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MINOR ALKALOIDS FROM *LYCORIS SANGUINEA*

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Key Word Index—*Lycoris sanguinea*; Amaryllidaceae; bulbs; norsanguinine; norbutsanguinine; sanguinine; lycorine; pseudolycorine; galanthamine; galanthine.

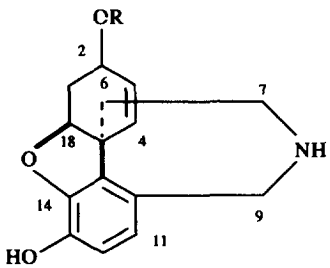
Abstract—From the bulbs of *Lycoris sanguinea*, two new alkaloids have been isolated and characterized as *nor*sanguinine and *nor*butsanguinine, in addition to other five known Amaryllidaceae alkaloids.

INTRODUCTION

As part of our studies on the chemical constituents of Amaryllidaceae plants [1–3], we report herein the isolation and characterization of two new alkaloids, namely *nor*sanguinine **1** and *nor*butsanguinine **2**, in addition to other known Amaryllidaceae alkaloids, namely sanguinine [4], lycorine [5, 6], pseudolycorine [5, 6], galanthamine [4, 7] and galanthine [4, 7]. Separation of the alkaloidal mixture was performed by silica gel column chromatography followed by purification by preparative TLC.

RESULTS AND DISCUSSION

Compounds **1** ($C_{15}H_{17}NO_3$) and **2** ($C_{19}H_{23}NO_5$) obtained as needles (mp 141–142°) and an oil, respectively, were both optically active and gave a positive $FeCl_3$ test for phenols.



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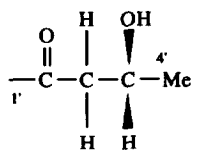
2 R = 

The ^1H NMR spectra of both compounds showed the presence of an AB system corresponding to the *ortho*-protons (H-11 and H-12) of ring A, as well as two olefinic protons, two methylene protons at the benzylic position and the absence of any *N*-methyl group. The UV spectra of these compounds were similar to that of galanthamine. These findings suggested that the compounds have a galanthamine-type skeleton. The ^1H NMR spectra of **1** and **2** were very similar, except for the signals around δ1.17, 4.04 and 2.45 ascribable to H-4′ and H-3′, respectively. These signals were assigned as follows. Monitoring of the higher lines (δ1.17) of the doublet (H-4′) gave internuclear double resonance (INDOR) at signals at *ca* δ4.04 assigned to (H-3′), whereas monitoring of the lowest lines (δ4.04) of (H-3′) gave INDOR peaks at δ1.17 (H-4′) and δ2.45 (H-2′). These data indicated that **2** has the partial formula $COCH_2CH(OH)Me$.

The other known compounds were identified by comparison of their physical and spectral data with those reported in the literature [8–12].

EXPERIMENTAL

General. Mps: uncorr. IR spectra were recorded in KBr or $CHCl_3$, EIMS were measured at 70 eV. NMR spectra were recorded in the solvent specified using TMS as int. standard at 200 MHz for ^1H and 50 MHz for ^{13}C. Silica gel Merck (70–230 mesh) was used for CC and flash CC. Silica gel 60 F_{254} (Merck) was used for analytical (0.25 mm) and prep. (1 mm) TLC. Spots on chromatograms were detected by spraying with Dragendorff's reagent and under UV light (254 nm), using the solvent system ($CHCl_3$–MeOH, 9:1).

Plant material. Lycoris sanguinea Maxim bulbs were collected in April 1991 at Assiut during the flowering period. Samples were authenticated by Prof. Dr N. El-Haddidy, Cairo University and a Voucher specimen (No. 2416) is deposited at the Herbarium of the Faculty of Pharmacy, Assiut University.

Extraction and isolation. Freshly collected bulbs (2 kg) were crushed and extracted with EtOH in a Soxhlet apparatus. After evapn, the extract was dissolved in 2% H_2SO_4 and the mixt. filtered. After removal of neutral material with Et_2O, the acidic soln was made basic (pH 8–9) with Na_2CO_3 and extracted with $CHCl_3$. Upon concn of the $CHCl_3$ extract, lycorine was pptd (300 mg). The concd $CHCl_3$ extract (2.8 g) was fractionated by flash CC eluting with $CHCl_3$–MeOH (9:1) affording pseudolycorine (60 mg), sanguinine (200 mg), galanthamine (90 mg), galanthine (10 mg) and alkaloidal mixt. A. Further purification of mixt. A by prep. TLC afforded *nor*sanguinine (80 mg) and *nor*butsanguinine (10 mg).

