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NORDITERPENOID ALKALOIDS FROM *ACONITELLA HOHENACKERI*

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Key Word Index—*Aconitella hohenackeri*; *Consolida hohenackeri*; Ranunculaceae; norditerpenoid alkaloids; 1-demethylwinkleridine; 18-demethyl-14-deacetylpubescenine; hohenackeridine.

Abstract—Two new norditerpenoid alkaloids, 1-demethylwinkleridine and 18-demethyl-14-deacetylpubescenine, and a new bisnorditerpenoid alkaloid, hohenackeridine, were isolated from the aerial parts of *Aconitella hohenackeri*, and their structures elucidated by 1D and 2D NMR spectroscopy techniques.

INTRODUCTION

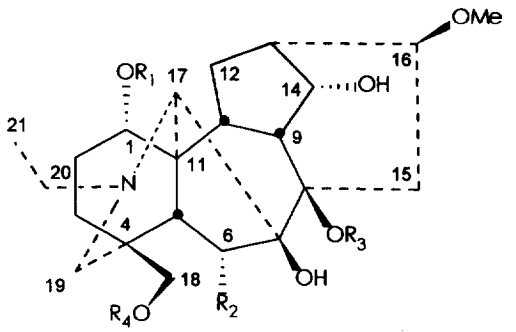
Aconitella hohenackeri (Boiss). Sojak, syn. *Consolida hohenackeri* (Boiss.) Grossh., is an annual herb distributed in northeast Turkey, from which seven norditerpenoid alkaloids, lycoctonine, delcorine, dehydrodelcorine, delectinine, bicolorine, hohenackerine, and tortumine, have been isolated [1]. We report here on the structure determination of two new norditerpenoid alkaloids, 1-demethylwinkleridine (**1**) and 18-demethyl-14-deacetylpubescenine (**2**), as well as that of a new bisnorditerpenoid alkaloid, hohenackeridine (**3**), isolated from the epigeal part of the said plant.

RESULTS AND DISCUSSION

The new alkaloids, 1-demethylwinkleridine (**1**), 18-demethyl-14-deacetylpubescenine (**2**), and hohenackeridine (**3**), were isolated as colourless crystals, and their molecular formulae, $C_{22}H_{35}NO_6$, $C_{23}H_{37}NO_7$, and $C_{22}H_{31}NO_7$, respectively, inferred from their HR-mass spectra and ^{13}C NMR spectra. The NMR spectra revealed that they belong to the lycoctonine type diterpenoid alkaloids, showing distinctive signals at δ_H 0.77–1.11 (3H, *t*), 2.59–3.06 (two 1H, *dq*), δ_C 13.8–14.1 *q* and 50.3–51.4 *t* for the *N*-ethyl group; δ_H 3.01–3.39 (3H, *s*) and δ_C 56.1–56.7 *q*, from HMQC [2] (Tables 1, 3 and 5), for the methoxyl group at C-16β; δ_H 3.34–4.04 (1H, *br t*) and δ_C 73.0–77.3 *d* (HMQC), for the hydroxyl group at C-1α (ring A boat); two carbon singles at δ_C 85.6–89.0 and δ_C 77.0–82.6, for the C-7 and C-8 oxygen functions, respectively; and δ_H 3.81–4.00 (1H, *t*, J = 4.5 Hz) and δ_C 75.7–75.4 *d* (HMQC), for a secondary hydroxyl group at C-14β, only in compounds **1** and **2** [3, 4].

The one-proton signal at δ_H 2.37 *s* (HMQC, δ_C 65.6 *d*), 2.72 *s* (δ_C 64.5 *d*) and 3.15 (*d*, J = 3.0 Hz) (δ_C 67.7 *d*) in compounds **1**, **2**, and **3**, respectively, gave three-bond connectivities with the C-20 and the methylene carbon resonance at δ_C 54.2–57.7, in the HMBC spectra (Tables 1, 3 and 5) [5], which in turn displayed one-bond correlation with the non-equivalent methylene protons at δ_H 2.09–2.55 and δ_H 2.42–3.44 (each *d*, J = 10.0–11.5 Hz), in the HMQC spectra, allowing us to assign the NMR signals at δ_H 2.37–3.15 *s* or *d*, δ_H 2.09–2.55 *d*, δ_H 2.42–3.44 *d*, δ_C 54.2–57.7 and δ_C 64.5–67.7 *d*, to H-17, H-19α, H-19β, C-19, and C-17, respectively, in alkaloids **1**–**3**.

