

UNIVERSITY OF RUHUNA
BACHELOR OF SCIENCE SPECIAL DEGREE LEVEL I (SEMESTER II)
EXAMINATIONS - DECEMBER 2017

SUBJECT: CHEMISTRY

COURSE UNIT: CHE 4213 (Advanced Organic Chemistry)

TIME: Three (03) hours

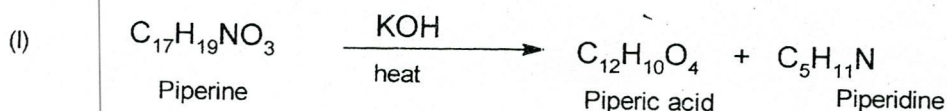
Answer **ALL** the Questions

01 Answer **all** parts.

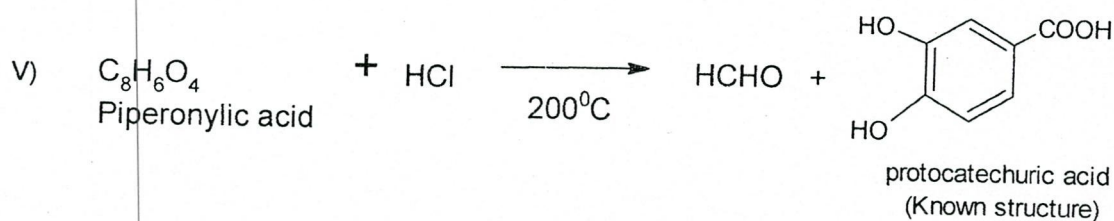
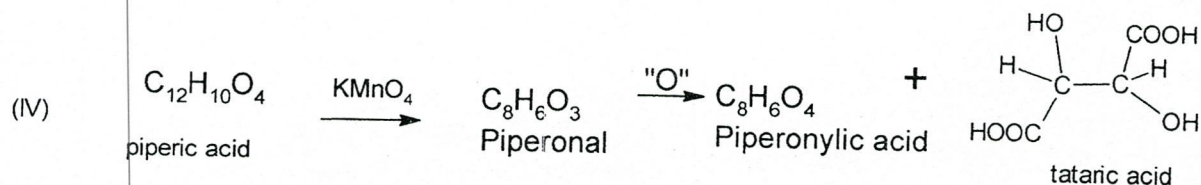
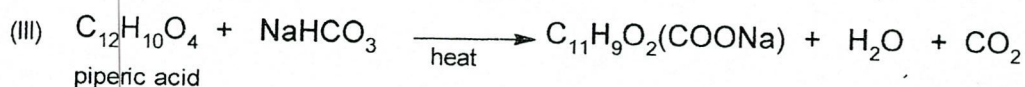
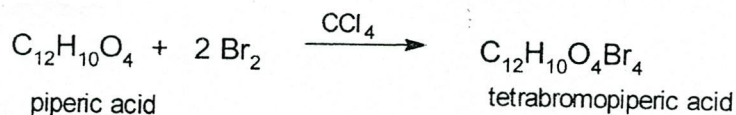
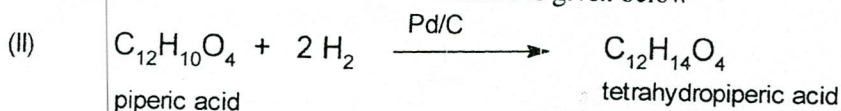
- (a) (i) Name **four (04)** sources of natural products.
 (ii) Give examples for functions of natural products biosynthesized in different sources.
 (iii) What are the principles applied in the extraction of natural products?
 (iv) What is "supercritical fluid extraction", state the advantages of applying it in natural product extraction process?

(25 marks)

- (b) Piperine ($C_{17}H_{19}NO_3$) and chavicine are main alkaloids present in black pepper. Piperine and chavicine are geometrical isomers. The given below are the chemical tests and the analyses of results during the structure determination of piperine.



