

(2 ½ hours)

Total Marks: 60

Please check whether you have got the right question paper.

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**

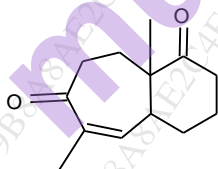
- Explain structural features and applications of
 - Starch
 - Heparin
- Explain Wohl degradation studies in structural determination of lactose.
- Draw the structure of β -Carotene. How will you prove the presence of
 - conjugated double bonds
 - bicyclic compound
 - β -Ionone units
- Give the synthesis of cyanin chloride.

Q.1 B. Attempt **any one** of the following: **4**

- Give synthesis of Bombykol from acetylene.
- Give synthesis of Coniine.
 - Draw the structure of morphine and atropine.

Q.2 A. Attempt **any two** of the following: **8**

- How is longifolene synthesized from



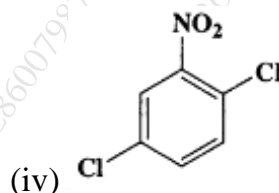
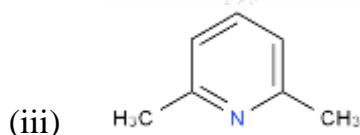
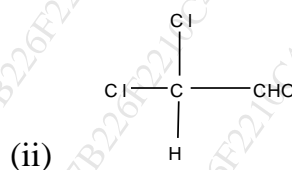
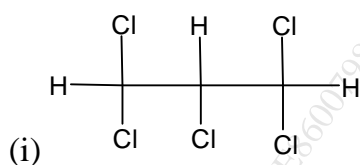
- How is phloroglucinol converted to 4,6-dimethyl benzofuranone? Draw the structure of 4-demethoxydaunomycin.
- What are lipids? Give its classification with suitable example.
- How is decalinedione prepared from resorcinol? Draw the configuration of the two enantiomers of Griseofulvin.

Q.2 A. Attempt **any one** of the following: **4**

- Write the structure of reserpine. Give the biological importance of prostaglandine.
- Write the synthesis of Triacntanol.

Q.3 A. Attempt **any two** of the following: 8

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



- b. Explain the term double resonance in NMR spectroscopy. Discuss its use in simplifying the complex NMR spectra.
- c. Calculate ^{13}C NMR chemical shifts for all the aromatic carbons using incremental shifts of all the aromatic carbon atoms from the table given below for the following compounds:

(I) *m*-chloroaniline(II) *o*-bromophenol

| Substituents | Increments in ppm | | | |
|------------------|-------------------|--------------|-------------|-------------|
| | <i>Ipso</i> | <i>Ortho</i> | <i>Meta</i> | <i>Para</i> |
| -Cl | +6.4 | +0.2 | +1.0 | -2.0 |
| -NH ₂ | +19.2 | -12.4 | +1.3 | -9.5 |
| -OH | +26.6 | -12.7 | +1.6 | -7.3 |
| -Br | -5.4 | +3.4 | +2.2 | -1.0 |

- d. Explain long range coupling in allylic compounds and hetero aromatic compounds.

Q.3 B. Attempt **any one** of the following: 4

- a. Explain the following statements:

(i) At 165°C the ^1H NMR spectrum of N,N-dimethylformamide shows only one methyl singlet.

(ii) At -40°C ^1H NMR spectrum of methyl alcohol shows one doublet and one quartet.

- b. The following chemical shifts were observed in ^1H NMR spectrum of 2,4-dichloroaniline in δ ppm.

6.60 (d, $J=9\text{Hz}$), 7.2 (d, $J=3\text{Hz}$), 6.95(dd), 4.0(s).

Match the chemical shifts with appropriate protons and justify your answer.

State whether the spectrum is First order or Second order.

Q.4 A. Attempt **any two** of the following: 8

- What is DEPT technique? Explain with suitable example how is it used to determine the number of attached hydrogens in an organic compound.
- Sketch and explain COSY spectrum of 3-methyl-2-butanone.
- What is NOE? What is its significance?
Explain with suitable example.
- A compound having molecular formula $C_3H_6O_2$ shows following spectral data:

Mass spectrum: molecular ion peak $m/z=74$, base peak $m/z=31$

IR (cm^{-1}): 1715(strong)

UV spectrum: no absorption above 205 nm

1H NMR δ (ppm): 8.026 (s,1H), 4.215(q,2H), 1.289(t,3H),1.8(m,2H)

^{13}C NMR δ (ppm): 14,60,161

The peak at 161 appears positive peak in DEPT-90 spectrum.

Assign suitable structure to the compound.

