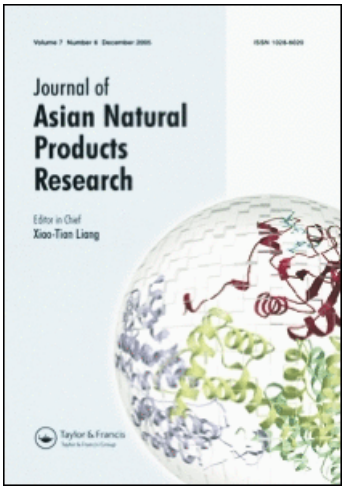

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

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Dong-Lin Chen[a]; Ling-Yun Lin[b]; Qiao-Hong Chen[a]; Xi-Xian Jian[a]; Feng-Peng Wang[a]
[a] Department of Chemistry of Medicinal Natural Products, West China College of Pharmacy, Sichuan University, Chengdu, China [b] Mental Health Center of Shantou University, Shantou, China

Online publication date: 12 May 2010

To cite this Article Chen, Dong-Lin , Lin, Ling-Yun , Chen, Qiao-Hong , Jian, Xi-Xian and Wang, Feng-Peng(2003) 'New C[19]-diterpenoid alkaloids from *Aconitum hemsleyanum* var *leueanthus* and *Delphinium potaninii*', Journal of Asian Natural Products Research, 5: 3, 209 — 213
To link to this Article: DOI: 10.1080/1028602031000093393
URL: http://dx.doi.org/10.1080/1028602031000093393

Journal of Asian Natural Products Research, 2003 VOL. 5 (3), pp. 209–213

NEW C_{19}-DITERPENOID ALKALOIDS FROM *ACONITUM HEMSLEYANUM* VAR *LEUEANTHUS* AND *DELPHINIUM POTANINII*

DONG-LIN CHEN[a], LING-YUN LIN[b], QIAO-HONG CHEN[a], XI-XIAN JIAN[a] and FENG-PENG WANG[a,*]

[a]*Department of Chemistry of Medicinal Natural Products, West China College of Pharmacy, Sichuan University, Chengdu 610041, China;* [b]*Mental Health Center of Shantou University, Shantou 515000, China*

(Received 26 September 2002; Revised 9 December 2002; In final form 3 January 2003)

A new franchetine-type (leueandine **1**) and two new lycoctonine-type [potanisines F (**3**) and G (**5**)] C_{19}-diterpenoid alkaloids have been isolated from the roots of *Aconitum hemsleyanum* var. *leueanthus* and *Delphinium potaninii*, respectively, and their structures were established on the basis of spectral data.

Keywords: Ranunculaceae; *Aconitum hemsleyanum* var. *leueanthus*; *Delphinium potaninii*; C_{19}-Diterpenoid alkaloid; Leueandine; Potanisine F

INTRODUCTION

Subsequent to a previous study on the plant *Aconitum hemsleyanum* var. *leueanthus* P. Guo et M. R. Jia (Ranunculaceae) by Guo *et al.* [1], we reported on the isolation of seven known C_{19}-diterpenoid alkaloids: indaconitine, 13,15-dideoxyaconitine, ezochasmanine, crassicaudine, franchetine, talatisamine, and chasmanine from this plant species [2]. Further research led to the isolation of the new franchetine-type C_{19}-diterpenoid alkaloid leueandine (**1**) and, in continuing studies on *Delphinium potanii* W. T. Wang [3–6], two C_{19}-diterpenoid alkaloids potanisine F (**3**) and G (**5**). Here we report the isolation and structural elucidation of the new alkaloids.

