Revised C Nmr Assignments for Norditerpenoid Alkaloids with 7,8-Methylenedioxy and 10#-OH Groups

Haridutt K. Desai, and W. William Pelletier

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REVISED ^{13}C NMR ASSIGNMENTS FOR NORDITERPENOID ALKALOIDS WITH 7,8-METHYLENEDIOXY AND 10β-OH GROUPS

HARIDUTT K. DESAI and S. WILLIAM PELLETIER*

Institute for Natural Products Research and The Department of Chemistry, The University of Georgia, Athens, Georgia 30602-2556

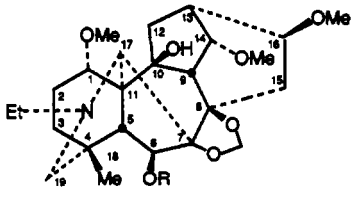
ABSTRACT.—^{13}C-nmr chemical shift assignments for the norditerpenoid alkaloids deltaline [**1**], deltamine [**2**], dictyocarpine [**3**], and 14-acetyldictyocarpine [**5**] have been revised on the basis of a study of their 1D, 2D, and selective INEPT nmr spectra. These revisions suggest that the ^{13}C-nmr chemical shift assignments for twenty-eight other norditerpenoid alkaloids possessing 7,8-methylenedioxy and 10β-OH groups may have to be revised. Complete ^{1}H-nmr chemical shift assignments for compounds **1–3** and **5** are also reported.

The alkaloid deltaline [**1**] was isolated from *Delphinium occidentale* S. Wats (Ranunculaceae) in 1936 by Couch (1). Deltaline (eldeline) [**1**] and deltamine (eldelidine) [**2**] were isolated by Rabinovich (2) from *Delphinium elatum* L. in 1952. The structures of **1** and **2** were established by Kuzovkov and Platonova in 1959 (3).

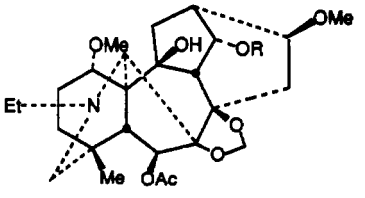
Dictyocarpine [**3**] was first reported from *Delphnium dictyocarpum* by Narzullaev *et al.* (4) in 1972. They established structure **3** for dictyocarpine on the basis of ^{1}H-nmr and mass spectral studies (5). The study also involved chemical correlation of **1–3** with the alkaloid delpheline [**4**]. Later the structure of dictyocarpine [**3**] was confirmed by a single crystal X-ray analysis of its acetone complex (6).

^{13}C-nmr chemical shift assignments for compounds **1–3** and **5** were reported from this laboratory in 1980 (7). The assignments were based on the determination of the noise-decoupled and single-frequency off-resonance decoupled (SFORD) spectra. The ^{13}C-nmr signals were assigned with the help of the single-frequency proton off-resonance decoupling technique, application of the known chemical shift rules for OH substitution and acetylation shifts, and steric effects, and from comparisons of spectra from compound to compound.

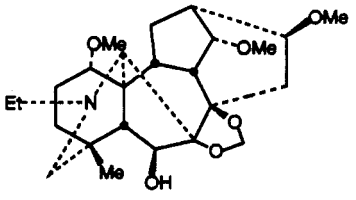
A growing need for the complete and unambiguous nmr chemical shift assignments for the naturally occurring complex diterpenoid alkaloids prompted us to examine the



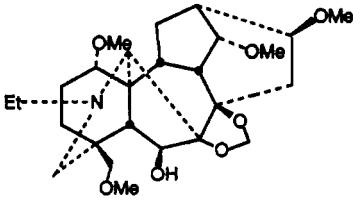
1 R=Ac (deltaline)
2 R=H (deltamine)



3 R=H (dictyocarpine)
5 R=Ac (14-acetyldictyocarpine)



4 (delpheline)



6 (delcorine)

TABLE 1. ^{13}C and ^{1}H nmr Chemical Shift Assignments of Deltaline [1] ($CDCl_3$).[a]

