



(University of Choice)

**MASINDE MULIRO UNIVERSITY OF  
SCIENCE AND TECHNOLOGY  
(MMUST)**

MAIN CAMPUS

UNIVERSITY EXAMINATIONS  
2022/2023 ACADEMIC YEAR

FIRST YEAR SECOND SEMESTER EXAMINATIONS  
MAIN EXAM

FOR THE DEGREE  
OF  
MASTERS OF SCIENCE (CHEMISTRY)

COURSE CODE: SCH 833

COURSE TITLE: ADVANCED NATURAL PRODUCTS CHEMISTRY

DATE: 18<sup>th</sup> April 2023

TIME: 8.00 to 11.00 AM

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**INSTRUCTIONS TO CANDIDATES**

1. Answer all questions

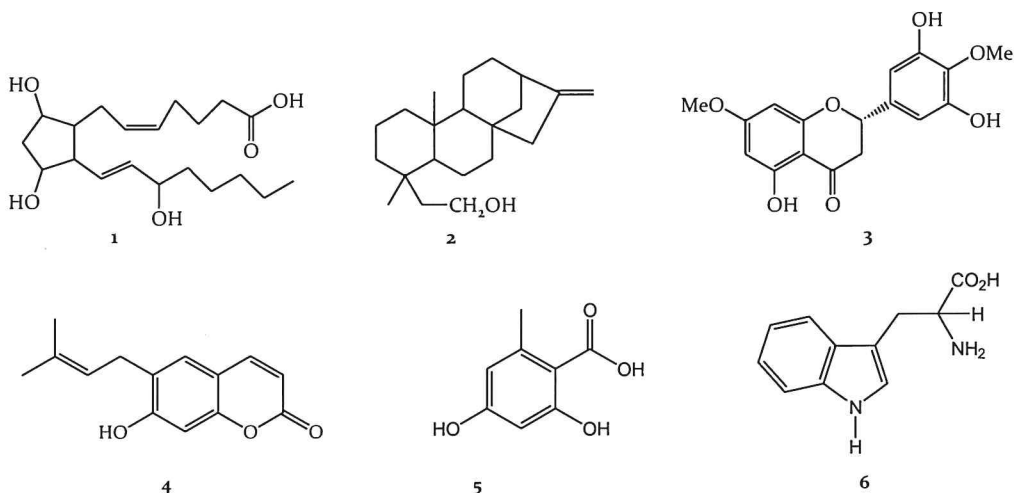
TIME: 3 Hours

MMUST observes ZERO tolerance to examination cheating

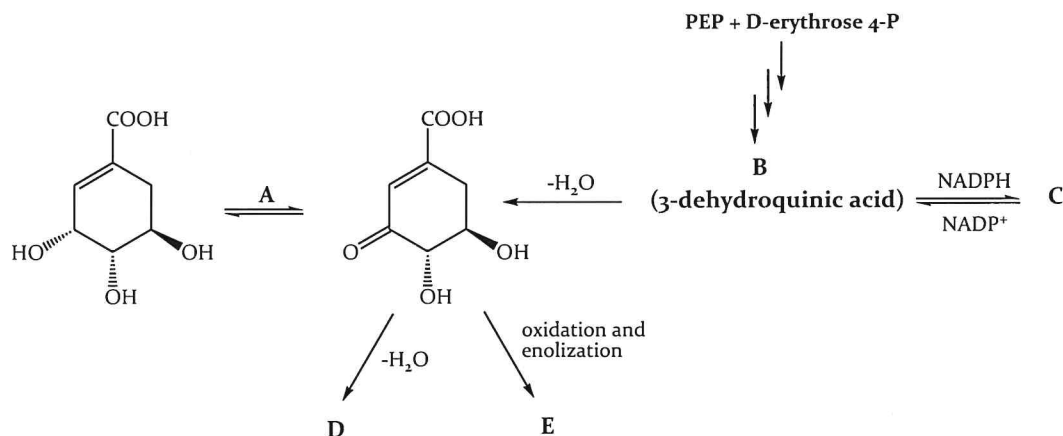
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### QUESTION 1 (14.5 Marks)

a) Giving reasons predict the biosynthetic origin of the compounds 1 to 6 given below **6 Marks**