Since the corresponding H-19β signal in compound **1** and **2** gave three-bond correlation (HMBC) with the methylene carbon resonance at δ_C 67.5–70.0, this carbon resonance was assigned to C-18, which also showed one-bond correlation (HMQC) with the non-equivalent protons at δ_H 3.08–3.84 and 2.90–3.69 (each *d*, J = 10.5–11.0 Hz); hence a secondary hydroxyl group was situated at C-18 in alkaloids **1** and **2**. In the ^1H COSY spectra of the compounds (Tables 2, 4 and 6) the H-17 signal showed *W* coupling to the one-proton signals at δ_H 1.46 (*d*, J = 8.0 Hz) (HMQC, δ_C 41.8 *d*), 2.07 (*d*, J = 7.0 Hz) (δ_C 46.5 *d*) and 1.44 (*d*, J = 2.0 Hz) (δ_C 48.7 *d*) that were assigned to H-5 in compounds **1**, **2**, and **3**, respectively. On the other hand, the H-5 signal gave: (a) scalar correlation with the non-equivalent methylene protons at δ_H 1.94 (*dd*, J = 15.0 and 7.5 Hz) (δ_C 33.5 *t*) and 1.21 (*d*,

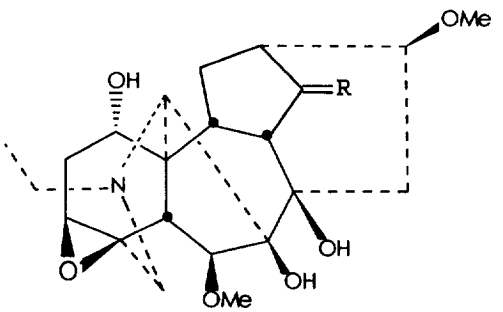


1 $R_1=R_2=R_3=R_4=H$

2 $R_1=R_4=H$; $R_2=\alpha$ OH; $R_3=Me$

4 $R_1=Me$; $R_2=R_3=R_4=H$

5 $R_1=H$; $R_2=\alpha$ OH; $R_3=R_4=Me$



3 R=O

6 R=βH, α OMe

J = 15.0 Hz) (δ_C 33.3 *t*) in compound **1** and the one-proton signal at δ_H 4.48 (*d*, J = 7.0 Hz) (δ_C 70.6 *d*) in alkaloid **2**; (b) spatial but not scalar correlation with the one-proton signal at δ_H 4.41 *s* (δ_C 89.8 *d*) in compound **3** (Tables 2, 4 and 6). In addition, the signal at δ_H 4.41 *s* showed spatial correlations (Table 6) with the methoxyl group at δ_H 3.38 *s* and the H-19β signal. These observations and the coupling constants observed between the protons involved indicating that there were no functional groups at C-6 in compound **1**, a secondary hydroxyl group at C-6α in compound **2**, and a secondary methoxyl group at C-6β in alkaloid **3**.

The C-7 and C-8 carbon singlet resonances of the new alkaloids were assigned by comparison of their ^{13}C NMR spectra with those of related lycoctonine-type alkaloids [3, 4], in particular with the spectra of winkleridine (**4**) [6], 14-deacetylpubescenine (**5**) [7] and tuguaconitine (**6**) [8] (Table 7). Furthermore, the following long-range correlations between the C-7 and C-8 carbon singlets and proton signals were observed in the HMBC spectra (Tables 1, 3 and 5): (a) δ_C 86.2 with H-5, H-6α and H-6β, and δ_C 77.0 with H-6α, H-6β and H-14β for alkaloid **1**; (b) δ_C 85.6 with H-5 and H-6β, and δ_C 81.0 with H-6β, H-14β, H-17 and the methoxyl group at δ_H 3.41 for alkaloid **2**; (c) δ_C 89.0 with H-6α and δ_C 82.6 with H-6α and H-17 for alkaloid **3**. These confirmed the C-7 and C-8 carbon resonance assignments, and the existence of two tertiary hydroxyl groups at C-7 and C-8 in compounds **1** and **3**, and a tertiary hydroxyl group at C-7 and a tertiary methoxyl group at C-8 in alkaloid **2**. The C-5, C-9, and C-10 carbon resonance of 14-deacetylpubescenine (**5**) (Table 7) have been reassigned considering the NMR data given in this work for 18-demethyl-14-deacetylpubescenine (**2**).

