UNIVERSITY OF SWAZILAND
SECOND SEMESTER FINAL EXAMINATION 2012

TITLE OF PAPER	:	Advanced Organic Chemistry
COURSE NUMBER	:	C403
TIME	:	Three Hours
INSTRUCTIONS	:	Answer any FOUR Questions. Each Question carries 25 Marks.

This Paper contains Nine (9) pages.

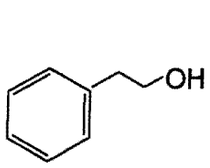
You must not open this paper until the Chief Invigilator so has granted permission to do.

SECTION A

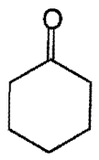
POLYCYCLIC AND HETEROCYCLIC AROMATIC COMPOUNDS

Question 1 **Polycyclic Aromatic Compounds**

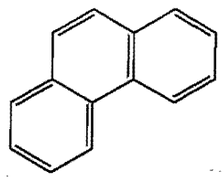
(a) Show a suitable laboratory synthesis of phenanthrene III starting with 2-phenylethanol I and cyclohexanone II and using other suitable reagents. (5 marks)



I

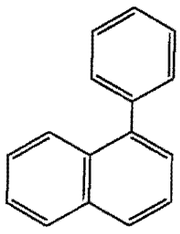


II

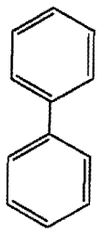


III

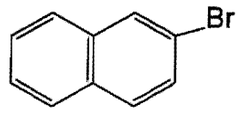
(b) Design a laboratory practical synthesis of each of the following compounds starting with a suitable benzene derivative: [(i) = 7; (ii) = 4; (iii) = 4 marks]



(i)



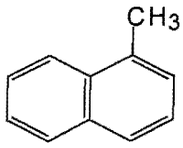
(ii)



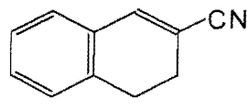
(iii)

(c) Give the expected dominant product or products in mononitration of each of the following compounds. (5 marks)

(i)



(ii)



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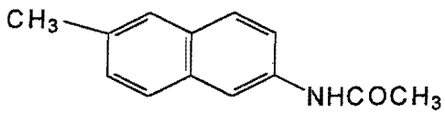

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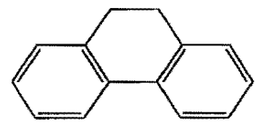
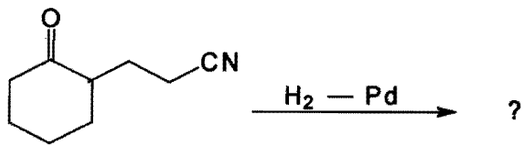


Question 2 **Heterocyclic Aromatic Compounds**

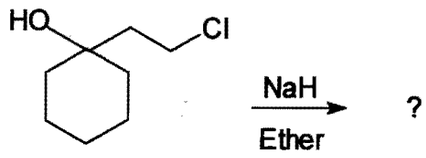
Non Aromatic Heterocycles

(a) Write down the structure of the principal product from each of the following reactions. (6 marks)

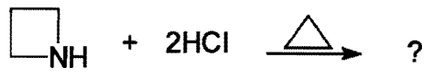
(i)



(ii)



(iii)



Aromatic Heterocycles

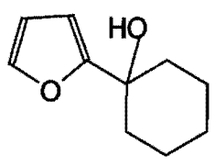
(b) (i) Briefly describe the structure and bonding characteristics in pyrrole and thiophene in terms of orbital hybridization. (2 marks)

Explain the following factual observations:

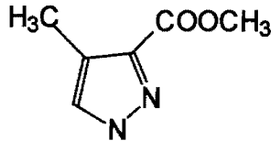
(ii) Pyridine is more basic than pyrrole even though both of them have a lone pair of electrons on nitrogen which can be protonated in an acid-base reaction. (2 marks)

(iii) Thiophene is none aromatic than furan. (2 marks)

(c) Outline a synthesis for each of the following compounds from the corresponding non-heterocyclic reagents or unsubstituted heterpcyclic systems.

