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DITERPENOID ALKALOIDS FROM *ACONITUM ORIENTALE*

AYHAN ULUBELEN,*† ALI H. MERIÇLI,* FILIZ MERIÇLI* and FUNDA YILMAZ*

*Faculty of Pharmacy, University of Istanbul, Istanbul 34452, Turkey; †TUBITAK Marmara Research Centre, Department of Chemistry, PK 21, 41470, Gebze-Kocaeli, Turkey

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Key Word Index—*Aconitum orientale*; Ranunculaceae; diterpenoid alkaloids; demethyllappaconitine; 7,11,14-trihydroxy-2,13-dioxohetisane; 6,13,15-trihydroxyhetisane; *N*-deethyldelphatine.

Abstract—Four new diterpenoid alkaloids demethyllappaconitine; 7,11,14-trihydroxy-2,13-dioxohetisane, 6,13,15-trihydroxyhetisane and *N*-deethyldelphatine, were isolated from *Aconitum orientale*, in addition to the previously known compounds, lappaconitine, lycoctonine and browniine. The structures of the new and the known alkaloids were established from spectral data.

INTRODUCTION

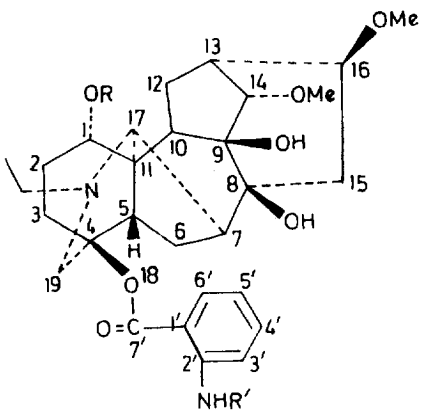
In previous studies with *Aconitum orientale* collected from the north Caucasus, a group of norditerpenoid alkaloids (lappaconitine, as the major compound, lappaconine, gigactonine, *N*-deacetyllappaconitine, and lycoctonine), together with an aporphine alkaloid, corydine [1], and a C_{20} diterpenoid alkaloid, orgetine [2], were isolated.

In the present study, with plant material collected from the eastern Black Sea area, we have obtained three of the above compounds, lappaconitine (**1**) [3] *N*-deacetyllappaconitine (**2**) [4], lycoctonine (**3**) and another known alkaloid, browniine (**4**) [5]. Four new alkaloids, demethyllappaconitine (**5**), orientinine (7,11,14-trihydroxy-2,13-dioxohetisane) (**6**), acorientine (6,13,15-trihydroxyhetisane) (**7**) and *N*-deethyldelphatine (**8**) were also isolated. The differences in the alkaloidal contents indicated that the two collections represent two different chemotypes. The structures of the known and the new compounds were assigned on the basis of their spectroscopic data.

