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DITERPENOID ALKALOIDS FROM *DELPHINIUM ALBIFLORUM*

AYHAN ULUBELEN,

Faculty of Pharmacy, University of Istanbul, 34452, Istanbul, Turkey and TUBITAK, Marmara Research Center, Department of Chemistry, P.O. Box 21, 41470, Gebze-Kocaeli, Turkey

HARIDUTT K. DESAI, BALAWANT S. JOSHI, VOBALABOINA VENKATESWARLU, S. WILLIAM PELLETIER,*

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

ALI H. MERIÇLI, FILIZ MERIÇLI,

Faculty of Pharmacy, University of Istanbul, 34452, Istanbul, Turkey

and HASAN ÖZÇELIK

Faculty of Sciences, Department of Biology, Suleyman Demirel University, Isparta, Turkey

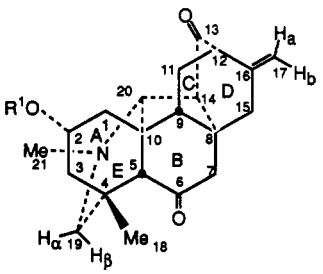
ABSTRACT.—Investigation of the aerial parts of *Delphinium albiflorum* resulted in the isolation and identification of deacetylheterophylloidine [**1**] along with hetidine [**2**] and lycoctonine [**3**]. Structure **1** for this previously unreported naturally occurring alkaloid was established on the basis of detailed nmr spectral studies and chemical correlation with deacetylheterophylloidine, obtained by the hydrolysis of heterophylloidine [**4**]. ^{1}H- and ^{13}C-nmr chemical shift assignments for **1** and **2** are reported herein.

In continuation of our chemical investigation of the genera *Aconitum* and *Delphinium* of the Ranunculaceae (1–3), we have examined alkaloids from the aerial parts of *Delphinium albiflorum* DC.

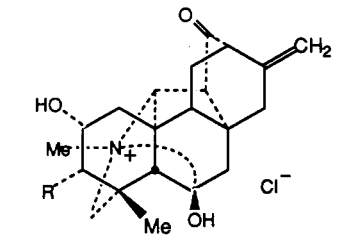
Delphinium albiflorum grows in the far-eastern region of Turkey (Van-Erek mountains) at an altitude of 2,500 m, and no phytochemical investigation has yet been reported on this plant. We report here the isolation and structure elucidation of three alkaloids [**1–3**] (Figure 1) from its aerial parts. One of the alkaloids has been identified as deacetylheterophylloidine [**1**]. Structure **1** was established on the basis of detailed spectroscopic data (hrms, ir, ^{1}H- and ^{13}C-nmr) and chemical correlation by the alkaline hydrolysis of heterophylloidine [**4**]. The other two alkaloids have been identified as hetidine [**2**] and lycoctonine [**3**] by comparison of their tlc, ir, ^{1}H- and ^{13}C-nmr spectral data with those of authentic samples. Structures **2** (5) and **4** (6) were established earlier by X-ray crystal structure determination. ^{1}H- and ^{13}C-nmr chemical shift assignments for **1**, **2**, and **4** have been made in the present study.

RESULTS AND DISCUSSION

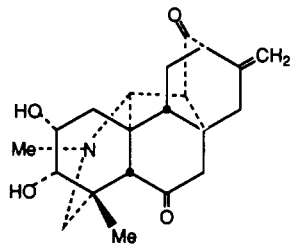
The three alkaloids [**1–3**, Figure 1] were isolated by chromatographic separation of the crude alkaloids isolated from the aerial parts of the plant by cc on Al_2O_3 and on Al_2O_3 rotors of a Chromatotron. The molecular formula, $C_{21}H_{27}NO_3$, for **1** was derived from hrms (*m/z* 341.1991) and ^{13}C-nmr data. Alkaloid **1** showed mp 160–162°, $[\alpha]_D$ −59.9° and exhibited a characteristic ^{1}H-nmr spectrum for the presence of an exocyclic methylene (δ 4.94, 4.76, each 1H), a tertiary Me (δ 1.08, 3H), and *N*-Me (δ 2.45, 3H), and the absence of OMe groups. These data indicated that **1** is a diterpenoid (not a norditerpenoid) alkaloid. The ^{13}C-nmr spectrum and DEPT experiments in $CDCl_3$ indicated the presence of two methyls at δ 27.2, 41.9; seven methylenes at δ 109.9, 57.5, 52.3, 48.3, 40.7, 36.2, and 23.4; six methines at δ 67.1, 64.5, 59.9, 56.6, 53.5, and 46.4; and six quaternary carbons at δ 210.5, 209.0 (weak), 142.7, 45.0, 40.9, and 37.1. The weak signal at δ 209.0