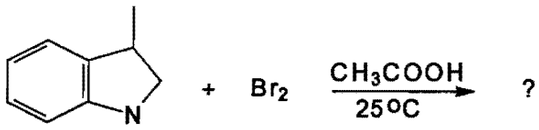


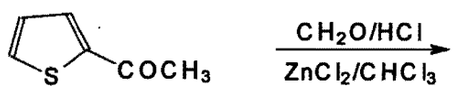
(i) (5 marks)

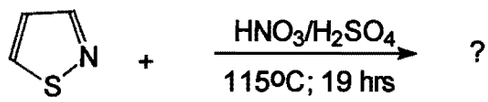


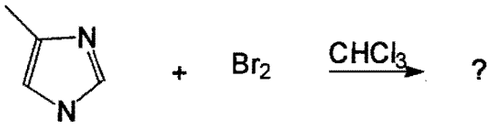
(ii) (2 marks)

(d) Predict the major product expected from each of the following reactions of heterocyclic aromatic compounds. (1½ marks each)

(iii) 

(iv) 

(v) 

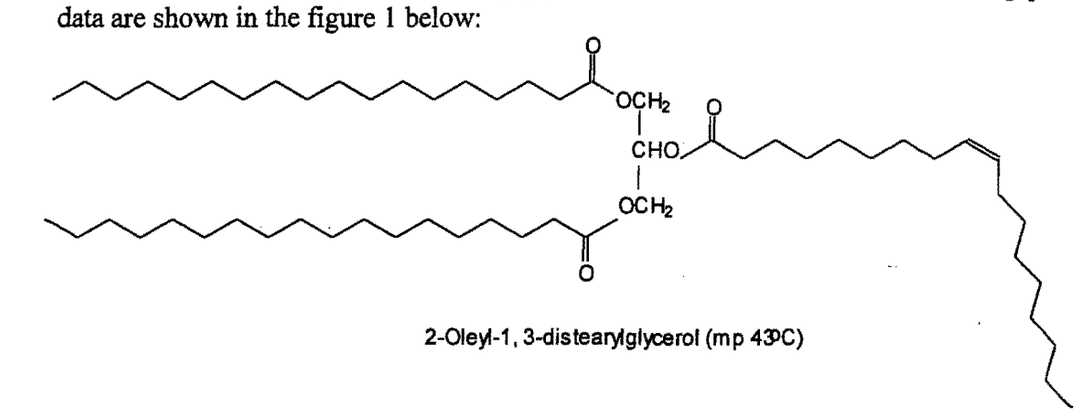
(vi) 

SECTION B

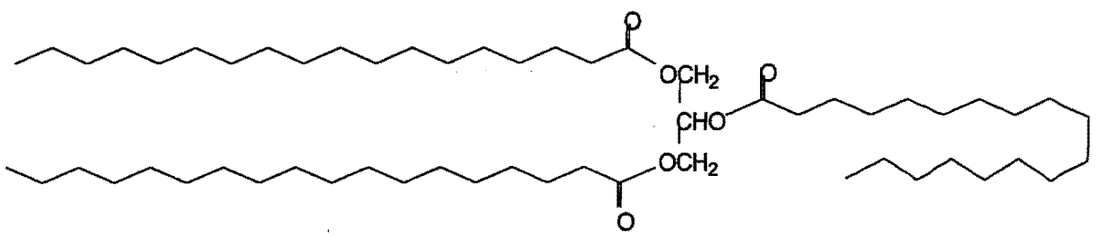
NATURAL PRODUCTS

Question 3 **Fatty Acids and Derivatives**

(a) The structures of 2-Oleyl-1, 3-distearylglycerol and Tristearin, and their melting point data are shown in the figure 1 below:



2-Oleyl-1, 3-distearylglycerol (mp 43°C)



Tristearin (mp 72 °C)

Fig1: The structure of two typical triacylglycerols: 2-Oleyl-1, 3-distearylglycerol and Tristearin and their melting point data.

Study these structures and accordingly, answer questions i and ii.

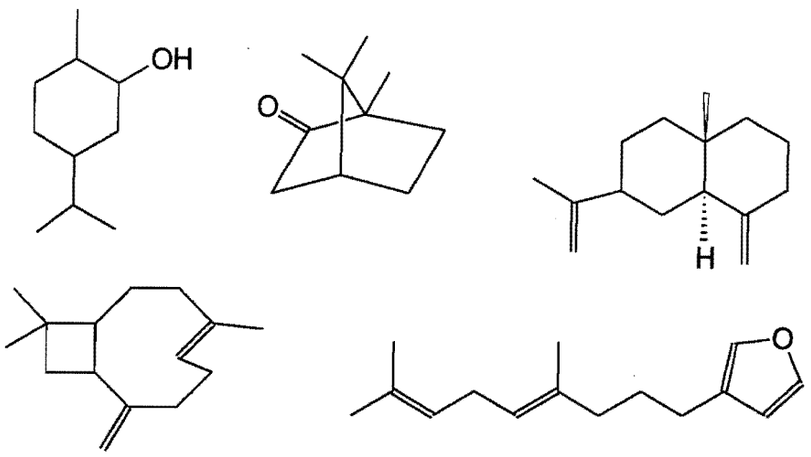
(i) The hydrolysis of 2-oleyl-1, 3-distearylglycerol affords two molecules of stearic acid and one molecule of oleic acid. Draw the structure and give the name of one other triacylglycerol that would, upon hydrolysis give the same fatty acids and in the same proportions as 2-oleyl-1, 3-distearylglycerol. (3 marks)