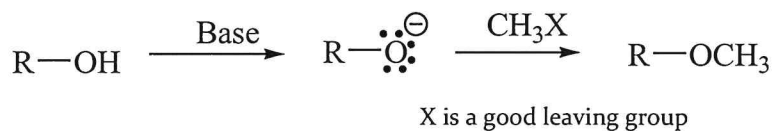


b) Study the biosynthetic process below then identify the missing reagent A and the structures labelled B to E. NB: PEP refers to phosphoenolpyruvate. **2.5 Marks**

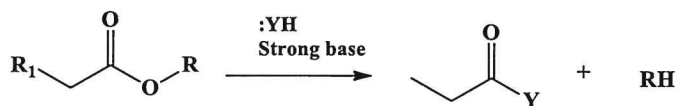


c) The reactions given below are “test tube reactions”. Give equivalents of these transformations in biological systems showing the reagents used. **2 Marks**

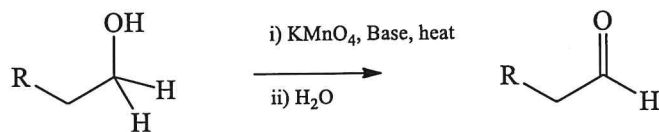
i)



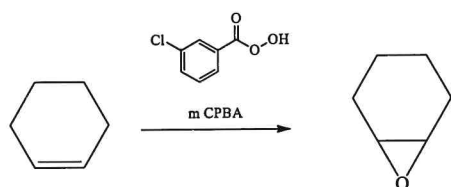
ii)



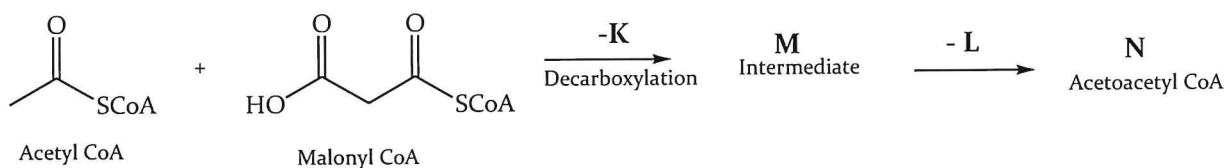
iii)



iv)

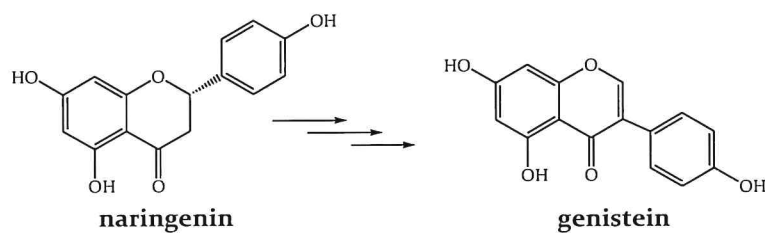


- d) The **Claisen** reaction achieves carbon-carbon bond formation and typical base-catalysed chemical reactions depend on the generation of a resonance-stabilized enolate anion from a suitable carbonyl system. This reaction is similar to the reaction joining together of C<sub>2</sub> acetate group to the C<sub>3</sub> malonyl group in biological systems as given in the scheme below. Determine species **K** and **L** and structures **M** and **N**. **4 Marks**

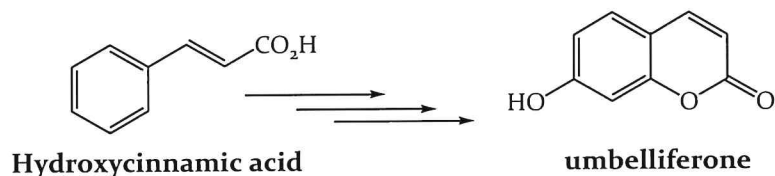


## QUESTION 2 (13 Marks)

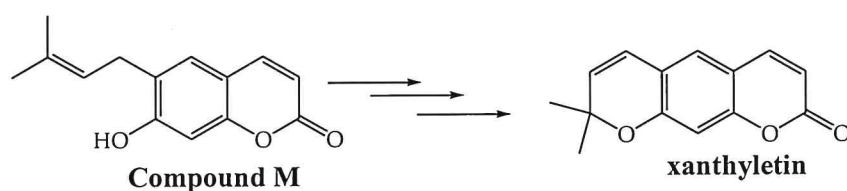
- a) Isoflavoids are produced from flavonoids by migration of the aromatic ring B. Through this process genistein is obtained from naringenin. Give a detailed mechanism for this process. **6 Marks**