1 R^1=H
4 R^1=Ac



1A R=H
2A R=OH



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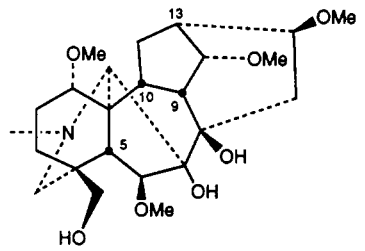

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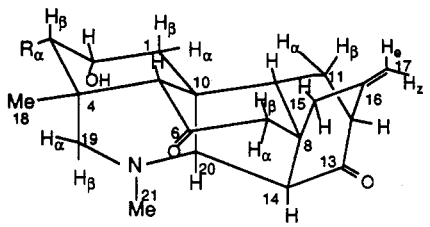

1 R=H
2 R=OH

FIGURE 1. For the convenience of depiction in the diagram, H-19$_\alpha$ and H-19$_\beta$ indicate the pseudo-axial and pseudo-equatorial protons, respectively, in the chair conformation of the E ring formed by C-4, C-5, C-10, C-20, N, and C-19. Also, Hα and Hβ in ring C are designated for the pseudo-axial and pseudo-equatorial protons of the twist-boat conformation of the ring formed by C-8, C-9, C-11, C-12, C-13, and C-14.

was observed at δ 206.6 when the spectrum was recorded in C_6D_6. The solvent effect on the chemical shifts upon changing from $CDCl_3$ to C_6D_6 was minor (Table 1).

The molecular formula $C_{21}H_{27}NO_3$ indicated nine degrees of unsaturation, of which three were accounted for by the presence of two carbonyls (δ 210.5 and 209.0) and the exocyclic methylene (δ 142.6 and 109.9). The remaining six degrees of unsaturation indicated the presence of a hexacyclic skeleton as in the atisane-type alkaloids. The C-16 carbon signal at δ 142.7 indicated that there was no OH group at C-15, as an OH at C-15 would have caused the C-16 signal to shift downfield by ca. 10 ppm as in atisine. The signals at δ 67.1 and δ 64.5 were assigned to C-20 and C-2, respectively, based on the COSY spectrum, which showed a correlation of H-2 (δ 3.92) with H-1 and H-3, and H-20 (δ 3.20) showed a correlation with H-14 (δ 2.60). In the HETCOR spectrum, the methine signals at δ 67.1 and δ 64.5 showed correlations with H-20 (δ 3.20) and H-2 (δ 3.92), respectively. Comparison of the ^{1}H- and ^{13}C-nmr spectral data of **1** with those of the known compounds suggested that the alkaloid may be identical with deacetylheterophylloidine which has been prepared by alkaline hydrolysis of

TABLE 1. ^{13}C-Nmr Chemical Shifts and Assignments of Deacetylheterophylloidine [**1**], Heterophylloidine [**4**],[a] and Hetidine [**2**].

