UNIVERSITY OF SWAZILAND
FINAL EXAMINATION 2015

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 8 (eight) printed pages.

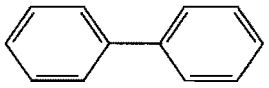
You must not open this paper until the Chief Invigilator so has granted permission to do.

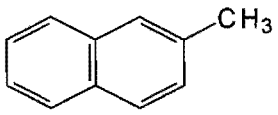
SECTION A

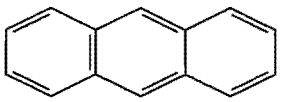
POLYCYCLIC AND HETEROCYCLIC AROMATIC COMPOUNDS

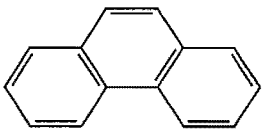
Question 1 **Polycyclic Aromatic Hydrocarbons**

(a) Write the major product formed in each of the following reactions:

(i)  + $\xrightarrow[CH_3COOH]{\text{Excess } Br_2}$? (2 marks)

(ii)  + $\xrightarrow[\text{Heat}]{96\%\ H_2SO_4/SO_3}$? (2 marks)

(iii)  + $\xrightarrow[CH_3CHOOH/H_2SO_4]{NaClO_3/V_2O_5}$? (2 marks)

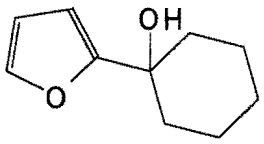
(iv)  + $\xrightarrow[CCl_4]{Br_2}$? (2 marks)

(b) Explain the regioselectivity of substitution in naphthalene using a resonance description. (7 marks)

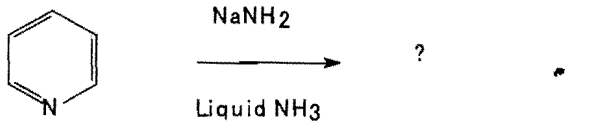
(c) Outline a synthesis for phenanthrene I using benzene, oxirane, and cyclohexanone as the only source of carbon along with any reagents. (10 marks)

Question 2 **Heterocyclic Aromatic Compounds**

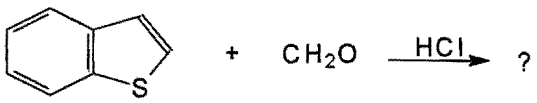
(a) Show how you could prepare the heterocycle below using furan and cyclo hexanone as the only source of carbon along with any inorganic reagents. (10 marks)



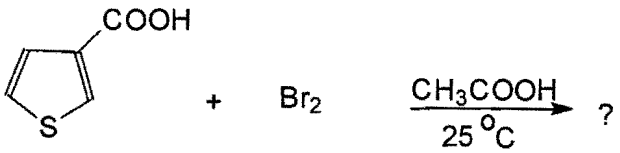
(b) Write the structure of the major product formed in each of the following reactions.



(3 marks)



(3 marks)



(3 marks)

(c) Account for the following factual information:

(i) Pyrrole is much more reactive than furan towards electrophilic aromatic substitution. (3 marks)

(ii) Pyridine is more basic than pyrrole even though both of them have lone pairs of electron on nitrogen, which can be protonated in an acid-base reaction. (3 marks)

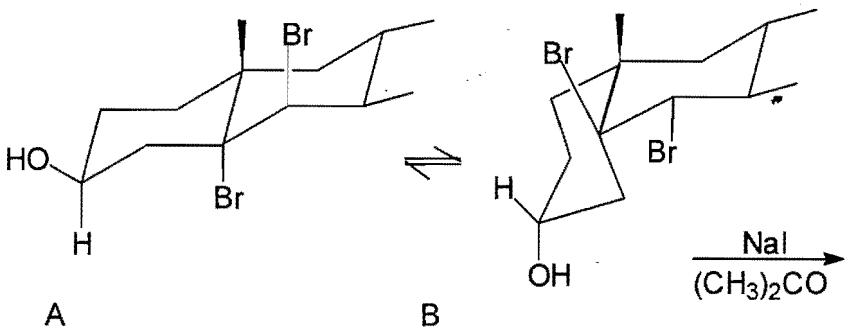
SECTION B

NATURAL PRODUCTS

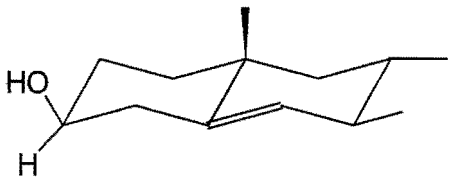
Question 3 **Terpenoid Compounds**

(a) Both compounds A and B are easily debrominated by sodium iodide in acetone to compound C. However, in the debromination process, compound A reacts faster than compound B. Why? Explain your reasoning clearly.

