DEHYDRODISCRETINE, AN INFREQUENTLY OCCURRING QUATERNARY PROTOBERBERINE ALKALOID FROM HEPTACYCLUM ZENKERI*

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Abstract—Dehydrodiscretine, a quaternary protoberberine alkaloid, has been isolated from Heptacyclum zenkeri Engl (syn Penianthus zenkeri Diels) This is the first reported isolation of this alkaloid from a member of the Menispermaceae and only the second reported isolation from nature

INTRODUCTION

Heptacyclum zenkeri Engl [1] Menispermaceae (syn Penianthus zenkeri Diels [2]) is a woody climber or small shrub indigenous to West Africa, where the roots and twigs have been used as an aphrodisiac and in the treatment of local infections and venereal disease [3] We have recently reported the occurrence of the quaternary protoberberine alkaloids palmatine and jatrorrhizine and the quaternary aporphine alkaloid magnoflorine from an extract of the stems and roots [4] This brief note is to report the isolation of dehydrodiscretine iodide (1), an infrequently occurring quaternary protoberberine alkaloid, from the same extract

RESULTS AND DISCUSSION

Careful re-examination of fractions 50–66 from CC of fraction C [4] revealed the presence of an additional yellow-orange colored alkaloid on TLC over Si gel G [4] Fractions 56–66 were combined to afford a brownish-orange residue (37 mg) which was dissolved in methanol (10 ml) and passed over a column of anion exchange resin (10 ml) [IRA-410 (I)] The column eluate plus its methanol rise (20 ml) was evaporated to dryness and the resulting dark orange residue crystallized from methanol to afford orange needles (16 mg) of a quaternary alkaloid iodide, mp 243–245° (dec), R_f 0.38 [CHCl3–MeOH–NH4OH (14 7 1)], R_f 0.49 [MeOH–NH4OH–H2O (8 1 1)], R_f 0.47 [n-PrOH–MeOH–NH4OH–H2O (4 2 2 1)], UV $\lambda_{\rm max}^{\rm MeOH}$ nm (log ε) 242 (4 24), 265 (4 13), 289 (4 32), 315 (sh) (4 15), 342 (3 97) and 381 (3 97) with no

shift in 01 N methanolic hydrochloric acid, UV² MeOH $+OH^{-}$ nm (log ε), 254 (446), 309 (424) and 379 (431), IRv_{max}^{KBr} cm⁻¹ 3440, 1615, 1575, 1518, 1500, 1430, 1357, 1290, 1260, 1220, 1175, 1129, 1032, 1009, 910 and 880, ¹H NMR [60 MHz, CDCl₃ + CD₃OD (1 1)] δ 4 03 (3H, s, OMe), 407 (3H, s, OMe), 415 (3H, s, OMe), 686–940 (6H, m, ArH) Treatment of this alkaloid (7 mg) with NaBH₄ (10 mg) in MeOH (10 ml) and work-up in the usual fashion [5] afforded a colorless amorphous residue (4 mg), $UV\lambda_{\text{max}}^{\text{HoOH}}$ nm (log ε) 224 (sh) (3 86) and 286 (3 41), MS m/z (rel int), 341 [M]⁺ (4%), 326(7), 257(9), 193(8), 185(13), 176(13), 165(39), 164(100), 150(10), 149(50), 124(17), 121(21), 97(26), 83(41), 71(44), 69(59), 59(46). 57(80), 55(84), 43(95) and 41(98) A consideration of the UV [6, 7] and ¹H NMR [5, 8] spectra of the quaternary alkaloid and the UV [6, 7] and mass [9] spectra of the reduced product suggested that the quaternary alkaloid was a 2, 3, 10, 11-tetraoxygenated protoberberine with one methoxy and one hydroxy group in ring A and two methoxy groups in ring D, while the reduced product was its tetrahydro-derivative. The alkaloid was identified as dehydrodiscretine iodide (1) by direct comparison (UV, IR, mp, co-TLC) with an authentic reference sample

Dehydrodiscretine was first isolated from *Thalictrum* fauriei Hayata (Ranunculaceae) in 1980 [5], and to our knowledge this is the first reported isolation of this alkaloid from a Menispermaceous species, and only the

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second reported isolation from nature Furthermore, discretine, the parent tetrahydroprotoberberine analog of dehydrodiscretine, appears to have been isolated only from Xylopia discreta (Anonaceae) [10] to date

Finally, dehydrodiscretine was found to be devoid of antimicrobial activity when tested against a standard collection of Gram-positive, Gram-negative, acid-fast micro- and fungal organisms [11]

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