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TATSIDINE, A NORDITERPENOID ALKALOID FROM *DELPHINIUM TATSIENENSE*

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Key Word Index—*Delphinium tatsienense*; Ranunculaceae, NMR spectra, alkaloid, tatsidine

Abstract—The isolation and structure determination of tatsidine, a new norditerpenoid alkaloid is reported The structure is derived on the basis of spectroscopic data.

INTRODUCTION

Earlier work on the alkaloids of *Delphinium tatsienense* Franch has resulted in the isolation and structure determination of tatsiensine, tatsinine, deltatsine and delelatine [1–4]. The plant also contains other norditerpenoid alkaloids: browniine, deacetylambiguine, delcosine, lycoctonine and the diterpenoid alkaloids: ajaconine, dictyzine, hetisine and hetisinone. We report here the isolation and structure of tatsidine, a new norditerpenoid alkaloid

RESULTS AND DISCUSSION

Purification by VLC [5] and by centrifugally accelerated thin layer chromatography (Chromatotron) [6] of the mother liquors left after the separation of some of the above mentioned alkaloids afforded a new alkaloid tatsidine (**1**), mp 191.5–193 5°. The molecular formula $C_{23}H_{35}NO_6$ was assigned for tatsidine on the basis of mass spectrum ($[M]^+$, *m/z* 421) and the ^1H and ^{13}C NMR data The ^1H NMR spectrum indicated the following functional groups· (δ) one *tert* methyl (0.85, 3H, *s*), an *N*-ethyl (1.08, 3H, *t*, $J = 7$ Hz), one methoxyl (3.30, 3H, *s*), a methylenedioxy (4.97, 5 06, each 1H, *s*). The ^{13}C NMR spectrum indicated 23 lines for 23 carbon atoms of the molecule and the SFORD and DEPT experiments showed five singlets due to quaternary carbons at δ32.9, 52.3, 78.6, 83.3, 89.7, seven doublets at 39.1, 43.2, 50.4, 62.6, 72.3, 80.4, 81.8, eight triplets at 26.4, 29 2, 30.1, 30 9, 36 5, 49.8, 60 4, 93.8 and three quartets at 13.4, 27.0, 56 3. On the basis of these data and comparison with the spectrum with tatsinine (**2**), the structure **1** is assigned to tatsidine.

The possibility of locating the methylenedioxy group on C-8 and C-9 in tatsidine was considered. In order to study the chemical shift of such a methylene group, we prepared **3** by methylenation [7] of lappaconitine. The methylene carbon of the methylenedioxy group appeared at δ96 2, whereas in all the compounds of type **1** this signal is observed at δ93 5 [8] The ^{13}C values for the new alkaloids are recorded in Table 1 Attempts to methylenate tatsinine (**2**) failed to give exclusively **1**, the ^{13}C NMR spectrum of the crude product indicated it to be a mixture which was predominantly methylenated at C-8, C-9. The structure **1** for tatsidine has been confirmed by assignment of all the protons and carbons by 2D NMR techniques [9]

EXPERIMENTAL

Mps corr ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ The roots of *Delphinium tatsienense* Franch were collected during the flowering stage in October 1981 in Gio-jia (Yunnan) China, and the plant was authenticated by Professor T L. Ming (Kunming Institute of Botany, Kunming, China) A herbarium specimen, voucher no 151476, is deposited in the Herbarium of the Department of Botany, The University of Georgia, Athens, GA 30602, U.S A

Isolation of tatsidine (**1**) The crude alkaloidal fraction E_1 obtained from the ethanol extract of the roots of *D tatsienense* at pH 8 afforded after chromatographic separation tatsiensine, deacetylambiguine, browniine, delcosine, hetsinine [1], tatsinine [2] and deltatsine [3]. The pooled mother liquors (3 69 g) were partitioned between $CHCl_3$ and 1 5% H_2SO_4 Basification of the acidic layer (aq NaOH, pH 12) gave a crude alkaloidal fraction (2 g) Chromatographic separation (VLC) [5] was carried out on Al_2O_3 and 182 fractions (20 ml each) were collected by elution with increasing amounts of hexane, hexane–$CHCl_3$ and $CHCl_3$–MeOH Fractions 107–110 were pooled (120 mg) on the basis of TLC (Al_2O_3, $CHCl_3$– 4% MeOH, 2 spots R_f 0 56, 0 5) and rechromatographed on a silica rotor (1 mm, EM 7741) of a Chromatotron [6] and eluted with Et_2O–0 75% MeOH–0 3% Et_2NH The slower moving band was collected (68 mg) and rechromatographed on two silica gel plates (0 5 mm, 20 × 20 cm) and developed with Et_2O–5% MeOH The homogeneous fraction gave tastsidine (**1**, 23 mg), crystallized from CH_2Cl_2–hexane, mp 191 5–193 5°, $[M]^+$ *m/z* 421 IR (nujol): 3400 cm^{-1} (OH)

