[Time: 2\frac{1}{2} Hours]

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:-
   i) Draw the structure of β-carotene & give analytical evidence of
      a) the presence of conjugated double bonds
      b) the presence of two β-ionone units
      c) presence of bicyclic compounds
   04
   ii) Write notes on:-
      a) Branched sugars
      b) Amino sugars
   04
   iii) Give the analytical evidences of
      a) Numbers and position of hydroxyl groups in cyanidine chloride.
      b) Numbers and position of glucose residue in cyanin chloride.
   04
   iv) Give the synthesis of grandisol from 2-methyl-1, 3-butadiene.
   04

b) Attempt any one of the following: -
   i) Explain the structural features and applications of
      I) chitin        II) flavones
   04
   ii) Give analytical evidence to prove the presence n-propyl side chain in coniine
       and give the synthesis of coniine from pyridine.
   04

Q.2 a) Attempt any two of the following: -
   i) How is reserpine synthesized from the following compounds?
   04
   ii) Give the synthesis of Griseofulvin from phloroglucinol.
   04
   iii) I) Write the structure of Taxol.
        II) Outline the steps involved in the following conversion as part of Longifolene synthesis.
iv) Outline the steps involved during D ring formation in the Taxol synthesis.

b) Attempt any one of the following:
   - I) Write structural features and give the applications of Gibberelic acid
   - II) Give analytical evidence for the structure determination of PGE_{\text{ia}}

Q.3 a) Answer any two of the following:
   - i) What are lantha shifts reagents? How are they useful in simplifying the complex NMR spectra?
   - ii) Using spin system notation, designate the type of spin system in the following compounds:
      - (I) 2, 5-dichloronitrobenzene
      - (II) dichloroacetaldehyde
      - (III) 2-chloroethanol
      - (IV) 2-bromo-5-chlorothiophene
   - iii) Calculate 13CNMR 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) o-fluoronitrobenzene
      - (II) p-nitroacetophenone

<table>
<thead>
<tr>
<th>Substituents</th>
<th>Increments in ppm</th>
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<tbody>
<tr>
<td></td>
<td>ipso</td>
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<tr>
<td>-NO2</td>
<td>+19.6</td>
</tr>
<tr>
<td>-F</td>
<td>+35.1</td>
</tr>
<tr>
<td>-COCH3</td>
<td>+7.8</td>
</tr>
</tbody>
</table>

iv) An organic compound A displays molecular ion peaks at m/e 166/168 in the ratio 1:1. On treatment with dimethyamine it yields another compound B showing the molecular ion peak m/e 131. The IR spectrum of B exhibits a strong absorption at 1730 cm\(^{-1}\) where as the 1H NMR spectrum displays signals at \(\delta ppm\) 1.3 (t, 3H), 2.4(s, 6H), 3.2(s, 2H), 4.2(q, 2H).
What are the structure of A and B?
b) Answer any one of the following:
   i) Explain the term double resonance in NMR spectroscopy. Discuss its use in simplifying complex spectra.
   ii) The following chemical shifts were obtained in the $^{13}$CNMR spectrum of acetophenone.
       197.7, 137.1, 132.9, 128.4, 128.2, 26.3
       Match the chemical shifts with the appropriate carbons and justify your answer.

Q.4 a) Attempt any two of the following:
   i) Draw the proton decoupled $^{13}$CNMR spectrum & DEPT-45, DEPT-90, DEPT-135 of the following compounds.
      (I) Isobutyl acetate  (II) 3,3-dimethylbutanoic acid
   ii) Explain COSY technique with suitable example.
   iii) What is NOE? What is its significance? Explain with suitable examples.
   iv) A compound with molecular formula $\text{C}_9\text{H}_{12}\text{O}$ exhibit strong absorption at 1715 cm$^{-1}$.
       Its $^1$HNMR data is as follows:
       2.312 (d, 2H), 2.133 (m, 1H), 2.123 (s, 3H), 0.926 (d, 6H)
       Its $^{13}$CNMR data is as follows:
       22.55 24.68 30.32 52.80 208.57
       Assign the structure to the compound and draw its HETCOR spectrum

b) Answer any one of the following:
   i) Explain NOESY technique with suitable example.
   ii) Assign a suitable structure to the organic compound having M$^+$ peak at 116 on the basis of following spectral data and draw its COSY spectrum
       UV ($\lambda_{max}$) : 283 nm
       IR (cm$^{-1}$): 3000-2500 (broad) 1715 (s) 1342 (w)
       $^1$HNMR (δppm): 2.12 (s, 3H) 2.60 (t, 2H) 2.25 (t, 2H) 11.9 (s, 1H)

Q.5 Attempt any four of the following:
   a) Give the synthesis of triacontanol.
   b) What are insect growth regulators?
      Give a brief account of aryl acetic acid as plant growth regulators.
   c) Give the synthesis of cyanidin chloride from phloroglucinaldehyde and $\omega,3,4$-trihydroxy acetophenone.
   d) Draw the structure of JH$_3$.
      Give the structural features and biological importance of anthocyanins.
e) State whether following statements are true or false and justify your answer:
   i) At 165°C the $^1$HNMR spectrum of N, N-dimethyl formamide shows only one methyl singlet.
   ii) At room temperature $^1$HNMR spectrum of cyclohexane shows only a single peak at δ 1.4.
   iii) At -40°C $^1$HNMR spectrum of methyl alcohol shows one doublet and one quartet.

f) Explain ‘W’ coupling with suitable examples.

g) Sketch and explain COSY Spectrum of 3-heptanone.

h) Fill in the blanks & justify
   i) DEPT-90 spectrum shows signals for ________. (CH, CH₃)
   ii) COSY spectrum explains ________ correlation. ($^1$H-$^1$H, $^1$H-$^13$C)
   iii) NOESY spectrum gives information about ________.
      (stereoisomers, $^{13}$C-$^1$H correlation)

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