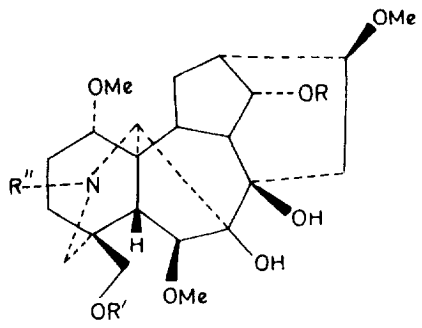
RESULTS AND DISCUSSION

The high resolution EI mass spectrum of the new compound **5** indicated a molecular formula $C_{31}H_{42}N_2O_8$ (*m/z* 570.2958, calc. 570.2941). The ^{1}H NMR spectrum showed the presence of an acetyl group at δ2.20 (3H, *s*), two methoxyl groups at δ3.44 and 3.33 (each 3H, *s*), four aromatic proton signals at δ8.67 (1H, *br d*, J = 8.0 Hz), 7.95 (1H, *dd*, J = 1.5 and 8.0 Hz), 7.49 (1H, *dd*, J = 1.5 and 8.0 Hz) and 7.06 (1H, *br d*, J = 8.0 Hz) and an amide proton at δ11.05 (1H, *br s*). All these signals were similar to those of **1**: only the signal for one of the methoxyl groups (at δ3.30) in **1** was missing. The lack of $[M - 31]^+$ and the presence of $[M - 17]^+$ ions in the mass spectrum indicated the presence of a hydroxyl group at C-1 instead of a methoxyl group [6, 7]. A HETCOR experiment made the assignment of the protons and carbon atoms possible (Table 1). The ^{13}C NMR (APT) spectrum correlated the presence of the hydroxyl at C-1 with the signals at δ26.2 and 27.0 for C-2 and C-3, instead of δ26.2 and 31.9, respectively. Also, C-1 appeared at δ74.5, while a C-1 methoxyl group would shift the C-1 signal to δ84.2 + 0.2 [8]. The ^{1}H NMR spectrum showed H-1β at δ3.70 as a multiplet. Two signals at δ3.45 (1H, *t*, J = 4.5 Hz, H-14β) and 3.28 (1H, *dd*, J = 3.0 and 9.0 Hz, H-16α) indicated the presence of methoxyl groups at C-14 and C-16. The ^{13}C NMR signals, except for C-1 and C-3, were in agreement with those of **1** (Table 2). These spectral data indicated that compound **5** was a 1-demethyllappaconitine.

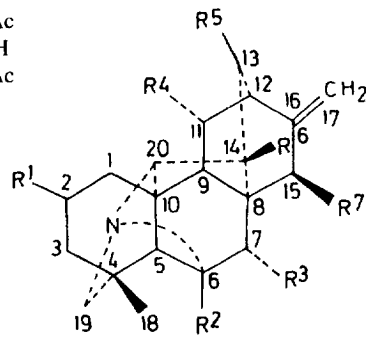
The HR mass spectrum of the new compound **6** indicated a molecular formula $C_{20}H_{23}NO_5$ (*m/z* 357.1566, cal. 357.1576). The ^{13}C NMR (APT) spectrum showed the presence of one methyl quartet at δ24.2, five methylene triplets at δ37.0, 46.0, 51.5, 62.7 and 108.2, seven methine doublets at δ49.5, 54.9, 60.0, 65.3, 68.6, 69.8 and 70.0 and seven quaternary carbon atoms at δ40.3, 44.2, 48.2, 79.1, 146.0, 211.4 and 214.1. The absence of methoxyl, *N*-methyl or *N*-ethyl groups suggested a hetisane-type diterpenoid alkaloid for **6**. The ^{1}H NMR spectrum indicated the presence of a methyl group at δ1.02 (3H, *s*) and an exocyclic methylene group at δ4.98 and 4.86. The presence of these groups were supported by the ^{13}C NMR signals at δ24.2 (*tert.* CH_3), δ108.2 (*t*) and 146.0 (*s*) ($C{=}CH_2$). There are five oxygen functions in the molecule, two of which are oxo groups, as revealed by ^{13}C NMR signals at δ211.4 and 214.1. The other three are hydroxyls attached to carbons, which were observed at δ79.1 (*s*), 70.0 (*d*) and 69.8 (*d*), indicating one tertiary and two



