

MAASAI MARA UNIVERSITY

REGULAR UNIVERSITY EXAMINATIONS 2021/2022 ACADEMIC YEAR FOURTH YEAR FIRST SEMESTER

SCHOOL OF PURE, APPLIED AND HEALTH SCIENCES BACHELOR OF SCIENCE (BSc.) & BACHELOR OF EDUCATION (SCIENCE)

COURSE CODE: CHE 4135

COURSE TITLE: NATURAL PRODUCTS CHEMISTRY

DATE: 5TH APRIL 2022 **TIME:** 1430 – 1630 HOURS

INSTRUCTIONS TO CANDIDATES

- 1. Answer the compulsory question ONE and any other TWO in section B.
- 2. All University Examinations rules and regulations apply.

This paper consists of 5 printed pages. Please turn over:

SECTION A

QUESTION ONE (30 MARKS)

a) Distinguish between the following terms citing relevant examples in each case:

(6 marks)

- (i) *in vivo* and *in vitro* reactions
- (ii) oxidative coupling and oxidative cleavage reactions
- (iii)Primary and secondary metabolites
- b) Suggest reasons for the following observations

(8 marks)

- (i) High levels of blood cholesterol is a health hazard
- (ii) Morphine is an important pharmacological drug whereas its diacetyl derivative heroine is outlawed
- (iii)Ecdysone is a key hormone in insect metamorphosis but is also regarded as a useful insect control hormone
- (iv) Animals grazing in dry lands for a longer period tend to have infertility problems
- c) Complete the following table by providing examples of natural drug or pharmacological effect/class: (4 marks)

Natural drug	Pharmacological effect	
	Analgesic	
Quinine		
Penicillin		
	Antioxidant	

d) Given the following scheme:

Geranyl pyrophosphate
$$\xrightarrow{-H^+}$$
 most stable olefin \mathbf{Y} OPP $\xrightarrow{\text{PhCH}_2\text{SH}}$ compound \mathbf{X} $\alpha\text{-thujene}$

- (i) Provide the structure of Geranyl pyrophosphate(GPP). Hint: GPP is an acyclic diene (2 marks)
- (ii) Draw the structures of X and Y

(2 marks)

- (iii)What is the structure of minor product Y? Why one product is preferentially formed over the other? (3 marks)
- (iv)Devise arrow pushing mechanism for the synthesis of α -thujene from the intermediate given (3 marks)
- e) What is isoprene rule?

(2 marks)

SECTION B

QUESTION TWO (20 MARKS)

- a) What structural clue do the following analytical techniques used to analyze natural products provide? (3 marks)
 - (i) Nuclear Magnetic Resonance
 - (ii) Infra-red spectroscopy
 - (iii)UV-Vis spectroscopy
- b) p-methylphenol undergoes oxidative coupling reaction when refluxed in presence of trace amounts ferric hexacyano complex. The C-C coupling process involves free radicals. Fe³⁺ is reduced to Fe²⁺. Propose a detailed half-arrow pushing mechanism for this reaction. (4 marks)

OH OH OH
$$(Fe(CN)_6)^{3-}$$
 CH_3 CH_3

- c) List the aromatic amino acids that are derived from Shikimate pathway (3 marks)
- d) Outline the biological significance of the following hormones

(4 marks)

- (i) Juvenile Hormone (JH)
- (ii) Inkosterone
- (iii)Testosterone
- (iv)Progesterone
- e) How are these sex hormones derived from cholesterol (C27)?

(2 marks)

f) Give four classes of terpenes indicating the number of carbon atoms present in each class. (4 marks)

QUESTION THREE (20 MARKS)

a) Define the following terms and provide examples:

(3 marks)

- (i) Biosynthesis
- (ii) Pharmacognosy
- (iii)Camphor
- b) Provide the intermediates and final products for the following reactions which mimic biological reactions: (6 marks)

i)
$$\stackrel{O}{\longrightarrow}$$
 + $\stackrel{N}{\longrightarrow}$ $\stackrel{1) \text{PhCH}_2\text{Br}}{\longrightarrow}$ (hydrolysis)

c) Explain the importance of the following biological molecules:

(3 marks)

- (i) Co-enzymes
- (ii) Cholesterol
- (iii)Riboflavins/Quinones
- d) Briefly discuss three important *in vivo* reactions. Compare reactions you have chosen with the related *in vitro* reactions. **(6 marks)**
- e) State any two general properties of alkaloids.

(2 marks)

QUESTION FOUR (20 MARKS)

- a) Name three different classes of terpenoids and indicate the carbon units' count in each case. (3 marks)
- b) Explain the importance of pheromones in insects

(3 marks)

- c) Write a sequence of reactions that describe the formation of Geranyl pyrophosphate (GPP) from isopentenyl pyrophosphate (IPP). (8 marks)
- d) Polyketides plays a central role in mammalian metabolic processes. They are formed by condensation acetate units without reduction of the β -carbonyl moieties. Provide a reasonable arrow pushing mechanism for the following ring folding reaction.

- e) State the pharmacological activities associated with the following alkaloids: (3 marks)
 - (i) codeine
 - (ii) colchicine
 - (iii)Cocaine

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