105

THE OPEN UNIVERSITY OF SRI LANKA

B. Sc DEGREE PROGRAMME / STAND ALONE COURSE 2006 / 2007

LEVEL 5 - FINAL EXAMINATION

CHU 3131 / CHE 5131

THE CHEMISTRY OF AMINO ACIDS, SUGARS AND RELATED COMPOUNDS

DURATION: 2 1/2 HOURS

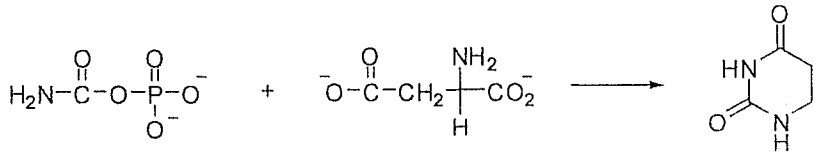
Monday 25th June 2007 1.30 - 4.00 p.m.

Answer any FOUR (04) questions only.
If you have answered more than four questions, only the first four answers will be marked.

1. (a) Compare and contrast the structural features and functions of RNA and DNA.

(25 Marks)

(b) Biosynthesis of pyrimidine involves the formation of dihydroorotate (**A**). The compound (**A**) is biosynthesized as shown below.

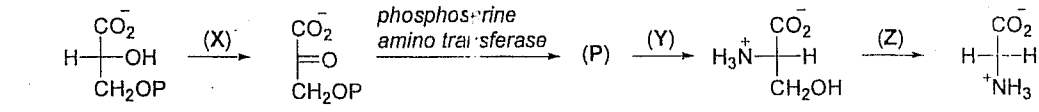


carbamoyl phosphate dihydroorotate (A)

(i) Explain briefly how carbamoylphosphate is formed.
(ii) Indicate the mechanism for the formation of (**A**) in the above reaction

(35 Marks)

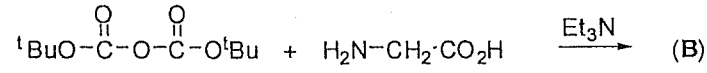
(c) Biosynthetic pathway involved in the formation of glycine is outlined below. Complete the pathway by filling the missing enzymes **X**, **Y** and **Z** and compound **P**.



3-phosphoglycerate glycine

(20 Marks)

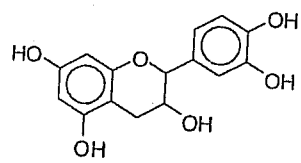
(d) Tertiary butyloxycarbonyl group is used as a protecting group in the synthesis of peptides. This group is introduced to protect the amino group using the anhydride as shown below.



(i) Identify the product **B**.
(ii) Indicate how the above protecting group is removed after synthesizing the peptide.

(20 Marks)

2. (a) Catechin is a flavonoid found in tea. Name the **two** pathways by which catechin is biosynthesized and clearly indicate the rings formed by each pathway.



catechin

(20 Marks)

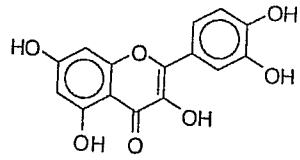
(b) (i) $^{14}CO_2$ was introduced into a plant and labeled malonyl CoA biosynthesized from acetyl CoA was isolated. Indicate the position of the labeled by ^{14}C in the malonyl CoA isolated.

$CH_3COSCoA$
acetyl CoA

$HOOC\text{-}CH_2COSCoA$
malonyl CoA

(10 Marks)

(ii) Labeled malonyl CoA obtained in (i) led to the formation of quercetin in the plant. Indicate the biosynthetic pathway leading to the formation of quercetin. Indicate the carbon atoms labelled by ^{14}C in quercetin isolated.



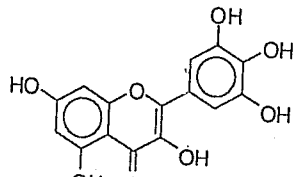
quercetin

(25 Marks)

(c) Explain briefly how coumarins prevent blood clotting.