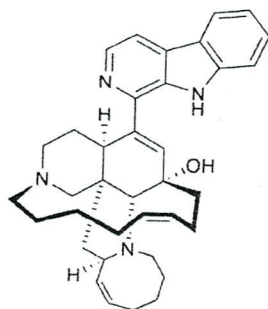
Piperic acid is known to possess *trans-trans* arrangement and the chemical analyses carried out for piperic acid in order to determine its structure is given below



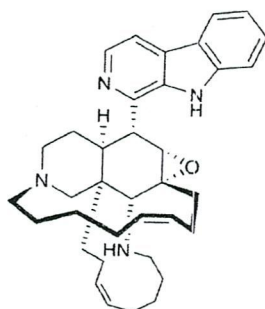
- (i) By analyzing above results of chemical analyses, suggest a structure for piperic acid.
- (ii) After knowing the structure of piperic acid, give the structure of piperine, giving reasoning.
- (iii) Using the structure of piperic acid proposed by you, explain the chemistry of the reactions given in (iv) and (v) above.
- (iv) Suggest possible structure(s) for chavicine which is a geometrical isomer of piperine.

(50 marks)

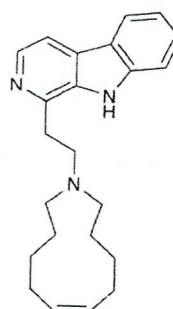
- (c) Manzamine alkaloids are novel marine alkaloids. According to the structural variety, many manzamine alkaloids are reported. The structures of a few manzamine alkaloids are shown below:



(+)-Manzamine A



(+)-Manzamine B



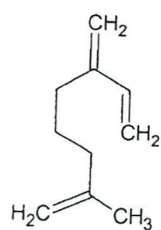
(+)-Manzamine C

- (i) Give five (05) pharmacological effects of manzamine alkaloids.
- (ii) When considering the structures of the manzamine alkaloids given above, what is the common structural feature of them?

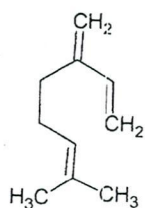
(25 marks)

02 Answer **all** parts.

- (a) Mycene is a simple monoterpene with the molecular formula $C_{10}H_{16}$. The structure of mycene could be either **A** or **B** given below;