Position	New δ_C	Previous[b] δ_C	δ_H	Multiplicity, J in Hz
1	77.3 d	79.2	3.50	m
2	27.2 t	27.1	2.10, 2.20	m, m
3	36.5 t	39.4	1.21, 1.57	m, m
4	33.7 s	33.7	—	—
5	50.4 d	50.4	1.58	br s W1/2=6.8
6	79.2 d	77.3	5.46	s
7	91.6 s	91.6	—	—
8	81.4 s	83.8	—	—
9	50.4 d	50.4	3.34	d, 6.0
10	83.8 s	81.6	—	—
11	56.0 s	56.0	—	—
12	39.4 t	36.5	1.75, 3.29	m, m
13	38.5 d	38.5	2.51	m
14	81.7 d	81.7	4.13	t, 4.9
15	34.8 t	34.8	1.82, 2.45	m, m
16	81.5 d	81.5	3.19	m
17	63.5 d	63.5	3.08	d, 2.1
18	25.7 q	25.7	0.88	s
19	56.9 t	56.9	2.47, 2.71	d, AB, 11.3, 11.3
N-CH_2	50.2 t	50.2	2.70, 2.82	m, m
Me	13.8 q	13.8	1.06	t, 7.1
O-CH_2-O	93.9 t	93.9	4.91, 4.96	s, s
1-OMe	55.3 q	55.3	3.26	s
14-OMe	57.7 q	57.8	3.45	s
16-OMe	56.2 q	56.2	3.33	s
C=O	169.8 s	169.9	—	—
Me	21.7 q	21.8	2.08	s
10-OH	—	—	1.67	s

[a]Chemical shifts in ppm downfield from TMS.
[b]Previous shifts are from Pelletier *et al.* (7).

chemical shift assignments with the aid of modern 2D nmr techniques. In many cases the 2D nmr spectra along with 1D DEPT studies resulted in minor revisions in the assignments (8,9). So far complete and unambiguous nmr assignments have been published for only one norditerpenoid alkaloid bearing a 7,8-methylenedioxy group (delpheline [**4**]) (9,10). Unambiguous ^{1}H- and ^{13}C-nmr chemical shift assignments for norditerpenoid alkaloids containing a 7,8-methylenedioxy group and a 10β-OH group have not been reported.

RESULTS AND DISCUSSION

A study of the 2D nmr spectra, i.e., COSY, HETCOR, COLOC, and selective INEPT experiments, of deltaline [**1**] indicated that some of the previously assigned ^{13}C-nmr chemical shifts should be revised. Because of this we decided to study other related alkaloids, viz., deltamine [**2**], dictyocarpine [**3**], and 14-acetyldictyocarpine [**5**], since authentic samples of these alkaloids were readily available. The study showed that as in deltaline [**1**], the compounds **2**, **3**, and **5** followed the same general pattern of revision.

The complete assignments of the protons of compounds **1–3** and **5** was first achieved by a study of their 2D homonuclear correlation spectra (COSY). The assignments for C-1 and C-6 were revised on the basis of a study of HETCOR spectra of compounds **1–3** and **5**. The protons H-1 and H-6 in all the four compounds could be assigned unambiguously, and in HETCOR the carbon signals showing correlation with these

TABLE 2. ^{13}C and ^{1}H nmr Chemical Shift Assignments of Deltamine [**2**] ($CDCl_3$).[a]

