DITERPENOID ALKALOIDS FROM DELPHINIUM PICTUM WILLD. THE STRUCTURE OF PICTUMINE

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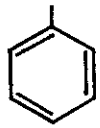
Abstract - A new C-19 diterpenoid alkaloid pictumine (1) was isolated from Delphinium pictum Willd. subsp. pictum together with the known bases neoline (2), bullatine C (14-acetylneoline) (3), delphisine (8,14-diacetylneoline) (4), delphinine (5), chasmaconitine (6), and chasmanthinine (7). The structure of the new alkaloid was established by ^{1}H and ^{13}C-nmr spectra. The ^{13}C-nmr data for alkaloids (3), (6), and (7) are also presented.

From seeds of Delphinium pictum Willd. subsp. pictum, collected in the mountains of Majorca,[1] we have isolated pictumine (1) as a homogeneous amorphous alkaloid, in a small amount.

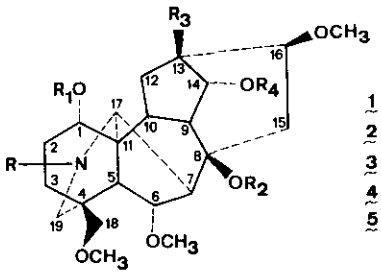
Its high-resolution ms displayed ions at m/z: 507.2911 (8%) M^+, $C_{27}H_{41}NO_8$, Δ-8.1; 490.2789 (100%) M^+-OH, $C_{27}H_{40}NO_7$, Δ+1.3; 474.2560 (50%) $M^+-H_2O|-CH_3$, $C_{26}H_{36}NO_7$, Δ7.1; 448.2749 (64%) M^+-OAc, $C_{25}H_{38}NO_6$, Δ-5.2; other peaks appearing at 447 (56%) M^+-AcOH, 432 (55%) M^+-AcOH|$-CH_3$, 430 (22%) M^+-OH|-AcOH, 416 (31%) $M^+-OCH_3|$-AcOH, 404 (40%), 402 (30%), 388 (47%), 223 (49%), 176 (48%), and 43 (88%). Ir ($CHCl_3$), 3345 (br, OH), 1724 and 1243 (acetate), 1105 and 1090 cm^{-1} (C-O).

The ^{1}H-nmr spectrum of pictumine (1) (200 MHz, $CDCl_3$) gave signals at δ 1.97 and 2.04 (3H each, s, two OAc), 2.33 (3H, s, N-CH_3), 3.10 and 3.66 (1H each, AB q, J = 8.2 Hz, H-18), 3.25, 3.31, and 3.32 (3H each, s, three OCH_3), 3.12 (1H, s, H-17), 3.66 (1H, m, $W\frac{1}{2}$ = 7.5 Hz, H-1β), 4.04 (1H, d, J = 6.4 Hz, H-6β), and 4.81 (1H, t, J = 5.0 Hz, H-14β).[2,3] The great similarity between the ^{13}C-nmr spectrum of pictumine and those of delphisine (4)[4] (Table 1), and other closed neoline-group

Table 1. ^{13}C-nmr chemical shifts and assignments for pictumine (1), neoline (2),[4] bullatine C (3), delphisine (4),[4] delphinine (5),[8] chasmaconitine (6), and chasmantine (7).

C	1	2	3	4	5	6	7	C	1	2	3	4	5	6	7
1	72.2	72.3	72.3	72.1	84.9	85.0	84.9	19	58.8	57.7	57.2	56.8	56.1	53.7	53.7
2	29.5	29.5	29.5	29.5	26.3	26.4	26.4	N							
3	29.8	29.9	29.7	30.1	34.7	35.0	34.9	(CH_2)		48.2	48.4	48.0		49.2	49.2
4	38.4	38.2	38.3	38.1	39.3	39.4	39.4	CH_3	42.0	13.0	13.1	12.9	42.3	13.5	13.5
5	43.5	44.9	44.7	44.1	48.8	50.2	49.5	1′					56.1	56.1	
6	84.1	83.3	83.5	84.2	83.0	83.2	83.2	6′	58.2	57.8	57.9	58.0	57.6	57.8	
7	47.5	52.3	52.9	48.3	48.2	49.6	49.1	16′	56.7	56.3	56.2	56.5	58.6	59.1	
8	86.0	74.3	74.8	85.2	85.4	85.7	85.7	18′	59.3	59.1	59.3	59.0	58.9	58.7	
9	43.2	48.3	46.3	43.3	45.1	45.2	45.2	CO	169.7 171.2		171.4	169.3 170.4	169.4	169.8	169.7
10	43.4	44.3	43.6	43.3	41.1	41.1	41.0	CH_3	21.4 21.5		21.3	22.3 21.1	21.4	21.6	22.3
11	50.1	49.6	49.9	49.8	50.2	49.2	50.2	CO					166.0	164.4	166.7
12	30.2	29.8	30.1	29.5	35.7	39.2	39.2	(CH)							130.5
13	38.5	40.7	37.0	38.5	74.8	74.9	74.8	(CH)							145.3
14	75.7	75.9	77.3	75.5	78.9	78.9	78.7						129.6 128.4	130.4 128.5	134.3 128.1
15	38.5	42.7	42.8	38.5	39.3	35.9	36.0						130.4 132.8	129.7 133.1	129.0 128.3
16	82.7	82.3	82.2	82.7	83.7	83.8	83.7								
17	65.3	63.6	63.6	62.7	63.3	62.0	61.9								
18	79.9	80.3	80.3	79.8	80.2	80.5	80.4								

Chemical shifts in ppm downfield from TMS. Solvent deuterochloroform.



1 R = Me ,R_1=R_3=H,R_2=R_4=Ac
2 R=Et,R_1=R_2=R_3=R_4=H
3 R=Et,R_1=R_2=R_3=H,R_4=Ac
4 R=Et,R_1=R_3=H,R_2=R_4=Ac
5 R=R_1= Me ,R_2=Ac,R_3=OH,R_4=Bz

6 R=Et,R_1= Me ,R_2=Ac,R_3=OH,R_4=Bz
7 R=Et,R_1= Me ,R_2=Ac,R_3=OH,R_4=(*E*)OC-CH=CH-C_6H_5

bases such as N-deethyldelphisine,[5] 8-acetyl-14-benzoylneoline,[6] and delstaphisine,[7] allowed its oxygen functions to be placed unambiguously on an aconitine skeleton. Furthermore, the DEPT ^{13}C-nmr spectrum of 1 showed a quartet at 42.0 ppm for the N-methyl group and lacked the characteristic signals, in this type of alkaloids, of an N-ethyl group at about 13 (q) and 48 (t) ppm.

The above-mentioned spectroscopic data enabled us to arrive at the structure depicted for pictumine (1).

We also isolated neoline (2),[3] bullatine C (14-acetylneoline) (3),[9] delphisine (8,14-diacetylneoline) (4),[3] delphisine (5),[10] chasmaconitine (6),[11] and chasmanthinine (7).[11] These alkaloids were identified by comparison with authentic samples or by spectroscopic methods, mainly ^{13}C-nmr spectra. The ^{13}C-nmr data for bullatine C (3), chasmaconitine (6), and chasmanthinine (7) in Table 1 are given by comparison with the spectra of neoline[4] and delphinine.[8] The C-10 and C-13 carbon resonances for neoline and delphisine have been reversed from those of the literature on the basis of the α- and β-effects observed upon acetylation of the C-14 and C-8 hydroxyl groups in neoline to give bullatine C and delphisine.

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