[2½ Hours]

[ 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
- 1. A. Attempt **any two** of the following:

8

- i) Explain structural features and applications of Starch and Chitin.
- ii) Give structural features and biological importance of
  - i) Porphyrin
  - ii) Anthocyanin
- iii) I. Give analytical evidence to prove presence of n-propyl side chain in coniine
  - II. Give physiological importance and structure of Morphine
- iv) Give the synthesis of grandisol from 2-methyl-1, 3-butadine
- B. Attempt **any one** of the following:

4

i) Write a note on

Deoxy sugars

Branched sugars

- ii) Draw the structure of  $\beta$ -carotene. How will you prove the following in the structure of  $\beta$ -carotene? the presence of conjugated double bonds the presence of two  $\beta$ -ionone units and the presence of bicyclic structure.
- 2. A. Attempt **any two** of the following:

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i) How is reserpine synthesized from the following compounds?

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

- iii) Give Gilbert-stork synthesis of Griseofulvin from phloroglucinol.
- iv) Give analytical evidence for the structure elucidation of PGE<sub>1</sub>.
- B. Attempt any one of the following:

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- i) (I) Write structure of Taxol
  - (II) Give the synthetic strategy for synthesis of Caryophyllene.
- ii) Give a brief account gibberellic acids as plant growth regulators and give its applications.

- 3. A. Attempt **any two** of the following:
  - i) Using spin system notations designate the type of spin system in the following compounds:
    - 1,1,2,2-tetrachloro ethane
- 1,2,4-tetchlorobenzene
- 1,1,2,3,3-pentachloropropane
- 2,5-dichloronitrobenzene
- ii) What are chemical shift reagents? Explain the use of shift reagents in NMR spectroscopy.
- iii) Calculate <sup>13</sup>CNMR chemical shifts for all the aromatic carbons using incremental shifts of the aromatic carbon atoms from the table given below for the following compounds

1-bromo-3-nitrobenzene and 1-chloro-3-iodobenzene

Substitute	Increments in ppm			
	ipso	ortho	meta	para
NO <sub>2</sub>	19.6	-4.9	0.9	6.0
Cl	5.3	0.4	31.4	-1.9
Br	-5.4	3.4	2.2	-1.0
I	-31.2	8.9	1.6	3.1.4

iv) assign the various peaks seen in the 1HNMR spectrum of the following compounds.

δppm: 2.15 (s,3H), 2.31 (t,24), 2.78 (t, 2H), 3.38 (S,3H) 5.18 (5, 2H), 7.18(S-5H), 9.58 (S, 1H)

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

i) Explain the term double resonance in NMR spectroscopy. Discuss its use in simplifying complex NMR spectra.

- ii) Explain <sup>13</sup>C proton decoupled spectrum of
  (I) CFBr<sub>3</sub> (II) CH<sub>3</sub> PO (OCH<sub>3</sub>)<sub>2</sub> on the basis of hetero nuclear coupling of <sup>13</sup>C to <sup>19</sup>F and <sup>13</sup>C to <sup>31</sup>p respectively.
- 4. A. Attempt **any two** of the following:

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- i) Explain HETCOR technique with suitable example.
- ii) Sketch the proton decoupled <sup>13</sup>CNMR spectrum and DEPT-45, DEPT-90, DEPT-135 spectra of the following compounds.
  - (I) Ethyl propionate
- (II) 1-methyl butyl acetate
- iii) Explain NOESY technique with suitable example.
- iv) An organic compound with molecular formula C<sub>4</sub>H<sub>10</sub>O IR (cm<sup>-1</sup>) 3500 (broad), 3000

  <sup>1</sup>HNMR (δppm):3.28 (2H, d) 1.68 (1H, m) 0.83 (6H d) 2.95 (1H, s) Deduce the structure of the compound and draw its COSY spectrum.

- B. Answer **any one** of the following:
  - i) What is NOE? What is its significance? Explain with suitable examples.

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12

ii) An organic compound shows following spectral data

 $M.F. C_6H_{12}O$ 

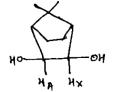
IR (cm<sup>-1</sup>): 1739, 1230

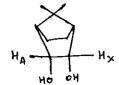
<sup>1</sup>HNMR (δppm) 2.1, 2.4, 1.6, 1.3, 0.9

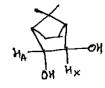
<sup>13</sup>CNMR (δppm) 208.93, 43, 30, 26, 22, 14

Deduce the structure and draw its HETCOR spectrum.

- 5. Answer **any four** of the following:
  - (a) Write the structures of Starch and cellulose and Bombykol
  - (b) Give the synthesis of ubiquinone from 3, 4, 5-trimethroxyacetophenone
  - (c) What are the Insect Growth Regulators? Give structure of JH<sub>3</sub>.
  - (d) What are lipids? Discuss their classification.
  - (e) How will you distinguish amongst the following compounds on the basis of NMR spectroscopy?







- (f) State whether the following statements are true or false and justify your answer.
  - 1. Cyclohexanone exhibits only 4 peaks in its <sup>13</sup>CNMR spectrum.
  - 2. A shift reagent leads to simplification of the spectra.
  - 3. At room temp <sup>1</sup>HNMR spectrum of cyclohexane shows only a single peak
- (g) Sketch and explain HETCOR spectrum of propyl acetate
- (h) Match the columns and justify your answer.

B B		
HETCOR	Determination of stereochemistry	
COSY	<sup>13</sup> C- <sup>1</sup> H correlation	
DEPT	<sup>1</sup> H- <sup>1</sup> H correlation	
	Identification of CH, CH <sub>2</sub> , CH <sub>3</sub> protons	

6-6-----