

F 6502

(Pages : 4)

Reg. No.....

Name.....

M.Sc. DEGREE (C.S.S.) EXAMINATION, JANUARY 2015

Third Semester

Faculty of Science

AN3C12/AP3C12/CH3C12/PH3C12/PO3C12—SPECTROSCOPIC METHODS IN CHEMISTRY

(Common to all Branches of Chemistry)

[2012 Admission onwards]

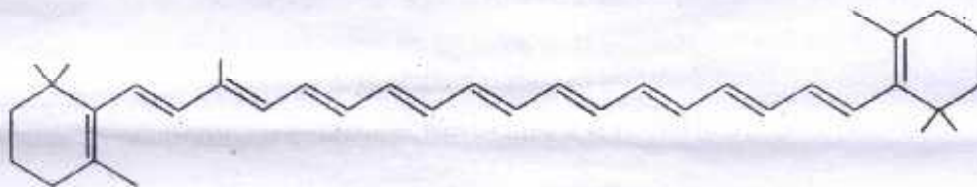
Time : Three Hours

Maximum Weight : 30

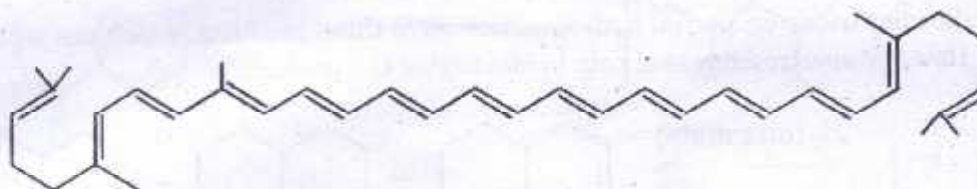
Section A

*Answer any ten questions.
Each question carries a weight of 1.*

1. Calculate the λ_{\max} and ϵ_{\max} for the following molecules using Woodward-Fieser Rules.

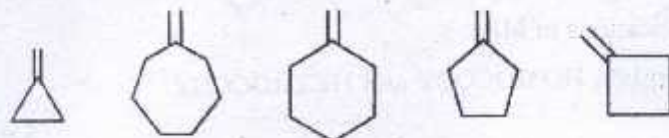


(1) Beta-Carotene



(2) All trans lycopene

2. What is optical rotatory dispersion ? Explain how this phenomena is helpful to distinguish the Enantiomeric pairs.
3. Arrange the following in the increasing order of their carbonyl stretching frequencies Ethyl acetate, valerolactone, γ -butyrolactone, β -propiolactone
4. Arrange in the decreasing order of olefinic stretching frequencies of the following compounds.



Turn over

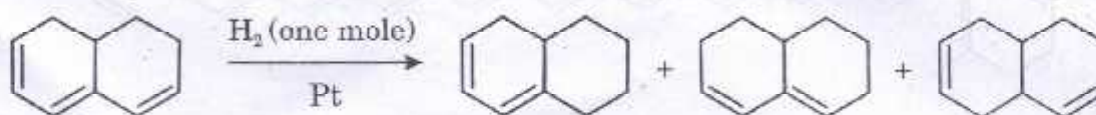
5. Explain why the increase in the solvent polarity the UV spectrum gives a blue shift to R-band while a red shift to the K-Band.
6. Describe the splitting patterns in the PMR spectra of the following molecules Z-1, 3-Dimethylcyclopropane, 2R, 3S-2, 3-Dibromopentane.
7. What is DEPT ? What is its use in structural determinations ?
8. Calculate DBE (Double bond equivalent) of the following molecules
 (a) $C_{12}H_{10}O_2$ (b) $C_{15}H_{13}Br$.
9. What is Nitrogen Rule ? What is its use in Mass spectrometry ?
10. What is MALDI ? What is its use ?
11. Explain Mc-Lafferty rearrangement ?
12. Using an example explain the special advantage in GC-MS.
13. Explain the use of UV spectra in distinguishing axial and equatorial conformations using a suitable example.

(10 × 1 = 10 marks)

Section B

Answer five questions.
 Each question carries a weight of 2.

14. What is "Cotton Effect" ? Explain how it is useful in distinguishing the Enantiomeric pairs using an example.
15. (a) How the ortho, Meta and Para disubstituted benzene derivatives are distinguished in IR spectra
 (b) The following triene on partial hydrogenation gave three products, which are separated by GLC. How UV spectroscopy is of help in identifying the products.



