20. (a) Establish the structure of Vitamin A.

Or

(b) Establish the structure of Zingeberene.

Reg. No. : .....

Code No. : 6395 **Sub. Code : HCHM 21**

M.Sc. (CBCS) DEGREE EXAMINATION,
APRIL 2016.

Second Semester

Chemistry — Main

ORGANIC CHEMISTRY — II

(For those who joined in July 2012 onwards)

Time : Three hours Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL questions.

Choose the correct answer :

1. Presence of an exocyclic double bond will shift the absorption maximum of a $\pi \rightarrow \pi^*$ transition in an UV spectrum by

(a) 5nm

(b) 30 nm

(c) 39 nm

(d) 42 nm

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2. The point at which the cotton effect curve crosses the X-axis corresponds to

(a) $[\alpha]$

(b) Specific rotation

(c) λ_{max}

(d) ϵ_{max}

3. Which of the following molecules will not have any cross contours in the H, H – Cosy spectrum?

(a) $(CH_3)_2\ CH\ CH_2\ Br$

(b) $(CH_3)_3\ C\ Br$

(c) $CH_3\ CH_2\ CH_2\ CH_2\ Br$

(d) $CH_3CHBr\ CH_2\ CH_3$

4. An AMX spin system will exhibit

(a) two doublets and one triplet

(b) three triplets

(c) three doublets of doublets

(d) two doublets of doublets

5. Which one of the following regarding mass spectroscopy in wrong?

(a) only cations can be detected by a normal mass spectrometer

(b) the intensity ratio of M^+ and $(M+Z)^+$ is 1:1, if the molecule has one bromine atom

(c) Molecular ion peaks will have even number of $\frac{m}{e}$ value

(d) initially a cation radical is generated in the mass spectral analysis

6. The base peak for ethylamine in EI mass spectrum will be at $\frac{m}{e}$

(a) 14 (b) 15

(c) 30 (d) 31

7. The number of chiral centres in quinine is

(a) 3 (b) 4

(c) 5 (d) 6

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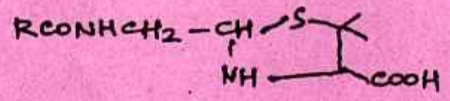
8. The following compound is known as



(a) penilloic acid (b) penicilloic acid

(c) penicillic acid (d) penilic acid

9. The molecular formula of camphoric acid is

(a) $C_8H_{14}O_4$ (b) $C_{10}H_{16}O_4$

(c) $C_{12}H_{18}O_4$ (d) $C_{12}H_{22}O_4$

10. Thiochrome is obtained from thiamine by the treatment of

(a) alkaline sodium hydroxide

(b) alkaline potassium ferricyanide

(c) sodium borohydride

(d) sodium and liquid ammonia

PART B — (5 × 5 = 25 marks)

Answer ALL questions, choosing either (a) or (b).

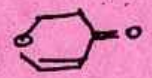
Each answer should not exceed 250 words.

11. (a) Explain how the solvent polarity changes the λ_{max} for (i) a $\pi \rightarrow \pi^*$ transition and (ii) a $n \rightarrow \pi^*$ transition.

Or

(b) Compare the carbonyl stretching frequency in the following cases.

(i) *Ph cooMe* and Me cooPh

(ii) and 

12. (a) Explain how a combination of DEPT 90, DEPT 45 and DEPT 135 spectra help us to differentiate between methyl, methylene, methine and quartenary carbons.

Or

(b) Predict the number of signals for diethyl maleate in the C-13 NMR spectrum. Indicate the order in which the chemical shifts of these signals increases.

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13. (a) Indicate the principle and application of FAB mass spectroscopy.

Or

(b) List out the popular fragmentation patterns associated with aliphatic ethers and esters.

14. (a) Establish the structure of chloramphinicol.

Or

(b) Write a note on the bio synthesis of alkaloids.

15. (a) (i) What is/are the $Ba(OH)_2$ hydrolysis product(s) of lumilacto flavin?

(ii) Indicate how N-methyl – 4, 5 – diamino-ortho – xylene can be obtained from ribo-flavin.

Or

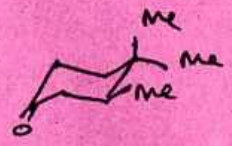
(b) What happens when santonin is treated with (i) kM_nO_4 (ii) $HCl/EtOH$ (iii) $I_2/HOAc$ (iv) Zn dust and distilled (v) alkali.

PART C — (5 × 8 = 40 marks)

Answer ALL questions, choosing either (a) or (b).

Each answer should not exceed 600 words.

16. (a) Explain the importance of octant rule. Describe how the sign of the cotton effect curve can be determined by octant rule. Predict the sign of the cotton effect curve of the following two compounds.

(i) 

(ii)

Or

(b) Account for the following:

(i) The primary amine gives a doublet around $3400cm^{-1}$

(ii) The terminal and non terminal alkynes can be distinguished by IR spectroscopy

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(iii) Trans-stilbene has its $\pi \rightarrow \pi^*$ band at a higher λ_{max} than the cis isomer

(iv) The $\gamma_{c=o}$ of an acid chloride is greater than that of a ketone.

17. (a) What is anisotropy? Draw the anisotropic cone for $C=0$ bond. Explain ring current effect. Discuss why anisotropic effect is not a problem with $C-13$ NMR spectra. What is Van der Waals deshielding?

Or

(b) (i) Describe the origin of spin-spin splitting.

(ii) Differentiate between geminal coupling and vicinal coupling. Indicate the factors that affect these coupling constants.

(iii) Predict the ^1H *NMR* split pattern for CH_2F_2 and $(CH_3)_3C-C(CH_3)_3$.

18. (a) (i) An organic compound of molecular formula C_7H_8O gives m/e ratio 108, 93, 77, 65 and 39. Discuss the fragmentation pattern corresponding to these values. (4)

(ii) Write a note on Mc Lafferty rearrangement. (4)

Or

(b) An organic compound with molecular formula $C_{11}H_{14}O$ has the following ^1H *NMR* spectral features: 7.5 – 7.6 ppm, multiplet, 3H; 7.9 ppm, doublet, 2H; 2.9 ppm, triplet, 2H; 1.7 ppm, pentet, 2H; 1.3 ppm, sextet, 2H; 0.9 ppm, triplet, 3H. The ^{13}C *NMR* signals appear at 14.1, 22.1, 26.2, 38.3, 128.4, 129.5, 133.6, 137.7 and 200.8 ppm. Suggest a structure for the compound.

19. (a) Elucidate the structure of morphine.

Or

(b) Hydrolysis of cephalosporin-C under different conditions give different products. Provide all the reaction conditions and the respective products formed.

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