Chinese Chemical Letters Vol. 16, No. 4, pp 475-478, 2005
http://www.imm.ac.cn/journal/ccl.html

Two New Norditerpenoid Alkaloids from *Aconitum spicatum* Stapf

Li Ming GAO[1,2]*, Xiao Mei WEI[2], Li YANG[2]

[1]Department of Chemistry, Key Laboratory of Polymer Materials of Gansu Province,
Northwest Normal University, Lanzhou 730070
[2]Department of Chemistry, National Laboratory of Applied Organic Chemistry,
Lanzhou University, Lanzhou 730000

Abtract: Two new norditerpenoid alkaloids, spicatine A (**1**) and spicatine B (**2**) were isolated from the root of *Aconitum spicatum*. The new compounds were deduced on the basis of their spectral data (IR, HREIMS, EIMS, 1D, 2D-NMR). This is the first whole report on the isolation of diterpenoid alkaloids from the *A.spicatum* Stapf.

Keywords: *Aconitum spicatum* Stapf, norditerpenoid alkaloids, spicatine A, spicatine B.

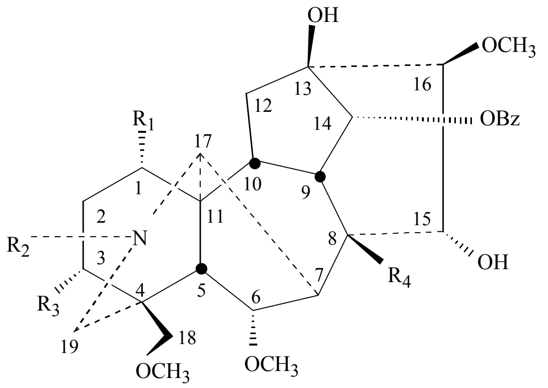
Aconitum spicatum as traditional herb its extracts have been employed in analgesic balms, sedatires and febrifugers in Tibet areas[1]. The analysis of the main norditerpene alkaloids of the root of *Aconitum spicatum* has been reported previously[2]. Further investigation on the alkaloids from the roots of this plant resulted in the isolation of thirteen norditerpenoid alkaloids, among them two were new compounds. In this paper, we report on the isolation and structural elucidation of two new norditerpene alkaloids spicatine A (**1**) and spicatine B (**2**).

Compound **1**[3]: The positive-SIMS M+H=632.3422 (calcd. 632.3429) indicated the molecular formula $C_{34}H_{49}NO_{10}$. The IR spectrum showed bands assigned to carbonyl groups (1721 cm^{-1}), hydroxyl group (3484 cm^{-1}) and aromatic ring (755, 711 cm^{-1}). The ^{1}H and ^{13}C NMR spectrum revealed the presence of five aromatic protons at δ 8.01 (*d*, 2H, *J*=7.6Hz), 7.53 (*t*, 1H, *J*=7.6Hz) and 7.41 (*t*, 2H, *J*=7.6Hz) combined with the carbon signals at δ 166.1 (*s*), 130.1 (*s*, 1C), 129.5 (*d*, 2C), 132.8 (*d*, 1C), 128.1 (*d*, 2C) indicating the presence of a benzoyl group. The presence of four methoxyl groups was indicated by the proton signals at δ 3.23, 3.23, 3.28, 3.71 (*s*, each 3H) and the methoxyl carbons at δ 55.8, 58.8, 59.0 and 62.3. An N-ethyl group and C-8-*O*-ethyl group were assigned at δ_H 1.07 (*t*, 3H, *J*=7.2Hz), δc 13.1 and δ_H 0.54 (*t*, 3H, *J*=6.4Hz), δc 15.2, respectively. In the ^{1}HNMR spectrum, the douplet signal at δ 4.79 (*d*, 1H, *J*=5.2Hz) and 4.52 (*d*, 1H, *J*=6.4Hz) were assigned C-14-βH and C-15-βH, and revealing that the two hydroxyl groups were located at C-13 and C-15, respectively. The NMR spectrum data of **1** was

