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Alkaloids from *Delphinium pentagynum*

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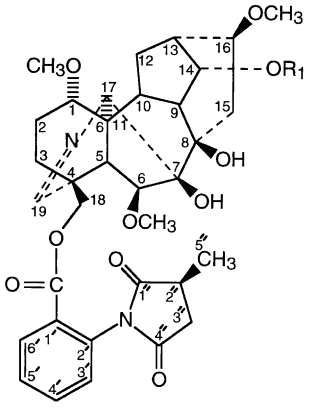
Abstract

Aerial parts of a collection of *Delphinium pentagynum* Lam. from Niebla, Southern Spain, furnished one diterpene alkaloid, 2-dehydrodeacetylheterophylloidine, two norditerpene alkaloids, 14-demethyl-14-isobutyrylanhweidelphinine and 14-demethyl-14-acetylanhweidelphinine, the known alkaloids 14-deacetylnudicauline, methyllycaconitine, 14-deacetyl-14-isobutyrylnudicauline, 14-acetylbrowniine, browniine, delcosine, lycoctonine, 18-methoxygadesine, neoline, karakoline and the aporphine alkaloid magnoflorine. Structures of the alkaloids were established by MS, 1D and 2-D NMR techniques.

Keywords: *Delphinium pentagynum*; Ranunculaceae; Diterpene alkaloids; Norditerpene alkaloids; 2-Dehydrodeacetylheterophylloidine; 14-Demethyl-14-isobutyrylanhweidelphinine; 14-Demethyl-14-acetylanhweidelphinine

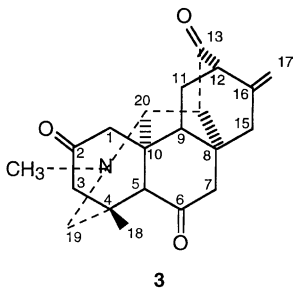
1. Introduction

In the early 1980s work in the La Laguna institute on a collection of *Delphinium pentagynum* Lam. from Cadiz in Southern Spain resulted in the isolation of nine norditerpene alkaloids gadesine, dihydrogadesine, 14-acetyldihydrogadesine, pentagynine, dihydropentagynine, pentagydine, pentagyline, gadenine and karakoline (González et al., 1979, 1982, 1983a,b, 1984). We have now studied a collection of this species from near Niebla in Huelva Province and report the isolation and structure determination of three new diterpene alkaloids, 14-demethyl-14-isobutyrylanhweidelphinine (**1**), 14-demethyl-14-acetylanhweidelphinine (**2**) and 2-dehydrodeacetylheterophylloidine (**3**). Ten previously known diterpene alkaloids also isolated from this collection were 14-deacetylnudicauline (Pelletier et al., 1988), methyllycaconitine (Pelletier et al., 1981), 14-deacetyl-14-isobutyrylnudicauline (Sherestha and Katz, 2000), 14-acetylbrowniine (Pelletier et al., 1980), browniine (Pelletier et al., 1981), delcosine (Pelletier et al., 1978), lycoctonine (Pelletier et al., 1981), 18-methoxygadesine (González et al., 1983a,b), neoline and karakoline (Konno et al., 1982) and in addition the aporphine alkaloid magnoflorine (Suess and Stermitz, 1981). All known alkaloids were identified by MS, ^{1}H and ^{13}C NMR spectrometry and comparison with data in the literature.



