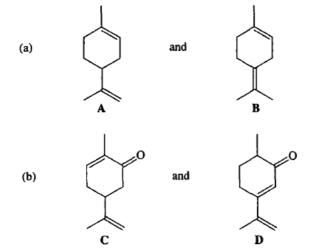
CHUKA UNIVERSITY EXAMINATIONS (2019/2020) CHEM 446: CHEMISTRY OF NATURAL PRODUCTS STREAMS: BSc (CHEMISTRY); BSc(Bio) TIME: 2 HRS **INSTRUCTIONS** Answer question **One** (Compulsory) and any other **Two** questions **QUESTION ONE [30 MARKS]** (a) Identify the isoprene units in each of the terpenes. Classify each teperne as monoterpene, diterpene, etc (4 Marks) (b) Write the stepwise mechanism for biosynthesis of α -pinene from geranyl pyrophosphate (6 Marks) α-pinene (c) Discuss the commercial importance of terpenoids and steroids (4 Marks)

(d) Explain how each of the following pairs can be distinguished using a physical and a

chemical method (4 marks)



- (e) Discuss the four stages of determining the structures of natural products (8 marks)
- (f) Explain four roles of secondary metabolites in plants and animals (4 marks)

QUESTION TWO [20 MARKS]

(a) Identify the acetate units in each of the following compounds (3 marks)

- (b) Describe how alkaloids are isolated from plant materials (6 marks)
- (c) A volatile plant product M, $C_8H_{14}O$, has strong IR absorption at 1717 cm⁻¹. It possess ¹H NMR signals at δ_H 1.65 (3H, s), 2.15 (3H, s), 2.4 (4H, m) and 5.20 (1H, t). On ozonolysis, compound M gives, among other products, propanone, and on treatment with iodine and alkali it gives triiodomethane (iodoform). What structural formula can be obtained from:
- (i) Its molecular formula (2 marks)
- (ii) Its IR spectrum (1 marks)
- (iii) Its ¹H NMR spectrum (3 marks)
- (iv) Its chemical reactions (2 marks)
- (v) Deduce the structure of compound M (3 marks)

QUESTION THREE [20 MARKS]

Alkaloid **G**, $C_8H_{13}NO$, is a tertiary base. It has IR absorption at 3500 cm⁻¹ and ¹H NMR signals at δ 3.0 (5H, m), 3.8 (2H, s) and 5.4 (1H, t, J = 7 Hz). It can be oxidized under mild conditions with MnO₂ to give compound **H**, $C_8H_{11}NO$, which had an IR absorption at 1680 cm⁻¹ and a UV absorption at 229 nm. Compound **H** formed a deep-red dinitrophenylhydrazone. On catalytic hydrogenation, **G** absorbed 1 mole of hydrogen to give **I**. This readily formed a monotoluene–*p*-sulfonate, which on reduction with LiAlH₄ gave **J**, $C_8H_{15}N$. When **J** was submitted to three successive Hofmann degradations with a hydrogenation after each stage, the C_8 hydrocarbon 3-methylheptane was obtained. Deduce the structure of **G** (20 marks)

QUESTION FOUR [20 MARKS]

- (a) Describe the stepwise biosynthesis of penicillins and cephalosporins (6 marks)
- (b) Explain the mode of action of penicillins and cephalosporins (2 marks)
- (c) State the functions of Vitamin A (2 marks)
- (d) Indicate the biosynthetic structural units [acetate, C₁ (methionine), C₅ (isoprene), C₆-C₃ (shikimate)] that form the carbon skeletons of the following compounds. Some of these compounds may be formed by combination of more than one pathway (5 marks)

(a)
$$CO_2H$$
 (b) MeO Me MeO M

(e) Describe the biosynthesis of steroid hormones from farnesyl pyrophosphate (5 marks)