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ALKALOIDS FROM *HYPERBAENA COLUMBICA*

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Key Word Index—*Hyperbaena columbica*; Menispermaceae; alkaloids; 3-demethoxy-2α,3α-methylenedioxy-erythroculine; erythroculine; protostephanine.

Abstract—Erythroculine, protostephanine and a new alkaloid have been isolated from *Hyperbaena columbica*, and the latter has been identified as 3-demethoxy-2α,3α-methylenedioxyerythroculine.

INTRODUCTION

In *Hyperbaena columbica* (Eichl.) Miers three alkaloids have been detected, but not identified [1]. According to the optical rotation [2], IR [2], UV [2] and ^{1}H NMR [2] as well as the mass spectral fragmentation (cf. [3]), one alkaloid is identical to erythroculine (**1**). According to melting point [4], UV [5], ^{1}H NMR and the high resolution mass spectrum the second alkaloid is protostephanine (**3**). Comparison of the IR, UV and ORD spectra (positive Cotton effect at 300 nm) of the third alkaloid with those of erythroculine (**1**) indicated a similar structure including absolute configuration.

RESULTS AND DISCUSSION

^{1}H NMR and mass spectrometry (Fig. 1) showed that the new alkaloid has the structure **2**. Spin–spin decoupling established the partial structure $R^1R^2R^3C$–CH_2–$CH(OR^4)$–$CH(OR^5)$–$CH=CR^6R^7$. The coupling constants $J_{3,4\alpha} = 11.5$ Hz and $J_{3,4\beta} = 6.0$ Hz proved the axial conformation of H-3 and hence its 3β-configuration. NOE enhancements of 6 and 11% were observed between H-2 (H-14) and H-3 (H-14), respectively. Such small positive values occur for the acute angle case of a three-spin system [6], pointing to the 2α,3α-configuration of the methylenedioxy group. In the case of a 2β,3α-configuration, a negative NOE enhancement between H-2 (H-14) would be expected.

Note added in proof: Considering additionally H-1, H-4α and H-4β a negative NOE enhancement between H-2 (H-14) for the 2β,3α-configuration was also calculated.

EXPERIMENTAL

Plant material. H. columbica (Eichl.) Miers was collected in May in Sierra del Rosario, Pinar del Río, Cuba, and identified by Lic. Pedro Herrera, Havana. A voucher specimen is retained in the Herbarium of the Institute of Botany, Academy of Sciences of Cuba, Havana.

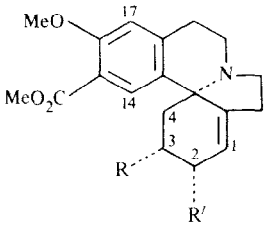
NOE studies. These were performed on a degassed sample of less than 5% concn (w/v) in Me_2CO-d_6. Each resonance was integrated 7 times in a homo-inverse-gated decoupled and a decoupled spectrum and the NOEs were calculated from the average areas. Accuracies of NOE values are *ca* ± 1.5%.

Extraction. Dried (40°) and ground leaves were extracted with EtOH at room temp. Evapn of the EtOH *in vacuo* gave a residue which was partitioned between 0.5 M HCl and C_6H_6–Et_2O (1:1). After addition of $KHCO_3$ to the aq. layer, the latter was extracted with $CHCl_3$–EtOH (2:1). Evapn of the solvent gave raw material which was chromatographed over silica gel using $CHCl_3$–MeOH mixtures.

3-Demethoxy-2α,3α-methylenedioxyerythroculine (**2**). Elution with $CHCl_3$–MeOH (99:1) and crystallization from MeOH afforded **2**; yield 0.003%; mp 94–97°, $[\alpha]_D^{25}$ +229° ($CHCl_3$; *c* 0.56). IR ν_{max}^{KBr} cm^{-1}: 1732 (CO_2R), 1612, 1500 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 305 (3.54), 238 (4.07, sh), 215 (4.55). ORD (EtOH): $[\phi]_{315}$ +2400° (peak), $[\phi]_{294}$ +2100° (trough). ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ1.55 (*t*, *J* = 11.5 Hz, 1H, H-4α), 2.27 (*dd*, *J* = 11.5 and 6.0 Hz, 1H, H-4β), 3.83 (*s*, 3H, OMe), 3.85 (*s*, 3H, OMe), 4.38 (*m*, 1H, H-3), 4.60 (*m*, 1H, H-2), 4.95 and 5.11 (each *s*, each 1H, OCH_2O), 5.90 (*m*, 1H, H-1), 6.68 (*s*, 1H, H-17), 7.26 (*s*, 1H, H-14). MS 70 eV, *m/z* (rel. int.): 357.1569 (calc. for $C_{20}H_{23}NO_5$: 357.1576; 16), 342.1340 (calc. for $C_{19}H_{20}NO_5$: 342.1341; 0.4), 326.1384 (calc. for $C_{19}H_{20}NO_4$: 326.1392; 7), 300.1230 (calc. for $C_{17}H_{18}NO_4$: 300.1236; 100), 285.1360 (calc. for $C_{17}H_{19}NO_3$: 285.1365; 83).