	R	R'
1	Me	Ac
2	Me	H
5	H	Ac



	R	R'	R''
3	Me	OH	Et
4	H	Me	Et
8	Me	Me	H



	R^1	R^2	R^3	R^4	R^5	R^6	R^7
6	O	H	OH	OH	O	OH	H
6a	O	H	OAc	OAc	O	OH	H
7	H	OH	H	H	OH	H	OH

secondary hydroxyl groups. Acetylation of **6** yielded a diacetyl derivative (**6a**). In the ^{1}H NMR spectrum of **6a**, the acetyl signals were at δ2.06 and 2.10, while in the ^{13}C NMR spectrum, signals appeared for these groups at δ170.4, 171.0 and 21.4, 21.0. The secondary hydroxyl groups were established by the shifts of the α-Cs and by OAc resonances. The tertiary hydroxyl group may be located at C-5, C-6, C-9, C-12, C-14 or C-20 of the hetisane skeleton to account for the quaternary carbon appearing at δ79.1. A hydroxyl at C-6 (carbinolamine) would have shifted the C-6 resonance downfield to δ97–101 [9, 10]. Location of the hydroxyl at C-5 or C-20 has not so far been observed in isolated hetisane-type diterpenoids. When C-12 carries a hydroxyl group it would produce a downfield shift of C-16 to δ150–156 analogous to the β-effect produced by hydroxylation of C-15 [11, 12]. A hydroxyl group at C-9 caused a 5–10 ppm downfield shift of C-10 (to 50–55 ppm) compared with hetisane-type alkaloids not having a hydroxyl at C-9 [12, 13]. Therefore, the hydroxyl group has to be located at C-14. The lack of a resonance at δ18–20 in the ^{13}C NMR spectrum indicated that one of the carbonyl or hydroxyl groups has to be located in ring A [14]. The chemical shifts of C-1 to δ46.0 and C-3 to δ51.5 suggested that there is an oxo group at C-2, rather than a hydroxyl [15, 16]. In this case, the second carbonyl group is C-6 and the skeleton atisine-type; Me-18 would be shifted downfield to δ1.40–1.50 [17, 18]. In the hetisane-type skeleton, the second oxo group could be in one of the following positions, C-7, C-11, C-13, C-15 or C-19. When the oxo group is at C-15 the protons at C-17 are shifted to δ5.20–5.90, as in atisinone and isoatisinone [19], but not as seen here. Also, the signals for the C-19 protons were observed at δ2.31 and 2.62 as broad doublets (J = 11 Hz). The possible places for the second oxo group and for the secondary hydroxyl groups are, therefore, at C-7, C-11 and C-13. The ^{1}H NMR signal at δ4.50 (1H, *t*, J = 2 Hz, H-7β) is typical for a C-7 α-hydroxyl group [20, 21], as also correlated by spin-decoupling experiments between H-6 (δ3.47, *br s*) and H-7 (δ4.50, *t*); when the former signal was irradiated, the latter one collapsed to a singlet. This leaves two locations, C-11 and C-13, for the remaining hydroxyl and the oxo groups. When the hydroxyl group is at C-13, both of the signals for C-13 and C-14 should appear at δ80.0–82.0 [13, 22], whereas an oxo group at C-13 and a hydroxyl at C-11 would give a signal at δ70.0–71.0 ppm [23]. In the present case, there are two signals as doublets at δ70.0 and 69.8 for C-11 and C-7 carrying the hydroxyl groups. In order to establish

Table 1. HETCOR assignments of compounds **5**–**7**

	5		**6**		**7**	
	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H
1	74.5	3.70	46.0	1.53; 2.03	39.3	1.35; 1.92
2	26.2	2.10	214.1	—	18.9	1.10; 1.55
3	27.0	2.30	51.5	1.75; 1.60	35.1	1.58
4	84.6	—	40.3	—	35.9	—
5	48.6	3.20	60.0	2.03	59.3	1.83
6	26.8	2.50	65.3	3.47	100.9	—
7	47.6	3.24	69.8	4.50	46.7	2.12; 2.35
8	75.8	—	44.2	—	40.9	—
9	78.7	—	54.9	2.00	54.1	2.10
10	36.5	2.85	48.2	—	49.6	—
11	51.1	—	70.0	4.24	37.6	1.95; 2.35
12	24.2	2.92	49.5	2.90	39.5	2.65
13	49.0	3.00	211.4	—	72.0	3.98
14	90.2	3.45	79.1	—	40.7	2.45
15	44.8	3.30	37.0	2.30	73.6	4.02
16	83.0	3.28	146.1	—	150.3	—
17	61.5	3.32	108.2	4.86; 4.98	116.1	5.16; 5.27
18	—	—	24.2	1.02	29.9	1.42
19	55.4	2.40; 2.80	62.7	2.31; 2.62	57.3	2.37; 2.67
20	—	—	68.6	3.64	67.2	3.86
N–CH_2	49.8	3.40	—	—	—	—
CH_3	13.6	1.10	—	—	—	—
14-OMe	57.9	3.33	—	—	—	—
16-OMe	56.2	3.44	—	—	—	—
NH–CO	169.2	—	—	—	—	—
CH_3	25.5	2.20	—	—	—	—
Ar-CO	168.5	—	—	—	—	—
C-1′	116.0	—	—	—	—	—
C-2′	141.6	—	—	—	—	—
C-3′	120.3	8.67	—	—	—	—
C-4′	134.6	7.95	—	—	—	—
C-5′	122.3	7.49	—	—	—	—
C-6′	131.0	7.06	—	—	—	—