1 R = $(CH_3)_2{}_{\beta}CHC{}_{\alpha}{}^{|}=O$

2 R = $CH_3{}_{\alpha}{}^{|}C=O$



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2. Results and discussion

The ^{1}H-NMR spectrum of compounds **1** and **2** (Table 1) displayed the distinctive resonances of norditerpenoid alkaloids (Table 1) containing the *N*-(methylsuccinimido)anthranoyl (MSA) ester group, i.e. the methyl signal on C-2 at δ 1.46, three methoxyl groups at δ 3.16, 3.29, 3.30, downfield resonances for the H-14 methine signal at δ 4.81 in **1** and at δ 4.79 in **2**, the C-18 methylene protons at δ 4.39 and 4.32, and the five signals of the aromatic moiety in the region δ 7.27–8.02. The ^{13}C NMR spectra (Table 1) and the mass spectra with a base peak at *m/z* 216 supported the presence of the MSA ester in both **1** and **2**. The ^{1}H NMR resonances of **1** and **2** compare closely with those reported for 14-deacetyl-14-isobutyrylnudicauline and nudicauline (Sherestha and Katz, 2000), except for the absence of the resonance attributable to an *N*-ethyl group. A broadened singlet at δ 7.47 was compatible with the presence of an azomethine proton on vinylic C-19 whose resonance appeared at δ 163.3 and which in turn was attached to C-4 at 47.2 (Desai et al., 1994); these assignments were verified by the three-bond correlations of H-19 with H-5 and H-18 (Table 1).

Table 1
^{13}C, ^{1}H-NMR and HMBC data for compounds **1** and **2**[a,b]

1			**2**		
Position	δ H	δ C	δ H	δ C	HMBC
1	3.26 *t* (4.6)	81.4 *d*	3.24 *t* (4.2)	81.4 *d*	C-3, 10, 11, 1-OMe
2a	1.76 *m*	21.3 *t*	1.75 *m*	21.4 *t*	C-1, C-11
2b	1.50 *m*		1.49 *m*		
3a	1.69 *m*	24.9 *t*	1.70 *m*	24.9 *t*	C-2, 5
3b	1.69 *m*		1.70 *m*		
4		47.2 *s*		47.2 *s*	
5	1.86 *brs*	45.6 *d*	1.87 *brs*	45.6 *d*	C-4, 10, 11, 19
6	3.76 *s*	91.5 *d*	3.74 *s*	91.5 *d*	C-4, 7, 8, 11, 6-OMe
7		86.4 *s*		86.4 *s*	
8		77.3 *s*		77.3 *s*	
9	2.96 *m*	42.7 *d*	3.00 *dd* (11, 6.3)	42.3 *d*	C-8, 10, 12, 13, 15
10	2.06 *m*	43.3 *d*	2.06 *m*	43.3 *d*	C-1, 8, 17
11		50.01 *s*		50.0 *s*	
12a	2.05 *m*	29.5 *t*	2.04 *m*	29.5 *t*	C-10, 11, 13
12b	1.58 *m*		1.58 *m*		C-10, 11, 13
13	2.45 *brt* (5.5)	38.3 *d*	2.45 *brt* (5.5)	38.3 *d*	C-10, 12, 15, 16
14	4.81 *t* (4.7)	75.6 *d*	4.79 *t* (4.7)	75.9 *d*	C-8, 16, C=O_{14}
15a	2.91 *dd* (15,9)	33.4 *t*	2.91 *dd* (15, 9)	33.3 *t*	C-7, 8, 9, 13, 16
15b	1.63 *m*		1.63 *m*		
16	3.30 *m*	81.9 *d*	3.32 *m*	82.0 *d*	C-12, 14, 16-OMe
17	3.88 *brs*	64.5 *d*	3.89 *brs*	64.5 *d*	C-5, 6, 19
18a	4.39 *brd* (11.5)	66.5 *t*	4.40 *brd*	66.5 *t*	C-3, 5, C=O_{81}
18b	4.32 *brd* (11.5)		4.32 *d*		
19	7.47 *brs*	163.3 *d*	7.48 *brs*	163.4 *d*	C-4, 17
1-OMe	3.29 *s*[b]	56.3 *q*	3.33 *s*[b]	56.3 *q*	
6-OMe	3.30 *s*[b]	58.3 *q*	3.30 *s*[b]	58.7 *q*	
16-OMe	3.16 *s*[b]	56.0 *q*	3.16 *s*[b]	56.2 *q*	
C=O_{Bz}		164.0 *s*		163.4 *s*	
1′		126.5 *s*		126.5 *s*	
2′		*s*	133.1 *d*	133.2 *d*	
3′	7.27 *brd* (7.5)	130.1 *d*	7.27 *brd* (7.5)	130.2 *d*	
4′	7.68 *td* (7.7, 1.5)	134.0 *d*	7.68 *td* (7.7, 1.5)	134.0 *d*	
5′	7.54 *td* (7.7, 1.1)	129.2 *d*	7.54 *td* (7.7, 1.1)	129.5 *d*	
6′	8.02 *brd* (7.7)	130.9 *d*	8.02 *brd* (7.7)	130.9 *d*	
1″		179.7 *s*			
2″		35.3 *d*		35.3 *d*	
3″		36.9 *t*		36.9 *t*	
4″		175.6 *s*		175.8 *s*	
5″	1.46 *brs*[b]	16.4 *q*	1.46 *brs*[b]	16.5 *q*	
C=O_{Ac}		177.2 *s*		171.7 *s*	
C_α	2.55 *sept* (7)	34.2 *d*		2.05 *s*[b]	
C_β	1.17 *d* (7)[b]	18.8 *q*		21.4 *q*	
	1.16 *d* (7)[b]	18.7 *q*			