(8 marks)



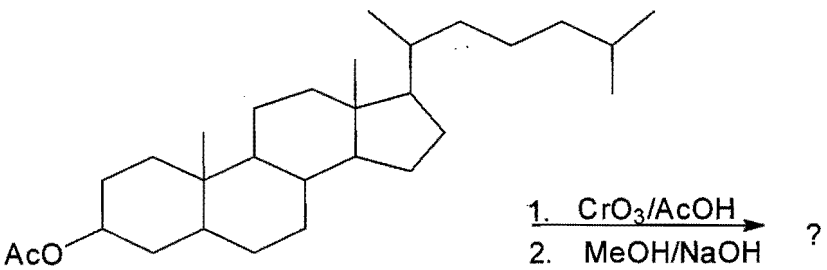
A B



C

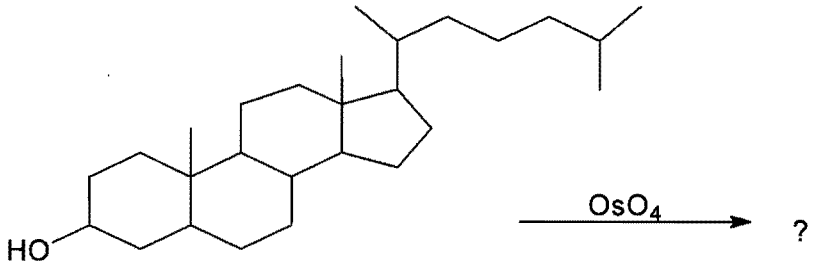
(b) Predict and draw the structure of the principal product in each of the following reactions:

(i)



(3 marks)

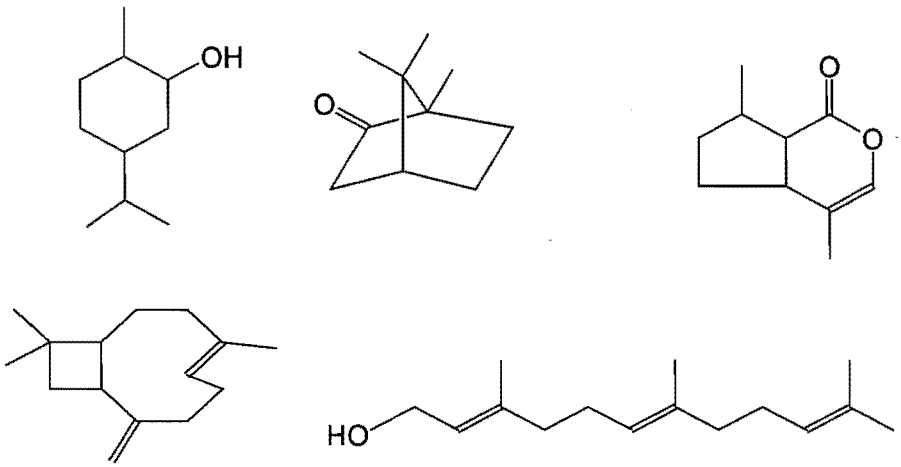
(ii)



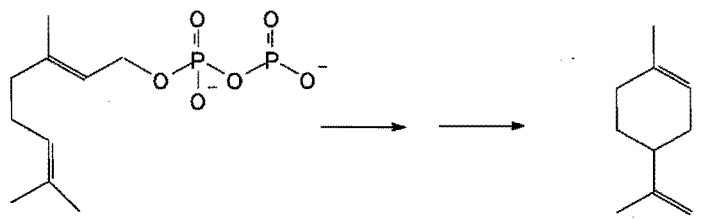
(3 marks)

(c) The following compounds are made up of more than one isoprene unit. Draw the structure of the compound and, using dotted lines, identify the five carbon fragments corresponding to the isoprene units in each compound.

(6 marks)



(d) Show the steps and mechanism for the synthesis of limonene from geranyl disphosphate (GPP). (5 marks)

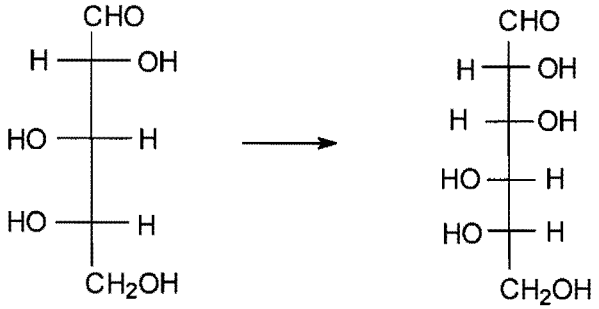


Geranyl Diphosphate (GPP)