Position	New δ_C	Previous δ_C	δ_H	Multiplicity, J in Hz
1	77.3 d	80.2	3.55	dd, 9.9, 7.5
2	27.0 t	27.0	2.03, 2.13	m, m
3	36.8 t	38.7	1.21, 1.57	m, br d, 13.3
4	33.6s	33.6	—	—
5	51.3 d	51.0	1.48	br s, W1/2=6.8
6	80.1 d	77.4	4.24	s
7	92.4 s	92.4	—	—
8	82.4 s	83.5	—	—
9	50.8 d	51.5	3.45	d, 6.1
10	83.5 s	82.4	—	—
11	56.0 s	56.2	—	—
12	38.7 t	36.8	1.76, 3.08	d, 15.4, d, 15.5
13	37.4 d	37.6	2.53	m
14	81.6 d	81.6	4.13	t, 4.7
15	34.3 t	34.3	1.83, 2.50	m, m
16	81.6 d	81.6	3.18	m
17	63.2 d	63.2	3.01	d, 2.1
18	25.6 q	25.6	0.94	s
19	57.2 t	57.3	2.25, 2.66	d, AB 11.3, 11.2
N-CH_2	50.4 t	50.4	2.64, 2.73	m, m
Me	13.9 q	13.9	1.04	t, 7.1
O-CH_2-O	93.3 t	93.3	5.05, 5.13	s, s
1-OMe	55.5 q	55.5	3.25	s
14-OMe	57.8 q	57.9	3.43	s
16-OMe	56.2 q	56.2	3.33	s
6-OH	—	—	3.36	s
10-OH	—	—	2.39	s

[a]Chemical shifts in ppm downfield from TMS.
[b]Previous shifts are from Pelletier *et al.* (7).

protons appeared to be reversed from the previous assignments (7). Thus the previous higher field signals assigned to C-6 correlated with H-1 and the downfield signal assigned to C-1 correlated with H-6 (Tables 1–4) in all compounds. The new assignments for C-1 and C-6 were confirmed by selective INEPT experiments (Table 5). Thus selective pulsing of the H-1 protons of **1–3** and **5** showed enhancement of the corresponding C-1 methoxy methyl carbons which are three bonds away from H-1. H-1 in turn correlated with the higher field carbon signal in the HETCOR spectrum. The assignments of C-6 were confirmed when H-5's were selectively pulsed (Table 5).

Revision of the assignments for C-3 and C-12 was based on the study of the COLOC spectra recorded for **1** and **3**. For deltaline [**1**], a methylene at δ 36.5 previously assigned to C-12 (Table 1) showed a long-range coupling with Me-18 (δ 0.88) and one of the H-19 protons (δ 2.47), which are both three bonds away from C-3. The methylene at δ 39.4 previously assigned to C-3 showed a long-range coupling with H-9 (δ 3.34), which is three bonds away from C-12. Similarly for dictyocarpine [**3**], a methylene at δ 36.3 previously assigned to C-12 (Table 3) showed a long-range coupling with Me-18 (δ 0.85), which is three bonds away from C-3. The methylene at δ 37.6, previously assigned to C-3, has been assigned to C-12 on the basis of selective INEPT experiments on dictyocarpine (Table 5). Thus when H-9 (δ 3.36) was selectively pulsed, a weak response was observed at the methylene carbon resonating at δ 37.6. This must be C-12, being three bonds away from H-9.

TABLE 3. ^{13}C and ^{1}H nmr Chemical Shift Assignments of Dictyocarpine [3] ($CDCl_3$).[a]

Position	New δ_C	Previous δ_C	δ_H	Multiplicity, J in Hz
1	77.2 d	78.6	3.61	dd, 10.0, 7.4
2	26.4 t	26.4	2.03, 2.12	m, m
3	36.3 t	37.6	1.20, 1.56	m, br d, 13.2
4	34.0 s	34.0	—	—
5	50.4 d	51.8	1.56	br s, W1/2=6.8
6	78.6 d	77.2	5.47	s
7	93.0 s	93.0	—	—
8	79.9 s	82.9	—	—
9	51.8 d	50.4	3.36	d, 5.1
10	82.9 s	79.9	—	—
11	55.1 s	55.1	—	—
12	37.6 t	36.5	1.75, 2.67	d, 4.5, d, 14.8
13	36.6 d	36.6	2.56	m
14	72.8 d	72.8	4.62	m
15	32.9 t	32.9	1.81, 2.49	m, dd, 14.7, 9.1
16	81.2 d	81.2	3.47	m
17	64.4 d	64.4	3.29	d, 2.2
18	25.5 q	25.5	0.85	s
19	56.9 t	56.9	2.44, 2.71	d, AB 11.8, 11.8
$N-CH_2$	50.4 t	50.4	2.77	m
Me	14.0 q	14.0	1.05	t, 8.6
$O-CH_2-O$	93.9 t	94.0	4.94, 4.98	s, s
1-OMe	55.6 q	55.5	3.25	s
16-OMe	56.3 q	56.2	3.34	s
C=O	170.2 s	170.1	—	—
Me	21.8 q	21.8	2.08	s
10-OH	—	—	2.17	s
14-OH	—	—	4.29	d, 6.5

[a]Chemical shifts in ppm downfield from TMS.
[b]Previous shifts are from Pelletier *et al.* (7).