RESULTS AND DISCUSSION

Compound **1**, $C_{33}H_{43}NO_6$ ([M^+] ion at *m/z* 549.3098 in HREIMS), showed the distinct NMR features of a franchetine-type C_{19}-diterpenoid alkaloid skeleton [7,8], bearing an *N*-ethyl

*Corresponding author. Tel.: +86-28-85501368. Fax: +86-28-85501368. E-mail: wfp@wcums.edu.cn

ISSN 1028-6020 print/ISSN 1477-2213 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/1028602031000093393

[δ_H 1.01 (3H, t, $J = 7.2$ Hz)], three methoxyl (δ_H 3.27, 3.29, 3.36), and cinnamoyl [δ_H 6.44 (1H, d, $J = 16.0$ Hz), 7.67 (1H, d, $J = 16.0$ Hz), 7.37-7.54 (5H, m)] functional groups as well as an *N*,*O*-mixed ketal moiety [δ_H 4.37 (1H, s), 5.77 (1H, d, $J = 5.6$ Hz); δ_C 128.7 d, 136.9 s]. A triplet signal at δ_H 5.01 (brs) was attributed to H-14β [9], indicating the presence of an ester group at C-14. Finally, a comparison of ^{13}C NMR data of **1** (Table I) with those of franchetine (**2**) [7,8] led us to locate the cinnamoyl group at C-14. All available evidence strongly suggested the structure of leueandine as depicted in **1**.

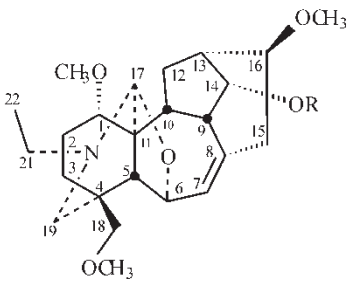
Compound **3**, an amorphous powder, $C_{38}H_{52}N_2O_{10}$ (LRMS + ^{13}C NMR), exhibited the characteristic NMR features of a lycoctonine-type C_{19}-diterpenoid alkaloid skeleton [10], bearing N-ethyl (δ_H 1.05, 3H, t, $J = 7.4$ Hz), five methoxyl (δ_H 3.23, 3.34, 3.35, 3.42, 3.44, each 3H, s) and a substituted anthranoyl [δ_H 7.25, 7.50, 7.65, 8.04 (each 1H, m); δ_C: see Table I (3‴-methyl succinimide)] functional groups. A comparison of the ^{13}C NMR data of **3** (Table I) and those of 8-*O*-methyllycaconitine (**4**) [10] indicated that an extra methyl group was located at C-3″. All of the above-mentioned evidence suggested the structure of potanisine F as **3**.

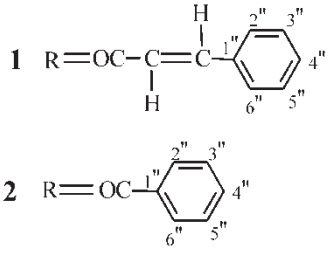
The structure of compound **5**, molecular formula $C_{38}H_{55}N_3O_{10}$, was inferred from its HRFABMS ([$M^+ + 1$] ion at *m/z* 714.4004), and ^{13}C NMR spectra. The NMR spectra of potanisine G (**5**) gave signals at δ_H 1.10 (3H, t, $J = 7.1$ Hz), δ_C 52.7 t, 11.3 q for an N-ethyl group; δ_H 1.25 (3H, d, $J = 6.8$ Hz), δ_C 17.6 q for a *C*-methyl group; δ_H 3.36, 3.39, 3.39, 3.41, 3.42 (each 3H, s) for five methoxyl groups; δ_H 7.11, 7.53, 7.97, 8.59 (each 1H, Ar-H), δ_H 10.9 (1H, brs, *NH*CO); δ_C: Table I for an N′-substituted anthranoyl moiety. The ^{1}H(^{13}C) NMR spectra of **5** showed a very close relationship to those of septentrionine (**6**) [11] and delsemine B (**7**) [12], except for the signals of the anthranoyl side chain or the carbon skeleton moiety, respectively These comparisons thus led to deduce the structure of potanisine G as **5**. However, it may be an artifact, formed from 8-*O*-methyllycaconitine (**4**) and the aqueous ammonium used in the separation procedures

TABLE I ^{13}C NMR data of leueandine (**1**), potanisine F (**3**), and potanisine G (**5**) (50 MHz, $CDCl_3$)