In the alkaloid hohenackeridine (**3**) a carbonyl group was situated at C-14 (IR, 1750 cm^{-1} for a five-membered ring ketone) because its ^{1}H and ^{13}C NMR spectra lacked the distinctive signals corresponding to the C-14βH,αOR [3, 4] and the similarity of its ^{13}C NMR spectrum, which gave a signal at δ_C 214.2 *s*, with those of the related alkaloids 14-dehydrodelcosine [9] and grandifloricine [10]. The NMR spectra of **3** did not show signals of an angular methyl group at C-4 or a C-18 functionality and, in agreement with its empirical formula, $C_{22}H_{31}NO_7$, and the ^{13}C NMR data, this compound must be a bisnorditerpenoid alkaloid having an epoxide group in the molecule. The comparison of the ^{13}C NMR spectrum of **3** with that of the related alkaloid tuguaconitine (**6**) [8] (Table 7) suggested that the oxirane ring is located at C-3–C-4 in the β position. In effect, the one-proton signal at δ_H 3.12 (*dd*, J = 7.0 and 5.5 Hz) (HMQC, δ_C 58.4 *d*) was assigned to H-3α since it gave three-bond correlations with the C-5 and C-19 carbon resonances in the HMBC spectrum (Table 5), and spatial correlation with the H-19α in the NOESY spectrum (Table 6). In addition, in the HMBC spectrum of **3**, the H-6α gave a long-range connectivity with the carbon signal at δ_C 58.4, that was 25% more intense that the highest of the remainder of the carbon signals, and was also assigned to C-4.

The new alkaloid 18-demethyl-14-deacetylpubescenine (**2**), together with pubescenine [7], delphiperegrine and pergoline [11], is another example of the rare lycoctonine-type norditerpenoid alkaloids with a C-6α oxygen function. Hohenackeridine (**3**), like tuguaconitine [12], monticoline [13] and delboxine [14], is an example of a lycoctonine-type bisnorditerpenoid alkaloid with an epoxy bridge between C-3 and C-4.

EXPERIMENTAL

General. Mps (uncorr) were taken on a Gallenkamp apparatus. Mixts of hexane–EtOAc and EtOAc–MeOH were used as solvents for crystallization. IR: Perkin–Elmer-1430 spectrophotometer. OR: Perkin–Elmer-241 polarimeter, MeOH, 1 cm cell. EIMS and