8,9-*Methylenedioxy lappaconitine* (**3**): A mixture of lappaconitine (100 mg), *p*-toluenesulphonic acid (50 mg), diethoxymethane

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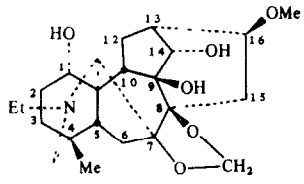

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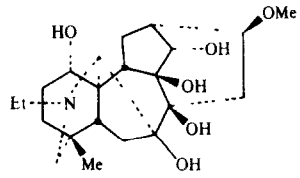

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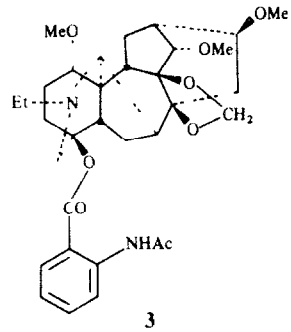

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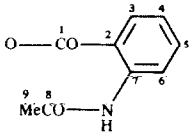
Table 1 ^{13}C chemical shifts and assignments for tatsidine (**1**), tatsinine (**2**) and 8,9-methylenedioxylappaconitine (**3**)

C	1	2 [2]	3‡
1	72.3 *d*	73.0	84.4 *d*
2	29.2 *t*	28.9	26.8[a] *t*
3	30.9 *t*	31.1	31.9 *t*
4	32.9 *s*	33.5	84.7 *s*
5	43.2 *d*	45.4	48.2 *d*
6	30.1 *t*	32.4	27.2[a] *t*
7	89.7 *s*	85.8	45.9 *d*
8	83.3 *s*	77.8	83.0 *s*
9	78.6 *s*	77.8	86.2 *s*
10	50.4 *d*	48.7	47.6 *d*
11	52.3 *s*	50.4	51.2 *s*
12	26.4 *t*	27.6	24.8 *t*
13	39.1 *d*	39.8	35.7 *d*
14	80.4 *d*	80.8	88.6 *d*
15	36.5 *t*	36.5	38.7 *t*
16	81.8 *d*	83.2	83.1 *d*
17	62.6 *d*	64.1	60.2 *d*
18	27.0 *q*	27.1	—
19	60.4 *t*	60.2	55.9 *t*
N-CH_2	49.8 *t*	49.9	49.0 *t*
Me	13.4 *q*	13.8	13.4 *q*
1-(OMe)	—		56.6 *q*
OCH_2O-	93.8* *t*	—	96.7† *t*
14-(OMe)	—	—	57.4 *q*
16-(OMe)	56.3 *q*	56.5	56.3 *q*

[a] These values may be interchanged.
*C(7)–C(8) -OCH_2O-
†C(8)–C(9) -OCH_2O-



1′–167.4 *s*, 2′–115.8 *s*,
3′-131.0 *d*, 4′–122.3 *d*,
5′-134.4 *d*, 6′-120.8 *d*,
7′-141.8 *s*, 8′–169.0 *s*,
9′-25.5 *q*

(1 ml) and C_6H_6 (100 ml) was refluxed in a Dean–Stark apparatus for 30 hr. The reaction mixture was filtered, dried over Na_2SO_4, evapd to a small vol. and chromatographed over neutral Al_2O_3. Elution with C_6H_6 gave a crude product which on crystallization from EtOH afforded **3** (30 mg) as colourless shining plates, mp 260–261° (Found: C, 66.26; H, 7.46. $C_{33}H_{44}N_2O_8$ requires: C, 66.44; H, 7.38%), $[\alpha]_D^{25}$ +20° (MeOH; *c* 0.3). $[M]^+$ *m/z* 596 (1%), 565 $[M-31]$, 417 $[M-C_9H_9NO_3]$. ^1H NMR ($CDCl_3$) δ: 1.12 (3H, *t*, J=7 Hz, N-CH_2Me), 2.22 (3H, *s*, NHAc), 3.29, 3.31, 3.34 (each 3H, *s*, OMe), 5.13 (1H, *d*, J = 1.5 Hz, H_a), 5.47 (1H, *d*, J = 1.5 Hz, H_b), 7.03 (1H, *ddd*, J = 8.5, 8.1 Hz, H-5′), 7.50 (1H, *ddd*, J = 8.5, 8.2 Hz, H-6′), 7.91 (1H, *dd*, J = 8.5, 2 Hz, H-4′), 8.67 (1H, *dd*, J = 8.5, 1 Hz, H-7′), 11.05 (1H, *br*, NH).

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