

**UNIVERSITY OF RUHUNA**  
**BACHELOR OF SCIENCE SPECIAL DEGREE LEVEL I (SEMESTER II)**  
**EXAMINATIONS – DECEMBER 2021**

**SUBJECT: CHEMISTRY**

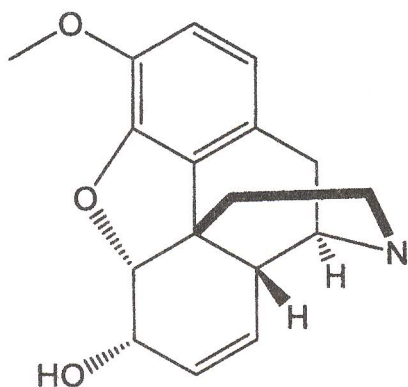
**COURSE UNIT: CHE 4213 (Advanced Organic Chemistry I) TIME: Three (03) hours**

Answer **all** the Questions

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01. Answer **all** parts.

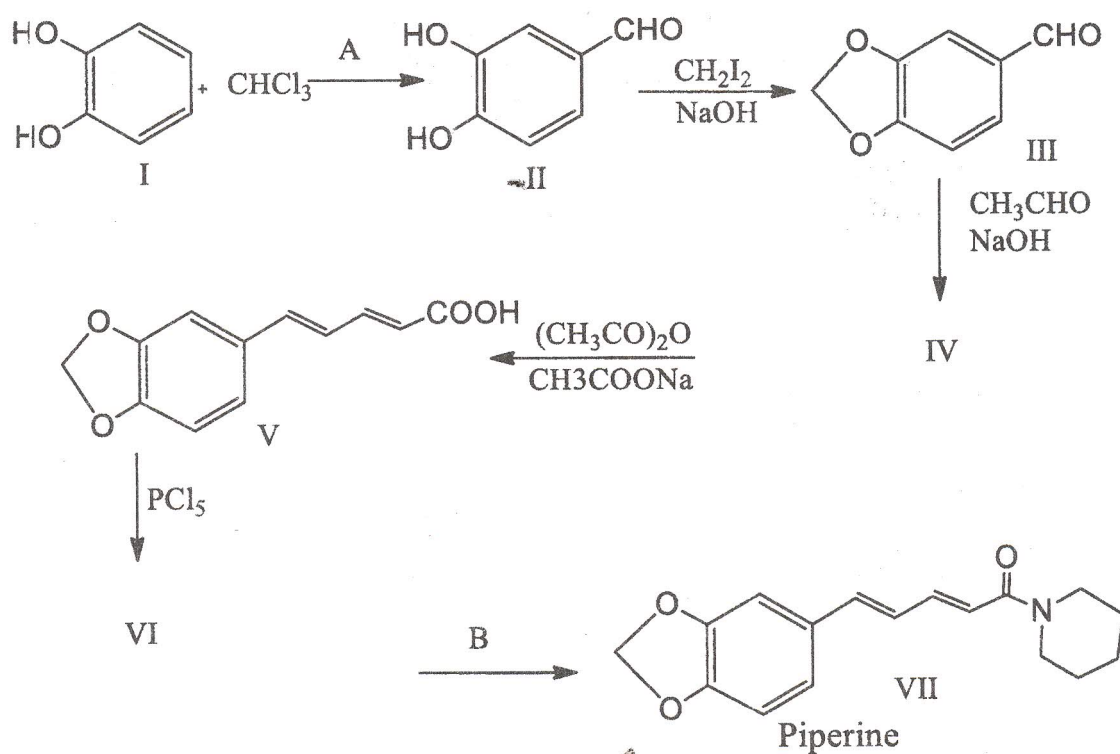
- (a) Alkaloids have remarkable physiological actions on humans and other animals upon administration, thus considered as medicinally important natural products.
- (i) Classify alkaloids based on its chemical structure and write down an example for each category.
  - (ii) Write the basic steps involved in extraction of alkaloids from plant parts and state the significances of each step based on alkaline nature.
  - (iii) Codeine, the structure given below, is considered as a prodrug and less potent than its active analgesic agent. Explain.



codeine

(35 marks)

- (b) Piperine, one of the main constituents in black pepper can be synthesized in laboratory following the given procedure.