Table 1. ^{1}H, HMQC and HMBC NMR data of 1-demethylwinkleridine (**1**)*

H		Correlated C-atom	
		HMQC	HMBC
1β	3.34 *br t* (4.3)	73.0 *d*	
2α	1.23 *m*	29.4 *t*	C-4, C-11
2β	1.21 *m*	29.4 *t*	C-4, C-11
3α	1.27 *ddd* (13.5, 12.5, 5.5)	26.6 *t*	
3β	1.59 *br d* (14.0)	26.6 *t*	
5	1.46 *d* (8.0)	41.8 *d*	C-4, C-7, C-17, C-19
6α	1.21 *d* (15.0)	33.5 *t*	C-4, C-5, C-7, C-8, C-11
6β	1.94 *dd* (15.0, 7.5)	33.5 *t*	C-4, C-7, C-8
9	1.79 *dd* (7.0, 5.5)	48.1 *d*	C-8, C-12, C-13, C-14
10	1.52 *ddd* (11.5, 7.0, 5.0)	44.0 *d*	C-8, C-11, C-17
12α	1.14 *dd* (14.5, 5.5)	30.0 *t*	C-11, C-16, C-14
12β	1.69 *ddd* (14.5, 11.5, 8.0)	30.0 *t*	
13	1.93 *dd* (7.5, 5.0)	40.6 *d*	
14β	3.81 *t* (4.5)	75.7 *d*	C-8, C-9, C-16
15α	2.53 *dd* (15.5, 9.5)	35.5 *t*	C-7, C-8, C-9, C-13, C-16
15β	1.41 *dd* (16.0, 6.5)	35.5 *t*	C-8, C-16
16α	2.97 *m*	83.3 *d*	
17	2.37 *s*	65.6 *d*	C-1, C-5, C-6, C-11, C-19, C-20
18A	3.08 *d* (11.0)	67.5 *t*	C-3, C-4, C-5, C-19
18B	2.90 *d* (11.0)	67.5 *t*	C-3, C-4; C-5, C-19
19α	2.09 *d* (11.0)	56.5 *t*	C-4, C-5, C-17
19β	2.42 *d* (11.5)	56.5 *t*	C-3, C-4, C-18
20A	2.72 *dq* (14.0, 7.0)	51.1 *t*	
20B	2.59 *dq* (14.0, 7.0)	51.1 *t*	
21	0.77 *t* (7.0)	13.8 *q*	C-20
16β-OMe	3.01 *s*	56.5 *q*	C-16

* Chemical shifts in ppm rel. to TMS. Coupling constants (*J*) in Hz. C-Multiplicities were determined by DEPT data.

exact mass measurements: Hewlett-Packard 5989A and VG-Micromass-ZAB-2F instruments, respectively, 70 eV. ^{1}H NMR, ^{1}H COSY, HMQC, HMBC and NOESY spectra: Varian-VXR-500 spectrometer; ^{13}C NMR and DEPT spectra: Varian-Gemini-300 spectrometer; $CDCl_3$, $CDCl_3$–CD_3OD, or CD_3OD, TMS and solvents as internal standard. DEPT and 2D NMR experiments were carried out with the standard pulse sequences given in the Varian manual. Alumina Merck Art. 1067 and 5581 were used for CC and TLC, respectively. Spots on chromatograms were detected under UV light (254 nm) and with Dragendorff's reagent.

Plant material. Plants were collected near Unçular, between Tortum and Artvin, Turkey, at an altitude of 1200 m, growing in dry fields, and authenticated by Professors J. Molero and C. Blanché, Botany Laboratory, Faculty of Pharmacy, University of Barcelona, where a voucher specimen, BCF 37765, has been deposited.

Extraction and isolation of alkaloids. Aerial parts of plants were air-dried (1.1 kg) and extracted with EtOH by percolation at room temp. The extract was evapd under vacuum and acidified with H_2SO_4 (0.5 M). After removing the insoluble part, the acidic soln was adjusted with Na_2CO_3 to pH 9 and extracted with $CHCl_3$ to give a crude alkaloidal extract. CC of this extract using EtOAc and EtOAc–MeOH step gradient led to the isolation of individual alkaloids, purified by further CC and by PTLC using the analyt pre-coated sheets, in the following elution order: **3** (8.5 mg), **1** (12.0 mg) and **2** (5.0 mg).

1-*Demethylwinkleridine* (**1**). Crystalline, mp 204–205°, from EtOAc–MeOH. $[\alpha]_D$ +25.6° (*c* 0.43). $[M]^+$ *m/z* 409.2463 for $C_{22}H_{35}NO_6$ (calc. 409.2464). IR ν_{max}^{NaCl} cm^{-1}: 3344, 2923, 2846, 1455, 1383, 1350, 1292, 1201, 1182, 1078, 1039, 1020, 1000, 980, 941. EIMS *m/z* (rel. int.): 409 (11) $[M]^+$, 395 (13), 394 (58), 393 (26), 392 (100), 376 (17), 374 (5), 366 (9), 360 (9), 353 (4), 351 (8), 334 (5), 328 (4), 310 (8), 91 (6), 71 (11), 58 (26). ^{1}H NMR and ^{13}C NMR ($CDCl_3$–CD_3OD, 8:1): Tables 1 and 7.