[a] Assignments based on cosy, HMQC and DEPT experiments. Chemical shifts in ppm relative to TMS; coupling constants in parentheses are in Hz.
[b] Intensity three protons.

That the isobutyrate resp. acetate esters were attached to C-14 and the MSA ester to C-18 in both **1** and **2** was established by three-bond correlations in the HMBC spectra (Table 1). Resonances at 91.5, 82.4 and 81.4 could be assigned to C-6, C-16 and C-1 with β-, β- and α-oriented methoxyls respectively, because of the similarity of the ^{13}C NMR resonances to those of anhweidelphinine (Sun and Benn, 1992) and other structurally related alkaloids (Pelletier et al., 1984) thus leading to the complete formulation of **1** as 14-demethyl-14-isobutyrylanhweidelphinine and **2** as 14-demethyl-14-acetylanhweidelphinine.

The ^{1}H-NMR spectrum of the third new alkaloid with the empirical formula $C_{21}H_{25}NO_3$ derived from the high resolution mass and the ^{13}C NMR spectra exhibited signals characteristic of an exocyclic methylene group at δ 4.96 and 4.90, a tertiary methyl at δ 1.38 and an *N*-methyl at δ 2.28, but no signals attributable to –OMe groups, thus leading to the conclusion that it was a diterpenoid, not a norditerpenoid alkaloid. The molecular formula indicated the presence of 10 degrees of unsaturation, four of which were accounted for by three carbonyl groups (^{13}C signals at δ 210.4, 207.2 and 205.1) and the exocyclic methylene (^{13}C singlet at δ 141.7 and triplet at δ 110.9). The remaining six degrees of unsaturation suggested that the substance possessed the hexacyclic carbon skeleton of an atisane alkaloid. This was verified and the location of the functional groups on the carbon skeleton established by analysis of the ^{1}H, ^{13}C-NMR, HMQC and HMBC spectra (Table 2).

The chemical shift of C-16 at δ 141.7 ruled out the location of one of the three carbonyl groups on C-15; in addition the signals of H-15a and H-15b were mutually coupled doublets ($J = 18$ Hz) at δ 2.47 and 2.37 split by allylic coupling to H-17a and H-17b. A choice among the remaining possibilities could be made as follows. The chemical shifts of C-1 (δ 48.2) and C-3 (δ 55.4), and the absence of a triplet near δ 20.0 ordinarily characteristic of C-2 indicated that one of the carbonyls was situated on C-2. The second carbonyl was placed on C-13 because of the chemical shifts of C-12 and C-14 (doublets at δ 52.8 resp. 60.5). Finally the chemical shifts of C-5 and C-7 (δ 58.6 and δ 50.9) were consistent with placement of the third carbonyl group on C-6. The locations of these carbonyl groups at C-2, C-6 and C-13 were verified by the HMBC experiments detailed in