The most interesting result of this study is the revision of the chemical shifts assigned to the quaternary C-8 and C-10, and this revision was found to be consistent in the case of the four compounds **1–3** and **5**. The assignment of these carbons was based on the selective INEPT experiments, since the COLOC spectra of **1** and **3** failed to show the correlations for the quaternary carbons. The previous assignments (7) for these compounds (Tables 1–4) were based on the comparison of the ^{13}C nmr chemical shifts of **3** with those of the lycoctonine-type alkaloid delcorine [**6**]. The oxygen-bearing quaternary C-8 in **6** resonates at δ 83.9, and in dictyocarpine [**3**] there are two oxygenated quaternary carbons resonating at δ 79.9 and 82.9 besides the common oxygenated quaternary C-7 present in **6** and **3**. Hence, the additional chemical shift at δ 79.9, which is not present in **6**, was assigned to C-10 in **3** (7).

In the selective INEPT experiments on dictyocarpine [**3**] (Table 5), selective pulsing of H-9 (δ 3.36) showed a strong response of both quaternary carbons at δ 79.9 and 82.9. These are two bonds away from H-9. Selective pulsing of H-1 (δ 3.61) showed a strong response to the quaternary carbon at δ 82.9 which can be assigned to C-10 being three bonds away from H-1. Selective pulsing of one of the methylenedioxy group protons (δ 4.95) showed a strong response to a signal at δ 79.9, which is three bonds away from this proton (as for this group oxygen is two bonds away) and can be assigned to C-8. The selective INEPT experiments on compounds **1**, **2**, and **5** (Table 5) also gave similar results.

TABLE 4. ^{13}C and ^{1}H nmr Chemical Shift Assignments of 14-Acetyldictyocarpine [**5**] $CDCl_3$.[a]

Position	New δ_C	Previous δ_C	δ_H	Multiplicity, J in Hz
1	77.2 d	79.0	3.56	dd, 10.2, 7.3
2	26.9 t	27.0	2.01, 2.13	m, m
3	36.4 t	37.3	1.21, 1.61	m, m
4	33.7 s	33.7	—	—
5	50.3 d	50.4	1.58	br s, W1/2=7.0
6	78.9 d	77.3	5.42	s
7	91.6 s	91.7	—	—
8	81.2 s	83.3	—	—
9	49.8 d	49.9	3.55	d, 4.5
10	83.3 s	81.3	—	—
11	55.7 s	55.8	—	—
12	38.6 t	36.6	1.78, 3.15	m, m
13	37.2 d	38.9	2.65	m
14	74.6 d	74.7	5.23	t, 4.9
15	34.9 t	35.0	1.70, 2.65	m, m
16	81.1 d	81.3	3.23	m
17	63.9 d	63.9	3.08	d, 2.2
18	25.6 q	25.6	0.88	s
19	56.7 t	56.9	2.45, 2.71	d, AB, 11.9, 11.9
N-CH_2	50.3 t	50.4	2.76	m
Me	13.9 q	13.9	1.06	t, 7.1
O-CH_2-O	93.8 t	93.8	4.87, 4.95	s, s
1-OMe	55.4 q	55.4	3.26	s
16-OMe	56.2 q	56.1	3.30	s
C=O	170.0 s	170.0	—	—
Me	21.7 q	21.7	2.08 (6H)	s
C=O (14)	171.6 s	171.7	—	—
Me	21.4 q	21.4	2.08 (6H)	s
10-OH	—	—	1.26	s

[a]Chemical shifts in ppm downfield from TMS.
[b]Previous shifts are from Pelletier *et al.* (7).