- Write down the reagents **A**, **B** chemical structures **IV** and **VI**.
- Draw a plausible mechanism for the conversion of **III** to **IV**.
- Discuss four chemical analyses with expected results to evaluate the structural features (functional groups, unsaturation etc.) of piperine.

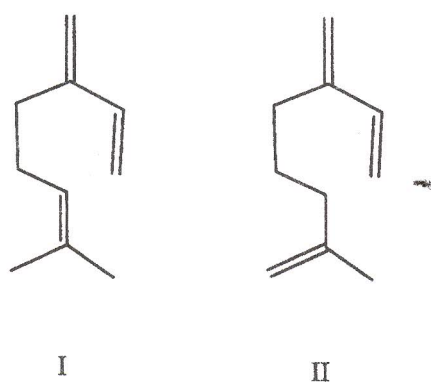
(45 marks)

- (c) Chromatography is one of the widely used techniques for analysis and purification of bioactive components from natural products. Discuss the underline principles of Thin Layer Chromatography (TLC) and Column chromatography.

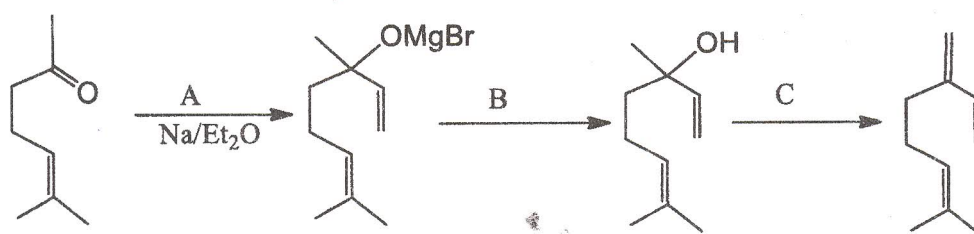
(20 marks)

02. Answer **all** parts.

- Enfleurage (extraction by using fat) is a technique use for the extraction of volatile oil in perfume industry. Briefly explain the process used in the enfleurage.
  - Giving appropriate chemical reactions, explain a chemical method that can be used to differentiate the two isomeric forms (I & II) of terpenes (MW  $C_{10}H_{16}$ ) given below.



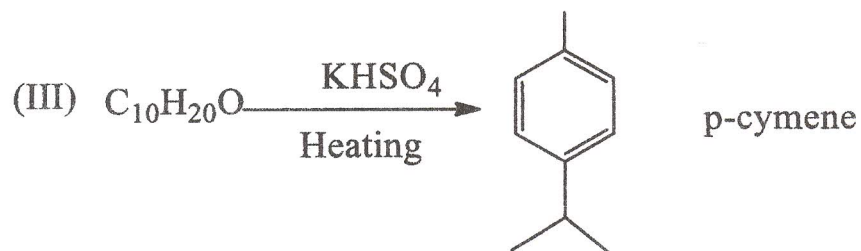
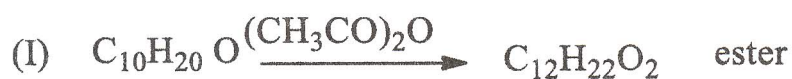
(iii) Fill the missing reagents in the conversion given below for the synthesis of isomer I.



(40 marks)

(b) Menthol is a cyclic monoterpenoid and naturally occurring in peppermint oil. The following data were obtained for its structure elucidation process.

Molecular formula :  $C_{10}H_{20}O$

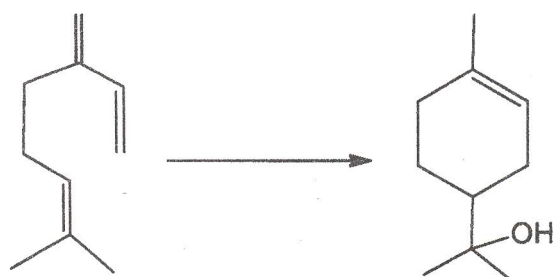


- (i) Based on above experimental data propose a structure for menthol.  
 (ii) Using the proposed structure explain the experimental data above with appropriate structures.