Carbon	**1**	**1**	**4**	**2**	**2**
	δ_C[b] $CDCl_3$	δ_C[b] C_6D_6	δ_C[b] $CDCl_3$	δ_C[b] $CDCl_3$ +drop of pyridine-d_5	δ_C[b] C_6D_6 +2 drops of $CHCl_3$
1	40.7 t	40.6 t	35.9 t	39.0 t	38.9 t
2	64.5 d	64.8 d	70.9[c] d	66.7 d	67.2 d
3	48.3 t	48.5 t	43.9 t	76.9 d	77.6 d
4	37.1 s	36.9 s	36.8 s	41.8 s	41.9 d
5	59.9 d	59.7 d	63.2 d	58.2 d	57.9 d
6	208.7 s	206.6 s	203.8 s	208.4 s	208.9 s
7	52.3 t	51.9 t	50.4 t	52.1 t	52.3 t
8	40.9 s	40.6 s	41.8 s	41.2 s	40.7 s
9	46.4 d	46.9 d	50.0 d	46.3 d	46.1 d
10	45.0 s	45.9 s	44.5 s	44.6 s	44.4 s
11	23.4 t	23.4 t	22.7 t	23.4 t	23.5 t
12	53.5 d	53.8 d	52.8 d	53.4 d	53.7 d
13	210.5 s	209.4 s	211.5 s	210.2 s	208.9 s
14	56.6 d	57.7 d	59.2 d	56.5 d	56.6 d
15	36.2 t	35.9 t	34.8 t	36.1 t	36.0 t
16	142.7 s	144.0 s	142.3 s	142.3 s	143.8 s
17	109.9 t	108.9 t	110.5 t	110.3 t	109.1 t
18	27.2 q	28.4 q	31.2 q	22.7 q	23.4 q
19	57.5 t	58.0 t	60.4 t	51.7 t	51.9 t
20	67.1 d	68.2 d	68.5[c] d	67.2 d	67.5 d
21	41.9 q	42.0 q	43.3 q	41.6 q	41.5 q
2-CO	—	—	109.8 s	—	—
$-CH_3$	—	—	21.6 q	—	—

[a]These values have been taken from Katz and Stahelin (7) and assignments have been made to fit the values found for **1** and **2**.

[b]The multiplicities were based on DEPT experiments.

[c]The assignments for these carbons have been reversed from those quoted by Wang and Liang (8).

heterophyllodine [**4**] (4). Alkaloid **1** has not been reported as a natural product. Heterophylloidine [**4**], isolated from *Aconitum heterophylloides* Stapf. and panicutine isolated from *A. paniculatum* Lam. (7), have been shown to be identical (4). The precise ^{1}H- and ^{13}C-nmr spectral assignments for **1** and **4** have not been published. Wang and Liang (8) have tabulated the assignments for **4** but have taken the values quoted for panicutine (carbonyl group at C-11 instead of at C-13 in **4**) prior to our publication, revising the structure of panicutine. In view of the present study, we have reassigned the chemical shifts for **4** (Table 1). Comparison of the tlc, mixture mp, and ir spectra confirmed the identity of the alkaloid isolated from *D. albiflorum* with deacetylheterophylloidine [**1**].

Three separate scalar spin-systems in **1** were delineated by the homonuclear COSY nmr spectrum in $CDCl_3$: [H-1α–H-1β–H-2β–H-3α–H-3β], [H-9–H-11–H-12] and [H-14–H-20]. Long-range coupling was observed between H-17a–H-17b–H-15β and H-17a–H-17b–H-12 and some more protons. *W*-Type coupling was noticed between H-9–H-12–H-14 (Table 2). The carbon multiplicities were assigned using the DEPT spectrum (Table 1). After establishing chemical shifts of the protons by COSY, the protonated carbons were assigned by the heteronuclear COSY (HETCOR) spectrum. The assignments of the quaternary carbon resonances were established by selective INEPT experiments (9).

TABLE 2. ^{1}H-Nmr Chemical Shift Assignments for Deacetylheterophylloidine [**1**].[a]

Proton	δ (ppm)	Multiplicity *J* (Hz)	COSY
H-1α	2.02	dd, $J_{1\alpha,1\beta}$=13.8 $J_{1\alpha,2\beta}$=4.4	H-1β, H-2β
H-1β	1.61	dd, $J_{1\beta,1\alpha}$=13.8 $J_{1\beta,2\beta}$=5.5	H-1α, H-2β
H-2β	3.92	br s $W_{1/2}$=5.0	H-1α, H-1β, H-3α, H-3β
H-3α	1.80	m	H-2β
H-3β	1.72	m	H-2β
H-5	1.85	s	
H-7α, 7β	2.41	m	
H-9	1.91	m	H-12[b], H-14[b]
H-11α	2.07	m	H-11β, H-12
H-11β	1.85	m	H-11α, H-12
H-12	2.92	br d $W_{1/2}$=7.5	H-9[b], H-11α, H-11β, H-14[b] H-17a[c], H-17b[c]
H-14	2.60	br t $W_{1/2}$=6.0	H-9[b], H-20
H-15α	2.35	AB J_{gem}=18.1	
H-15β	2.49	AB J_{gem}=18.1	H-11α[c], H-11β[c], H-17b[c]
H-17a	4.76	br s $W_{1/2}$=5.0	H-12[c], H-15β[c], H-17b[c]
H-17b	4.94	br s $W_{1/2}$=5.0	H-12[c], H-15β[c], H-17a[c]
H-18	1.08	s	H-19α, H-19β
H-19α	2.10	AB J=8.0	H-18[c], H-19β
H-19β	2.40	AB J=8.0	H-18[c], H-19α
H-20	3.21	s	H-14
H-21	2.45	s	
OH-2	6.62	br s	