(10 Marks)

(d) Myricetin (**C**) is a flavonoid. Ethanolic solution of **C** shows a UV absorption band in the region 250 – 270 nm.



myricetin (**C**)

(i) Deduce the effect on the above UV absorption on adding the following compounds.
   (I) Sodium acetate
   (II) Aluminum chloride

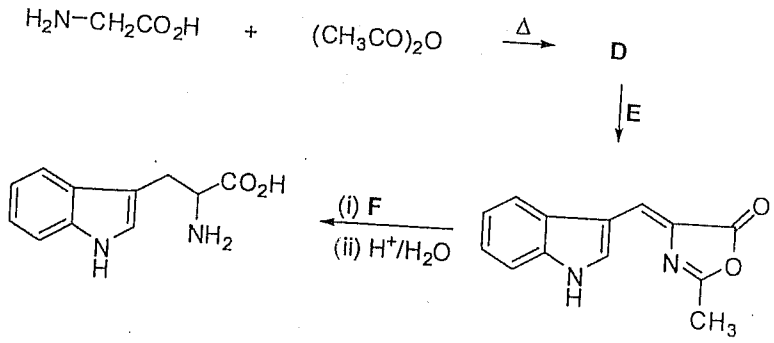
(ii) Explain why the OH group at C-5 of **C** is less acidic than that at C-7.

(iii) Indicate clearly the carbon atoms that contain hydrogen atoms which could show *meta* coupling in the ^1H NMR spectrum of **C**.

(iv) Does the compound **C** react with vanillin in sulphuric acid? Explain briefly.

(35 Marks)

3. (a) Amino acid tryptophane can be synthesized using the reaction scheme given below. Give the structures of the missing compounds **D** – **F** and complete the reaction scheme.



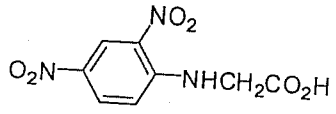
(25 Marks)

(b) (i) Deduce the structure of the pentapeptide **G** from the following data.

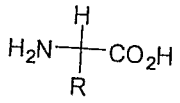
(I) **H**, Ala, Phe, Met and Pro were obtained on hydrolysis of the product obtained by treating **G** with 2,4-dinitrofluorobenzene.

(II) Initially a high concentration of Phe was observed when **G** was reacted with carboxypeptidase.

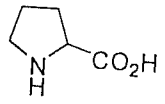
(III) Partial acid hydrolysis of **G** yielded peptides Pro.Phe, Met.Ala and Ala.Pro.Phe.



(**H**)



R = H Gly
= CH_3 Ala
= $C_6H_5CH_2$ Phe
= $CH_3SCH_2CH_2$ Met

Pro = 

(30 Marks)

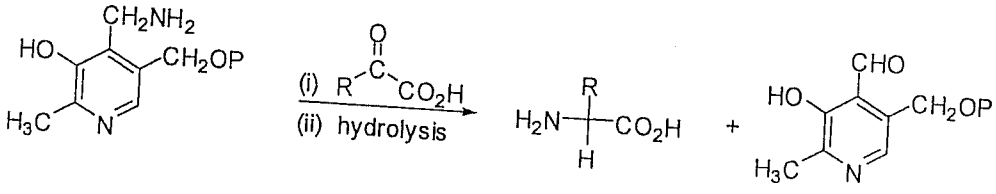
(ii) Explain briefly whether the peptide **G** reacts with cyanogen bromide or not.

(10 Marks)

(iii) Peptide **I** was obtained when **G** was acetylated and permethylated. Deduce the structure of the positively charged ion corresponding to the base peak (m/z= 114) seen in the mass spectrum of **I**.

(20 Marks)

(c) Biological transamination of α-keto acids is shown below. Give the mechanism for the transamination reaction.