18-*Demethyl*-14-*deacetylpubescenine* (**2**). Crystalline, mp 139–140°, from EtOAc–MeOH. $[\alpha]_D$ −10.8° (*c* 0.37). $[M]^+$ *m/z* 439.2571 for $C_{23}H_{37}NO_7$ (calc. 439.2570). IR ν_{max}^{NaCl} cm^{-1}: 3348, 2928, 2872, 1456, 1378, 1229, 1240, 1155, 1120, 1099, 1032, 1007, 987, 954, 935, 863, 837, 805, 720. EIMS *m/z* (rel. int.): 439 (5) $[M]^+$, 424 (11), 423 (11), 422 (41), 409 (15), 408 (52), 407 (38), 406 (23), 392 (42), 390 (32), 378 (19), 376 (24), 364 (20), 362 (16), 351 (17), 350 (14), 348 (16), 332 (16), 318 (12), 302 (10), 265 (14), 264 (65), 223 (19), 210 (21), 192 (12), 164 (15), 91 (23), 58 (100). ^{1}H NMR (CD_3OD) and ^{13}C NMR ($CDCl_3$–CD_3OD, 1:8): Tables 2 and 7.

Hohenackeridine (**3**). Crystalline, mp 224–225°,

Table 2. Scalar and spatial correlation of the protons of 1-demethylwinkleridine (**1**)

H	COSY	NOESY
1β	H-2α, H-2β	H-2α, H-2β, H-10, H-12α, H-12β
2α	H-1β, H-2β, H-3α, H-3β	H-1β, H-3α, H-3β
2β	H-1β, H-2α, H-3α, H-3β	H-1β, H-3α, H-3β, H-5
3α	H-2α, H-2β, H-3β	H-2α, H-2β, H-3β, H-19α
3β	H-2α, H-2β, H-3α	H-2α, H-2β, H-3α, H-18A, H-18B
5	H-6α, H-6β, H-17 (W)	H-2β, H-6α, H-6β, H-10, H-18A
6α	H-5, H-6β	H-5, H-6β, H-18A, H-18B, H-19β
6β	H-5, H-6α	H-5, H-6α, H-9
9	H-10, H-14β	H-6β, H-10, H-14β
10	H-9, H-12α, H-12β	H-1β, H-5, H-9, H-12β, H-14β
12α	H-10, H-12β	H-1β, H-12β, H-16α, H-17
12β	H-10, H-12α, H-13	H-1β, H-10, H-12α, H-13, H-14β
13	H-12β, H-14β	H-12β, H-14β, H-16α, 16β-OMe
14β	H-9, H-13	H-9, H-10, H-12β, H-13
15α	H-15β, H-16α	H-15β, H-16α, H-17
15β	H-15α, H-16α	H-15α, H-16α, 16β-OMe
16α	H-15α, H-15β	H-12α, H-13, H-15α, H-15β, H-17
17	H-5 (W)	H-12α, H-15α, H-20A, H-16α
18A	H-18B	H-3β, H-5, H-6α, H-19β, H-18B
18B	H-18A	H-3β, H-6α, H-18A, H-19α
19α	H-19β	H-3α, H-18B, H-19β, H-20B, H-21
19β	H-19α	H-6α, H-18A, H-19α, H-20B, H-21
20A	H-20B, H-21	H-17, H-20B, H-21
20B	H-20A, H-21	H-19α, H-19β, H-20A, H-21
21	H-20A, H-20B	H-19α, H-19β, H-20A, H-20B
16β-OMe		H-13, H-15β

Table 3. ^{1}H, HMQC and HMBC NMR data of 18-demethyl-14-deacetylpubescenine (**2**)*