- b) Hydroxycinnamic acid is a precursor to a number of  $C_6C_3$  natural products like coumarins. Show the biosynthetic process through this precursor to the coumarin umbelliferone common to the plant family Umbelliferae. 3 Marks



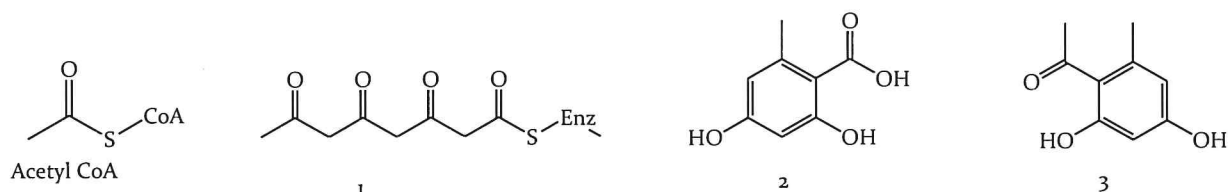
- c) Isoprenylation of umbelliferone gives compound M which can be transformed to xanthyletin as shown below.



- i) What is the origin of the prenyl group? 1 Mark  
 ii) Show mechanism how xanthyletin is obtained from umbelliferone. 3 Marks

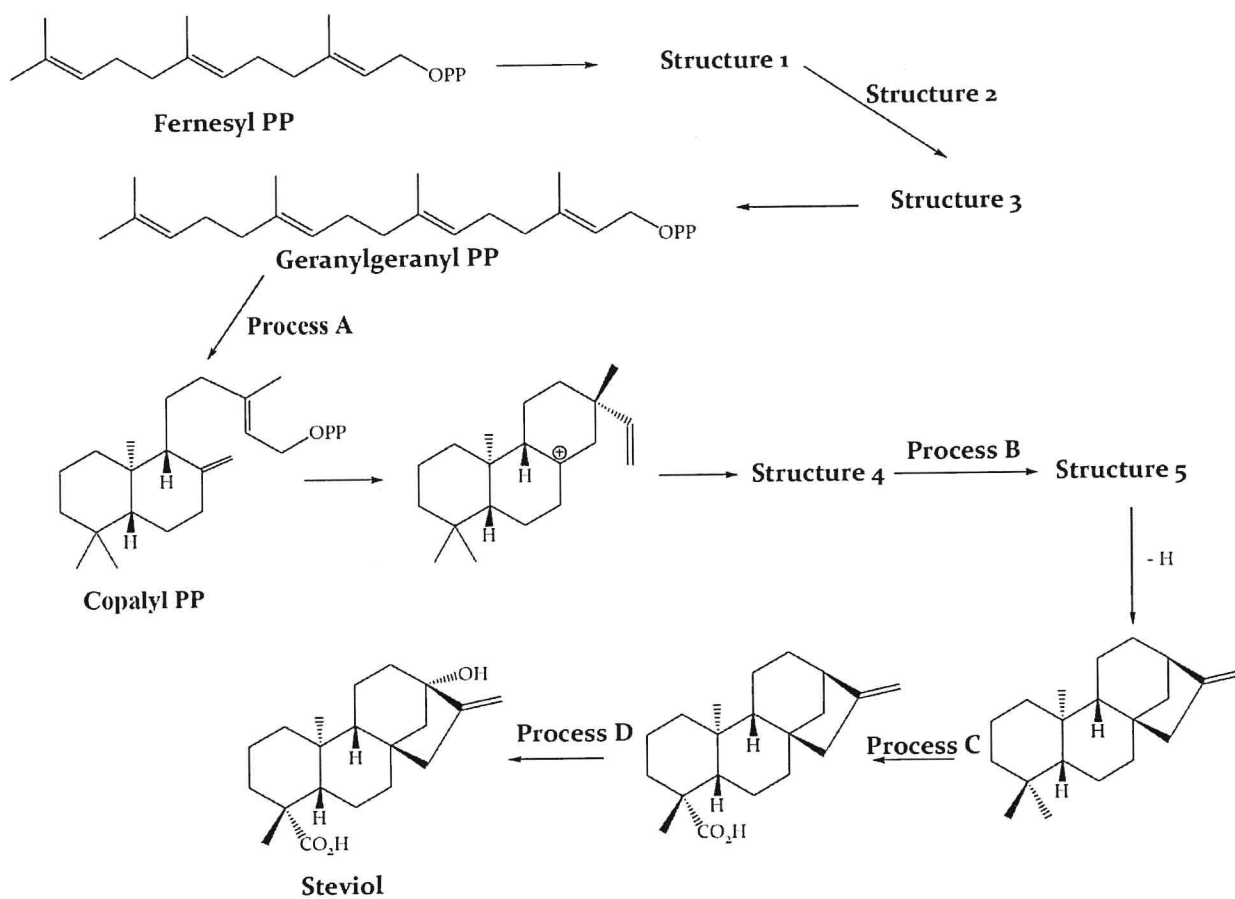
### QUESTION 3 (19.5 Marks)

- a) Consider structures acetyl CoA (given) derived natural products below.