A

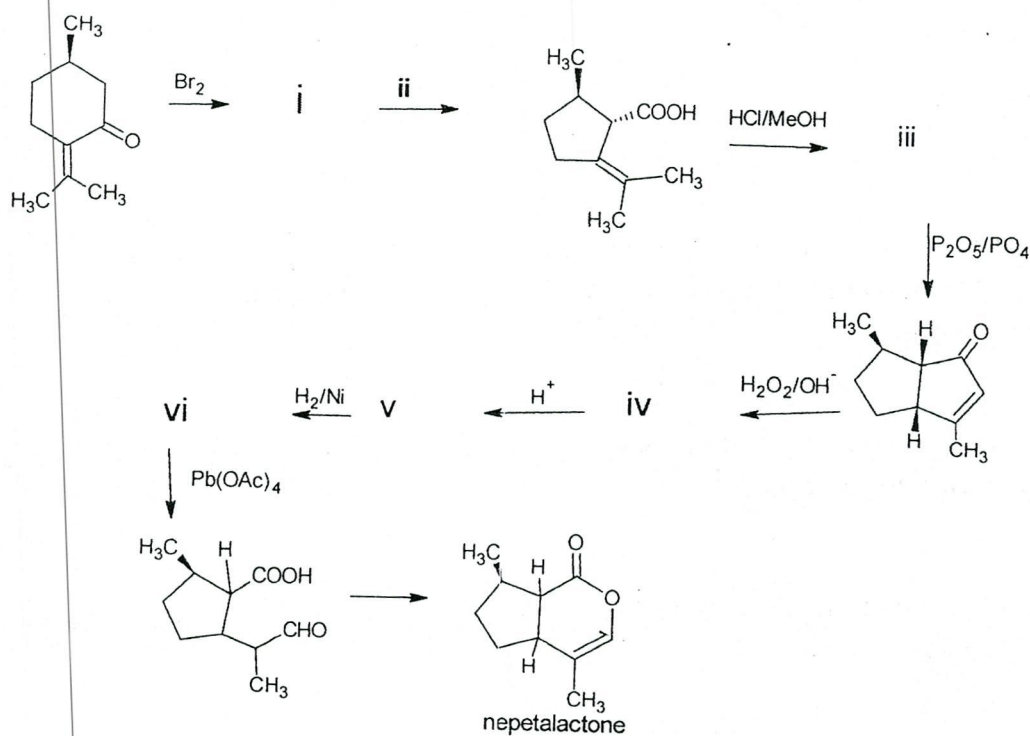


B

- (i) Give a chemical test to identify unsaturated nature of mycene.
- (ii) Specify a chemical test to identify number of double bonds present in **A** and **B**.
- (iii) How can the result of ozonolysis under reducing condition be applied to identify the correct structure of mycene as the structure **B** out of the two structures given above.

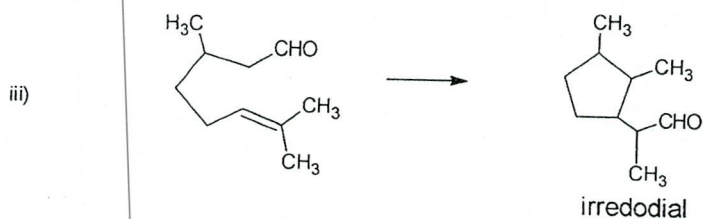
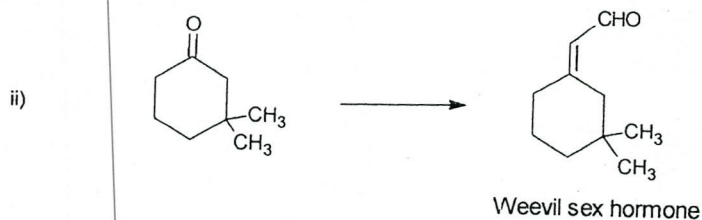
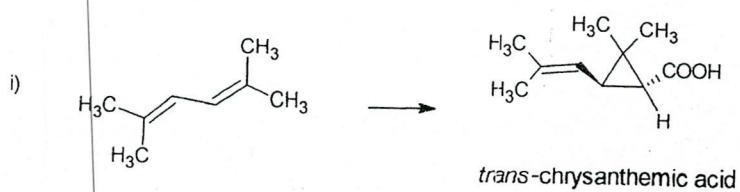
(28 marks)

- (b) Using pulegone as the starting compound, a synthetic scheme for cyclopentano-monoterpenes, nepetalactone is given below. Complete the synthesis by giving missing reagents and the intermediates formed (i-vi).



(42 marks)

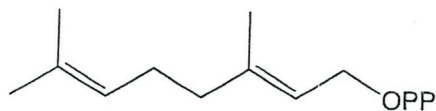
- (c) Indicating the necessary reagents and intermediates formed, show how you would transform starting compound to the given terpene in each case.



(30 marks)

03 Answer **all** parts.

(a) Geranyl pyrophosphate (GPP) is the precursor to most monoterpenes.



Geranyl pyrophosphate

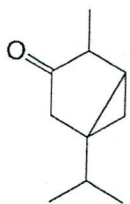
(i) “The different reactivity of the two isomers, Isopentyl^{en} pyrophosphate (IPP) and Dimethylallyl pyrophosphate (DMAPP) are the basis of terpenoid biosynthesis.” Explain this statement using IPP and DMAPP structures.

(12 marks)

(ii) Giving suitable mechanism show how Geranyl pyrophosphate (GPP) is formed from biological isoprene units.

(18 marks)

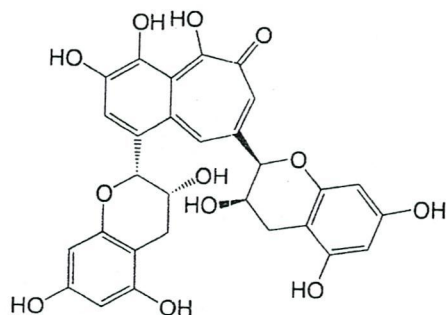
(iii) Outline a synthetic pathway for the synthesis of bicyclic monoterpene thujone, from GPP via α -terpinyl cation.



thujone

(25 marks)