H		Correlated C-atom	
		HMQC	HMBC
1β	3.64 *br t* (4.5)	73.3 *d*	C-10
2α	1.52 *m*	29.8 *t*	
2β	1.49 *m*	29.8 *t*	
3α	1.52 *m*	29.6 *t*	C-2, C-19
3β	1.86 *m*	29.6 *t*	C-1, C-4, C-18, C-19
5	2.07 *d* (7.0)	46.5 *d*	C-4, C-7, C-10, C-11, C-17, C-18, C-19
6β	4.48 *d* (7.0)	70.6 *d*	C-4, C-7, C-8, C-17
9	2.01 *dd* (7.0, 5.0)	47.9 *d*	C-8, C-10, C-12
10	1.87 *m*	44.3 *d*	C-1, C-8, C-11, C-12, C-17
12α	1.58 *dd* (14.0, 5.0)	31.0 *t*	C-11, C-13, C-14, C-16
12β	2.00 *ddd* (14.0, 11.5, 7.5)	31.0 *t*	C-13, C-14
13	2.21 *dd* (7.0, 4.5)	41.5 *d*	C-9, C-10, C-14, C-15, C-16
14β	4.00 *t* (4.5)	75.4 *d*	C-8, C-16
15α	2.60 *dd* (14.0, 8.5)	29.2 *t*	C-7, C-8, C-9, C-13, C-16
15β	2.11 *dd* (14.0, 8.0)	29.2 *t*	C-8, C-16
16α	3.40 *m*	84.2 *d*	
17	2.72 *s*	64.5 *d*	C-5, C-6, C-8, C-10, C-11, C-19, C-20
18A	3.84 *d* (10.5)	70.0 *t*	C-3, C-4, C-5, C-19
18B	3.69 *d* (10.5)	70.0 *t*	C-3, C-4, C-5, C-19
19α	2.36 *d* (11.0)	57.7 *t*	C-3, C-4, C-5, C-17
19β	2.87 *d* (11.5)	57.7 *t*	C-3, C-4, C-18, C-20
20A	3.06 *dq* (14.0, 7.0)	51.4 *t*	C-17, C-19, C-21
20B	2.90 *dq* (14.0, 7.0)	51.4 *t*	C-17, C-19, C-21
21	1.11 *t* (7.5)	14.0 *q*	C-20
8-OMe	3.41 *s*	53.3 *q*	C-8
16β-OMe	3.39 *s*	56.7 *q*	C-16

* Chemical shifts in ppm rel. to TMS. Coupling constants (*J*) in Hz. C-Multiplicities were determined by DEPT data.

Table 4. Scalar and spatial correlation of the protons of 18-demethyl-14-deacetylpubescenine (**2**)

H	COSY	NOESY
1β	H-2α, H-2β	H-2α, H-2β, H-10, H-12α, H-12β
2α	H-1β, H-2β, H-3α, H-3β	H-1β, H-2β, H-3β
2β	H-1β, H-2α, H-3α, H-3β	H-1β, H-2α, H-3β, H-5, H-10
3α	H-2α, H-2β, H-3β	H-3β, H-5, H-19α
3β	H-2α, H-2β, H-3α	H-2α, H-2β, H-3α, H-18A, H-18B
5	H-6β, H-17 (W)	H-2β, H-3α, H-6β, H-10, H-18A
6β	H-5	H-5, H-9
9	H-10, H-14β	H-6β, H-10, H-14β
10	H-9, H-12α, H-12β	H-1β, H-2β, H-9, H-5, H-12β, H-14β
12α	H-10, H-12β	H-1β, H-12β, H-16α, H-17
12β	H-10, H-12α, H-13	H-1β, H-10, H-12α, H-13, H-14β
13	H-12β, H-14β	H-12β, H-14β, H-16α, 16β-OMe
14β	H-9, H-13	H-9, H-10, H-12β, H-13
15α	H-15β, H-16α	H-15β, H-16α, H-17
15β	H-15α, H-16α	H-15α, H-16α, 8-OMe, 16β-OMe
16α	H-15α, H-15β	H-12α, H-13, H-15α, H-15β, H-17
17	H-5 (W), H-19α (W)	H-12α, H-15α, H-16α, H-20A, H-21, 8-OMe
18A	H-18B	H-3β, H-5, H-18B, H-19β
18B	H-18A	H-3β, H-18A, H-19β
19α	H-17 (W), H-19β	H-3α, H-19β, H-20A, H-20B, H-21
19β	H-19α	H-18A, H-18B, H-19α, H-20A, H-21
20A	H-20B, H-21	H-17, H-19α, H-19β, H-20B, H-21
20B	H-20A, H-21	H-19α, H-20A, H-21
21	H-20B, H-20A	H-17, H-19α, H-19β, H-20A, H-20B
8-OMe		H-15β, H-17
16β-OMe		H-13, H-15β