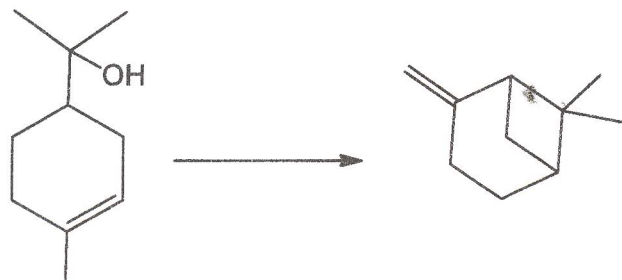
(40 marks)

(c) With necessary chemical reagents and intermediates show how you would carry out following transformations.

(i)



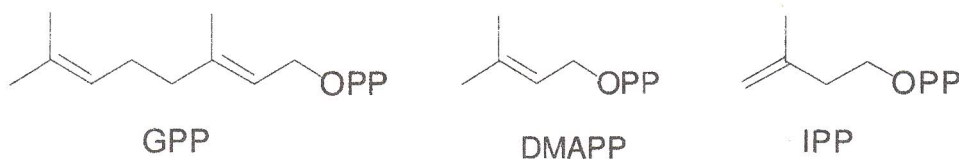
(ii)



(20 marks)

03. Answer **all** parts.

(a) Geranyl pyrophosphate (GPP) is the precursor for the majority of monoterpenes and it is formed by the combination of two isomers, isopentenyl pyrophosphate (IPP) and dimethylallyl pyrophosphate (DMAPP).



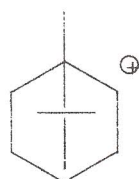
- (i) Using basic concepts of Organic Chemistry, explain the characteristic behaviors of DMAPP and IPP in the biosynthesis of terpenes.

(10 marks)

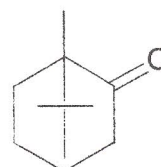
(ii) Giving a suitable mechanism show the formation of GPP from DMAPP and IPP.

(10 marks)

(iii) Giving appropriate chemical structures, explain the biosynthetic pathway for production of camphor from GPP *via* bornyl cation.



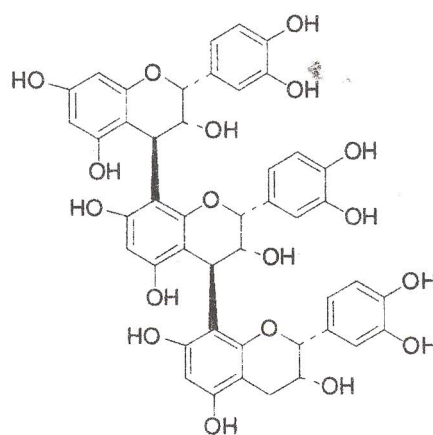
bornyl cation



camphor

(10 marks)

(b) The epicatechin trimer shown below is a condensed tannin which contributes to astringency in our foods and drinks.



epicatechin trimer

(i) Write down the structure of catechin that polymerizes to form epicatechin trimer.

(10 marks)