Q.4 B. Attempt **any one** of the following: 4

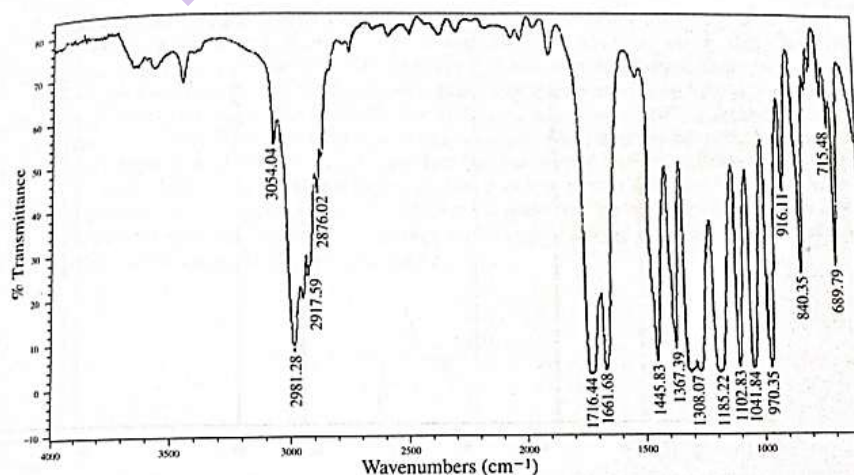
- Explain NOESY technique with suitable example.
- Determine the structure of a compound with molecular formula $C_6H_{10}O_2$.

1H NMR (\square ppm):

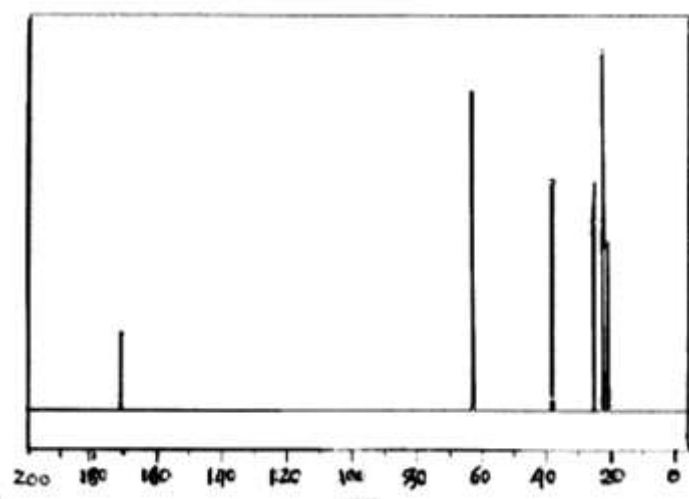
6.97(dq,1H),5.84(dq,1H),1.87(dd,3H),1.3(t,3H),4.2(q,2H)

The IR spectrum, ^{13}C NMR, DEPT, COSY and HETCOR spectra are shown.