Carbon	***1***	***3***	***5***	*Carbon*	***1***	***3***	***5***
1	86.6 t	82.5 d	82.8 d	1′	57.1 q	55.1 q	55.5 q
2	24.4 t	25.1 t	25.2 t	6′	–	59.5 q	59.8 q
3	32.8 t	31.2 t	31.4 t	8′	–	51.5 q	54.0 q
4	37.3 s	37.9 s	37.7 t	14′	–	57.2 q	57.5 q
5	47.9 d	40.0 d	46.5 t	16′	56.1 q	55.9 q	56.5 q
6	74.8 d	90.8 d	91.2 d	18′	59.4 q	–	–
7	128.7 d	89.8 s	90.1 s	O═C	166.7 s	163.9 s	167.9 s
8	136.9 s	80.4 s	80.6 s	α	144.6 d	–	–
9	42.9 d	53.6 d	51.6 d	β	118.5 d	–	–
10	49.3 d	46.1 d	37.5 d	1″	134.4 s	127.0 s	115.1 s
11	55.5 s	47.3 s	47.6 s	2″	128.8 d	132.5 s	141.2 s
12	29.9 t	27.5 t	27.9 t	3″	127.9 d	129.6 d	120.6 d
13	38.2 d	37.3 d	40.3 d	4″	130.2 d	130.8 d	134.5 d
14	78.5 d	82.5 d	83.8 d	5″	127.9 d	130.8 d	122.6 d
15	38.5 t	27.6 t	27.9 t	6″	128.8 d	128.9 d	129.4 d
16	85.5 d	82.2 d	82.6 d	1‴	–	175.6 s	170.4 s
17	92.4 d	65.6 d	65.8 d	2‴	–	37.2 t	41.8 t
18	79.0 t	69.9 t	70.3 t	3‴	–	37.3 d	36.3 d
19	52.1 t	52.7 t	53.2 t	4‴	–	176.6 s	176.7 s
21	49.1 t	51.3 t	51.8 t	5‴	–	15.9 q	17.6 q
22	13.2 q	14.3 q	11.3 q				

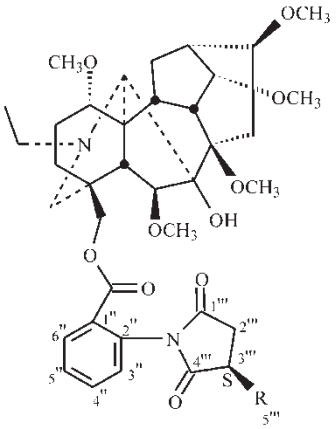
[13], also implying that the stereochemistry of C(3‴) (*S*) in **5** is the same as **4** and methyllycaconitine (**8**) [13].





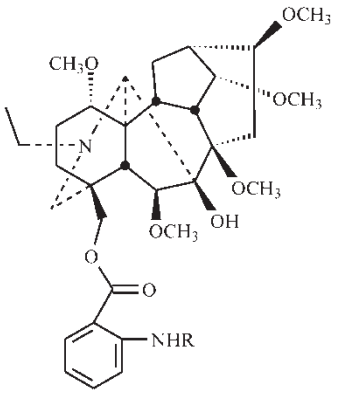
1 R=OC–C(H)=C(H)–C$_6$H$_4$

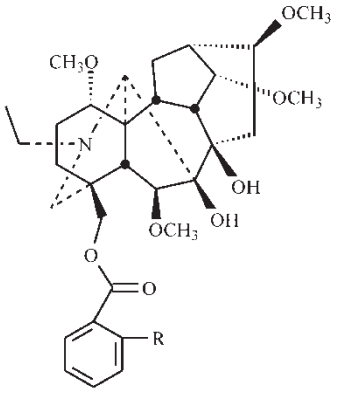
2 R=OC–C$_6$H$_4$

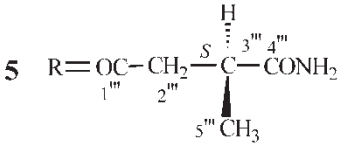


3 R=CH_3

4 R=H



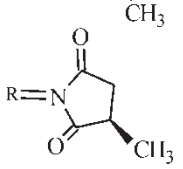




5 R=OC–CH_2–C(H)(S)(CONH$_2$)–CH_3

6 R=OC–$CH_2CH_2COOCH_3$

7 R=NHCO CH_2 CH(CONH$_2$)–CH_3



8 R=N(succinimide)–CH_3

EXPERIMENTAL

General Experimental Procedures

Optical rotation measurements were made using a Perkin-Elmer 241 polarimeter. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA 400/45 spectrometer, in $CDCl_3$ with TMS as internal standard. MS was measured on a VG Auto Spec 3000 mass spectrometer.