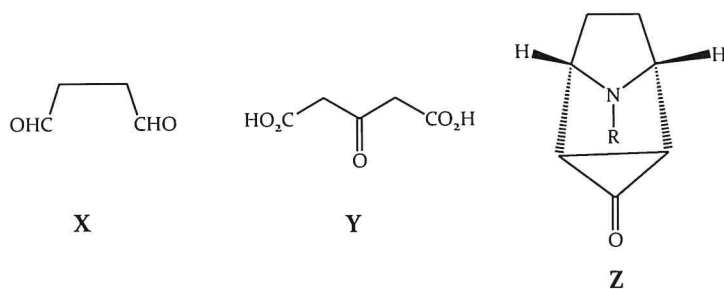
- i) Starting from acetyl CoA illustrate how polyketide 1 is biosynthetically formed. 3 Marks  
 ii) Name and outline mechanistically how orsellinic acid 2 and 3 may be obtained from the polyketide 1. 6 Marks
- b) The diterpene **steviol** is synthesized through a series of biochemical reactions presented in the scheme below starting from precursor farnesyl pyrophosphate. Refer to the scheme to answer the question below.

- i) Giving the mechanism and structures **1, 2** and **3** show how geranylgeranyl pyrophosphate is obtained from farnesyl pyrophosphate **4.5 Marks**
- ii) Process A leads to the formation of copalyl pyrophosphate a cyclised precursor to steviol. Give details of how the straight chain GGPP is transformed to copalyl PP. **3 Marks**
- iii) Identify structure **5** and structurally what necessitates its formation in process B. **2 Marks**
- iv) Identify processes **C** and **D** **1 Mark**

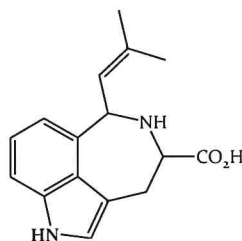


#### QUESTION 4 (13 Marks)

- a) Racemic tropinone **Z** could be prepared from components depicted as **X** and **Y** under virtually physiological conditions in a biomimetic reaction. Propose a plausible mechanism for this reaction. **5 Marks**

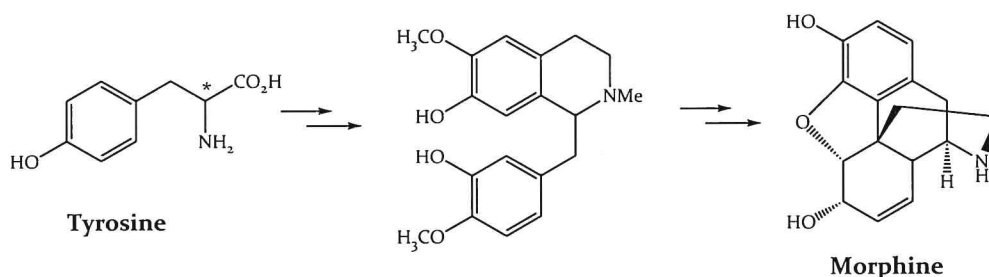


- b) The metabolite clavicipitic acid is produced by the ergot fungus, *Claviceps purpurea*. Identify the building blocks. 2 Marks



Clavicipitic acid

- c) Isotopic labeling studies using radioisotopes ( $^3\text{H}$  and  $^{14}\text{C}$ ) together with enzymatic methods have been used to establish biosynthetic pathways. Study the structure of morphine and its intermediate then mark with asterisk the sites that would be labeled in morphine and its precursor if biosynthesized from  $[2-^{14}\text{C}]$ tyrosine. 4 Marks



- d) The antibiotic Methicillin is prepared from 6-aminopenicillanic acid (6-APA) and 2,6-dimethoxybenzoyl chloride as shown below. Give the structure of Methicillin! 2 Marks