Table 2
^{1}H-NMR (500 MHz) and ^{13}C (125 MHz) spectral data for compound **3**[a]

$CDCl_3$			C_6D_6		
Position	δ H	δ C	δ H	δ C	HMBC
1a	24.5 *dd* (15, 1.5)	48.2 *t*	2.14 *dd* (15.2, 1.5)	47.8 *t*	C-2, 3, 5, 20
1b	2.23 *d* (15)		1.42 *d* (15)		C-2, 5, 9, 10, 20
2		207.2 *s*		204.9 *s*	
3a	2.21 *d* (15.3)	55.4 *t*	1.98 *dd* (15.3, 1.7)	55.2 *t*	C-2, 4, 19
3b	2.17 *dd* (15.3, 1.6)		1.68 d (15.3)		C-2, 4, 18, 19
4		40.3 *s*		39.4 *s*	
5	2.14 *brs*	58.6 *d*	1.43 *brs*	58.1 *d*	C-3, 4, 6, 18, 19, 20
6		205.1*s*		203.4 *s*	
7a	2.64 *d* (19.2)	50.9 *t*	2.19 *d* (19)	50.7 *t*	C-6, 8, 9, 14
7b	2.36 *dd* (19.2, 1.3)		1.88 *brd* (19)		C-6, 8, 14, 15
8				41.7 *s*	
9	2.10 *m*	47.9 *d*	1.23 *m*	46.7 *s*	C-10, 12, 14, 20
10		47.3 *s*		49.7 *s*	
11a	1.90 *m*	22.9 *t*	1.27 *dd* (13.5, 1.5)	22.7 *t*	C-8, 9, 12, 13, 16, 20
11b	1.88 *m*		1.25 *dd* (13.5, 3.8)		C-8, 9, 12, 13, 16, 20
12	2.93 *t* (2.6)	52.8 *d*	2.70 *brd* (3.2)	52.9 *d*	C-9, 11, 14, 15, 16, 17
13		210.4 *s*		208.5 *s*	
14	2.50 *brd* (2.5)	60.5 *d*	2.05 *brs*	60.4 *d*	C-7, 8, 13, 20
15a	2.47 *dt* (18, 2.5)	35.2 *t*	1.78 *dt* (18, 2.5)	34.9 *t*	C-16, 17
15b	2.37 *dt* (18, 2)		1.72 *dt* (18, 2)		C-8, 9, 14, 16, 17
16		141.7 *s*		143.0 *s*	
17a	4.96 *brt* (2.5)	110.9 *t*	4.78 *brs*	109.4 *t*	C-12, 15, 16
17b	4.80 *t* (2)		4.54 *brs*		C-12, 15, 16
18	1.38 *s*[b]	28.4 *q*	1.25 *s*[b]	28.4 *q*	C-3, 4, 5, 19
19a	2.43 *d* (12.5)	60.6 *t*	1.97 *d* (12.3)	60.6	C-3, 4, 5, 18, 20, 21
19b	1.92 *d* (12.5)		1.54 *d* (12.3)		C-3, 4, 5, 18, 20, 21
20	2.30 *brs*	72.5 *d*	2.15 *brs*	72.7 *d*	C-1, 8, 9, 10, 13, 14, 19
21	2.10 *s*[b]	43.1 *q*	1.96 *s*[b]	4.28 *q*	C-19, 20

*Solvent C_6D_6.
[a] 500 MHz, $CDCl_3$; assigments based on COSY, HMQC and DEPT experiments.
[b] Chemical shifts in ppm relative to TMS; coupling constats in parentheses are in Hz.

