be crystallized; however, repeated recrystallization or prolonged standing in solution effects a change in its properties, and it becomes very sparingly soluble in most solvents. This could be due to opening of the lactone rings by hydrolysis followed by the formation of a betaine. A more rigorous examination of the compound was precluded by lack of material.

EXPERIMENTAL

The isolation of **1** has been described [1]. IR, ^{1}H NMR, ^{13}C NMR and EIMS: see text. UV λ_{max}^{EtOH} (log ε): 207 (3.20), 275 (2.42). Found: C, 57.62; H, 6.89; N, 4.38. $C_{15}H_{21}NO_6$ requires C, 57.88; H, 6.75; N, 4.50%. The base formed a picrate, mp 209–211°.

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THE C_{19}-DITERPENOID ALKALOIDS OF *ACONITUM DELPHINIFOLIUM*

V. NAMBI AIYAR, PALANIAPPAN KULANTHAIVEL and MICHAEL BENN

Chemistry Department, The University, Calgary, Alberta, Canada, T2N 1N4

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Key Word Index—*Aconitum delphinifolium*; Ranunculaceae; diterpenoid alkaloids; 14-*O*-acetylsachaconitine.

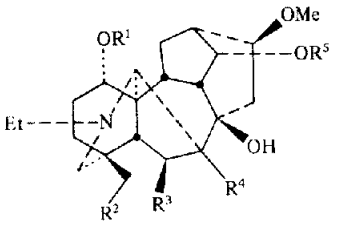
Abstract—Nine C_{19}-diterpenoid alkaloids were isolated from *Aconitum delphinifolium*, one of which was the apparently previously unknown 14-*O*-acetylsachaconitine.

INTRODUCTION

One of the few aconites native to N. America, *Aconitum delphinifolium* DC., has a range that extends from the Aleutian islands and Alaska down through the mountains of W. Canada into British Columbia and Alberta [1]. In all these places the plant has the reputation of being toxic, and it has been reported to have been used as an ingredient in an arrow-poison used by the aboriginal inhabitants of the Pacific North-West [2]. Such toxic properties appeared to us to be most likely due to the diterpenoid alkaloids to be expected in an aconite [3] and we therefore undertook an investigation of the alkaloids present in Albertan communities of *A. delphinifolium*.

RESULTS AND DISCUSSION

Whole plants were collected while in blossom and divided into flowers, leaves and stems, and roots. These all proved to contain substantial amounts of alkaloids, the flowers being particularly rich, but there seemed to be no qualitative differences in the distribution of individual components within the plant parts. Fractionation of the mixed alkaloids by conventional chromatographic procedures resulted in the isolation of nine C_{19}-diterpenoids. Analyses of the IR, mass, ^{1}H and ^{13}C NMR spectra of these compounds resulted in the identification of eight of these as known alkaloids: 14-*O*-acetylbrowniine (**1**), 14-*O*-acetyltalatisamine (**2**), browniine (**3**), condelphine (**4**), delcosine (**5**), delphinifoline (**6**), isotalatizidine (**7**) and virescenine (**8**) [4]. The ninth was similarly deduced to be 14-*O*-acetylsachaconitine (**9**), a compound which, so far as we have been able to ascertain, has not been described before. Thus MS suggested a $C_{25}H_{39}NO_5$ molecular formula; IR spectroscopy revealed the presence of hydroxyl and ester functionalities; and the ^{1}H NMR spectrum contained absorptions due to a quaternary *C*-methyl, an *N*-ethyl, an *O*-acetyl, two methoxy groups and, as well, one expected for H-14 of a lycoctonine-skeleton acyloxylated in this position [4]. The ^{13}C NMR data (see Table 1) was consistent with this information, and the



1 R^1 = Me, R^2 = R^3 = OMe, R^4 = OH, R^5 = Ac
2 R^1 = Me, R^2 = OMe, R^3 = R^4 = H, R^5 = Ac
3 R^1 = Me, R^2 = R^3 = OMe, R^4 = OH, R^5 = H
4 R^1 = H, R^2 = OMe, R^3 = R^4 = H, R^5 = Ac
5 R^1 = H, R^2 = R^3 = OMe, R^4 = OH, R^5 = H
6 R^1 = H, R^2 = OMe, R^3 = OH, R^4 = OH, R^5 = H
7 R^1 = H, R^2 = OMe, R^3 = R^4 = R^5 = H
8 R^1 = H, R^2 = OMe, R^3 = H, R^4 = OH, R^5 = H
9 R^1 = OMe, R^2 = R^3 = R^4 = H, R^5 = Ac
10 R^1 = OMe, R^2 = R^3 = R^4 = R^5 = H