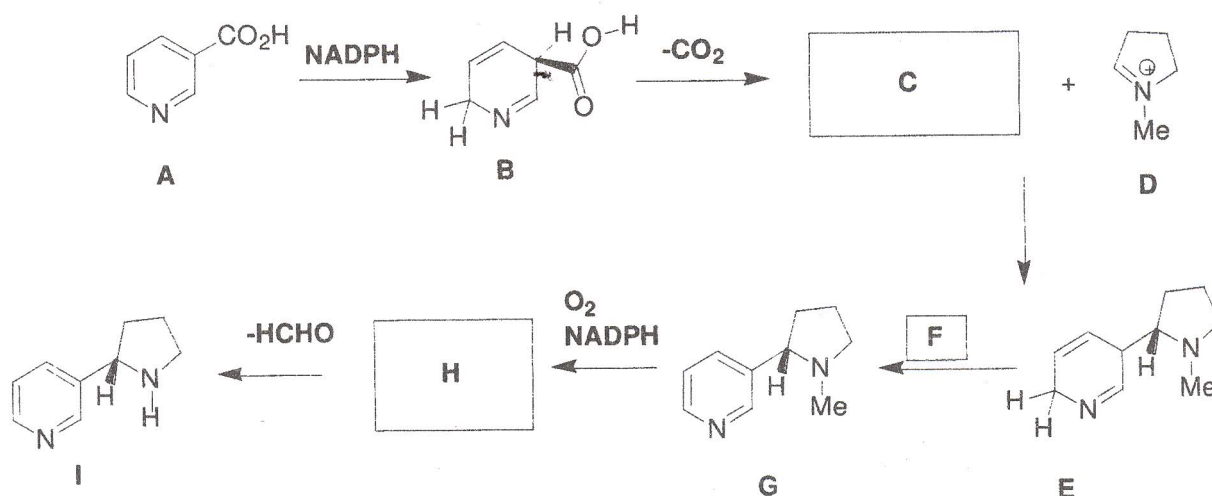
(ii) What are the precursors for the biosynthesis of catechin?

(10 marks)

(iii) Write down the first step of the biosynthesis pathway of catechin using the above precursors.

(10 marks)

(c) The biosynthetic pathway for nornicotine (I) from nicotinic acid (A) is given below.



(i) Draw the structures of the missing intermediates C and H.

(10 marks)

(ii) Name the transformation that takes place from E → G.

(05 marks)

(iii) Name the biological reagent(s) (F) involved in the conversion of E → G.

(05 marks)

(iv) Write down the mechanism for the formation of E from A.

(20 marks)

04. Answer **all** parts.

(a) Briefly describe the following terms related to <sup>1</sup>H NMR spectroscopy.

(i) Scalar coupling or J-coupling.

(10 marks)

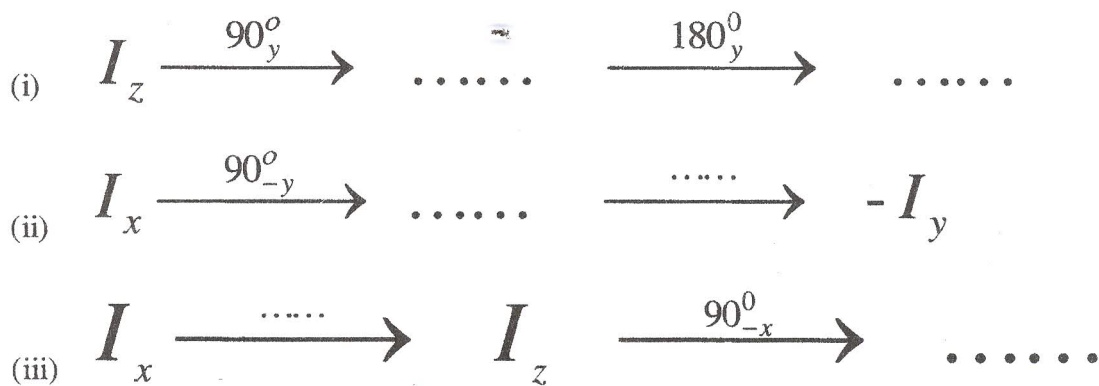
(ii) First order spin system or first order spectrum.

(10 marks)

(b) The splitting patterns of AMX spin system differ from AX<sub>2</sub> spin system. Justify this statement using suitable stick diagrams.

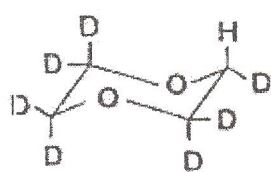
(20 marks)

(c) Fill the following blank positions with the suitable operation or correct component of net magnetization.