[a]Solvent used was $CDCl_3$.
[b]*W*-type coupling.
[c]Long-range coupling.

Saturation of the ^{1}H-nmr signals of **1** at δ 3.21, δ 2.60, and δ 2.92, assigned to H-20, H-14, and H-12, respectively, showed enhancements of the carbonyl carbon at δ 210.5 (C-13). The second carbonyl at δ 209.0 was assigned to C-6. Selectively pulsing H-14 (δ 2.60), showed enhancement of signals at δ 67.1 (C-20, two bonds separated), and δ 46.4 (C-9), δ 45.0 (C-10) (both three bonds away) (Table 3). The quaternary carbon at ca. 209 ppm in **1** was observed as a weak signal in $CDCl_3$ and was clearly observed in C_6D_6 because the trace amounts of HCl in $CDCl_3$ form a quaternary salt as in **1A**. The methine signal at δ 59.9 was assigned to C-5, as saturation of the C-18 methyl at δ 1.08 showed enhancement of the resonances at δ 37.1 (C-4) (two bonds away) and δ 59.9 (C-5), δ 48.3 (C-3), and δ 57.5 t (C-19) (all three bonds away) (Table 3). When H-12 (δ 2.92, ^{13}C 53.5), was selectively pulsed, the carbon signals showing a response were δ 142.7 (C-16) (two bonds separated), and δ 109.9 (C-17), δ 56.5 (C-14), δ 46.4 (C-9), and δ 36.2 (C-15) (all three bonds away).

Another alkaloid, mp 217–220°; [α]D −77.1°, $C_{21}H_{27}NO_4$, hrms (*m/z* 357.1940) was identified as hetidine [**2**]. A comparison of the tlc, ir, and their ^{1}H- and ^{13}C-nmr spectra of the alkaloid with those of an authentic sample of hetidine [**2**] showed them to be identical. Hetidine was isolated in a very small yield from *A. heterophyllum* Wall. (10) and its structure established by single-crystal X-ray analysis of its hydroiodide (5). As in **1**, the ^{13}C-nmr spectrum of **2** in $CDCl_3$ (Table 1) did not show a significant signal for C-6, due to the formation of a quaternary salt as in **2A**. Alkaline hydrolysis of episcopalidine is reported to give **2**, and the ^{13}C-nmr assignments for **2** have been recorded (8). By a detailed ^{1}H-nmr study, accurate chemical shift assignments have been

TABLE 3. Selective INEPT Nmr Data of **1** and **2**.

Pulsed ^{1}H (δ)	Responding carbons ^{13}C (δ)
Deacetylhetaphylloidine [**1**]	
4.76 (H-17b)	142.7 (C-16), 36.2 (C-15)
3.92 (H-2β)	45.0 (C-10), 37.1 (C-4)
3.21 (H-20)	210.5 (C-13), 59.9 (C-5), 57.5 (C-19), 45.0 (C-10)
2.91 (H-12)	210.5 (C-13), 142.7 (C-16), 109.9 (C-17), 56.6 (C-14), 46.4 (C-9), 36.2 (C-15)
2.60 (H-14)	210.5 (C-13), 67.1 (C-20), 46.4 (C-9), 45.0 (C-10)
2.49 (H-15β)	142.7 (C-16), 109.9 (C-17), 46.4 (C-9), 40.9 (C-8)
2.45 (*N*-CH_3)	67.1 (C-20)
2.41 (H-7)	59.9 (C-5), 46.4 (C-9), 40.9 (C-8), 36.2 (C-15)
2.40 (H-19)	59.9 (C-5), 67.1 (C-20), 41.9 (C-21)
2.35 (H-15α)	142.7 (C-16), 109.9 (C-17), 40.9 (C-8)
2.07 (H-11α)	46.4 (C-9), 45.0 (C-10)
2.02 (H-1α)	64.5 (C-2), 59.9 (C-5)
1.80 (H-3α)	64.5 (C-2), 59.9 (C-5), 37.1 (C-4)
1.08 (H-18)	59.9 (C-5), 57.5 (C-19), 48.3 (C-3), 37.1 (C-4)
Hetidine [**2**]	
4.79 (H-17a)	36.1 (C-15)
3.95 (H-2β)	76.9 (C-3), 44.6 (C-10), 41.8 (C-4)
3.36 (H-3β)	22.7 (C-18)
3.17 (H-20)	210.2 (C-13), 51.7 (C-19), 44.6 (C-10)
2.49 (H-7, H-15)	41.2 (C-8)
2.47 (*N*-CH_3)	67.2 (C-20), 51.7 (C-19)
1.18 (H-18)	76.9 (C-3), 58.2 (C-5), 51.7 (C-19), 41.8 (C-4)