the position of the second hydroxyl group at C-11, a spin-decoupling experiment was performed. When the signal at δ4.24 (H-11, *br d*) was irradiated, the signal at δ2.0 (H-9, *d*) collapsed to a singlet, the signal at δ2.90 (H-12, *d*) was sharpened. After examining the Dreiding model and measuring the *J* values, the hydroxyl group at C-11 was deduced as α. A HETCOR spectrum was recorded to assign the carbons and hydrogens. The spectral data indicated that orientinine (**6**) is 7,11,14-trihydroxy-2,13-dioxo-hetisane.

The molecular formula $C_{20}H_{27}NO_3$ (*m/z* 329.1984, calc. 329.2001) was derived for **7** from its HR mass spectrum. The ^{13}C NMR (APT) spectrum indicated one methyl quartet at δ29.9, seven methylene triplets at δ18.9, 35.1, 37.6, 39.3, 46.7, 57.3 and 116.1, seven methine doublets at δ39.5, 40.7, 54.1, 59.3, 67.2, 72.0 and 73.6, and five quaternary carbons at δ35.9, 40.9, 49.6, 100.9 and 150.3, indicating a C_{20} diterpenoid alkaloid. The lack of methoxyl, *N*-methyl or *N*-ethyl signals showed that **7** is also a hetisane-type alkaloid. A C-6 hydroxyl group was deduced to be present from the ^{1}H NMR shift of the C-18 methyl group to δ1.42 and from the carbinolamine signal at δ100.9 in the ^{13}C NMR spectrum. Due to the β-effect of the C-15 hydroxyl group, the signal for C-16 is shifted to δ150.3. In the ^{1}H NMR spectrum, the exomethylene (C-17) signals were observed as broad singlets at δ5.16 and 5.27, indicating the presence of a β-hydroxyl group at C-15 [24]; H-15 was observed at δ4.02 as a broad singlet. Since no carbonyl signal was present in the IR and ^{13}C NMR spectra of **7**, the third oxygen function is also a hydroxyl group. It is placed at C-13, as evident from the ^{1}H NMR signal at δ3.98 (1H, *d*, $J = 5$ Hz) and the ^{13}C NMR signal at δ72.0 (*d*), as well as from spin-decoupling experiments, in which the signal at δ2.45 (1H, *s*, H-14) was sharpened when the signal at δ3.86 (1H, *s*, H-20) was irradiated. Irradiation of the H-14 signal collapsed the doublet at δ3.98 (H-13) to a broadened singlet. A HETCOR experiment made the assignment of the