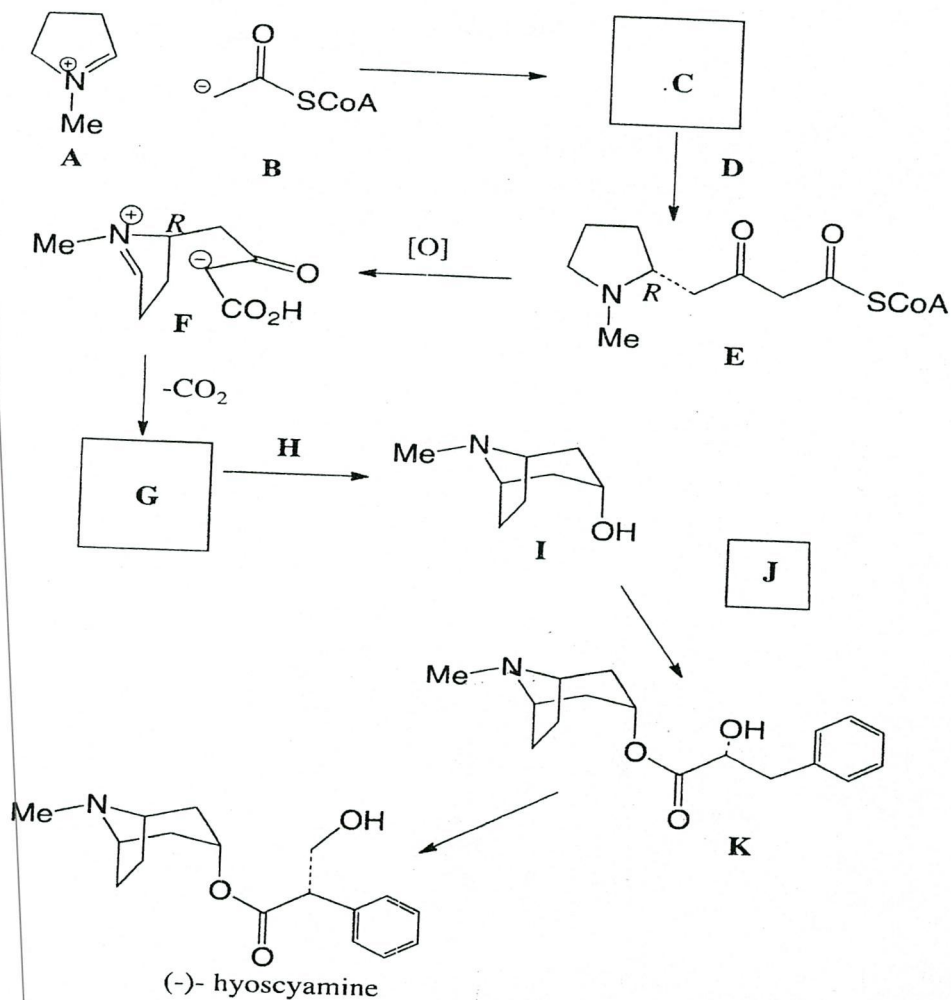
(b) **Theaflavin**, an antioxidant found in fermented tea is a dimeric catechin (a flavan-3-ol) structure in which oxidative processes have led to the formation of a seven-membered tropolone ring. Write down the structure of catechin that dimerized to form theaflavin



theaflavin

(10 marks)

(c) The biosynthetic pathway for (-)-hyoscyamine from Δ^1 -pyrolium cation is given below.



- Draw the structures of missing intermediates and reagents **C**, **D**, **G**, **H** and **J**.
- What other reaction take place, in addition to the oxidation of pyrrolidine ring from **E** to **F**.
- Write down the mechanism for the formation of **I** from **G**

(35 marks)

04 Answer **all** parts.

(a) Explain briefly the following pertaining to NMR spectroscopy.

