

THE OPEN UNIVERSITY OF SRI LANKA

B.Sc. DEGREE PROGRAMME/ STAND ALONE COURSES 2007/2008

LEVEL 5 – FINAL EXAMINATION

CHU 3130/CHE 5130

209

INTRODUCTION TO NATURAL PRODUCTS CHEMISTRY

TIME 2 ½ HOURS

Date: 23rd January 2008

Time: 9.30 a.m. - 12.00 noon

Answer any four (04) questions only. If more questions are answered only the first four answers will be marked.

1. (a) A student inferred that a sample of plant extract contained triterpenoids and anthroquinones by tlc using spray reagents. Fill the table given below with the spray reagent used and the colour observed by the student.

Class of compound	Spray Reagent	Colour Observed
Triterpenoid		
Anthroquinone		

(12 marks)

(b) (i) 'In biological systems RCOOH forms RCOSCoA in preference to esters of alcohols or anhydrides before undergoing nucleophilic reactions'. Explain the above statement.

(15 marks)

(ii) Complete the following synthetic pathway by providing the missing reagents and products (A - C).

(c) (i) Dissect the terpenoids **D** and **E** into isoprene units. Show the isoprene units bylines. Label the head of the isoprene units with a circle and tail with a rectangle.

(ii) Fill the table given below by writing the number of isoprene units present and the class of terpenoids it belongs to, in column M and N respectively.

Compound	Number of isoprene units M	Class of terpenoids N
D		
E		

(12 marks)

(d) Suggest the mechanism for the following reactions met in the study of terpenoids.

(i)
$$H_2SO_4$$
 OH H_2SO_4 (ii) H_2SO_4

(30 marks)

(e) Give the structures of the products **F** and **G** you would expect from the following reactions.

O (i)
$$ZnBrCH_2CH=CHCO_2C_2H_5$$
 (ii) H^+ (16 marks)

- 2. (a) To improve the properties rubber is vulcanized by heating with sulphur.
 - (i) Give five advantages of the use of vulcanized rubber.
 - (ii) Draw the structure of vulcanized rubber

$$- \begin{bmatrix} -CH_2 & CH_2 \\ C=C \\ H_3C & H \end{bmatrix}_n$$

Natural Rubber

(iii)How does the structure and properties of natural rubber and Gutta – percha differ from each other?

(20 marks)

(b) Zingiberene is the major constituents in ginger oil. Draw the structures of the products $\mathbf{H} - \mathbf{N}$ you would expect when zingiberene reacts with the given compounds.

(30 marks)

(c) Give the biosynthetic pathways leading to the following terpenoids indicating clearly the mechanism of the reactions.

(32 marks)

3. (a) The mechanism of pathway leading to 3-phosphoglyceric acid (3PGA) from ribulose -1,5 - diphosphate has been elucidated using *CO₂. Indicate the steps involved in the biosynthetic pathway and clearly indicate the position of the labeled carbon atom(s) in the PGA formed.

Ribulose-1,5-diphosphate

(25 marks)

(b) (i) The biosynthetic pathway leading to citric acid by the citric acid cycle is shown below. If \(^{14}CH_3COCO_2\) is used to study the mechanism of the path way indicate the position of the C atom labeled with \(^{14}C\) in the citric acid formed (Use *C to show \(^{14}C\) labeled atom). Draw the structures of the missing compounds **O** and **P**.

$$CH_3COCO_2$$
 + O \longrightarrow $CH_3COSCoA$ $\stackrel{\mathbf{P}}{\longrightarrow}$ $HO-C-CO_2$ CH_2CO_2

(14 marks)

(ii) Give the benefits of the citric acid cycle.

(16 marks)

- (c) Explain briefly what is meant by the following terms.
 - (i) Pre-infectional allomones.
 - (ii) Alarm pheromones

(10 marks)

(d) Complete the glycolysis pathway by drawing the structures of the missing compounds $\mathbf{Q} - \mathbf{V}$. If glucose labeled with ¹⁴C (*C) at C-6 is used in the study, indicate the position of labeling in the pyruvic acid formed.

(35 marks)

4. (a) 5β-cholanic acid was subjected to Barbier-Wieland degradation.

5ß-cholanic acid

- (i) Give the structure of the product.
- (ii) Indicating the appropriate reagents, give the reactions involved in the Barbier-Wieland degradation.

(30 Marks)

(b) Squalene undergoes oxidation and series of ring closure reactions and backbone rearrangements to form lanosterol. Show the reactions and mechanism that converts squalene to lanosterol.

(c) Show how the methyl group at C-14 of lanosterol is lost during the formation of cholesterol.

(20 Marks)

(d) Explain why only the 3β -hydroxyl group is esterified in the following reaction.

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5. (a) Give the names of following cholestane derivatives.

(15 marks)

(b) Explain why 5α , 6β -dibromocholestrol undergoes elimination with NaI in acetone to give cholesterol faster than 5β , 6α -dibromocholestrol under the same conditions.

(30 marks)

(c) Give the products (showing the appropriate stereochemistry) of the following reactions.

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(30 marks)

(d) Giving necessary reagents and conditions show how **ONE** of the following synthesis is carried out.

(25 marks)

6. (a) Giving molecular structures show the formation of polyketide chain produced from acetyl co-enzyme A and two moles of malonyl co-enzyme A, when 1-¹³C labeled acetate (CH₃¹³CO₂) fed into a plant. (show the ¹³C label in all the structures)

(20 Marks)

(b) Clearly state the basic skeleton giving the appropriate carbon number and the class of each of the following compounds. (See the example).

Example		
	MeQ	MeO
	но	HO—CO ₂ H
Basic skeleton	$C_6 - C_3$	$C_6 - C_3$
Class	Phenyl propene	Hydroxycinnamic acid

(20 Marks)

(c) Give the biosynthetic pathways leading to trihydroxyacetophenone, orcellinic acid and 6-methylsalicylic acid starting from the polyketide **P**.

(30 Marks)

(d) Explain how aspirin (Acetyl salicylic acid) reduces pain.

Acetylsalicylic acid

(30 Marks)