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THE STRUCTURE OF TATSININE, A NOVEL C_{19}-DITERPENOID ALKALOID FROM *DELPHINIUM TATSIENENSE* FRANCH

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A novel C_{19}-diterpenoid alkaloid designated as tatsinine has been isolated from the roots of Delphinium tatsienense and its structure (3) has been derived from ^1H NMR and ^{13}C NMR spectroscopic evidence.

In a previous communication[1], we have reported the identification of tatsiensine, deacetylambiguine, and six other diterpenoid alkaloids from the roots of *Delphinium tatsienense* Franch. We now wish to report the isolation and structure elucidation of an additional new C_{19}-diterpenoid alkaloid from the roots of the same plant. The crude alkaloids isolated at pH-8 from the ethanol extract of the roots, gave on chromatographic separation, *tatsinine*, m.p. 163-164°: $[\alpha]_D$ +9° (EtOH). The mass spectrum M^+, m/z 409 and elemental analysis of its perchlorate salt, m.p. 132-133°, indicated the molecular formula $C_{22}H_{35}NO_6$ for tatsinine.

The infrared spectrum showed ν_{max} 3660, 3540, 3510 cm^{-1} (OH), no bands in the carbonyl region and the ^1H NMR spectrum exhibited the following signals: δ 0.97 (3H, s, *tert* -$C\underline{H}_3$), 1.13 (3H, t, J = 7.5 Hz, CH_2-$C\underline{H}_3$), 3.43 (3H, s, $OC\underline{H}_3$), 3.7 (1H, t, J = 8 Hz), 3.95 (1H, d, J = 5 Hz). Biogenetic considerations and the presence of an ethyl and one methoxyl group in the molecule suggest that tatsisine is a new C_{19}-diterpenoid alkaloid. Acetylation under mild conditions afforded diacetyltatsinine, $C_{26}H_{39}NO_8$, m.p. 186°: M^+, m/z 493, δ 2.15 (3H, s, $OCOC\underline{H}_3$), 2.20 (3H, s, $OCOC\underline{H}_3$), indicating the presence of two readily acylable hydroxyl groups. Because almost without exception the naturally occurring C_{19}-diterpenoid alkaloids possess a methoxyl group at C(16) and oxygen functions at C(1)[2] and C(14), a partial structure (1) can be written for tatsinine.

The noise decoupled ^{13}C NMR spectrum of tatsinine in pyridine-d_5 showed twenty-two signals due to 22 carbon atoms of the molecule. The SFORD spectrum showed the presence of five singlet carbons at 86.2, 78.4, 78.1, 50.5 and 33.5 ppm., and three quartets at 55.8, 27.6 and 13.8 ppm. The remaining were seven doublets and seven triplets. The signals for two quaternary carbons at 33.5 and 50.5 ppm can be ascribed to C(4) and C(11), respectively. The other three quaternary carbons bear hydroxyl groups which can only be attached to C(7), C(8), C(9), C(10) and/or C(13). A hydroxyl

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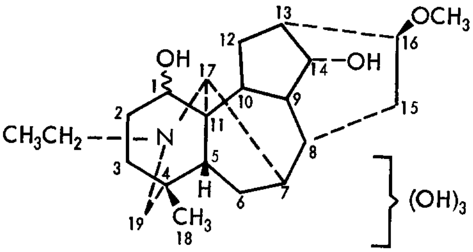

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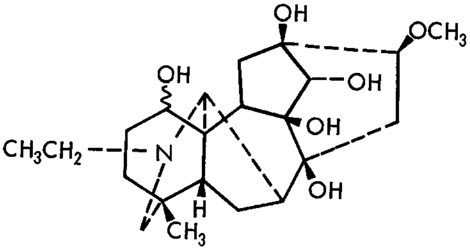
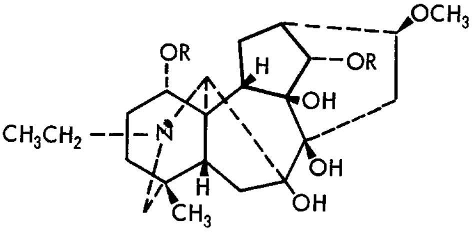


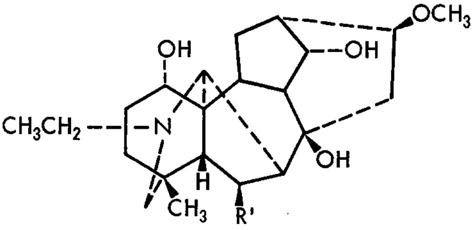
2

group at C(10) is expected to shift the C(11) singlet to ~ 55-56 ppm. As there is no signal near this position, an OH group at C(10) can be ruled out. The singlet at 86.2 ppm can only be assigned to C(7) or C(8) bearing a hydroxyl group. This evidence leads to the alternative structures (**2**) or (**3**) for tatsinine, the former belonging to the aconitine and the latter to the lycoctonine-type of C_{19}-diterpenoid alkaloids.



