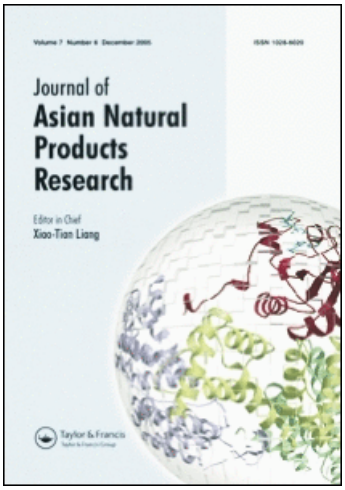

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Note: Two new C_{19}-diterpenoid alkaloids from *Aconitum kongboense*

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Note

TWO NEW C_{19}-DITERPENOID ALKALOIDS FROM *ACONITUM KONGBOENSE*

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Two new C_{19}-diterpenoid alkaloids, kongboentine A (**1**) and kongboentine B (**3**), were isolated from the roots of *Aconitum kongboense* Lauener and their structures were elucidated by spectral data.

Keywords: *Aconitum kongboense* Lauener; *Ranunculaceae*; C_{19}-diterpenoid alkaloids; Kongboentine A; Kongboentine B

INTRODUCTION

The roots of *Aconitum kongbense*, native to China, are used in folk medicine to treat arthritic pain [1]. In previous papers [2,3], a number of C_{19}-diterpenoid alkaloids were reported from this plant, and further investigation led to the isolation of two new C_{19}-diterpenoid alkaloids, kongboentine A and kongboentine B. We report here the isolation and structure elucidation of these compounds.

RESULTS AND DISCUSSION

Kongboentine A (**1**) was isolated as an amorphous powder with mp 94–96°C. The HR-EIMS showed $[M]^+$ at *m/z* 420.2992, corresponding to the molecular formula $C_{24}H_{40}N_2O_4$. The NMR spectra gave distinctive signals at δ_H 1.05 (3H, t, $J = 7.0$ Hz), δ_C 49.1 and 14.1, for the *N*-ethyl group, δ_H 3.33, 3.28 and 3.26 (s, each 3H), δ_C 56.2, 56.8 and 59.2 for three methoxyl groups. The ^{13}C signals of four oxygenated carbons at δ_C 75.3, 79.4, 82.3 and 86.1 indicated that **1** has a hydroxyl group besides three methoxyl groups. Analysis of these spectral data of **1** led to the experimental formula $C_{19}H_{25}N$ [NCH_2CH_3-$(OCH_3)_3$-OH], in addition to biogenetical considerations, suggesting that

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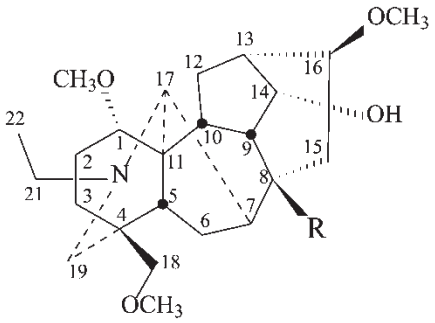
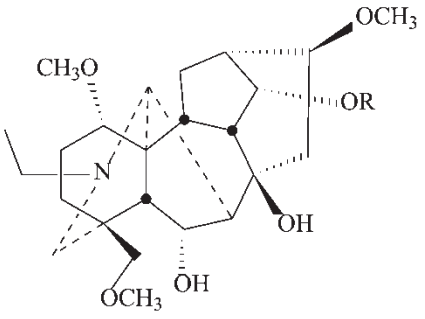
kongboentine A (**1**) is a C_{19}-diterpenoid alkaloid. The ^1H triplet ($J = 4.8$ Hz) signal at δ_H 4.04 was assigned to H-14β, suggesting the presence of 14α-OH [4]. The NMR spectra of **1** and talatisamine (**2**) [5] were very similar except that the chemical shift of C-8 in ^{13}C NMR spectrum of **1** (Table I) was shifted upfield from δ 72.7 to 54.7. Moreover, its MS showed the even molecular ion peak at *m/z* 420, indicating that **1** possessed an amino group at the C-8 position instead of a hydroxyl group as in **2**. The structure of **1** thus was confirmed.

Kongboentine B (**3**) was isolated as an amorphous powder with mp 96–98°C. The HR-EIMS exhibited $[M]^+$ at *m/z* 541.3044, corresponding to the molecular formula $C_{31}H_{43}NO_7$. The NMR spectra showed the presence of an *N*-ethyl group (δ_H 1.08, 3H, t, $J = 7.2$ Hz, δ_C 49.1 and 14.1), three methoxyl groups (δ_H 3.19, 3.25 and 3.29, each 3H; δ_C 56.2, 56.8 and 59.2) and a benzoyl group (δ_H 7.39–7.98, 5H, m; δ_C 166.4, 130.4, 129.5, 128.4 and 132.8). The ^{13}C signals of six oxygenated carbon at δ_C 85.1, 72.6, 74.6, 76.9, 81.1 and 81.1 suggested that **3** has two hydroxyl groups in addition to three methoxyl groups and a benzoyl group. Thus, the experimental formula is $C_{19}H_{22}$ [NCH_2CH_3–$(OCH_3)_3$–$(OH)_2$–C_6H_5COO], which, along with biogenetic considerations, suggests that kongboentine B (**3**) is a C_{19}-diterpenoid alkaloid. The benzoyl group was located at C-14 due to the triplet ($J = 4.8$ Hz) signal at δ_H 5.10 [4]. The NMR spectra of kongboentine B and geniconitine (**4**) [6] are very similar except for the signals of the aromatic ester moieties (Table I). The structure of **3**, therefore, was determined.