(i) Fourier transformation

(10 marks)

(ii) Polarization transfer

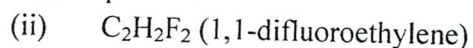
(10 marks)

(iii) First order spin system

(10 marks)

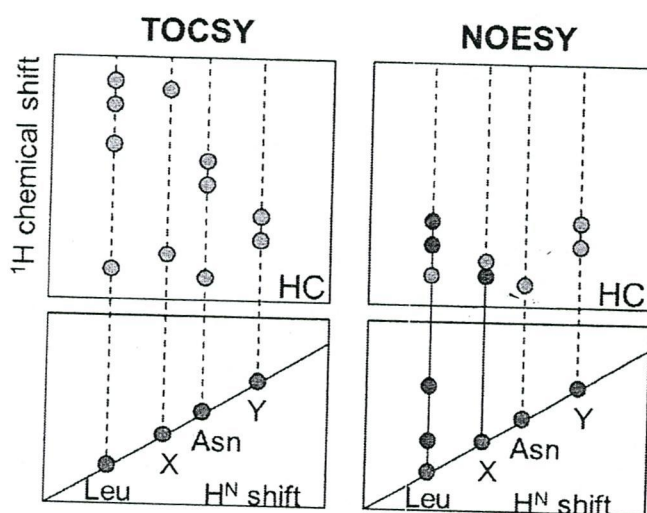
(b) Derive the resultant magnetization at each stage after applying two consecutive 90°_x pulses followed by two 90°_y pulses, and finally 180°_x pulse for the magnetization on z-axis (I_z).
(15 marks)

(c) Discuss briefly the ^1H NMR spectra that would be obtained for the following molecules taking into account the chemical and magnetic equivalence of protons.



(20 marks)

(d) Slices of 2D TOCSY and 2D NOESY spectra given below represent the amino acids Ala, Asn, Gly and Leu.



(i) Giving reasons assign Ala and Gly for the respective lines of the peaks, X and Y, using the TOCSY spectrum.

(15 marks)

(ii) Of the above four amino acids, identify the order of amino acids of a tripeptide using the given NOESY and TOCSY spectra. Explain.

(20 marks)

05 Answer all parts.

(a) (i) What is the important difference between hard ionization and soft ionization used in mass spectroscopy?

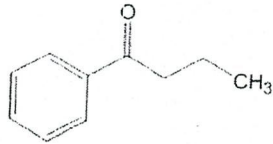
(ii) Name four types of ionization methods commonly used in mass spectrometry

(iii) Classify each as either a “hard” or “soft” ionization method.

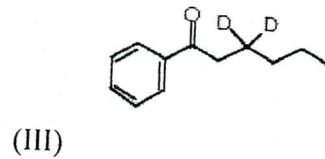
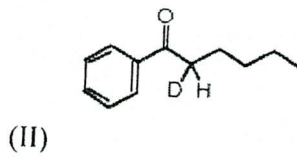
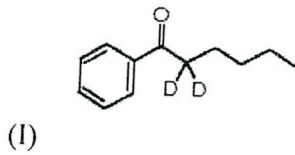
(iv) What is the source of ionization for the each method mentioned above?

(25 marks)

- (b) (i) Draw the structure of the McLafferty rearrangement fragment(s) that the following compound will produce during mass spectrometry: Also draw the mechanism of the McLafferty rearrangement