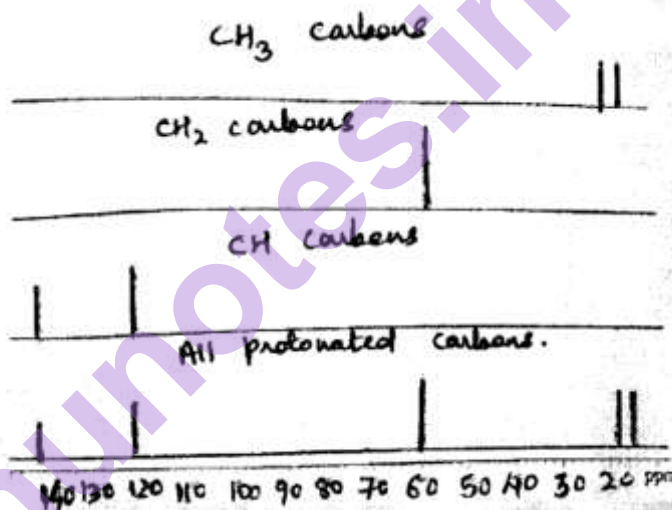
IR



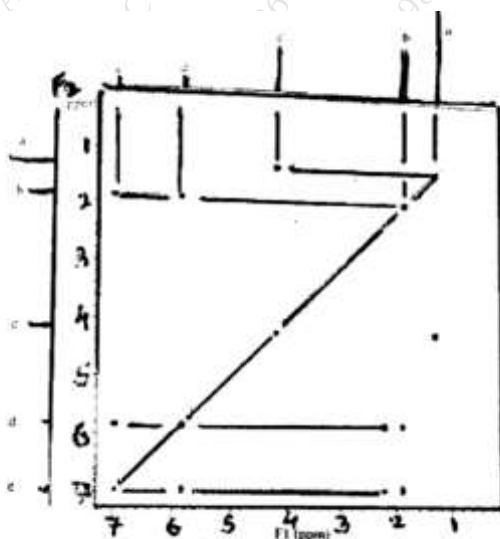
^{13}C NMR



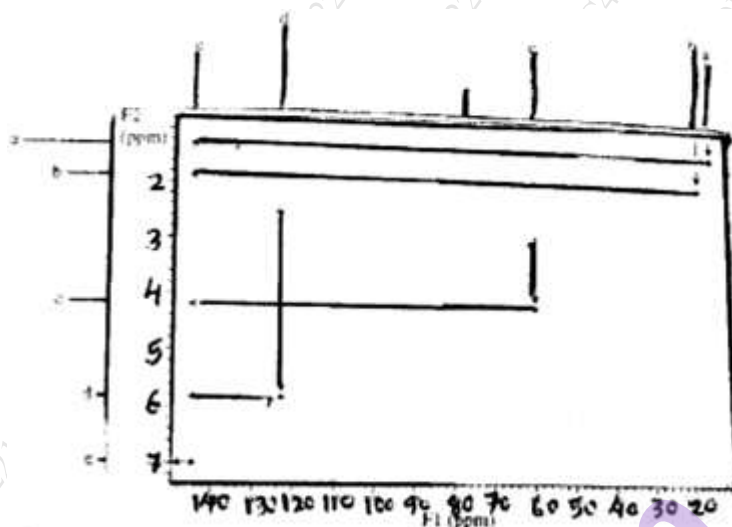
DEPT



COSY



HETCOR

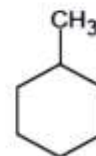
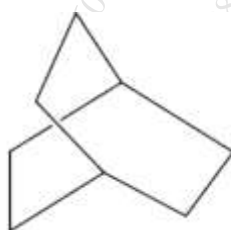


Q.5

Answer **any four** of the following:

12

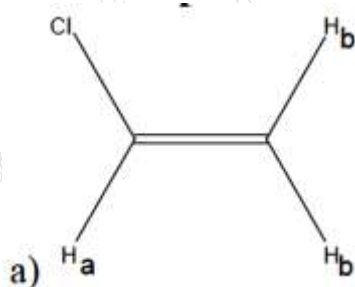
- Write a note on Amino sugars.
 - Draw the structure of Ubiquinone.
- Explain Alarm pheromones.
 - Write any two biological importance of porphyrins.
- What are insect growth regulator? Discuss the structure features of gibberellic acid.
- Draw the structure of Texol. Give the applications of JH₂ and JH₃
- How many signals you expect in the proton decoupled spectra of following compounds?



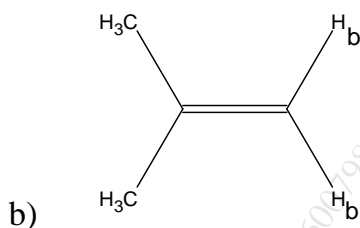
- f. Match the columns:

Compound

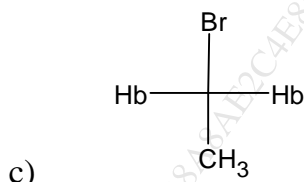
H_b protons



1) homotopic



2) enantiotopic



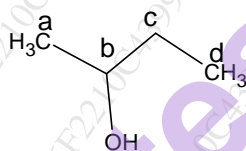
3) diastereotopic

g. State whether the following statements are true or false, justify your answer.

(i) NOESY spectra gives information about stereoisomers.

(ii) Quaternary carbon exhibit small NOE.

h. Select the correct option:



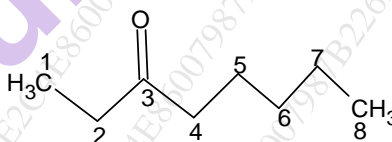
(i) In the compound the methyl triplet $\text{CH}_3(\text{d})$ at δ 0.9 ppm correlates ^{13}C NMR signal at δ _____ ppm in its HETCOR spectrum.

a) 10.2

b) 22.9

c) 32.3

d) 69.0



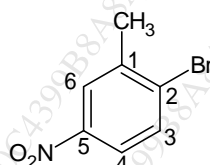
(ii) In the compound C-3 carbon will be detected only in _____ spectrum.

a) FTIR

b) COSY

c) ^{13}C NMR

d) DEPT



(III) In the compound CH_3 protons give a signal at δ 2.5 ppm. It correlates with ^{13}C NMR signal at δ _____ ppm in its HETCOR spectrum.

a) 122.1

b) 23.1

c) 147.1

d) 139.8