Revision of the ^{13}C-nmr chemical shifts for C-5 and C-9 in compounds **1–3** is also based on a study of 2D and selective INEPT nmr experiments (Tables 1–3 and 5).

We have found that selective INEPT experiments on norditerpenoid alkaloids having more than one -OMe and -OCOMe group such as in **1–3** and **5** can be successfully used to locate their attachment and assign the carbons bearing these groups. Selective pulsing of the methoxy methyl protons at δ 3.26 and 3.30 in compound **5** showed strong responses of signals at δ 77.2 and 81.1, respectively. As in **5**, the signal at δ 77.2 is assigned to C-1; the three-proton singlet at δ 3.26 for the methyl protons of the -OMe group belongs to the C-1 methoxyl and that at δ 3.30 belongs to C-16 (δ 81.1).

Similarly in the case of compound **5** bearing two acetoxyl groups, when H-6 (δ 5.42) was selectively pulsed a strong response to a signal at δ 170.0 was observed. Hence, the signal at δ 170.0 can be assigned to the carbonyl carbon of the acetoxyl group attached to C-6 and that at δ 171.6 to C-14. Unfortunately, the methyl protons of the two acetoxyl groups in the ^{1}H-nmr spectrum of **5** appear as a 6H singlet (δ 2.08) and thus could not be distinguished. As in the case of deltaline [**1**], selective pulsing of the signal at δ 2.05 assigned to the methyl protons of the C-6 acetoxyl group enhanced the ^{13}C-nmr signal at δ 169.8 (Table 5).

Revision of the ^{13}C nmr chemical shift assigned to the methine C-13 (δ 38.9) in **5** was derived from the DEPT experiments, where the signal at δ 38.9 was found to be a

TABLE 5. Nmr Data from Selective INEPT Experiments on **1–3** and **5**.[a]

Irradiation of Proton assigned to	δ (ppm)	Enhancement of the carbon signal assigned to (δ)		
		Strong	Medium	Weak
Deltaline [**1**]				
18-Me	0.88	33.7 (C-4)	50.2 (C-5)	56.9 (C-19)
N-CH_2CH_3	1.06	50.2 t (N-CH_2Me)	—	—
H-5	1.58	56.0 (C-11)	83.8 (C-10)	91.6 (C-7)
			79.1 (C-6)	25.7 (C-18)
			63.5 (C-17)	—
			33.7 (C-4)	—
OAc	2.05	169.8	—	—
H-17	3.08	50.2 (C-5)	56.0 (C-11)	—
H-9	3.34	83.8 (C-10)	81.4 (C-8)	38.5 (C-13)
				34.8 (C-15)
H-1	3.50	56.0 (C-11)	55.3 (C-1′)	—
		83.8 (C-10)	63.5 (C-17)	
H-14	3.50	81.4 (C-8)	—	—
		81.5 (C-16)		
		57.8 (C-14′)		
O-CH_2-O	4.96	81.4 (C-8)	—	—
H-6	5.46	56.0 (C-11)	33.7 (C-4)	81.4 (C-8)
			91.6 (C-7)	
Deltamine [**2**]				
H-5	1.48	80.1 (C-6)	83.5 (C-10)	92.4 (C-7)
		63.2 (C-17)	33.6 (C-4)	25.6 (C-18)
		56.0 (C-11)		
H-17	3.01	56.0 (C-11)	80.1 (C-6)	82.4 (C-8)
				83.5 (C-10)
H-1	3.55	56.0 (C-11)	83.5 (C-10)	63.2 (C-17)
			55.5 (C-1′)	
H-14	4.13	82.4 (C-8)	57.8 (C-14′)	50.8 (C-9)
			81.6 (C-16)	
H-6	4.24	56.0 (C-11)	33.6 (C-4)	—
			82.4 (C-8)	
			92.4 (C-7)	
O-CH_2-O	5.05	92.4 (C-7)	—	—
	5.13	82.4 (C-8)	—	—
Dictyocarpine [**3**]				
H-5	1.56	82.9 (C-10)	56.9 (C-19)	—
		78.6 (C-6)	25.5 (C-18)	
		64.4 (C-17)		
		55.1 (C-11)		
		34.0 (C-4)		
H-17	3.29	55.1 (C-11)	79.9 (C-8)	50.3 (C-5)
			82.9 (C-10)	50.4 (N-CH_2)
H-9	3.36	82.9 (C-10)	36.6 (C-13)	37.6 (C-12)
		79.9 (C-8)	32.9 (C-15)	
H-16	3.47	79.9 (C-8)	56.3 (C-16′)	—
		72.8 (C-14)		
H-1	3.61	82.9 (C-10)	64.4 (C-17)	—
		55.6 (C-1′)		
		55.1 (C-11)		
H-14	4.62	79.9 (C-8)	81.2 (C-16)	—
			36.6 (C-13)	
O-CH_2-O	4.95	79.9 (C-8)	—	—
		93.0 (C-7)		