Plant Material

Aconitum hemsleyanum var. *leueanthus* was colleted from An County of Sichuan province, China, in August 1998. Roots of *Delphinium potaninii* were collected in Peng County, Sichuan Province, China in September 1991. Two plants were identified taxonomically by Professor W.T. Wang (Institute of Botany, Chinese Academy of sciences, Beijing). Voucher specimens have been deposited in the herbarium of the West China College of Pharmacy, Sichuan University.

Extraction and Isolation

Fraction C (5.0 g) (see Experimental Section in Ref. [2]) was chromatographed on a silica gel H column (160 g) eluting with $CHCl_3$-acetone-NH_4OH (60 : 40 : 1 → 85 : 15 : 1) to give the fraction C-1 (92 mg), which was chromatographed on a Chromatotron over silica gel G, eluting with light petroleum-acetone (20 : 1 → 4 : 1) to give leueandine (**1**) (20 mg). Fraction D (5.2 g) (see Experimental Section in Ref. [5]) was chromatographed on a silica gel H column (210 g) eluting with $CHCl_3$—MeOH (9 : 1 → 85 : 1) to give the potanisines F (**3**) (9 mg) and G (30 mg).

Leueandine (**1**): Amorphous powder, mp. 138–140°C; $[\alpha]_D^{25}$ −71.4 (*c*, 0.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): 1.01 (3H, t, $J = 7.2$ Hz, N—CH_2CH_3), 3.27, 3.29, 3.36 (each, 3H, s, 3 × OCH_3), 4.37 (1H, s, H-17), 4.41 (1H, d, $J = 6.0$ Hz, H-6β), 5.01 (1H, brs, H-14β), 5.77 (1H, d, $J = 5.6$ Hz, H-7), 6.44 (1H, d, $J = 16.0$ Hz, H-α), 7.67 (1H, d, $J = 16.0$ Hz, H-β), 7.37–7.54 (5H, m, Ar-H); ^{13}C NMR: Table I; EI-MS: *m*/*z* 549 (M^+, 10); HREIMS *m*/*z* 549.3098, calcd for $C_{33}H_{43}NO_6$ 549.3090.

Potanisine F (**3**): White amorphous powder, $[\alpha]_D^{10}$ −23.1 (*c*, 1.00, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): 1.05 (3H, t, $J = 7.4$ Hz, N-CH_2CH_3), 3.23, 3.34, 3.35, 3.42, 3.44 (each, 3H, s, 5 × OCH_3), 7.25, 7.50, 7.65, 8.04 (each 1H, m, Ar-H); ^{13}C NMR: Table I; EI-MS: *m*/*z* 696 (M^+, 3), 665 (M—OCH_3, 100).

Potanisine G (**5**): White amorphous powder, $[\alpha]_D^{10}$ −24.5 (*c*, 1.00, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): 1.10 (3H, t, $J = 7.1$ Hz, N—CH_2CH_3), 1.25 (3H, d, $J = 6.8$ Hz, CH—CH_3), 3.36, 3.39, 3.39, 3.41, 3.42 (each, 3H, s, 5 × OCH_3), 7.11, 7.53, 7.97, 8.59 (each 1H, m, Ar-H), 10.9 (1H, brs, *N*HCO); ^{13}C NMR: Table I; FABMS: *m*/*z* 713 (M^+, 100), 682 (M—OCH_3, 15); HRFABMS: *m*/*z* 714.4004 (M + 1), calcd for $C_{38}H_{56}N_3O_{10}$ 714.3966.

Acknowledgements

This work was supported by the Doctoral Foundation of Ministry of Education, P. R. China (2002–2004).

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