

DITERPENOID ALKALOIDS FROM DELPHINIUM PICTUM WILLD.

THE STRUCTURE OF PICTUMINE

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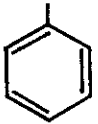
Abstract - A new C-19 diterpenoid alkaloid pictumine (1) was isolated from Delphinium pictum Willd. subsp. pictum together with the known bases neoline (2), bullatine C (14-acetylneoline) (3), delphisine (8,14-diacetylneoline) (4), delphinine (5), chasmaconitine (6), and chasmanthinine (7). The structure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

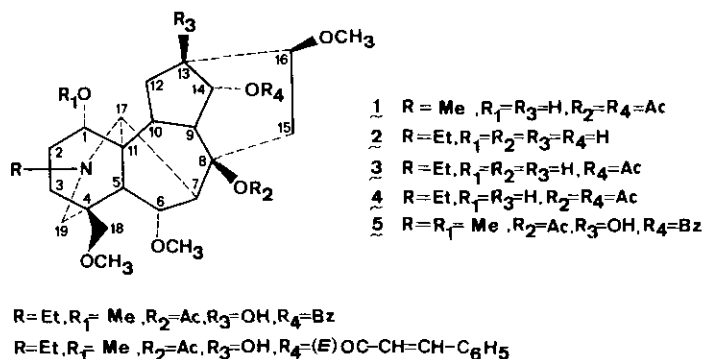
Its high-resolution ms displayed ions at m/z : 507.2911 (8%) M^+ , $\text{C}_{27}\text{H}_{41}\text{NO}_8$, Δ -8.1; 490.2789 (100%) M^+-OH , $\text{C}_{27}\text{H}_{40}\text{NO}_7$, Δ +1.3; 474.2560 (50%) $\text{M}^+-\text{H}_2\text{O}-\text{CH}_3$, $\text{C}_{26}\text{H}_{36}\text{NO}_7$, Δ 7.1; 448.2749 (64%) M^+-OAc , $\text{C}_{25}\text{H}_{38}\text{NO}_6$, Δ -5.2; other peaks appearing at 447 (56%) M^+-AcOH , 432 (55%) $\text{M}^+-\text{AcOH}-\text{CH}_3$, 430 (22%) $\text{M}^+-\text{OH}-\text{AcOH}$, 416 (31%) $\text{M}^+-\text{OCH}_3-\text{AcOH}$, 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 ^1H -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, $W_{1/2} = 7.5$ Hz, H-18), 4.04 (1H, d, $J = 6.4$ Hz, H-6 β), and 4.81 (1H, t, $J = 5.0$ Hz, H-14 β).^{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		171.4	169.3	169.4	169.8	169.7
10	43.4	44.3	43.6	43.3	41.1	41.1	41.0	CH ₃	171.2			170.4			
11	50.1	49.6	49.9	49.8	50.2	49.2	50.2	CO	21.4		21.3	22.3	21.4	21.6	22.3
12	30.2	29.8	30.1	29.5	35.7	39.2	39.2	(CH)	21.5			21.1			
13	38.5	40.7	37.0	38.5	74.8	74.9	74.8	(CH)					166.0	164.4	166.7
14	75.7	75.9	77.3	75.5	78.9	78.9	78.7						129.6	130.4	134.3
15	38.5	42.7	42.8	38.5	39.3	35.9	36.0						128.4	128.5	128.1
16	82.7	82.3	82.2	82.7	83.7	83.8	83.7						130.4	129.7	129.0
17	65.3	63.6	63.6	62.7	63.3	62.0	61.9						132.8	133.1	128.3
18	79.9	80.3	80.3	79.8	80.2	80.5	80.4								

Chemical shifts in ppm downfield from TMS. Solvent deuteriochloroform.



bases such as N-deethyldehphisine,⁵ 8-acetyl-14-benzoylneoline,⁶ and delstaphisine,⁷ allowed its oxygen functions to be placed unambiguously on an aconitine skeleton. Furthermore, the DEPT ¹³C-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 ¹³C-nmr spectra. The ¹³C-nmr data for bullatine C (3), chasmaconitine (6), and chasmanthinine (7) in Table 1 are given by comparison with the spectra of neoline⁴ 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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