TABLE 5. Continued.

Irradiation of Proton assigned to	δ (ppm)	Enhancement of the carbon signal assigned to (δ)		
		Strong	Medium	Weak
H-6	5.47	170.2 (COMe) 93.0 (C-7) 55.1 (C-11)	79.9 (C-8) 34.0 (C-4)	—
14-Acetyldictyocarpine [**5**]				
H-5	1.58	63.9 (C-17)	78.9 (C-6) 83.3 (C-10)	55.7 (C-11) 25.6 (C-18)
H-17	3.08	55.7 (C-11)	81.2 (C-8)	—
1-OMe	3.26	77.2 (C-1)	—	—
16-OMe	3.30	81.1 (C-16)	—	—
O-CH_2-O	4.95	81.2 (C-8)	—	—
H-14	5.23	81.2 (C-8)	—	—
H-6	5.42	91.6 (C-7) 170.0 (6-COMe)	81.2 (C-8) 55.7 (C-11) 33.7 (C-4)	—

[a]Strong 61-100%; Medium 40-60%; Weak<40% as compared with the strongest peak in the spectrum being 100%.

methylene carbon and that at δ 37.2 was found to be a methine carbon which was previously assigned to C-3.

We suggest that the ^{13}C-nmr chemical shift assignments reported for twenty-eight other norditerpenoid alkaloids bearing a 10β-OH group and a 7,8-methylenedioxy group (11,12), may now be revised according to the results of the present study.

EXPERIMENTAL

SOURCES OF ALKALOIDS.—The samples of deltaline [**1**], deltamine [**2**], dictyocarpine [**3**], and 14-acetyldictyocarpine [**5**] used for this study were of 30–40 mg size and were authentic from our file.

INSTRUMENTATION.—All the nmr spectra were recorded in $CDCl_3$ on a Bruker AC 300 spectrometer operating at 300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C. The residual $CHCl_3$, and $^{13}CDCl_3$ in $CDCl_3$ were used as internal references (^{1}H δ 7.27, ^{13}C δ 77.0). The pulse sequences employed in the 1D and 2D nmr experiments were those of the standard Bruker software. The pulse sequence for the selective INEPT experiments was obtained by modifying the Bruker standard INEPT sequence according to Bax (13). A long range coupling value (^{lr}J) for the COLOC and selective INEPT experiments was 6 Hz. In the selective INEPT experiments the decoupling powers used were S1=45L (for soft pulse) and S2=0L (for decoupling with CPD). The power 0L in the Bruker AC 300 spectrometer is approximately 1 W. The following delays were utilized: D1=3S (for ^{1}H), D2=1/4J LR−0.015 sec (refocusing delay), D3 was variable depending on the protons being selected, D3=1/4J LR−0.0075 sec (for polarization transfer from a CH), D3=1/8J LR−0.0075 sec (for polarization transfer from a CH_2), D3=1/10J LR−0.0075 sec (for polarization transfer from an Me), D5=0.0075 sec (for allowing evolution of antiphase magnetization), D6=0.015 sec (to refocus shifts, and to set decoupler power). The protons of the hydroxyl groups were assigned on the basis of the deuterium exchange studies with D_2O.

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