Table 2. ^{13}C NMR data (50 MHz) for compounds **1** and **5–8**

C	1*	5	8	6	7
1	84.2	74.5	83.6	46.0	39.3
2	26.2	26.2	26.2	214.1	18.9
3	31.9	27.0	32.4	51.5	35.1
4	84.7	84.6	37.7	40.3	35.9
5	48.6	48.6	42.5	60.0	59.3
6	26.8	26.8	88.4	65.3	100.9
7	47.6	47.6	86.7	69.8	46.7
8	75.6	75.8	78.2	44.2	40.9
9	78.6	78.7	49.5	54.9	54.1
10	36.4	36.5	38.3	48.2	49.6
11	51.0	51.1	50.5	70.0	37.6
12	24.2	24.2	29.0	49.5	39.5
13	49.0	49.0	44.2	211.4	72.0
14	90.2	90.2	83.5	79.1	40.7
15	44.9	44.8	33.5	37.0	73.6
16	82.9	83.0	81.9	146.0	150.3
17	61.5	61.5	64.3	108.2	116.1
18	—	—	78.0	24.2	29.9
19	55.5	55.4	52.0	62.7	57.3
20	—	—	—	68.6	67.2
N–CH_2	49.9	49.8	—	—	—
CH_3	13.5	13.6	—	—	—
1 OMe	56.5	—	55.8	—	—
6 OMe	—	—	56.5	—	—
14 OMe	57.9	57.9	57.9	—	—
16 OMe	56.1	56.2	56.3	—	—
18 OMe	—	—	59.8	—	—
NH–CO	169.0	169.2	—	—	—
CH_3	25.5	25.5	—	—	—
ArCO	167.5	168.5	—	—	—
C-1′	115.8	116.0	—	—	—
C-2′	141.7	141.6	—	—	—
C-3′	120.3	120.3	—	—	—
C-4′	134.4	134.6	—	—	—
C-5′	122.3	122.3	—	—	—
C-6′	131.1	131.0	—	—	—

*Data from ref. [26].

carbon and the protons possible (Table 2). These spectral data indicated that acorientine (**7**) was 6,13,15-trihydroxyhetisane.

The new compound (**8**) is a norditerpene alkaloid. The HR EI mass spectrum of **8** indicated a molecular formula $C_{24}H_{39}NO_7$ (*m/z* 453.2720, calc. 453.2726). The $[M-31]^+$ ion indicated the presence of a C-1 methoxyl group. The ^{1}H NMR spectrum indicated five methoxyl groups at δ3.46, 3.42, 3.40, 3.36 and 3.32. The lack of *N*-ethyl or *N*-methyl group signals and the presence of a singlet at δ3.12 (D_2O-exchangable) indicated the presence of a N–H group in the molecule. A triplet at δ3.65 (1H, *t*, J = 4.5 Hz, H-14β) and a multiplet at δ3.70 (1H, *m*, H-16α) indicated that the two methoxyl groups are at C-14 and C-16, respectively [25]. The third is assigned to C-1, based on the signal at δ3.20 (1H, *t*, J = 6 Hz, H-1β). The C-6 methoxyl group was evident from the signals at δ4.20 (1H, *d*, J = 6 Hz, H-6β) and 2.63 (1H, *d*, J = 6 Hz, H-5). The relation between these two signals was shown by spin-decoupling experiments. The latter methoxyl is at C-18 as evidenced from ^{1}H NMR signals at δ3.60 (1H, *d*, J = 9 Hz) and 3.54 (1H, *d*, J = 9 Hz) (H_2-18) and from the ^{13}C NMR signal of the C-18 OMe group at δ59.8 ppm. ^{13}C NMR (APT) revealed the presence of five methyl quartets at δ55.8, 56.3, 56.5, 57.9 and 59.8, six methylene triplets at δ26.2, 29.0, 32.4, 33.5, 52.0 and 78.0, nine methine doublets at δ38.3, 42.5, 44.2, 49.5, 64.3, 81.9, 83.5, 83.6 and 88.4, and four quaternary carbon singlets at δ37.7, 50.5, 78.2 and 86.7, consistent with the proposed molecular formula. The spectral data for **8** was similar to that of delphatine, except that the *N*-ethyl group is missing. Therefore, the structure of **8** was established as *N*-deethyldelphatine.

