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NARCISINE, AN ALKALOID FROM *NARCISSUS TAZETTA*

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Key Word Index—*Narcissus tazetta*; Amaryllidaceae; bulbs; alkaloids; narcisine; lycorine; pseudolycorine; galanthamine; haemanthamine; tazettine; pretazettine.

Abstract—I report the isolation of lycorine, pseudolycorine, galanthamine, haemanthamine, tazettine, pretazettine and the new alkaloid narcisine from *Narcissus tazetta* bulbs. Structural elucidation was carried out by spectroscopic analysis.

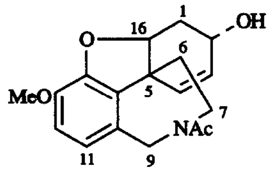
INTRODUCTION

The genus *Narcissus* comprises many species which have been reported to elaborate a variety of alkaloids [1, 2]. Moreover, most of these alkaloids are known for their medicinal properties and several isolated alkaloids have shown a wide range of biological activities [3]. As part of our studies on the chemical and biological constituents of the Amaryllidaceae [4, 5], I have isolated from the bulbs of *N. tazetta* the new alkaloid narcisine **1**, in addition to six known alkaloids, lycorine **2** [5], pseudolycorine **3** [2], galanthamine **4** [6, 7], haemanthamine **5** [1, 8], tazettine [9] and pretazettine **6** [10].

RESULTS AND DISCUSSION

Compound **1**, $C_{18}H_{21}NO_4$, was isolated by silica gel CC from $CHCl_3$–MeOH (9:1) eluates of extract B. It was recrystallized from methanol as needles (mp 158–140°) and gave a negative $FeCl_3$ test for phenols. Its UV maxima were similar to those of galanthamine-type alkaloids [11]. The IR spectrum was also similar to that of galanthamine and showed an intense absorption at 1706 cm^{-1} characteristic of a *N*-acetyl group and 3380 cm^{-1} for a hydroxyl group.

A careful examination of the ^1H NMR spectrum of **1** revealed the following: two singlets at δ3.86 and 2.01 due to the *O*-methyl and *N*-acetyl protons, respectively; two vicinal protons at δ8.12 and 6.84 corresponding to the two *ortho*-aromatic protons C-12 and C-11; two doublets at δ4.48 and 3.68 due to the β- and α-protons of the C-9 methylene group. The assignment of the β-proton at lower fields is in accordance with its *cis*-disposition with respect to the axial lone-pair of the nitrogen atom [12]. Two *dd* and *ddd* signals at δ6.68 and 6.08 were assigned to the protons H-4 and H-3.



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The ^{13}CNMR data of **1** in comparison with other Amaryllidaceae alkaloids [6, 13] are compiled in Table 1.

EXPERIMENTAL

All mps are uncorr. EIMS were recorded at 70 eV. NMR spectra were recorded at 200 and 50.3 MHz for ^1H and ^{13}C, respectively; chemical shifts are in δ with TMS as int. standard. TLC was carried out on silica gel using

Table 1. ^{13}CNMR (50.6 MHz) spectral data for narcisine (**1**)

C	δ ($CDCl_3$)
1	29.2 (*t*)
2	61.4 (*d*)
3	128.2 (*d*)^a
4	125.1 (*d*)^a
5	48.1 (*s*)
6	35.1 (*t*)
7	35.2 (*t*)
9	58.4 (*t*)
10	127.1 (*s*)^b
11	121.2 (*d*)
12	111.3 (*d*)
13	146.8 (*s*)^c
14	144.5 (*s*)^c
15	131.2 (*s*)^b
16	88.7 (*s*)
OMe	55.6 (*q*)
NCO Me	161.2/21.4 (*s*/*q*)

$^{a-c}$Values may be interchanged.

$CHCl_3$–MeOH (9:1). Spots were visualized by their fluorescence at 254 nm or after spraying with Dragendorff's reagent.

Plant material. Bulbs of *N. tazetta* L. were obtained from plants cultivated in the Experimental Station of Medicinal Plants, Faculty of Pharmacy, Assiut, and collected in July 1989 during flowering. Identity was confirmed by Prof. Dr N. El-Hadidy, Professor of Taxonomy, Cairo University. A voucher sample is kept in the Pharmacognosy Dept, Faculty of Pharmacy, Assiut.