Table 2. Compound **3** was therefore 2-dehydrodeacetylheterophylloidine, an oxidation product of deacetylheterophylloidine from *D. albiflorum* (Ulubelen et al., 1995) which contains an α-orientated hydroxyl group on C-2.

The only alkaloid encountered in both the original study of *D. pentagynum* from Cadiz and the present study of the same plant from near Niebla in a nearby district was karakoline. The difference between the two collections is apparently not due to time of collection, but may be due to different environmental and climatic conditions. The methylsuccinimidoanthranoyllycoctonine (MSAL) norditerpene alkaloids constitute a unique group of alkaloids within the norditerpenoid complex commonly found in larkspurs (*Delphinium* spp.). Two of these, methyllycaconitine and 14-deacetylnudicauline which were present in our collection of *D. pentagynum* have been shown to be potent neurophysiological toxins in mammalian systems (Benn and Jacyno, 1983). The alkaloids found in *D. pentagynum* thus make this species a highly poisonous plant.

3. Experimental

3.1. General experimental procedures

Mps are uncorrected and were taken on a Reichert Thermovar apparatus. IR spectra were run on a Bruker-IFS-55 spectrometer. Optical rotations were determined using a Perkin–Elmer-241 polarimeter with a 1-dm cell. EIMS and exact mass measurements were determined on a Micromass Autospec mass spectrometer at 70 eV. ^{1}H and ^{13}C NMR spectra were run on Bruker-AMX-400 or AMX-500 spectrometers. Merck Al_2O_3 (neutral, 200–300 mesh), Schleicher and Schuell 394 732, and Sephadex LH-20, were used for column chromatography (CC) and TLC, respectively. Spots on chromatograms were detected with Dragendorff's reagent.

3.2. Plant material

Aerial parts of *D. pentagynum* L. were collected on July 20, 1998 near Niebla, Huelva Province, Spain. The collection was identified by Prof. Julián Molero and César Blanché, Faculty of Pharmacy, Department of Botany, Universidad de Barcelona. A voucher specimen (No. BCF 46243) has been deposited in the herbarium of that department.

3.2.1. Extraction and isolation

Air-dried and powdered aerial parts (2.56 kg) were extracted with H_2O (90%) EtOH at room temperature for eight days. Filtration and removal of solvent at red press afforded a dark brown residue (117 g). This residue was treated with 0.5 M H_2SO_4 and filtered. The acidic solution was extracted three times with CH_2Cl_2 (350 ml each) to give crude material (6.7 g). This residue was subjected to column chromatography on basic Al_2O_3 (activity I). The eluting solvent was a gradient of hexane, EtOAc and MeOH, 100 fractions (100 ml each) being collected. On the basis of TLC analyses, the fractions were pooled to give nine fractions. Fractions 1–4 and 9 contained non-alkaloidal residues and were not investigated further. Fraction 5 (480 mg) was applied to a column of basic Al_2O_3 and eluted with hexane–EtOAc of increasing polarity. Subfractions 12–13 after further purification on alumina preparative plates using EtOAc as eluent gave 14-deacetyl-14-isobutyrylnudicauline (Sherestha and Katz, 2000) (6.5 mg). Subfractions 45–49 were subjected to prepared TLC on Al_2O_3 (EtOAc–MeOH, 4:1, twice), with two bands were cut. The upper band gave **1** (4.5 mg), whereas the lower was extracted with MeOH to give **2** (6 mg). Fractions 6 (622 mg) afforded after purification over Sephadex LH-20 (hexane–$CHCl_3$–MeOH, 2:1:1) (560 mg) methyllycaconitine (Pelletier et al., 1981), which was the major alkaloid isolated. Repeated chromatography of fraction 7 (250 mg) of the initial chromatogram over Sephadex LH-20 (hexane–MeOH–$CHCl_3$, 2:1:1) furnished additional methyllycaconitine (120 mg) and 14-deacetylnudicauline (8 mg) (Pelletier et al., 1988). Fraction 8 (360 mg) was applied to Sephadex LH-20 (hexane–MeOH–$CHCl_3$, 1:1:1) afforded methyllycaconitine (115 mg) and 18-methoxygadesine (González et al., 1983a,b) (4.5 mg). The acid aqueous phase was neutralized to pH 7 and extracted with CH_2Cl_2 to give crude material (720 mg). Chromatography of this residue on alumina, using gradient elution with hexane–EtOAc, followed by further purification over Sephadex LH-20 (hexane–MeOH–$CHCl_3$, 2:1:1) when necessary, allowed the isolation, in order of increasing polarity, 2-dehydrodeacetylheterophylloidine **3** (3.5 mg), 14-acetylbrowniine (Pelletier et al., 1980) (7 mg), browniine (Pelletier et al., 1981) (11 mg), neoline (De la Fuente et al., 1989) (15 mg) delcosine (Pelletier et al., 1978) (4.5 mg) and karakoline (Konno et al., 1982) (8 mg). The neutral aqueous phase was basified with 20% NaOH to pH 12 and extracted with CH_2Cl_2 to give crude alkaloidal material (570 mg). Repeated chromatography of this residue over Sephadex LH-20 (hexane–MeOH–$CHCl_3$, 1:1:1) afforded lycoctonine (Jacyno et al., 1996) and magnoflorine as a zwitterion (Suess and Stermitz, 1981). Known alkaloids were identified by comparison of m.p. and spectral data (IR, MS, ^{1}H and ^{13}C NMR) with literature values.