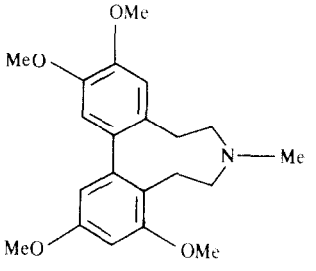
Erythroculine (**1**). Elution with $CHCl_3$–MeOH (49:1) and crystallization from Et_2O–pentane afforded **1**; yield 0.03%; mp 79–82°, $[\alpha]_D^{25}$ +216° ($CHCl_3$; *c* 1.05), lit. [2]: $[\alpha]_D$ +194° ($CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1716 (CO_2R), 1611, 1500 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 303 (3.49), 238 (3.93, sh), 214 (4.38). ORD (EtOH): $[\phi]_{315}$ +1250° (peak); $[\phi]_{296}$ +1150° (trough). ^{1}H NMR (100 MHz, $CDCl_3$, TMS): δ1.57 (*t*, *J* = 12 Hz, 1H, H-4α), 2.28 (*dd*, *J* = 12 and 4 Hz, H-4β), 3.29 (*s*, 3H, 3-OMe), 3.89 (*s*, 6H, 16-OMe, CO_2Me), 5.62 (*m*, 1H, H-1), 6.71 (*s*, 1H, H-17), 7.52 (*s*, 1H, H-14). MS 70 eV, *m/z* (rel. int.): 343.1780 (calc. for $C_{20}H_{25}NO_4$: 343.1783; 7), 328.1556 (calc. for $C_{19}H_{22}NO_4$: 328.1549; 0.5), 312.1602 (calc. for $C_{19}H_{22}NO_3$: 312.1600; 13), 285.1366 (calc. for $C_{17}H_{19}NO_3$: 285.1365; 100).

Protostephanine (**3**). Further elution with $CHCl_3$–MeOH (49:1) and crystallization from MeOH afforded **3**; yield 0.01%; mp 52–54°, lit. [4]: mp 75°. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1603, 1513 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 283 (3.92). ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ2.42 (*s*, 3H, NMe), 3.87 (*s*, 3H, OMe), 3.89 (*s*, 6H, OMe), 3.99 (*s*, 3H, OMe), 6.41 (*d*, *J* = 3 Hz, 1H), 6.54 (*d*, *J* = 3 Hz, 1H), 6.74 (*s*, 1H), 6.82 (*s*, 1H) (aromatic protons). MS 70 eV, *m/z* (rel. int.): 357.1932 (calc. for $C_{21}H_{27}NO_4$: 357.1940; 100), 342.1702 (calc. for $C_{20}H_{24}NO_4$: 342.1705; 18), 326.1756 (calc. for $C_{20}H_{24}NO_3$: 326.1756; 20).



1 R = OMe, R' = H

2 R + R' = OCH_2O



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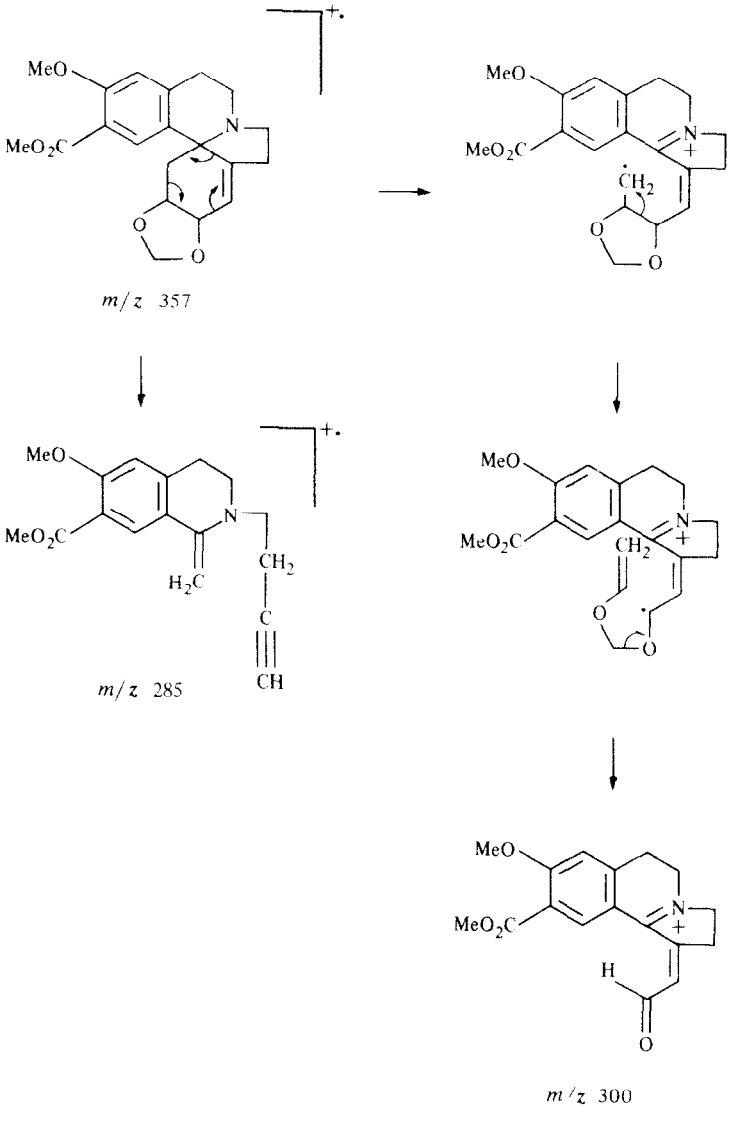

Fig. 1. MS fragmentation of 3-demethoxy-2α,3α-methylenedioxycrythroculine (cf. [3]).

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