EXPERIMENTAL

General. Kieselgel $60F_{254}$ (E. Merck) plates were used for prep. sepn and Sephadex LH-20 (Fluka) for further purification.

Plant material. Aconitum orientale Mill. was collected from the eastern Black Sea area of Trabzon-Hamsiköy at an altitude of *ca* 1500 m in August 1993. The species was identified by A. H. M. and a voucher specimen is deposited in the Herbarium of the Faculty of Pharmacy, University of Marmara (Istanbul) MARE 4152.

Isolation of alkaloids. Dried and powdered aerial parts (700 g) were extracted with MeOH at room temp. and the solvent evapd to dryness. The residue (45 g) was acidified with 0.1 N H_2SO_4 (pH 1.5) and extracted with $CHCl_3$. The pH of the aq. part was brought to 10 by addition of 5% NaOH and extracted with $CHCl_3$. The basic $CHCl_3$ extract (1.5 g) was fractionated on a basic Al_2O_3 column (5 × 70 cm) eluting with petrol, then petrol–EtOAc (1:1) followed by EtOAc and a gradient of EtOH up to 100%. The following compounds were obtained, lappaconitine (15 mg), 1-demethyllappaconitine (8 mg), *N*-deacetyllappaconitine (12 mg), lycoctonine (65 mg), orientinine (15 mg), acorientine (8 mg), *N*-deethyldelphatine (10 mg) and browniine (15 mg).

1-Demethyllappaconitine (**5**). $[\alpha]_D$ + 52° (*c* 0.1, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3340, 2960, 2850, 1720 (sh), 1695, 1605, 1595, 1525, 1510, 1450, 1375, 1300, 1260, 1130, 1095, 760. ^{1}H NMR 200 MHz ($CDCl_3$) δ: 1.10 (3H, *t*, *N*–CH_2CH_3), 2.20 (3H, *s*, $NHCOCH_3$), 3.28 (1H, *dd*, J = 3.0, 9.0 Hz, H-16α), 3.33, 3.44 (each 3H, *s*, OMe), 3.45 (1H, *t*, J = 4.5 Hz, H-14β), 3.70 (1H, *m*, H-1β), 7.06 (1H, *br d*, J = 8.0 Hz, H-6′), 7.49 (1H, *dd*, J = 1.5, 8.02 Hz, H-5′), 7.95 (1H, *dd*, J = 1.5, 8.0 Hz, H-4′), 8.67 (1H, *br d*, J = 8.0 Hz, H-3′) (aromatic protons), 11.05 (1H, *br s*, NHAc). ^{13}C NMR, see Table 1. HREIMS *m/z* (rel. int.): 570.2958 ($C_{31}H_{42}N_2O_8$) $[M]^+$ (15), 553 $[M-OH]^+$ (10), 492 $[M-2\times OMe-H_2O]^+$ (8), 465 (27), 435 (50), 392 (82), 162 (100), 119 (98).

Orientinine (**6**). $[\alpha]_D$ + 42.0° (*c* 0.1, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 2930, 2850, 1725, 1717 (sh), 1650, 1570, 1460, 1400, 1380, 1170, 1100, 1070, 1050, 1030, 890, 760. ^{1}H NMR 200 MHz ($CDCl_3$) δ: 1.02 (3H, *s*, Me-18), 2.0

(1H, *d*, $J = 9$ Hz, H-9), 2.31 (1H, *d*, $J = 11$ Hz, H-19a), 2.62 (1H, *d*, $J = 11$ Hz, H-11b), 2.90 (1H, *br s*, H-12), 3.47 (1H, *br s*, H-6), 4.24 (1H, *br d*, $J = 9$ Hz, H-11β), 4.50 (1H, *t*, $J = 2$ Hz, H-7β), 4.86 (1H, *br s*), 4.98 (1H, *br s*) (H_2-17). ^{13}C NMR, see Table 1. HREIMS *m/z* (rel. int.): 357.1566 ($C_{20}H_{23}NO_5$) $[M]^+$ (47), 340 $[M - OH]^+$ (62), 321 $[M - 2 \times H_2O]^+$ (25), 314 (30), 300 (15), 284 (25), 274 (45), 256 (30), 213 (17), 185 (15), 115 (37), 97 (55), 83 (60).