---

* E-mail: gaolm@nwnu.edu.cn

Figure 1 Structure of compounds **1** and **2**



1	R_1=OCH_3	R_2=Et	R_3=OH	R_4=OEt
2	R_1=OH	R_2=H	R_3=H	R_4=OAc

similar to that of compounds polyschistine A[4] and aljesaconitine B[5]. Comparison **1** with aljesaconitine B, the only difference is the C-14 substitute group, the former is benzoyl group and the latter is anisoyl group. The 2D-NMR supported this conclusion. Therefore, the structure **1** was assigned as 8-*O*-ethyl-14-benzoylaconine and named spicatine A (**1**).

Compound **2**[6]: The molecular formula $C_{31}H_{41}NO_{10}$ was derived from the ESI positive M+H=588.2794 (calcd. 588.2803) and its ^{13}C NMR, DEPT spectral data. Its IR spectrum showed absorptions at 3496 (OH), 3319 (NH), 1720 (C=O), 1105 (C-O-C) and 731, 711 cm^{-1} (aromatic ring). The ^1H NMR spectrum exhibited signals at δ 1.34 (*s*, 3H, C(8)-$OCOCH_3$), 3.12, 3.26, 3.70 (*s*, each 3H, OCH_3), 7.40-7.97 (*ttd*, 5H, J_1=J_2= 7.6Hz, J_3=7.6Hz, aromatic protons), 4.85 (*d*, 1H, *J*=4.9, C (14)-βH), 3.05, 3.50 (*dd*, each 1H, *J*=9.2Hz, C (18)-2H), 3.95 (*d*, 1H, *J*=6.4Hz, C (6)-βH), 3.66 (*br s*, 1H, C (1)-βH), 3.37 (*d*, 1H, *J*=5.2Hz, C (16)-αH), 4.46 (*dd*, 1H, *J*=5.2, 2.6Hz, C (15)-βH)[7]. The ^{13}C NMR and DEPT spectrum of **2** showed thirty-one signals including seven quartemery, fifteen methine, five methylene and four methyl carbons. The pattern of carbon chemical shifts was similar to that of 1-demethylhypaconitine[7] except nitron heterocycles (see **Table 1**). The disappearance of N-CH_3 signal at δ 42.7 and up field shifts of C-17, C-19 signals from δ 64.4→57.5, δ 58.5→48.6, respectively, suggested that the methyl at N-atom must be insteaded by proton. Also the chemical shifts of C-17, C19 were similar to that of flavaconitine[8]. Further studies in the 2D-NMR experiment, H-17 correlated to H-7 in the ^1H COSY; the C-17, C-19 correlated to H-5, H-10, H-19 and to H-17, H-18, respectively in the HMBC. The evidence of above spectral data confirmed that the structure of **2** assigned as N-demethyl-1-demethylhypaconitine and named spicatine B (**2**).

Table 1 NMR data of compound **1** and **2** (in $CDCl_3$, δ ppm)