3.3. 14-Demethyl-14-isobutyrylanhweidelphinine (*1*)

Amorphous substance; $[\alpha]_D^{25} + 65.2°$ (*c* 0.14, $CHCl_3$); IR ν_{max}^{NaCl} 3491, 2922, 2850, 1715, 1602, 1493, 1455, 1391, 1259, 1190, 1089 cm^{-1}. ^{1}H and ^{13}C NMR (Table 1); HREIMS *m/z* 708.3265 (Calc. for $C_{38}H_{48}N_2O_{11}$,

708.3258; EIMS m/z 708 (M^+, 46), 693) M^+–CH_3, 49), [677 M^+–OMe] 30), 676 (10), 662 (10), 216 (100).

3.4. 14-Demethyl-14-acetylanhweidelphinine (**2**)

Amorphous; $[\alpha]_D^{25} + 67.1°$ (c 0.16, $CHCl_3$); IR ν_{max}^{NaCl} 3476, 2930, 2850, 1715, 1602, 1493, 1455, 1391 1256, 1188, 1089 753 cm^{-1}.^1H, ^{13}C NMR (Table 1); HREIMS m/z 680.2963 (Calc. for $C_{36}H_{44}N_2O_{11}$, 680.2945); EIMS m/z 680 (M^+, 11), 655 (M^+–Me,14), 649 M^+–OMe, 9), 634 (25), 619 (9), 603 (6), 430 (8), 216 (100).

3.5. Dehydrodeacetylheterophylloidine (**3**)

Amorphous; $[\alpha]_D^{25} - 73.3°$ (c 0.17, $CHCl_3$); IR ν_{max}^{NaCl} 2923, 1707 broad, 1457, 1305, 1254, 1216, 1105, 1033, 905, 755 cm^{-1}. ^1H and ^{13}C NMR (Table 2); HREIMS m/z 339.1833, Calc. for $C_{21}H_{25}NO_3$, 339.1834; EIMS m/z 339 M^+,100), 322 (27), 311 (28), 296 (11), 282 (30), 268 (18), 254 (12).

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References

Benn, M.H., Jacyno, J.M., 1983. In: Pelletier, S.W. (Ed.), Alkaloids: Chemical and Biological Perspectives, vol. 1. J. Wiley and Sons, New York, NY, pp. 153–210.

De la Fuente, G., Díaz Acosta, R., Orribo, T., 1989. Diterpenoid alkaloids from *Delphinium pictum* Willd. The structure of pictumine. Heterocycles 29, 205–208.