3 R = H

4 R = Ac



5 R' = H Karakoline

6 R' = OH Alkaloid B

A choice was made between **2** and **3** on the basis of the ^{13}C NMR chemical shift of C(12). When C(13) bears a hydroxy group as in structure **2**, the C(12)-signal normally appears in the range of 33.5 ppm - 38.0 ppm. The triplet appearing at 36.8 ppm has to be assigned to C(15). The C(6)-methylene adjacent to an OH group at C(7) is expected to exhibit a signal around 32.5-34.0 ppm, and the triplet at 33.1 ppm is assigned to this carbon. On the basis of these data, tatsinine has been assigned the structure (**3**) and the diacetate (**4**). The pattern of ^{13}C chemical shifts in tatsinine is similar to that of the known alkaloids karakoline (vilmorriamine B) (**5**)[3],

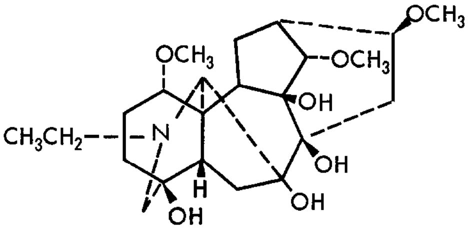
Table 1. Carbon-13 chemical shifts and assignments for tatsinine (**3**), 1,14-diacetyl tatsinine (**4**), karakoline (**5**), Alkaloid B (**6**) and ranaconine (**7**).†

Carbons	**3 (C_5D_5N)**	**3**	**4**	**5**[3]	**6**[4]	**7**[5]
C(1)	73.3 d	73.0	78.2	72.6 d	72.9	84.9
C(2)	29.8 t	28.9	26.1	29.1 t	29.7	27.1
C(3)	32.0 t	31.1	36.5	31.5 t	32.2	36.8
C(4)	33.5 s	33.5	34.6 s	33.1 s	32.8	71.1
C(5)	46.0 d	45.4	49.5	47.0 d	46.1	51.1
C(6)	33.1 t	32.4	33.2	25.4 t	72.0	32.4
C(7)	86.2 s	85.8	86.6 s	45.4 d	54.8	86.5
C(8)	78.1[a] s	77.8	77.1[a] s	74.6 s	76.0	78.0
C(9)	78.4[a] s	77.8	78.0[a] s	47.0 d	50.2	78.7
C(10)	40.8 d	39.8	36.5	40.5 d	40.0	37.5
C(11)	50.5 s	50.4	49.5 s	49.1 s	48.4	51.4
C(12)	27.9 t	27.6	28.0	29.9 t	29.7	26.3
C(13)	50.0 d	48.7	48.7	44.3 d	44.4	51.1
C(14)	81.5 d	80.8	82.3[b]	75.9 d	76.0	90.2
C(15)	36.8 t	36.5	37.2	42.5 t	42.4	38.1
C(16)	84.0 d	83.2	82.8[b]	82.5 d	82.4	83.0
C(17)	64.1 d	64.1 d	62.3	63.5 d	64.9	63.2
C(18)	27.6 q	27.1	26.4	27.8 q	27.4	-
C(19)	60.5 t	60.2	56.5	60.5 t	61.8	56.8
N-CH_2	50.4 t	49.9	50.9	48.6 t	48.4	50.0
CH_3	13.8 q	13.8	14.4	13.3 q	13.0	14.5
C(1)'						56.3
C(14)'						57.9
C(16)'	55.8 q	56.5	56.1	56.6 q	56.3	56.3
C=O			172.3s, 170.4s			
CH_3			22.0, 21.2			

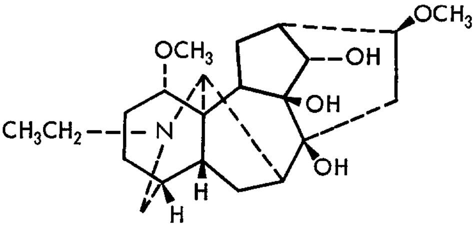
† In ppm downfield from TMS. Except as noted, spectra were taken in $CDCl_3$.

a,b These assignments may be interchanged in any vertical column.

c Values given for primed carbons refer to chemical shifts for methoxyls.



7 **Ranaconine**



8 **Episcopalisinine**

alkaloid B (**6**)[4], and ranaconine (**7**)[5]. (Table 1). The signal for C(14) shows an expected downfield shift of about 5 ppm due to the presence of an OH group at C(10), as is observed in episcopalisinine (**8**).[6] Among the aconitinine type of alkaloids, there are only two examples, viz: delphirine and talatizidine having a hydroxyl group at C(1) in the β-configuration. The remaining aconitine alkaloids and all lycoctonine alkaloids appear to bear the C(1)-hydroxyl or methoxyl group in an α-configuration[7]. The general range for the shift for a C(1)-α-OH is 72.0-73.0 ppm except where a C(10)-OH or a C(2)-C(3) double bond is present. The value for the C(1)-β-OH in delphirine is 69.0. [8],[9] Since the value for the C(1)-OH in tatsinine is 73.0 ppm, the C(1)-hydroxyl in tatsinine is assigned an α-configuration.

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