obtained for **2** (Table 4). A revision of the ^{13}C-nmr chemical shifts for C-4, C-8, C-11, and C-18 from the published values (8) has been made. Also in the case of **2**, the solvent effect on the chemical shifts upon changing from $CDCl_3$ to C_6D_6 was found to be minor

TABLE 4. ^{1}H-Nmr Chemical Shift Assignments for Hetidine [**2**].[a]

Proton	δ (ppm)	Multiplicity	*J* (Hz)	COSY
H-1α	2.15	dd	$J_{1\alpha,1\beta}$=14.5 $J_{1\alpha,2\beta}$=3.5	H-1β, H-2β
H-1β	1.73	dd	$J_{1\beta,1\alpha}$=14.5 $J_{1\beta,2\beta}$=3.5	H-1α, H-2β
H-2β	3.95	br t	$J_{2\beta,1\alpha}$=3.5 $J_{2\alpha,1\beta}$=3.5 $J_{2\beta,3\beta}$=5.3	H-1α, H-1β, H-3β, H-5[c], H-18[c]
H-3β	3.36	d	$J_{3\beta,2\beta}$=5.3	H-2β, H-5[c], H-18[c]
H-5	1.83	s		H-3β[c], H-20[c]
H-7α, 7β	2.48	m		
H-9	1.92	m		H-12[b], H-14[b], H-15β[c]
H-11α	2.07	m		H-11β, H-12
H-11β	1.85	m		H-11α, H-12, H-15[c]
H-12	2.95	br d	$W_{1/2}$=7.0	H-9[b], H-11α, H-11β, H-14[b], H-17a[c]
H-14	2.61	br d	$W_{1/2}$=3.0	H-9[b], H-20
H-15α	2.38	AB	J_{gem}=18.0	H-11β[c]
H-15β	2.49	AB	J_{gem}=18.0	H-9[c], H-17b[c]
H-17a	4.79	br s	$W_{1/2}$=7.0	H-12[c], H-15β[c], H-17b[c]
H-17b	4.96	br s	$W_{1/2}$=7.0	H-12[c], H-15β[c], H-17a[c]
H-18	1.18	s		H-19α, H-19β
H-19α	1.94	AB	*J*=12.4	H-18, H-19β
H-19β	2.73	AB	*J*=12.4	H-18, H-19α
H-20	3.17	br d	$W_{1/2}$=3.0	H-5[c], H-14
H-21	2.47	s		

[a]Solvent used was $CDCl_3$+drop of pyridine-d_5.
[b]*W*-type coupling.
[c]Long-range coupling.

(Table 1). Revision of the C-4 and C-8 assignments was based on selective INEPT experiments (Table 3). When the Me-18 signal at δ 1.18 was selectively pulsed, the carbons showing responses were C-3 (δ 76.9), C-5 (δ 58.2), and C-19 (δ 51.7) (all three bonds away), and C-4 (δ 41.8) (two bonds away). When the *N*-Me protons at δ 2.47 were selectively pulsed, the carbons responding were C-20 (δ 67.2), C-19 (δ 51.7) (both three bonds away). Saturation of the H-20 proton (δ 3.17) showed enhancement of the signals for C-13 (δ 210.2), C-19 (δ 51.7) (three bonds away), and C-10 (δ 44.6). The revision of the C-11 and C-18 chemical shifts resulted from DEPT studies in which the signals at δ 22.7 and δ 23.4 appeared as Me and CH_2, respectively.