Alkaloid isolation. Bulbs (4 kg) were ground in 96% EtOH and macerated for 24 hr. The EtOH soln was filtered, concd *in vacuo* and then acidified with 5% aq. HCl and extracted with $CHCl_3$ (4 × 500 ml). The combined $CHCl_3$ extracts yielded, after evapn of solvent, fr. A (40 g). The aq. phase was basified with conc. NH_3 and extracted with $CHCl_3$ (5 × 100 ml). Evapn of solvent gave fr. B (15 g). Fr. B was triturated in MeOH (100 ml) to give lycorine (1 g) as a creamy powder. The filtrate was concd and passed through a silica gel column (80 × 4 cm) eluting with $CHCl_3$–MeOH (9:1) and 300 frs (*ca* 50 ml) were collected over 48 hr. Frs 50–60 upon concn gave **3** (40 mg) while frs 70–75 gave impure **1** which was purified further by prep. TLC to give 50 mg. The remaining frs contained a mixt. of several compounds and were combined and passed through another silica gel column (4 × 60 cm) eluting with $CHCl_3$–MeOH (9:1). Frs 20–26 gave **4** (200 mg), frs 50–64 **5** (20 mg) and frs 71–72 **6** (30 mg).

Narcisine (**1**). Needles (MeOH) mp 158–160°. $[\alpha]_D^{20}$ $-18°$ ($CHCl_3$; *c* 0.5). UV λ_{max}^{MeOH} nm: 203, 231, 286. IR ν_{max}^{KBr} cm^{-1}: 3380, 2990, (Ac) 1620 and 1035. ^1H NMR (200 MHz, $CHCl_3$): δ8.12 (*d*, $J = 8.5$ Hz, H-12), 6.84 (*d*, $J = 8.5$ Hz, H-11), 6.68 (*d*, $J = 10$ Hz, H-4), 6.08 (*ddd*, $J = 10$, 4.4, 0.5 Hz, H-3), 5.22 (*m*, H-16), 4.48 (*d*, $J = 16$ Hz, H-9β), 3.86 (*s*, OMe), 3.68 (*d*, $J = 16$ Hz, H-9α), 3.18 (*m*, H-7), 2.71 (*m*, H-7), 2.67 (*m*, H-1), 2.01 (*s*, NCOOCH), 2.05 (*m*, H-6), 1.95 (*m*, H-1), 1.7 (*m*, H-6). ^{13}C NMR; see Table 1, EIMS *m/z* (rel. int.) 315, 1472 (100); $C_{18}H_{21}NO_4$ require, 315, 1470, 301 ($C_{17}H_{19}NO_4$) (27).

Lycorine (**2**). Needles (EtOH), mp 252–259°, undepressed on admixture with an authentic sample [5].

Pseudolycorine (**3**). Mp 236–240° (lit. 247–249° [2]). IR ν_{max}^{KBr} cm^{-1}: 3390–1570, 1500, 1470. UV λ_{max}^{MeOH} nm: (log ε) 211 (4.21), 287 (3.60). MS *m/z* (rel. int.) 289 $[M]^+$ (40), 288 (16), 270 (25), 229 (81), 228 (100).

Galanthamine (**4**). Cubes, mp 120–128° (lit. 127–129° [7]). HRMS *m/z* (rel. int.), $C_{17}H_{21}M_4O$, 287 $[M]^+$ (100). Identical to an authentic sample (TLC, mmp, ^1H NMR) [4].

Haemanthamine (**5**). Mp 194–198° (lit. 195–197° [1]). IR ν_{max}^{KBr} cm^{-1}: 3400, 2950, 1460, 1310. UV λ_{max}^{MeOH} nm: (log ε) 212 (3.05), 242 (3.20). MS *m/z* (rel. int.) 310 $[M]^+$ (41), 227 (100). ^1H NMR ($CDCl_3$) in agreement with lit. [1, 8].

Pretazettine (**6**). Mp 220–222° as HCl. Direct comparison (UV, IR, ^1H NMR [9] and co-TLC) with a ref. sample established identity.

Tazettine (**7**). A soln of pretazettine in 0.1 M NaOH was kept for 24 hr [10], giving tazettine (mp 219–223° as HCl).

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