Desai, H.K., Cartwright, B.T., Pelletier, S.W., 1994. Ajadinine: A new norditerpene alkaloid from the seeds of *Delphinium jacis*. The complete NMR assignments for some lycoctonine alkaloids. J. Nat. Prod. 57, 677–682.

González, A.G., de la Fuente, G., Díaz, R., Fayos, J., Martínez-Ripoll, M., 1979. Gadesine, a new C-19 kiterpene alkaloid from *Delphinium pentagynum* Lam. Tetrahedron Lett. 1, 79–80.

González, A.G., de la Fuente, G., Díaz, R., 1982. Four new diterpenoid alkaloids from *Delphinium pentagynum*. Phytochemistry 21, 1781–1782.

González, A.G., de la Fuente, G., Díaz, R., Jones, P.G., Sheldrick, G.M., 1983a. The structure of pentagydine, a new diterpene alkaloid. Tetrahedron Lett. 24, 959–960.

González, A.G., de la Fuente, G., Munguía, O., 1983b. 18-Methoxygadesin, a new diterpenoid alkaloid. Heterocycles 20, 409–411.

González, A.G., de la Fuente, G., Díaz Acosta, R., 1984. Structures of gadenine and pentagyline, two new diterpene alkaloids. Heterocycles 22, 17–20.

Jacyno, J.M., Harwood, J.S., Lin, N.H., Campbell, J.E., Sullivan, J.P., Holladay, M.W., 1996. Lycaconitine revisited: Partial synthesis neuronal nicotinic acetylcholine receptor affinities. J. Nat. Prod. 59, 707–709.

Konno, C., Shirasaka, M., Hikino, H., 1982. Structure of senbusin A, B and C, diterpene alkaloids of *Aconitum michaeli* roots from China. J. Nat. Prod. 45, 128–133.

Pelletier, S.W., Sawhney, R.S., Mody, N.V., 1978. Ambiguine and dihydroajaconine: two new diterpenoid alkaloids from *Consolida ambigua*. Heterocycles 9, 1241–1247.

Pelletier, S.W., Sawhney, R.S., Desai, H.K., Mody, N.V., 1980. The diterpene alkaloids of *Consolida ambigua*. J. Nat. Prod. 43, 395–406.

Pelletier, S.W., Dailey Jr., O.D., Mody, N.V., Olsen, J.D., 1981. Isolation and structure elucidation of the alkaloids of *Delphinium glaucescens* Rydb. J. Org. Chem. 46, 3284–3293.

Pelletier, S.W., Mody, N.V., Joshi, B.S., Schramm, L.C., 1984. In: Pelletier, S.W. (Ed.), Alkaloids: Chemical and Biological Perspectives, vol. 2. John Wiley and Sons, New York, NY, pp. 205–462.

Pelletier, S.W., Panu, A.M., Kulanthaivel, P., Olsen, J.D., 1988. New alkaloids from *Delphinium andersonii* Gray. Heterocycles 27, 2387–2393.

Sherestha, P.M., Katz, A.S., 2000. Norditerpenoid alkaloids from the roots of *Delphinium stapeliosum*. J. Nat. Prod. 63, 2–5.

Suess, T.R., Stermitz, F.B., 1981. Alkaloids of *Mahonia repens* with a brief review of previous work in the genus *Mahonia*. J. Nat. Prod. 44, 680–687.

Sun, F., Benn, M., 1992. Norditerpenoid alkaloids of *Delphinium zalil*. Phytochemistry 31, 3247–3250.

Ulubelen, A., Desai, H.K., Yoshiro, B.S., Venkateswarlu, V., Pelletier, S.W., Meriçli, A.H., Meriçli, F., Özçelik, H., 1995. Diterpenoid alkaloids from *Delphinium albiflorum*. J. Nat. Prod. 58, 1555–1561.