The least polar fraction in the chromatographic separation of the crude alkaloid on Al_2O_3 afforded lycoctonine [**3**], which was identified by comparison with an authentic sample. The ^{13}C-nmr chemical shift assignments for C-5, C-9, C-10, and C-13 must be revised according to a study by Beul and Katz (11) from the reported values (12). The new assignments for these carbons are C-5 (49.7), C-9 (43.3), C-10 (46.1), and C-13 (38.0).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps are reported corrected and were determined on a Thomas-Koffler hot stage equipped with a microscope and a polarizer. Optical rotations were measured on a Perkin-Elmer model 141 polarimeter in $CHCl_3$. Ir spectra were recorded in nujol on a Perkin-Elmer model 1420 spectrophotometer. Hrms were determined on a Fisons Auto Spec ETOFFPD mass spectrometer. Nmr spectra including DEPT and 2D experiments 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 pulse sequences employed for the nmr experiments were those of the standard Bruker software. The pulse sequence for the selective INEPT nmr experiments was obtained by modifying the Bruker standard INEPT sequence and the critical parameters used were as described (13). Chromatographic separations on a Chromatotron (14) were carried out on rotors coated with 1-mm thick layers of Merck Al_2O_3 60 PF_{254}, 365 (EM 1104).

PLANT MATERIAL.—The aerial parts of *D. albiflorum* were collected from Eastern Turkey, Van Erek mountain, at an altitude of 2,500 m. The plant was identified by one of us (H.Ö.), Faculty of Sciences, Department of Biology, Suleyman Demirel University, Isparta, Turkey, and the voucher specimen (No. H. O. 6342) has been deposited in that department.

EXTRACTION AND ISOLATION.—Dried and powdered aerial parts of *D. albiflorum* (0.634 kg) were extracted exhaustively by percolation at room temperature with 95% EtOH (5×1.5 liters). Evaporation *in vacuo* of the combined extracts gave a dark gummy residue (76.1 g). The residue was mixed with CH_2Cl_2 (500 ml) and the mixture was extracted with 5% H_2SO_4 (250 ml×10). The acidic extract was washed with CH_2Cl_2 (200 ml×3) and then basified, in the cold, with aqueous Na_2CO_3 to pH 10. Extraction with CH_2Cl_2 (300 ml×10) and evaporation *in vacuo* yielded a crude mixture of alkaloids (5.2 g) which was chromatographed on an Al_2O_3 column (5×70 cm). The eluting solvent was a gradient of petroleum ether, EtOAc, and EtOH and 130 fractions (100 ml each) were collected. On the basis of tlc results the fractions were pooled to give nine fractions. Fractions 1, 2, and 9 contained non-alkaloidal residues. Fractions 3–5 (98.3 mg) on SiO_2 prep. tlc yielded lycoctonine [**3**] (45.3 mg).

Deacetylheterophylloidine [**1**] *and hetidine* [**2**].—Fractions 6–8 from the cc (235 mg) were fractionated on an Al_2O_3 rotor of a Chromatotron. A gradient of hexane, $CHCl_3$, and MeOH was used for elution and 104 fractions were collected according to the uv- (λ 254 or 365 nm) visible bands eluting from the rotor. Fractions 19–30 (eluted with hexane-$CHCl_3$ 80:20, 70:30, and 60:40) gave deacetylheterophylloidine [**1**] (28.1 mg), mp 160–162°, $[\alpha]_D$ −59.9° (*c*=0.76); hrfabms *m/z* 341.1991 (calcd for $C_{21}H_{27}NO_3$ *m/z* 341.1984); ir ν max 3420, 2920, 2800, 1725, 1690, 1640, 1450, 1430, 1335, and 1210 cm^{-1}, and fractions 65–74 (eluted with $CHCl_3$ and $CHCl_3$-2% MeOH) gave hetidine [**2**] (27.3 mg), mp 217–220°; $[\alpha]_D$ −77.1° (*c*=0.49); hrfabms *m/z* 357.1940 (calcd for $C_{21}H_{27}NO_4$ *m/z* 357.1933); ir ν max 3400, 2920, 2850, 1725, 1660, 1465, 1455, 1375 cm^{-1}.

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