(ii) Using suitable illustrations explain why the melting point of 2-oleyl-1, 3-distearylglycerol is lower than that of tristearin? (2 marks)

(iii) Outline a biosynthetic pathway for butanoic acid from acetylcoenzyme A. (5 marks)

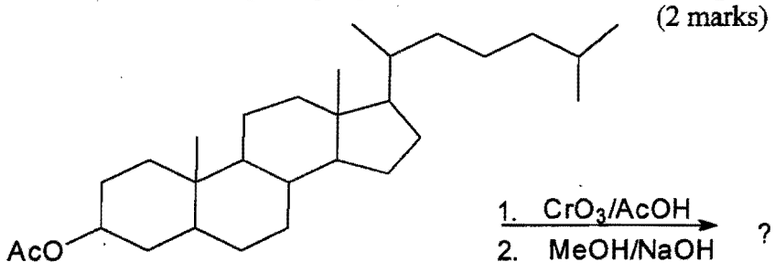
Terpenoid compounds

(b) The following compounds are made up of more than one isoprene unit. Using dotted lines, identify the isoprene units in each compound. (6 marks)



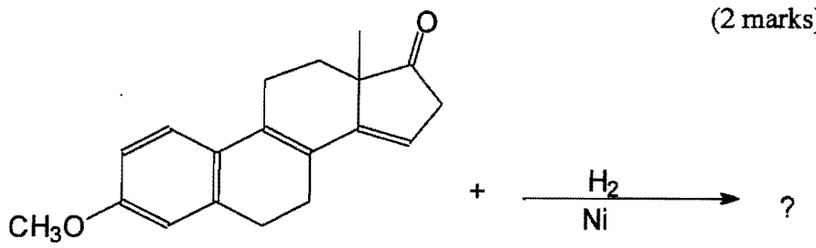
(c) Predict and draw the structure of the principal product in each of the following reactions: (2 marks)

(i)

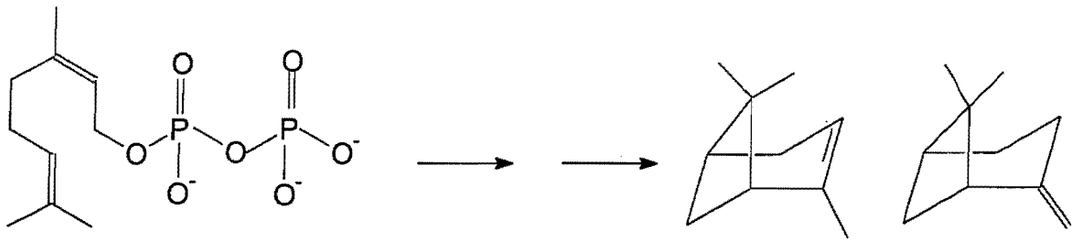


(2 marks)

(ii)



(d) Show the biosynthetic pathway to α-pinene(1) and β-pinene(II) from nerol pyrophosphate. (5 marks)

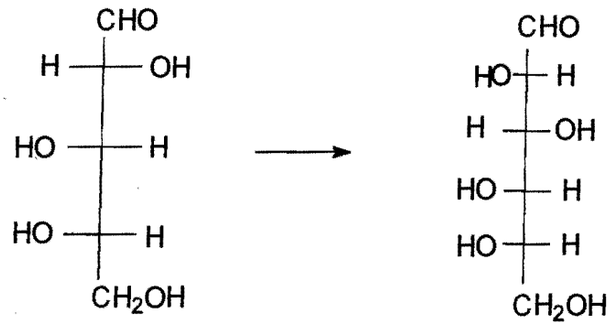


Nerol pyrophosphate

(i) (ii)

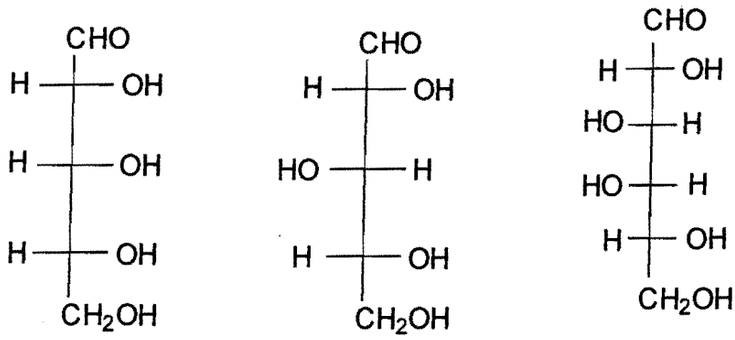
Question 4 **Carbohydrates**

(a) Show the steps and reagents in the synthesis of L-Glucose from L-Arabinose. (10 marks)