1 R=NH_2
2 R=OH

3 R = OC–⟨benzene⟩
4 R = OC–⟨benzene⟩–OCH_3

EXPERIMENTAL

General Experimental Procedures

Melting points were determined on a Kofler block and are uncorrected. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$, with TMS as internal standard, on a Varian INOVA 400/54 spectrometer. MS data were recorded with a VG Autospec 3000. Silica gel (GF_{254} and H, Qingdao Sea Chemical Factory, China) was used for TLC (S_1: $CHCl_3$–MeOH, 95:5; S_2: petroleum ether–acetone 7:3; S_3: cyclohexane–acetone 2:1), Chromatotron and column chromatography. Spots on chromatograms were detected with Dragendorff's reagent. A polyvinyl sulfonic ion exchange resin (H-form, cross-linking 1 × 1, Nankai University Chemical Factory, China) was used in the extraction of total alkaloids.

TABLE I ^{13}C NMR data of compounds **1**, **2** [5], **3**, and **4** [6]

Carbon	***1***	***2***	***3***	***4***
1	86.0 d	86.1	85.1 d	85.1
2	25.8 t	25.7	22.6 t	22.6
3	32.5 t	32.6	31.9 t	31.9
4	38.4 s	38.6	39.3 s	38.4
5	37.6 d	37.7	56.8 d	56.8
6	24.8 t	24.8	72.6 d	72.4
7	45.1 d	45.7	56.8 d	56.8
8	54.7 s	72.7	74.6 s	74.6
9	46.7 d	46.9	47.0 d	47.0
10	46.0 d	46.0	45.0 d	45.0
11	48.5 s	48.6	50.7 s	50.8
12	29.2 t	28.6	29.3 t	29.6
13	46.0 d	45.7	37.0 d	37.2
14	75.3 d	75.7	76.9 d	76.5
15	36.2 t	36.2	41.2 t	41.2
16	82.3 d	82.2	81.8 d	82.0
17	62.6 d	62.8	62.0 d	62.0
18	79.4 t	79.4	81.1 t	81.0
19	52.9 t	53.1	54.6 t	56.2
21	49.4 t	49.4	49.1 t	49.1
22	13.6 q	13.6	14.0 q	14.1
1′	56.2 q	56.1	56.2 q	56.0
16′	56.3 q	56.3	56.8 q	56.8
18′	59.3 q	59.3	59.2 q	59.2
O=C	–	–	166.4 s	166.1
1″	–	–	130.4 s	122.7
2″,6″	–	–	129.5 d	131.6
3″,5″	–	–	128.4 d	113.7
4″	–	–	132.8 d	163.2
4″-OCH_3	–	–	–	55.3

Plant Material

Aconitum kongboense lauener roots were collected in August 2001 in the Can district area of South mountain, Tibet, China. The plant was identified by Associate Professor Sang Ge of the Tibet Institute of Pharmaceutical Inspection, China, where a voucher specimen has been deposited.

Extraction and Isolation

The total alkaloids (89 g) obtained from 8.5 kg of the roots of *Aconitum kongboense* lauener [2] were chromatographed on a silica gel H column, eluting with petroleum ether–acetone (3:1), to afford ten fractions (A–J). Fraction I was subjected to silica gel H column chromatography, eluting with chloroform-methanol (95:5) to give fractions I-1 to I-8. Fraction I-6 was repeatedly chromatographed on a silica gel column, eluting with petroleum ether–acetone (6:4), to provide kongboentine A (1) (12 mg). Repeated column chromatography of fraction I-8 using petroleum ether–acetone (6:4), cyclohexane–ethyl acetate–acetone (7:1:0.5, containing 1% diethylamine) and cyclohexane–acetone (10:0.5, containing 1% diethylamine) as solvent systems successively afforded kongboentine B (3) (10 mg) .

Kongboentine A (1)

White amorphous powder, mp 92–94°C; ^1H NMR (400 MHz): δ 1.05 (3H, t, $J = 6.8$ Hz, NCH_2CH_3), 3.24, 3.29, 3.35 (each 3H, s, 3 × OCH_3), 4.05 (1H, t, $J = 5.2$ Hz, H-14β);

^{13}C NMR (100 MHz): see Table I; EIMS *m/z* (%): 420 [M^+] (8), 389 [$M-OCH_3$]$^+$ (100); HREIMS *m/z*: 420.2993 (calcd for $C_{20}H_{40}N_2O_4$: 420.2988).

Kongboentine B (3)

White amorphous powder, mp 96–98°C; ^{1}H NMR (400 MHz): δ 1.08 (3H, t, $J = 7.2$ Hz, NCH_2CH_3), 3.19, 3.25, 3.29 (each 3H, s, 3 × OCH_3), 4.77 (1H, d, $J = 6.8$ Hz, H-6β), 5.10 (1H, t, $J = 4.8$ Hz, H-14β), 7.39–7.98 (5H, m, aromatic protons); ^{13}C NMR (100 MHz): see Table I; EIMS *m/z* (%): 541 [M^+] (10), 510 [$M-OCH_3$]$^+$ (100), 482 (56); HR-EIMS *m/z*: 541.3044 (calcd for $C_{31}H_{43}NO_7$: 541.3039).

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