(15 Marks)

4. (a) How does D-fructose act as a reducing sugar?

(10 Marks)

(b) Explain using appropriate structures, how when crystalline α-D-Glucose ($[\alpha]_D = +113°$) dissolved in water the specific rotation ($[\alpha]_D$) slowly changes to + 52.5° with time.

(15 Marks)

(c) In the ^{1}H NMR spectra of aldopyranoses and their derivatives, the signal from one proton (C*H*) is found at lower fields than any of the others.

i. Which proton is this and why?

ii. In the ^{1}H NMR spectrum of the two anomers of D-tetra-*O*-acetylxylopyranose the down field peak appear as follows:

Anomer **X**: doublet, δ 5.39, J = 6Hz

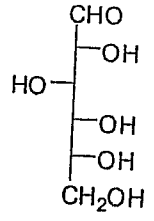
Anomer **Y**: doublet, δ 6.03, J = 3Hz

Identify **X** and **Y**. explain your answer.

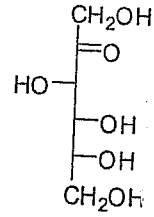
(25 Marks)

(d) (+)-Gentibiose, **J** ($C_{12}H_{22}O_{11}$) gave a silver mirror when treated with Tollens reagent. Complete hydrolysis followed by GLC analysis of alditol acetates showed that **J** contains only glucose. Treatment of (+) gentibiose with MeI in the presence of dimsyl anion gave the product **K**, which upon acid hydrolysis gave 2,3,4,6-tetra-*O*-methyl-D-glucopyranose and 2,3,4-tri-*O*-methyl-D-glucopyranose. ^{1}H NMR spectrum of **K** showed a doublet at δ 4.8 (J = 7.0 Hz) among the other signals, which was assigned to the anomeric proton at the glycoside linkage. Deduce the structure of (+)-gentibiose.

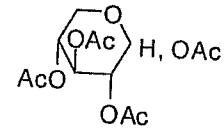
(50 Marks)



D-glucose

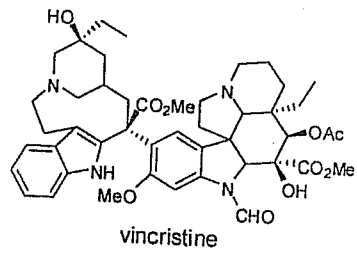


D-fructose

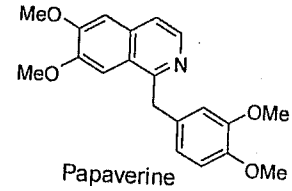


D-tetra-O-acetylxylopyranose

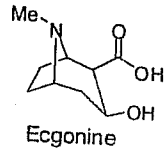
5. (a) Classify the following alkaloids in their groups according to the nucleus present.



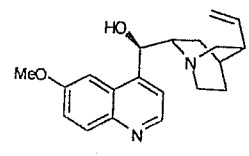
vincristine



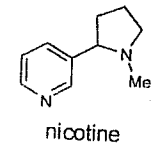
Papaverine



Ecgonine



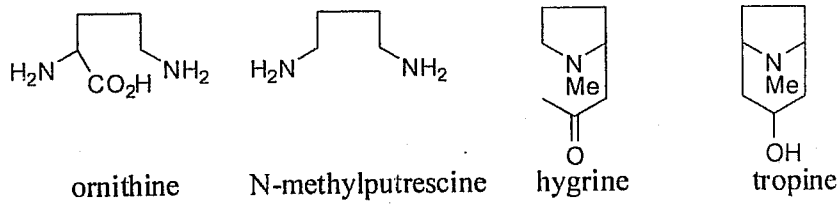
quinine



nicotine

(20 Marks)