Limonene

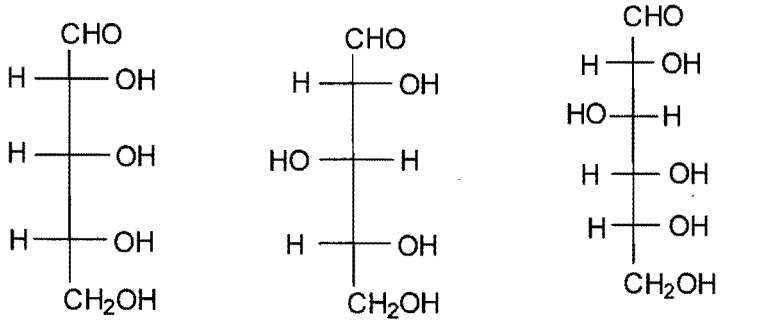
Question 4 **Carbohydrates**

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



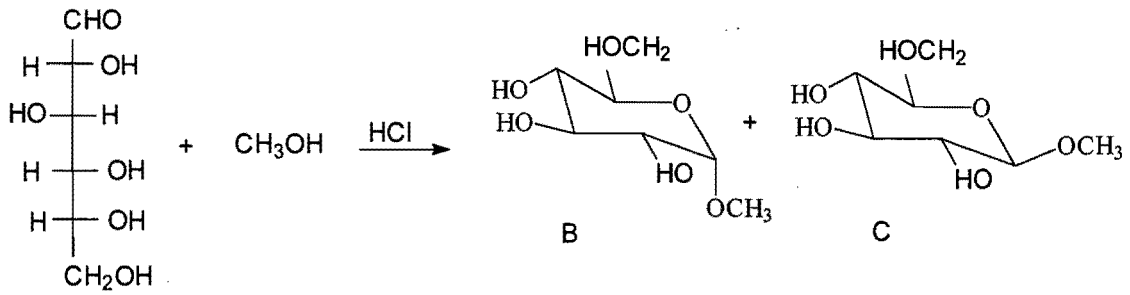
L-Arabinose L-Mannose

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



D-(-)-Ribose D-(+)-Xylose D-(+)-Glucose

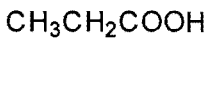
(c) Glycosides are easily prepared in the laboratory by allowing a carbohydrate compound and an alcohol to stand in the presence of an acid catalyst, as shown below for the conversion of Glucose to the Methyl D-Glucopyranosides B and C. Suggest a reasonable mechanism for this reaction. (9 marks)



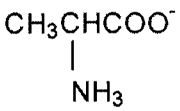
D-Glucose B C

Question 5 **Amino Acids**

(a) Suggest a synthesis of Alanine from propionic acid. (5 marks)

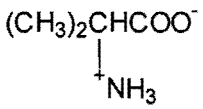


Propionic Acid



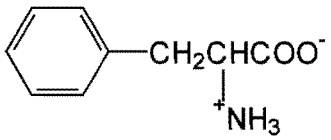
Alanine

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

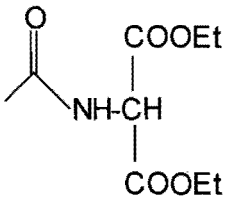


Valine

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



Phenylalanine



Diethylacetamidomalonate

(d) Predict and draw the structure of the major product of the reaction of glycine with the following reagents: (8 marks)

(i) $NaNO_2$ and dilute HCl

(ii) Acetic anhydride $[(CH_3CO)_2O]$

(iii) NaOBr

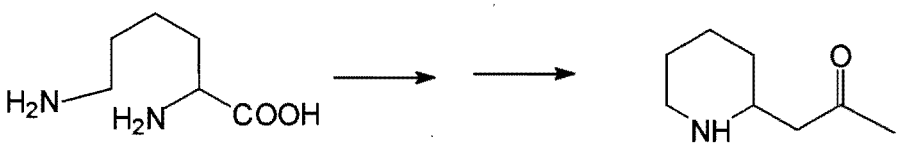
(iv) CH_3CH_2OH and dry HCl

Question 6 **Alkaloids**

(a) Show the main steps in the following biosynthetic conversion of amino acids to alkaloids.

(i) Lysine to the piperidine alkaloid Pelletierine.

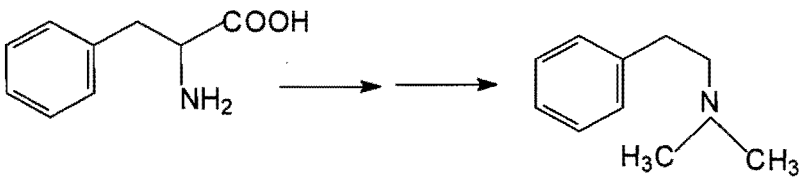
(10 marks)



Lysine Pelletierine

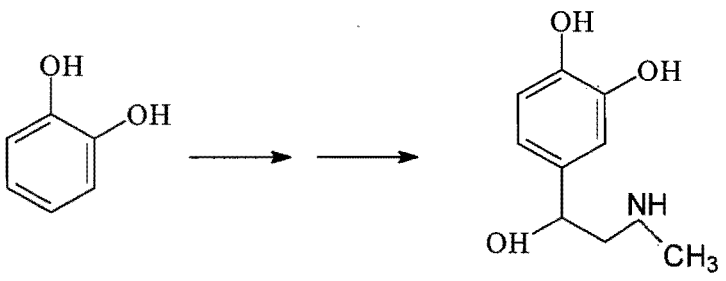
(ii) Phenylalanine to the germination inhibitor hordenine.

(6 marks)



Phenylalanine Hordenine

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



Catechol Adrenaline