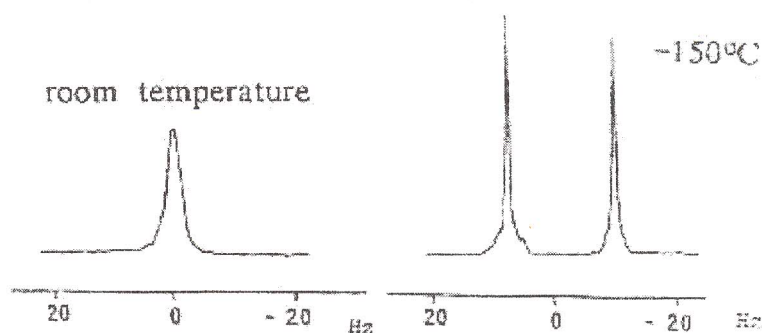


(15 marks)

(d) The  $^1\text{H}$  NMR spectrum of 1,4-dioxan-d7 consists of a singlet at room temperature (with broadband decoupling of  $^2\text{H}$ ). However, it gives two singlets of equal intensity at  $-150^\circ\text{C}$ . Using your knowledge on conformational mobility of 6-membered rings, explain briefly why the room temperature and low temperature spectra appear as follows.



1,4-dioxan-d7



(20 marks)

(e) Two-dimensional NMR spectroscopy provides more information about a molecule than one-dimensional NMR spectroscopy and they are especially useful in determining the structure of a molecule.

Explain briefly the use of 2D COSY and 2D TOCSY techniques in NMR spectroscopy.

(25 marks)

05. Answer **all** parts.

- (a) Consider the fragmentary spectral data sets (i) and (ii) given below and assign a reasonable elemental composition for each. Calculate the double bond equivalent for each elemental composition you proposed.

**Note:** Natural isotopic abundances of a few common elements are given in the table below.

(i)

m/z	Relative Abundance
43	100
78	23.6
79	1.00
80	7.55
81	0.25

(ii)

m/z	Relative Abundance
130	0.3
131	0.6
132	28.6
133	2.8
134	0.2

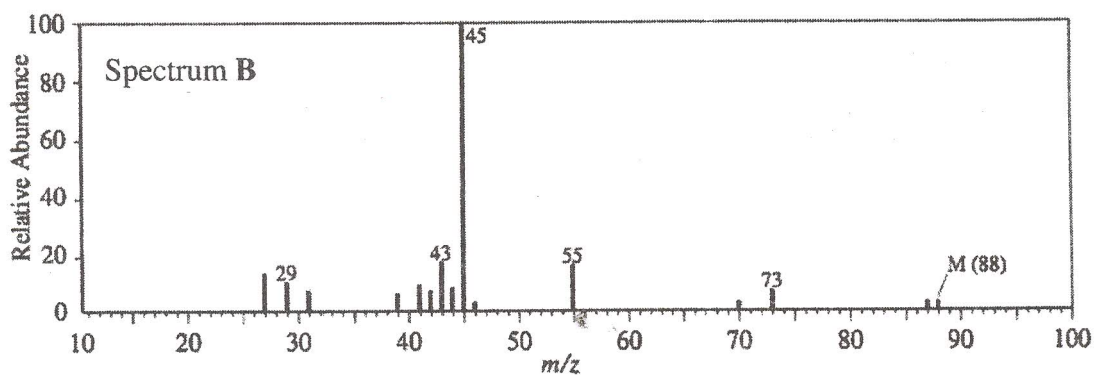
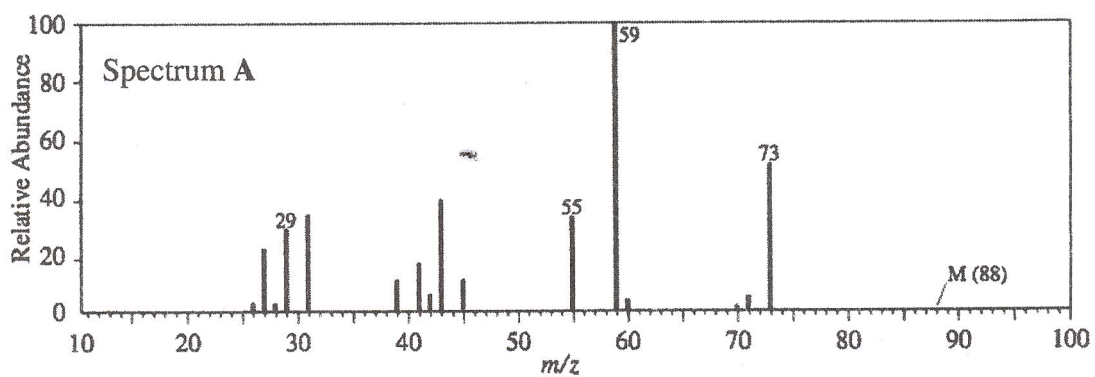
Element	A		A + 1		A + 2		Element type
	Mass	%	Mass	%	Mass	%	
H	1	100	2	0.015			"A"
C	12	100	13	1.1 <sup>a</sup>			"A + 1"
N	14	100	15	0.37			"A + 1"
O	16	100	17	0.04	18	0.20	"A + 2"
F	19	100					"A"
Si	28	100	29	5.1	30	3.4	"A + 2"
P	31	100					"A"
S	32	100	33	0.79	34	4.4	"A + 2"
Cl	35	100			37	32.0	"A + 2"
Br	79	100			81	97.3	"A + 2"
I	127	100					"A"