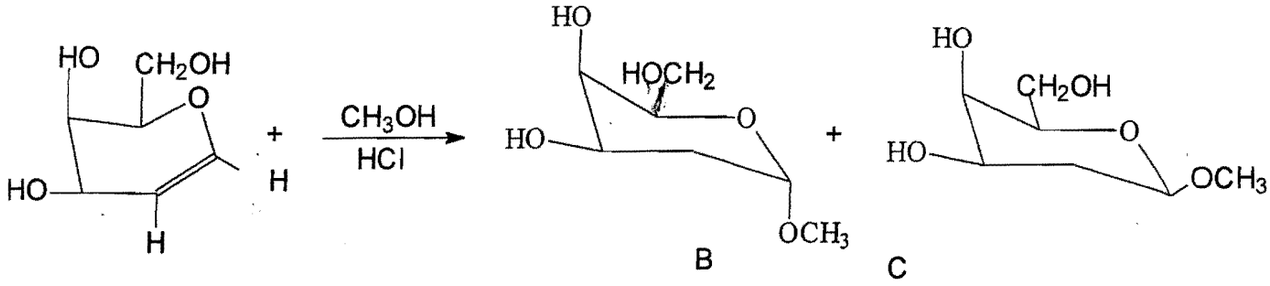
L-Arabinose L-Glucose

(b) Write the Harworth formulas corresponding to the α- and β-pyranose forms of D-Xylose, D-Ribose and D-Galactose. (6 marks)



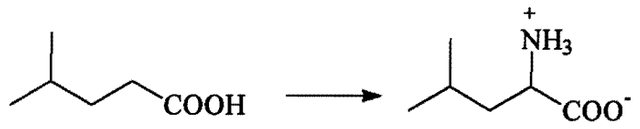
D-(-)-Ribose D-(+)-Xylose D-(+)-Galactose

(c) Glycosides are easily prepared in the laboratory by allowing a carbohydrate compound and an alcohol to stand in the presence of an acid catalyst, as shown below for the conversion of Glycal to the Methyl D-Deoxy-lyxohexopyranosides B and C. Suggest a reasonable mechanism for this reaction. (9 marks)



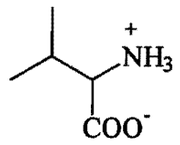
Question 5 Amino Acid, Peptides and Proteins

(a) Suggest a synthesis of Leucine from 4-methylpentanoic acid. (5 marks)

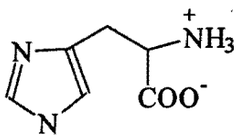


4-methylpentanoic acid Leucine

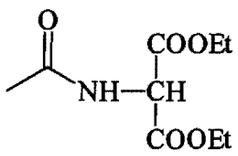
(b) Outline the steps in the preparation of Valine by the Strecker Synthesis. (5 marks)



(c) Using diethylacetamidomalonate and any other appropriate reagents, outline a synthesis for histidine. (7 marks)



Histidine



Diethylacetamidomalonate

(d) Glycine undergoes acid catalysed esterification more slowly than does propionic acid. Explain. (4 marks)

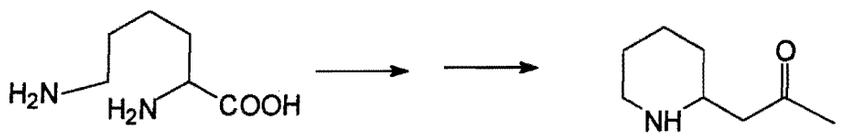
(e) Write the structural formula of the Glycylalanine (Gly-ala) dipeptide showing:

(i) the constitution and
(ii) the stereochemistry at the α-carbib atom. (4 marks)

Question 6 **Alkaloids**

(a) Write briefly on alkaloids indicating what they are, their major sources, how they are usually isolated from their major sources and their importance to human beings. (6 marks)

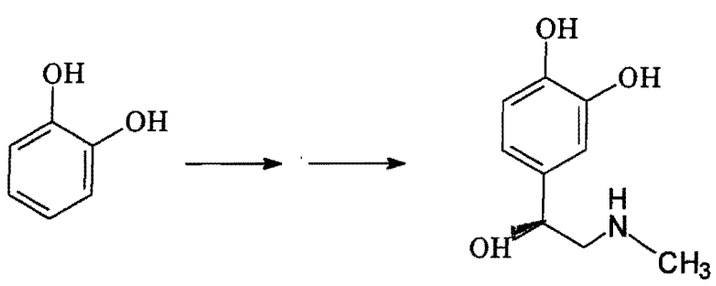
(b) Show the main steps in the following biosynthetic conversion of Lysine to the piperidine alkaloid Pelletierin. (10 marks)



Lysine

Pelletierine

(c) Outline the sequence of steps and show the appropriate reagents in the laboratory synthesis of adrenaline from catechol. (9 marks)



Catechol

Adrenaline