Acetylation of **6**. Ac_2O (1 ml) was added to 5 mg **6** dissolved in 1 ml pyridine and left at room temp. for 4 hr. The reaction mixt. was evapd to dryness and the product purified by prep. TLC yielding 4.5 mg **6a**. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3380, 2950, 2840, 1730, 1725, 1715, 1650, 1560, 1460, 1410, 1370, 1150, 1240, 1100, 1050, 1020, 880. ^{1}H NMR ($CDCl_3$) δ: 1.04 (3H, *s*, Me-18), 2.06, 2.10 (each 3H, *s*, 2 × OAc), 4.86, 4.96 (each 1H, *br s*) (H_2-17), 4.76 (1H, *br d*, $J = 8.5$ Hz, H-11β), 5.15 (1H, *t*, $J = 2.5$ Hz, H-7β). ^{13}C NMR 50 MHz ($CDCl_3$) δ: C-1 45.7, C-2 213.8, C-3 51.5, C-4 40.2, C-5 58.9, C-6 65.5, C-7 68.6, C-8 44.2, C-9 53.8, C-10 48.2, C-11 69.8, C-12 49.4, C-13 211.0, C-14 79.0, C-15 37.1, C-16 146.2, C-17 107.9, C-18 23.9, C-19 63.0, C-20 68.5.

Acorientine (**7**). $[\alpha]_D + 13.5°$ (*c* 0.1, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3360, 2940, 2820, 1660, 1560, 1450, 1410, 1220, 1100, 1040, 1020, 910, 760. ^{1}H NMR 200 MHz ($CDCl_3$) δ1.42 (3H, *s*, Me-18), 2.45 (1H, *br s*, H-14), 3.86 (1H, *s*, H-20), 3.98 (1H, *d*, $J = 5$ Hz, H-13), 4.02 (1H, *s*, H-15α), 5.16 (1H, *br s*), 5.27 (1H, *br s*) (H_2-17). ^{13}C NMR, see Table 1. HREIMS *m/z* (rel. int.): 329.1984 ($C_{20}H_{27}NO_3$) $[M]^+$ (23) 314 $[M - Me]^+$ (7), 301 $[M - CO]^+$ (7), 284 (5), 162 (100), 127 (50), 63 (75).

N-*Deethyldelphatine* [**8**]. $[\alpha]_D + 52°$ (*c* 1, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420, 2940, 2850, 1650, 1460, 1380, 1240, 1190, 750. ^{1}H NMR 200 MHz ($CDCl_3$) δ: 2.63 (1H, *d*, $J = 6$ Hz, H-5), 3.12 (1H, *br s*, NH) (D_2O-exchange), 3.20 (1H, *d*, $J = 6$ Hz, H-1β), 3.54 (1H, *d*, $J = 9$ Hz), 3.60 (1H, *d*, $J = 9$ Hz) (H_2-18), 3.65 (1H, *t*, $J = 4.5$ Hz, H-14β), 32.70 (1H, *m*, H-16α), 4.20 (1H, *d*, $J = 6$ Hz, H-6β), 3.32, 3.36, 3.40, 3.42, 3.46 (each 3H, *s*, OMe). ^{13}C NMR, see Table 1. HREIMS *m/z* (rel. int.): 453.2720 ($C_{24}H_{39}NO_7$) $[M]^+$ (50), 422 $[M - OMe]^+$ (25), 406 (10), 392 (14), 371 (10), 340 (45), 292 (15), 141 (30), 85 (55).

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