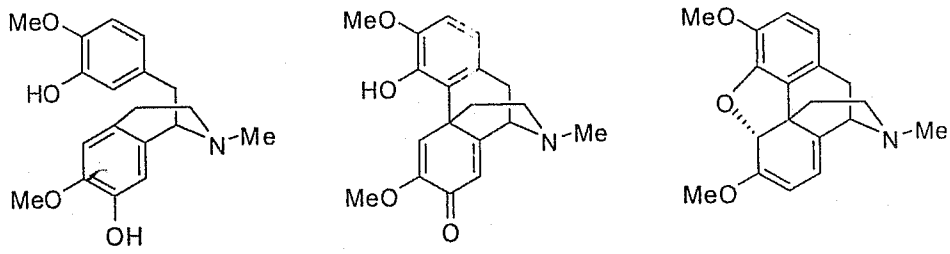
(b) Labeled studies have shown that tropine is biosynthesized from ornithine *via* N-methylputrescine and hygrine. Postulate the possible biosynthetic pathway to tropine.



ornithine N-methylputrescine hygrine tropine

(30 Marks)

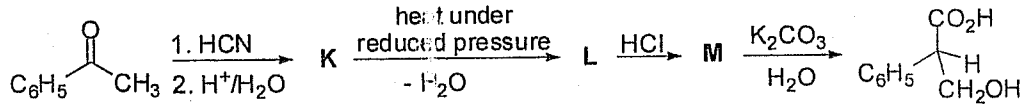
(c) Phenolic oxidative coupling is an important reaction that occurs during alkaloid biosynthesis. Suggest the possible biosynthetic pathway leading to thebaine from reticuline *via* salutaridine.



reticuline salutaridine thebaine

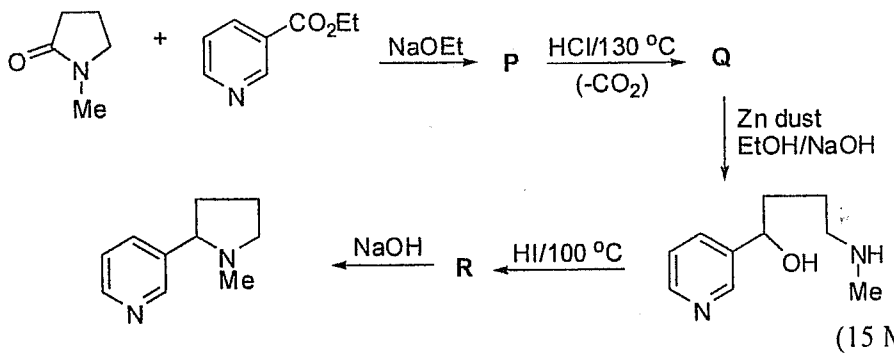
(20 Marks)

(d) i. Reactions involved in the synthesis of tropic acid are given below. Identify the compounds **K** – **M** in the reaction scheme.



(15 Marks)

ii. Reactions involved in the synthesis of nicotine are given below. Identify the compounds **P** – **R** in the reaction scheme.



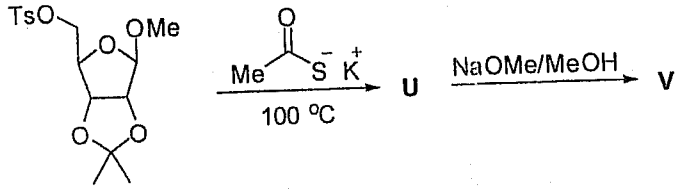
(15 Marks)

6. (a) Both starch and cellulose are made up from D-glucopyranosyl residues. Explain giving appropriate structures, how they differ from each other with respect to their structure and function.

(40 Marks)

(b) Give the structures of **S - V** of the following reaction sequences.

i. D-glucose $\xrightarrow{Br_2/H_2O}$ **S** $\xrightarrow{\text{high temperature}}$ **T**

ii. 

(20 Marks)

(c) Alkaloids are important class of natural products because of their physiological action on humans and animals. Giving five examples (with their structures) illustrate the above statement.

(40 Marks)