Table 5. ^{1}H, HMQC and HMBC NMR data of hohenackeridine (**3**)*

H		Correlated C-atom	
		HMQC	HMBC
1β	4.04 *br t* (2.5)	77.3 *d*	
2α	2.27 *ddd* (14.5, 6.0, 3.0)	31.6 *t*	C-1
2β	1.26 *ddd* (14.5, 7.5, 2.5)	31.6 *t*	C-3, C-4
3α	3.12 *dd* (7.0, 5.5)	58.4 *d*	C-2, C-5, C-19
5	1.44 *d* (2.0)	48.7 *d*	C-3, C-4, C-11, C-19
6α	4.41 *s*	89.8 *d*	C-4, C-5, C-7, C-8, C-11, C-6′
9	2.84 *dd* (8.0, 1.0)	52.8 *d*	C-8, C-12, C-13, C-15
10	2.18 *ddd* (12.0, 8.0, 5.0)	39.6 *d*	C-5, C-9, C-11
12α	1.90 *dd* (14.0, 5.0)	27.8 *t*	C-10, C-11, C-13
12β	2.34 *ddd* (14.0, 11.5, 8.0)	27.8 *t*	C-13
13	2.44 *br d* (6.5)	46.8 *d*	C-12, C-16
15α	2.70 *dd* (16.0, 7.5)	34.9 *t*	C-7, C-8, C-9, C-13, C-16
15β	1.30 *ddd* (16.0, 9.0, 1.5)	34.9 *t*	C-7, C-8, C-16
16α	3.61 *t* (7.5)	86.6 *d*	C-12, C-13, C-16′
17	3.15 *d* (3.0)	67.7 *d*	C-8, C-10, C-11, C-19, C-20
19α	2.55 *dd* (10.0, 0.5)	54.2 *t*	C-3, C-4, C-5, C-17
19β	3.44 *d* (10.0)	54.2 *t*	C-3, C-4, C-20
20A	3.04 *dq* (14.0, 7.0)	50.3 *t*	C-17, C-19, C-21
20B	3.01 *dq* (14.0, 7.0)	50.3 *t*	C-17, C-19, C-21
21	1.09 *t* (7.5)	14.1 *q*	C-20
6β-OMe	3.38 *s*	58.9 *q*	C-6
16β-OMe	3.32 *s*	56.1 *q*	C-16

* Chemical shifts in ppm rel. to TMS. Coupling constants (*J*) in Hz. C-Multiplicities were determined by DEPT data.

Table 6. Scalar and spatial correlation of the protons of hohenackeridine (**3**)

H	COSY	NOESY
1β	H-2α, H-2β	H-2α, H-2β, H-10, H-12α, H-12β
2α	H-1β, H-2β, H-3α	H-1β, H-2β, H-3α
2β	H-1β, H-2α, H-3α	H-1β, H-2α, H-3α, H-5
3α	H-2α, H-2β	H-2α, H-2β, H-19α
5	H-17 (W), H-19α (W)	H-2β, H-6α, H-10, 6β-OMe
6α		H-5, H-19β, 6β-OMe
9	H-10, H-13 (W)	H-10
10	H-9, H-12α, H-12β	H-1β, H-5, H-9, H-12α, H-12β
12α	H-10, H-12β, H-13	H-1β, H-10, H-12β, H-13, H-16α, H-17
12β	H-10, H-12α, H-13	H-1β, H-10, H-12α, H-13
13	H-9 (W), H-12α, H-12β	H-12α, H-12β, H-16α, 16β-OMe
15α	H-15β, H-16α	H-15β, H-16α, H-17
15β	H-15α, H-16α	H-15α, H-16α
16α	H-15α, H-15β	H-12α, H-13, H-15α, H-15β, H-17, 16β-OMe
17	H-5 (W)	H-12α, H-15α, H-16α, H-20A
19α	H-5 (W), H-19β	H-3α, H-19β, H-20A, H-21
19β	H-19α	H-6α, H-19α
20A	H-20B, H-21	H-17, H-19α, H-20B, H-21
20B	H-20A, H-21	H-20A, H-21
21	H-20A, H-20B	H-19α, H-20A, H-20B
6β-OMe		H-5, H-6α
16β-OMe		H-13, H-16α