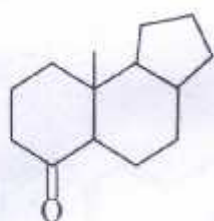
16. Sketch the 1H NMR and ^{13}C NMR spectra of Hept-3-ene. Explain the spectral features.
17. What is Nuclear Overhauser effect (NOE) ? Explain its use in structural elucidations using a suitable example.
18. Explain Karplus Curve. How it is helpful in determining the conformations ?
19. What are shift reagents ? What is their use in NMR spectra ? Name two common shift reagents used.
20. Write briefly on the theory and applications of MRI.
21. Explain the principle of 2DNMR. Explain HOMOCOSY and HETROCOSY.

(5 × 2 = 10)

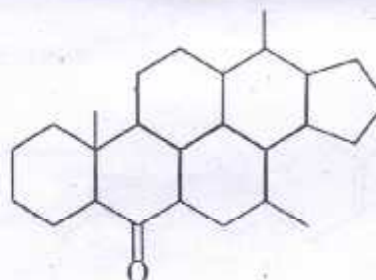
Section C

Answer any **two** questions.
Each question carries a weight of 5.

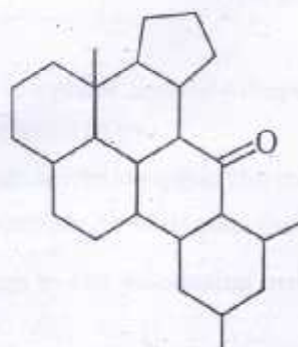
22. (a) Write down the fragmentation pattern for the following compounds and suggest the probable mass spectra peaks : (1) n-Hexyl benzene ; (2) 2-Hexanol.
- (b) What are Meta stable peaks ? How they are identified in mass spectra. Explain the formation of a broad peak at 46.4 in the mass spectrum of Toluene.
23. The phyto toxic fungal metabolite Pyrenocine (Molecular formula- $C_{11}H_{14}O_4$) had IR absorptions at 3410, 1710 and 1640 cm^{-1} and an intense UV absorption at 284 nm. It possessed 1H NMR signals at δ_H 1.71 (3H, d, $J = 5.5$ Hz), 2.31 (3H, S), 2.64 (1H, exchanged on shaking with D_2O), 3.86 (3H, S), 5.15 (1H, d, $J = 7H_z$), 5.50 (1H, S), 5.6 (1H, d, $J = 15.5 H_z$ of q, $J = 5.5 H_z$) and 5.75 (1H, d, $J = 15.5 H_z$ of d, $J = 7H_z$). Irradiation of the signal δ_H 1.71 collapsed the multiplet at δ_H 5.60 to a doublet ($J = 15.5 H_z$) and irradiation of the signal at δ_H 5.15 collapsed the signal at 6115.75 to a doublet ($J = 15.5 H_z$). The signal at δ_H 5.15 received nuclear Overhauser effect enhancements on irradiation of the signal δ_H 2.31 and 3.86, but the signal at δ_H 5.50 only received an enhancement from irradiation at δ_H 3.86. Suggest a structure for Pyrenocine.
24. State and explain "Octant Rule" Apply this rule and draw the octants for the following compounds and predict the sign of their optical activity



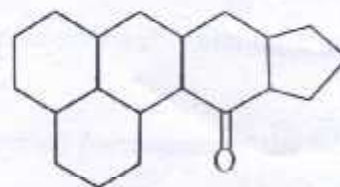
(1)



(2)



(3)



(4)

Turn over

25. A natural product A (MF $C_{11}H_{14}O_5$) had IR absorption at 3400 and 1600 cm^{-1} and UV absorption at 260 nm . It showed ^1H NMR signals at δ_{H} 1.03 (3H , d, $J = 7\text{ Hz}$), 2.60 (2H , broad, s, exchangeable with D_2O), 3.74 (1H , quintet, $J = 7\text{ Hz}$), 3.90 (3H , s), 4.20 (1H , d, $J = 7\text{ Hz}$), 5.95 (2H , s), and 6.55 (2H , s). Irradiation at δ_{H} 1.03 collapsed the signal at δ_{H} 3.74 to a doublet ($J = 7\text{ Hz}$). Oxidation of A with Sodium Iodate gave B (MF $C_9H_8O_4$) which showed IR absorption at 1690 and 1600 cm^{-1} . Compound B had ^1H NMR signals δ_{H} 3.90 (3H , s), 5.95 (2H , s), 7.30 (2H , s) and 9.85 (1H , s). There was a NOE enhancement of the signal at δ_{H} 7.30 on irradiation of the signal at 9.85 . Suggest a structure for the compounds A and B.

(2 × 5 = 10)