No	**1**		**2**	
	δ_H (*J=Hz*)	δ_C	δ_H (*J=Hz*)	δ_C
1	3.12 t (6.4)	82.4	3.66 br s	71.8
2	1.86 dt (β) (13.6, 4.8) 2.34 dt (α) (13.6, 6.4)	33.0	1.85 m (α), 1.60 m (β)	28.8
3	3.80 dd (6.4, 4.8)	71.5	1.61 m (α, β)	29.9
4	—	42.9	—	38.2
5	2.08 m	45.2	2.70 br s	50.4
6	4.03 d (6.4)	83.3	3.95 d (6.4)	83.2
7	2.67 m	42.9	2.25 m	43.9
8	—	82.1	—	91.4
9	2.61 m	45.0	2.75 t (5.2)	42.9
10	2.06 m	41.2	2.1 m	39.5
11	—	50.4	—	49.0
12	2.10 m (α), 2.55 dd (β) (14, 4)	36.1	2.20 m (α), 2.25 m (β)	36.1
13	—	74.6	—	73.9
14	4.79 d (5.2)	79.4	4.85 d (4.9)	78.9
15	4.52 d (6.4)	78.1	4.46 dd (5.2, 2.6)	78.8
16	3.24 m	93.3	3.37 d (5.2)	89.5
17	2.87 br s	61.1	3.06 br s	57.5
18	3.43 d (a) (8.8), 3.55 d (b) (8.8)	77.2	3.05 d (a) (9.2), 3.50 d (b) (9.2)	79.6
19	2.43 m (b), 2.70 m (a)	48.8	2.25 m (b), 3.22 m (a)	48.6
NCH_2CH_3	2.43 m (a), 2.91 m (b); 1.07 t (7.2)	47.3, 13.1	—	—
OCH_2CH_3	3.29 m (a), 3.46 m (b); 0.54 t (6.4)	57.1, 15.2	—	—
$COCH_3$	—	—	1.34 s	172.3, 21.2
1′	3.23 s	55.8	—	—
6′	3.23 s	58.5	3.12 s	57.9
16′	3.71 s	62.3	3.70 s	61.2
18′	3.28 s	59.0	3.26 s	59.0
COC_6H_5	—	166.1	—	165.7
1′	—	130.1	—	129.6
2′, 6′	8.01 d (7.6)	129.5	7.97 d (7.6)	129.4
3′, 5′	7.41 t (7.6)	128.1	7.40 t (7.6)	128.5
4′	7.53 t (7.6)	132.8	7.55 t (7.6)	133.2

Assignments based on DEPT, COSY, HSQC and HMBC

References and Notes

1. The Flora Committee of Chinese Academy of Sciences, "*The Chinese Flora*", Vol. 27. Science press, Beijing, **1979**, p.219.

2. L. G. Qiu, M. Lian, Z. W. Ma, G. F. He, *Zhongcaoyao* (Chinese Herb Medicine), **1988**, *19*(8), 4.
3. Spicatine A (**1**): amorphous powder, $[\alpha]^{27}_{D}$ -1 (c 1.0, $CHCl_3$); IR (KBr) cm^{-1}: 3484 (hydroxyl), 3065 2972, 2929, 1279, 1721 (carbonyl), 1602, 1564, 1098 (C-O-C), 755, 711 (aromatic ring); HR positive-SIMS (M+H=632.3422, calcd. for $C_{34}H_{49}NO_{10}$ 632.3429); EI-MS *m/z* (rel. int): 631 (M^+, 0.07), 600 (M-OMe, 17.8), 586 (2.3), 496 (3.8), 105 (100), 84 (92.0), 77 (28.7), 45 (33.3); ^{1}H-NMR and ^{13}C-NMR data are listed in **Table 1.**
4. H. C. Wang, A. N. Lao, *Heterocycles*, **1985**, *23* , 803.
5. H. Bando, K. Wada, M. Watanabe, T. Mori, T. Amiya, *Chem. Pharm. Bull.*, **1985**, *33*, 4717.
6. Spicatine B (**2**): white needle crystals, mp 126-127℃, $[\alpha]^{27}_{D}$ +39 (c 1.0 $CHCl_3$); IR (KBr) cm^{-1}: 3496 (hydroxyl), 3319 (NH), 2934, 2893, 2822, 1720 (carbonyl), 1603, 1585, 1454, 1105 (C-O-C), 731, 711 (aromatic ring); HRESI positive (M+H=588.2794, calcd. for $C_{31}H_{41}NO_{10}$ 588.2803); EI-MS *m/z* (rel. int): 587 (M^+, 0.9), 570 (M-OH,12.3), 554 (5.2), 538 (4.8), 105 (93.8), 77 (27.4), 60 (55.1), 43 (100); ^{1}H-NMR and ^{13}C-NMR data are listed in **Table 1.**
7. Z. G .Chen, A. N. Lao, H. C. Wang, S. H. Hong, *Heterocycles*, **1987**, *26*, 1455.
8. Z. G .Chen, A. N. Lao, H. C. Wang, S. H. Hong, *Heterocycles*, **1989**, *29*, 997.

Received 10 March, 2004