13</sup>CNMR spectrum of the compound



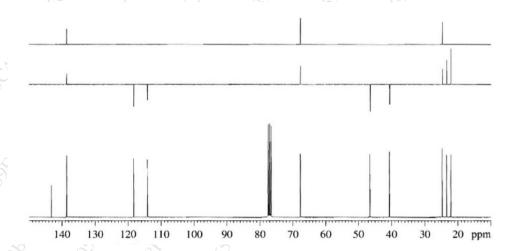
<sup>1</sup>HNMR(δppm):0,93,1.28,1.42,1.8,1.82,2.21,2.48,3.83,5.08,5.15,5.24, 5.26,6.40.

<sup>13</sup>CNMR(δppm):22.0,23.5,25.0,40.8,47.0,67.8,118.2,138.5,143,143.3

Its <sup>13</sup>CNMR, DEPT-90, DEPT-135, COSY and HETCOR spectra are given.

Match the values to appropriate protons and carbons and justify your answer by using the spectra.

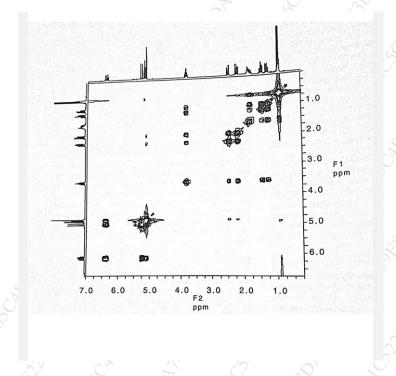
DEPT:



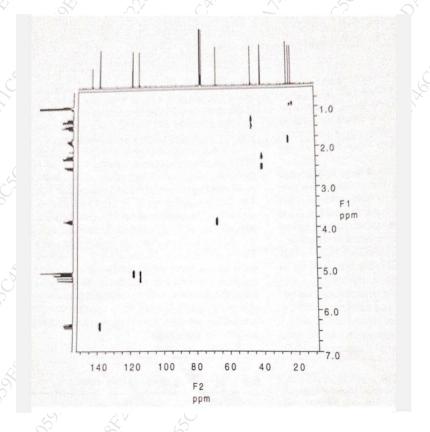
31198

Page 4 of 7

## COSY:



## HETCOR:



31198 Page 5 of 7

- Q.5 Answer **any four** of the following:
  - a. i) Write a note on aminosugar.
    - ii) Draw the structure of Disparlure.
  - b. Give the synthesis of Grandisol from 2-methyl-1, 3-butadine.
  - c. How glycerol is derived from oils and fats?
  - d. What are the Insect Growth Regulators? Give structure of JH3.
  - e. How many signals you expect in the proton decoupled <sup>13</sup>C-spectra of following compounds?
    - i)o-Dichlorobenzene ii) Methyl acetate iii) Acetone
  - f. A compound gives following <sup>1</sup>HNMR spectra by using operating frequency 200 MHz. Coupling constant is 8 Hz.
    - <sup>1</sup>H NMR  $\delta$  (ppm): 3.9, 3.2

Calculate the frequency difference between these two signals and state whether the spectra is of first order or second order.

- g. Sketch and explain HETCOR spectrum of 1-Chloro-2-propanone.
- h. i) Identify the spectral technique that gives the signal for carbon bonded to only one hydrogen.
  - a) DEPT 135
  - b) DEPT 90
  - c) <sup>13</sup>C NMR
  - d) <sup>19</sup>F NMR

31198

$$O_2N$$
 $H_4$ 
 $H_6$ 

- ii) In the COSY spectrum of H<sub>2</sub> proton is coupled by a cross peak to \_\_\_\_\_ protons.
- a)  $H_4$ ,  $H_5$
- b)  $H_5$ ,  $H_6$
- c)  $H_4$ ,  $H_6$
- d)  $H_4$ ,  $H_5$  and  $H_6$

$$H_{b}$$
  $CI$   $H''$   $(a)$ 

iii) In the compound (a) the methyl doublet of  $^{1}$ H NMR at 1.2  $\delta$  ppm correlates  $^{13}$ C NMR signal at  $\delta$  \_\_\_\_\_ ppm in its HETCOR spectrum.

- a) 20
- b) 67
- c) 51
- d) 51 and 67