[Time: $2\frac{1}{2}$ 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.

Q.1 a) Attempt **any two** of the following:-

i) Draw the structure of β-carotene & give analytical evidence of **04**
   a) the presence of conjugated double bonds
   b) the presence of two β-ionone units
   c) presence of bicyclic compounds

ii) Write notes on:- **04**
   a) Branched sugars
   b) Amino sugars

iii) Give the analytical evidences of **04**
   a) Numbers and position of hydroxyl groups in cyanidine chloride.
   b) Numbers and position of glucose residue in cyanin chloride.

iv) Give the synthesis of grandisol from 2-methyl-1, 3-butadiene. **04**

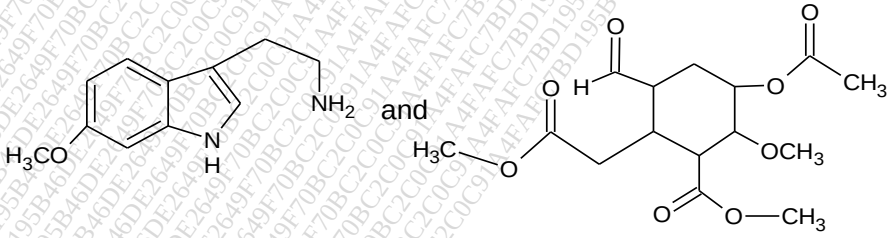
b) Attempt **any one** of the following: -

i) Explain the structural features and applications of **04**
   I) chitin II) flavones

ii) Give analytical evidence to prove the presence n-propyl side chain in coniine and give the synthesis of coniine from pyridine. **04**

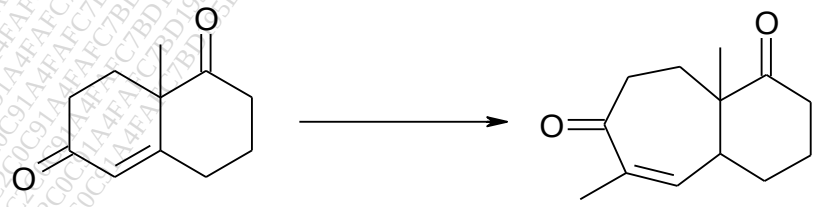
Q.2 a) Attempt **any two** of the following: -

i) How is reserpine synthesized from the following compounds? **04**

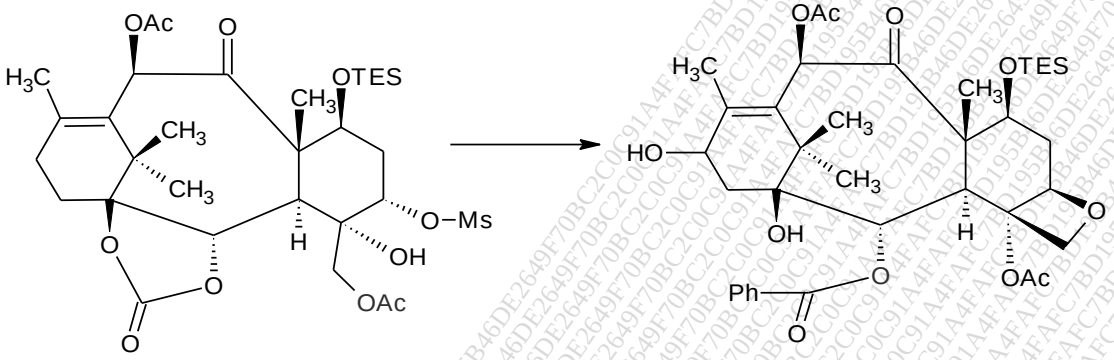


ii) Give the synthesis of Griseofulvin from phloroglucinol. **04**

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 **04**

II) Give analytical evidence for the structure determination of $PGE_{1}\alpha$ **04**

Q.3 a) Answer **any two** of the following: **08**

i) What are lanthanide shift reagents? How are they useful in simplifying the complex NMR sepctra?

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 ^{13}CNMR 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

Substituents	Increments in ppm			
	ipso	*ortho*	*meta*	*para*
$-NO_2$	+19.6	-5.3	+0.9	+6.0
-F	+35.1	-14.3	+0.9	-4.5
$-COCH_3$	+7.8	-0.4	-0.4	+2.8

iv) An organic compound A displays molecular ion peaks at m/e 166/168 in the ratio 1:1. On treatment with dimethylamine 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 ^{1}HNMR spectrum displays signals at δppm 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: **04**

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: **08**

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 $C_6H_{12}O$ exhibit strong absorption at 1715cm^{-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: **04**

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 (λ_{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: **12**

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 ω,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 165^0C 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 -40^0C ^{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, CH_3)
   ii) COSY spectrum explains _____ correlation. (^{1}H-^{1}H, ^{1}H-^{13}C)
   iii) NOESY spectrum gives information about _____. (stereosiomers, ^{13}C-^{1}H correlation)

****