Table 1. ^{13}C NMR data for 14-*O*-acetylsachaconitine [at 50.3 MHz in $CDCl_3$, shifts (δ) in ppm rel. to TMS, off-resonance multiplicities as indicated]

C	δ	C	δ
1	85.8 *d*	13	44.9 *d*
2	26.4 *t*	14	77.1 *d*
3	37.6 *t*	15	41.1 *t*
4	34.5 *s*	16	81.8 *d*
5	45.4 *d**	17	61.8 *d*
6	25.4 *t*	18	26.4 *q*
7	46.2 *d**	19	57.0 *t*
8	73.9 *s*		
9	50.5 *d*	NCH_2	49.4 *t*
10	35.6 *d*	Me	13.5 *q*
11	49.0 *s*		
12	28.6 *t*	MeO-1	56.2 *q*†
		16	56.3 *q*†
		–C=O	170.8 *s*
		Me	21.4 *q*

*†Assignments may be interchanged.

individual chemical shifts and multiplicities enables us to arrive at the structure **9**. Furthermore, saponification of **9** gave sachaconitine (**10**).

Curiously, none of the alkaloids which we identified corresponds to highly toxic aconitines, and we also found that chewing the flowers of *A. delphinifolium* did not produce the tingling and subsequent numbness of the tongue and lips which is produced by aceonitine and its congeners [3]. While Albertan populations of the plant probably contain enough of diterpenoid alkaloids to be toxic to grazing stock it seems highly unlikely that they would contribute much towards an effective arrow-poison.

EXPERIMENTAL

Plant material. Plants were collected in blossom near the Little Berland River and Cabin Creek crossings of the Forestry Trunk Road, Alberta. Voucher specimens are deposited in the Herbarium of the University of Calgary.

Extraction and isolation of the alkaloids. The freshly collected plants were separated into flowers, stems and leaves, and roots. These were then repeatedly macerated in EtOH to afford extracts from which the alkaloids were isolated in the usual way [5]. The alkaloid content of both roots, and stems and leaves was about 0.3% wt/marc, but the flowers contained much more, *ca* 2.5%.

Analysis by TLC (silica gel 60, $CHCl_3$–MeOH, 4 : 1; with I_2 vapour to detect the components) indicated no qualitative differences in the alkaloid mixtures obtained from the various plant parts, so they were combined. A portion of this material (1.6 g) was then subjected to CC over neutral alumina. Individual fractions were analysed by TLC, and pooled accordingly. If the products thus obtained were still impure, they were subjected to prep. TLC (1 mm thick silica gel 60, $CHCl_3$–MeOH 5 : 1). By these means we isolated 14-*O*-acetylbrowniine (550 mg), isotalatizidine (230 mg), browniine (195 mg), 14-*O*-acetyltalatisamine (60 mg), virescenine (35 mg), condelphine (30 mg) and delcosine (25 mg): all of which had IR, mass, ^{1}H and ^{13}C NMR spectra in accord with the data reported in the literature for these bases [4]. Delphinifoline was also isolated: but in an amount (*ca* 5 mg) that was insufficient for a ^{13}C NMR spectrum, although the other spectroscopic data agreed with that previously recorded for this alkaloid [6].

In addition we obtained 14-*O*-acetylsachaconitine as an amorphous but homogeneous solid (110 mg) with the following properties: IR $\nu_{max}^{(film)}$ cm^{-1}: 3450 (br), 1743, 1495, 1458, 1443, 1365, 1239, 1094 and 1056; EIMS (70 eV) *m/z* (rel. int.): 433 (13) ($[M]^{+\cdot}$ for $C_{25}H_{39}NO_5$) and 402 (98) (loss of a methoxy group from C-1 [7]); ^{1}H NMR (200 MHz, $CDCl_3$; $CHCl_3$ as internal ref.: δ7.24; rel. TMS): δ0.76 (3H, *s*), 1.05 (3H, *t*, J = 7 Hz, Me of N-Et), 2.03 (3H, *s*, AcO), 3.25 and 3.20 (each 3H, *s*, 2 × MeO), and 4.79 (1H, *dd*, J = 5 Hz, H-14); the ^{13}C NMR data is in Table 1; $[\alpha]_D$ + 24.8° (*c* 0.6; $CHCl_3$). The base formed a crystalline $HClO_4$ salt, mp 182–184°.

Saponification of **9** (25 mg) with NaOH–MeOH gave the desacetyl compound (*ca* 20 mg) which was shown to be sachaconitine (**10**) by direct (IR) comparison with an authentic specimen.

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