(20 marks)

- (b) Mass spectra A and B given below were obtained for the constitutional isomers 2-pentanol and 2-methyl-2-butanol.

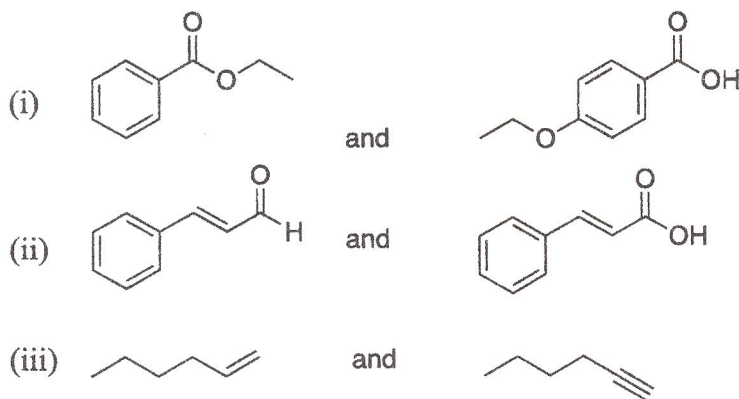
- Giving reasons assign each of the two spectra to 2-pentanol and 2-methyl-2-butanol.
- Give the possible structures for fragments with m/z: 73, 59, 55, and 45.
- Draw plausible mechanisms for the formation of all **four** fragments above.





(45 marks)

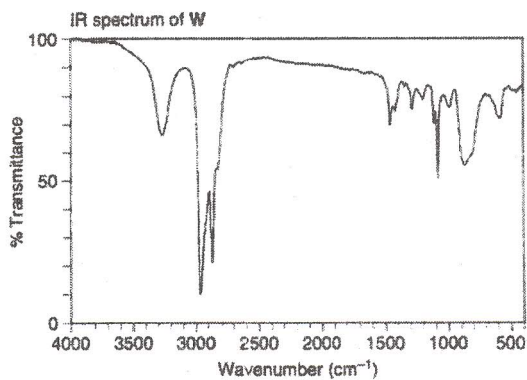
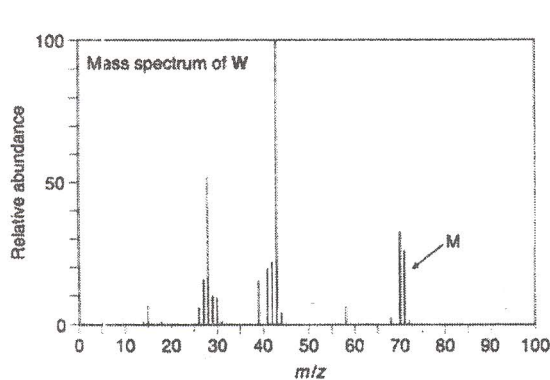
(c) Explain how you would distinguish the following pairs of molecules using IR spectroscopy.



(15 marks)

(d) Reaction of  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  with  $\text{NaH}$  forms compound **W**, which gives the IR and mass spectra shown below.

- (i) Giving reasons propose a structure for **W**.
- (ii) Assign two major peaks in each spectrum.



(20 marks)

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