Nor*sanguinine* (**1**). Obtained as a solid residue recrystallized from $CHCl_3$–MeOH (1:1) as crystals, mp 141–142°. Blue–violet colour with $FeCl_3$ reagent. $[\alpha]_D^{20}$ −14° ($CHCl_3$; *c* 0.1). Molecular formula $C_{15}H_{17}NO_3$ deduced by EIMS *m/z* (rel. int.) 259.0637 $[M]^+$ (18) [calc. for $C_{15}H_{17}NO_3$, 259. 0633]. IR ν_{max}^{KBr} cm^{-1}: 3400, 1640, 1040, UV λ_{max}^{MeOH} nm 210 (log ε 3.4) and 296 (log ε 2.9). ^1H NMR ($CDCl_3$): δ2.03 (*m*, H-1α), 2.59 (*m*, H-1β), 4.18 (*m*, H-2), 5.99 (*d*, *J* = 10.5 Hz, H-3), 6.08 (*d*, *J* = 10.5 Hz, H-4), 1.77–1.83 (*m*, H-6), 3.22–3.35 (*m*, H-7), 3.92 (*d*, *J* = 15 Hz, H-9α), 4.04 (*d*, *J* = 15 Hz, H-9β), 4.56 (*m*, H-16), 6.43 (*d*, *J* = 8 Hz, H-11), 6.72 (*d*, *J* = 8 Hz, H-12). ^{13}C NMR ($CDCl_3$): δ29.8 (C-1, *t*), 61.3 (C-2, *d*), 127.8 (C-3, *d*), 127.3 (C-4, *d*), 48.3 (C-5, *s*), 39.1 (C-6, *t*), 46.2 (C-7, *t*), 53.6 (C-9, *t*), 132.3 (C-10, *s*), 120.1 (C-11, *d*), 111.6 (C-12, *d*), 144.8 (C-13, *s*), 142.1 (C-14, *s*), 133.8 (C-15, *s*), 88.1 (C-16, *d*).

Nor*butsanguinine* (**2**). Oil. Blue–violet colour with $FeCl_3$ reagent. $[\alpha]_D^{20}$ −26° ($CHCl_3$; *c* 0.1). Molecular formula $C_{19}H_{23}NO_5$ deduced by EIMS *m/z* (rel. int.) 345.1162 $[M]^+$ (63). [Calc. for $C_{19}H_{23}NO_5$, 345. 1159]. IR ν_{max}^{KBr} cm^{-1}: 3550, 2930, 1630, 1507. ^1H NMR ($CDCl_3$): δ2.45 (*d*, *J* = 7 Hz, H-2′), 4.04 (*m*, H-3′), 1.17 (*d*, *J* = 7 Hz, H-4′), 2.08 (*m*, H-1α), 2.61 (*d*, *J* = 16 Hz, H-1β), 5.38 (*t*-like, H-2), 5.93 (*dd*, *J* = 10, 6 Hz, H-3), 6.22 (*d*, *J* = 10.5 Hz, H-4), 1.53 (*d*, *J* = 13 Hz, H-6a), 2.04 (*d*, *J* = 13 Hz, H-6b), 3.01–3.11 (*m*, H-7), 3.48 (*d*, *J* = 14.5 Hz, H-94α), 4.01 (*d*, *J* = 14.5 Hz, H-9b), 4.68 (*br s*, H-16), 6.44 (*d*, *J* = 8 Hz, H-11), 6.75 (*d*, *J* = 8 Hz, H-12). ^{13}C NMR ($CDCl_3$): δ28.6 (C-1, *t*), 60.8 (C-2, *d*), 129.3 (C-3, *d*), 127.1 (C-4, *d*), 48.7 (C-5, *s*), 36.9 (C-6, *t*), 45.1 (C-7, *t*), 51.2 (C-9, *t*), 130.2 (C-10, *s*), 121.6 (C-11, *d*), 110.9 (C-12, *d*), 146.1 (C-13, *s*), 143.3 (C-14, *s*), 131.5 (C-15, *s*), 87.8 (C-16, *d*), 168.7 (C-1′, *s*), 39.6 (C-2′, *t*), 69.3 (C-3′, *d*), 24.3 (C-4′, *q*).

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