Table 7. ^{13}C NMR chemical shifts assignments for compounds **1–6**

Carbon	**1**	**4**	**2**	**5**	**3**	**6**
1	73.0 *d*	81.9 *d*	73.3 *d*	72.4 *d*	77.3 *d*	77.9 *d*
2	29.4 *t*	31.4 *t*	29.8 *t*	29.5 *t*	31.6 *t*	31.6 *t*
3	26.6 *t*	29.7 *t*	29.6 *t*	29.6 *t*	58.4 *d*	58.6 *d*
4	38.9 *s*	39.7 *s*	39.9 *s*	38.4 *s*	58.4 *s*	58.7 *s*
5	41.8 *d*	45.2 *d*	46.5 *d*	46.1 *d*	48.7 *d*	48.7 *d*
6	33.5 *t*	34.2 *t*	70.6 *d*	70.7 *d*	89.8 *d*	90.3 *d*
7	86.2 *s*	89.9 *s*	85.6 *s*	85.3 *s*	89.0 *s*	89.4 *s*
8	77.0 *s*	76.8 *s*	81.0 *s*	80.8 *s*	82.6 *s*	78.5 *s*
9	48.1 *d*	48.7 *d*	47.9 *d*	47.1 *d*	52.8 *d*	43.3 *d*
10	44.0 *d*	42.7 *d*	44.3 *d*	44.2 *d*	39.6 *d*	42.7 *d*
11	49.1 *s*	50.0 *s*	47.8 *s*	47.5 *s*	54.4 *s*	53.9 *s*
12	30.0 *t*	31.4 *t*	31.0 *t*	29.2 *t*	27.8 *t*	30.7 *t*
13	40.6 *d*	39.7 *d*	41.5 *d*	40.6 *d*	46.8 *d*	37.9 *d*
14	75.7 *d*	75.3 *d*	75.4 *d*	75.2 *d*	214.2 *s*	84.3 *d*
15	35.5 *t*	39.7 *t*	29.2 *t*	29.9 *t*	34.9 *t*	33.3 *t*
16	83.3 *d*	89.4 *d*	84.2 *d*	82.6 *d*	86.6 *d*	82.8 *d*
17	65.6 *d*	58.9 *d*	64.5 *d*	63.8 *d*	67.7 *d*	67.0 *d*
18	67.5 *t*	67.4 *t*	70.0 *t*	80.8 *t*		
19	56.5 *t*	56.4 *t*	57.7 *t*	56.7 *t*	54.2 *t*	54.3 *t*
20	51.1 *t*	53.4 *t*	51.4 *t*	50.7 *t*	50.3 *t*	50.0 *t*
21	13.8 *q*	14.1 *q*	14.0 *q*	13.8 *q*	14.1 *q*	14.0 *q*
6′					58.9 *q*	58.8 *q*
8′			53.3 *q*	52.9 *q*		
16′	56.5 *q*	58.6 *q*	56.7 *q*	56.5 *q*	56.1 *q*	56.3 *q*

Chemical shifts in ppm rel. to TMS. Carbon Multiplicities were established by DEPT data.

from hexane–EtOAc. $[\alpha]_D$ +39.5° (*c* 0.38). $[M]^+$ *m/z* 421.2101 for $C_{22}H_{31}NO_7$ (calc. 421.2100). IR ν_{max}^{NaCl} cm^{-1}: 3360, 3295, 2924, 2846, 1750, 1461, 1383, 1260, 1207, 1180, 1143, 1088, 961, 883, 798, 740. EIMS *m/z* (rel. int.): 422 (2) $[M+1]^+$, 421 (2) $[M]^+$, 406 (4), 391 (2), 390 (2), 378 (1), 348 (1),252 (2), 246 (2), 212 (2), 206 (2), 180 (3), 162 (5), 136 (10), 129 (9), 128 (6), 118 (9), 107 (10), 91 (19), 85 (31), 71 (30), 55 (100). ^1H NMR and ^{13}C NMR ($CDCl_3$): Tables 3 and 7.

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