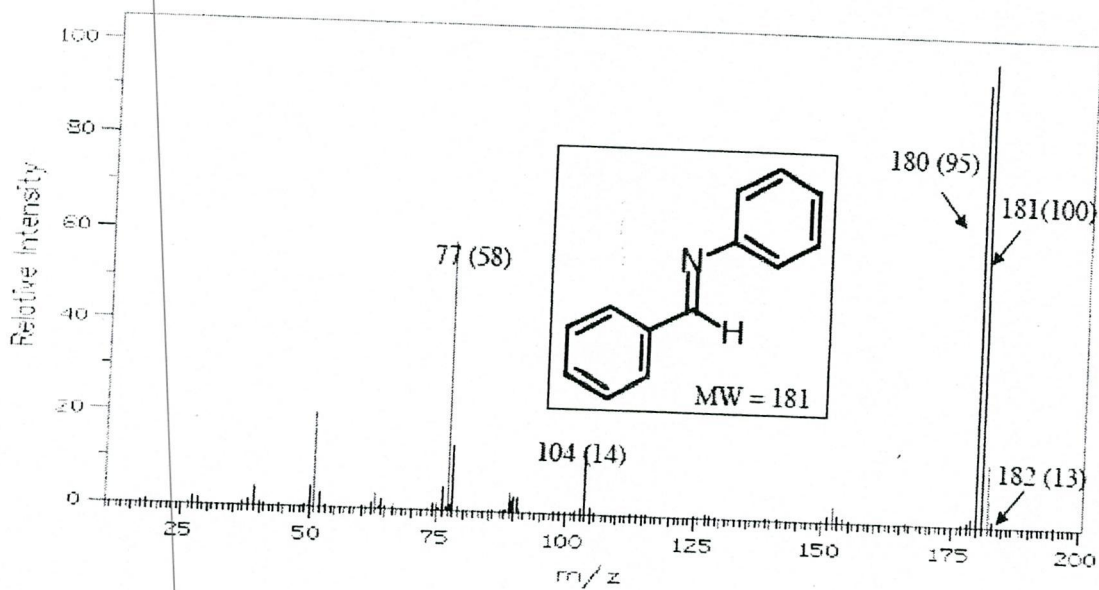


- (ii) How the following isomeric compounds would be differentiated by mass spectrometry using their McLafferty rearrangement fragment ions.



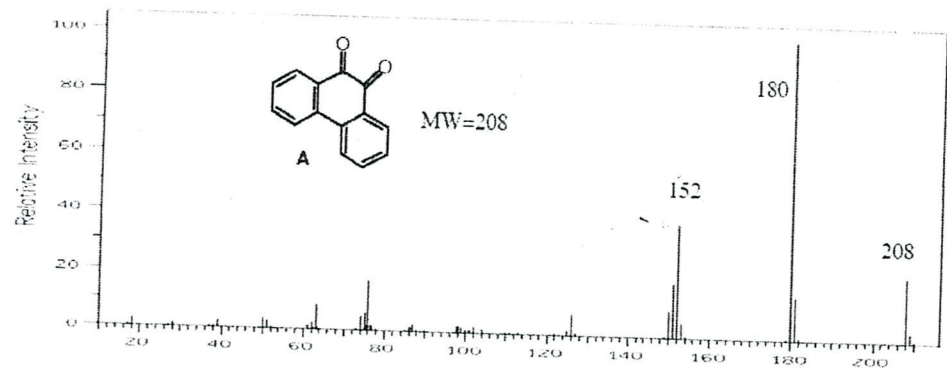
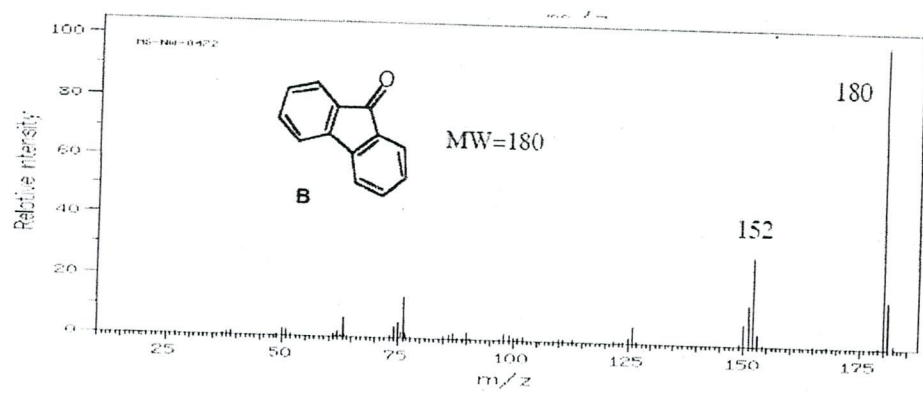
(25 marks)

- (c) Draw structures and explain how the indicated fragments are observed in the mass spectrum of the following compound.



(25 marks)

(d) The mass spectra of the compounds **A** and **B** are shown below. They are nearly identical, except for the additional peak at 208 in the spectrum of **A**. Explain why and assign the labeled peaks in the mass spectrum to corresponding fragments



(25 marks)

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