

## Diterpenoid Alkaloids from *Aconitum Nagarum* var. *Lasiandrum*

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**Abstract:** Two new diterpenoids, nagadine **1** and 14-benzoylsachaconitine **2** were isolated from the roots of *Aconitum nagarum*. Their structures were elucidated as **1** and **2** on the basis of spectral analysis.

**Keywords:** *Aconitum nagarum*, diterpenoid, alkaloid, nagadine, 14-benzoylsachaconitine.

*Aconitum* species have been used as a traditional chinese medicine having analgesic activity. Several groups<sup>1-3</sup> have studied the components of the roots of *Aconitum nagarum* var. *lasiandrum* W.T. Wang. Further chemical investigation of this plant led to isolate two new diterpenoid alkaloids, nagadine **1** and 14-benzoylsachaconitine **2**. This type of norditerpenoid alkaloid has not been reported before.

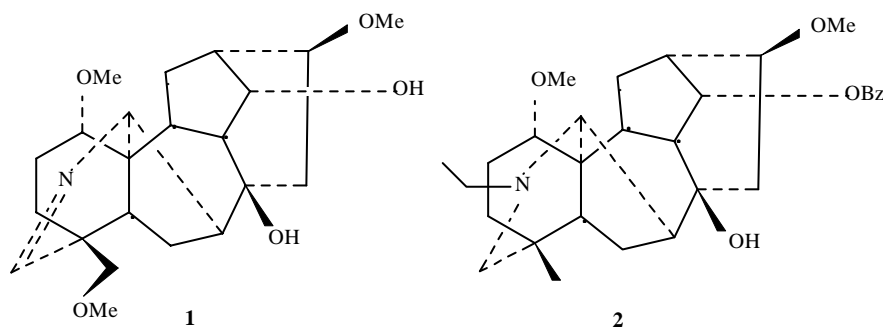
Nagadine **1**,  $[\alpha]_D^{255} +43.0$  (c, 0.00273, CHCl<sub>3</sub>), was isolated as white amorphous powder. The HREIMS of **1** exhibited the  $[M]^+$  peak at  $m/z$  391.2382 corresponding to the molecular formula C<sub>22</sub>H<sub>33</sub>NO<sub>5</sub> (calcd. 391.5044). Spectral data indicated the presence of hydroxyl groups, an azomethine (-N=C) (IR: 3300~3600 and 1633cm<sup>-1</sup>, respectively) and three methoxyl groups ( $\delta_H$ :  $\delta$ 3.31, 3.30 and 3.22, each 3H, s). The <sup>1</sup>HNMR spectrum of **1** showed no signals for NCH<sub>3</sub> or NEt groups, and a broad singlet at  $\delta$  7.24 was consistent with the presence of C (19)-azomethine<sup>4</sup>. The doublet at  $\delta$ 165.0 was assigned to C (19) and the downfield signals at  $\delta$  47.75 adjacent double bond as N=C (19). Comparison of the <sup>13</sup>CNMR data of **1** with those of talatisamine<sup>5</sup> suggested that the three quartet signals at  $\delta$ 55.9, 56.5, 59.5 in **1** can be assigned to C(1)-OMe, C(16)-OMe, C(18)-OMe, respectively: the secondary carbon signal at  $\delta$  75.72 also was assigned to the C-18. The EIMS spectrum of **1** showed a strong  $[M^+-31]$  fragment peak at 360 indicating the C (1)-OMe<sup>6</sup>. Therefore, the structure of nagadine was assigned as **1**.

14-benzoylsachaconitine **2**,  $[\alpha]_D^{255} +33.3$  (c, 0.00466, CHCl<sub>3</sub>), was obtained as white amorphous powder. The HREIMS of **2** exhibited the  $[M]^+$  peak at  $m/z$  495.2945 corresponding to the molecular formula C<sub>30</sub>H<sub>41</sub>NO<sub>5</sub> (calcd. 495.6556). The <sup>1</sup>HNMR and <sup>13</sup>CNMR of **2** exhibited the presence of an N-ethyl group ( $\delta_H$ : 1.03, 3H, t, J=7.1 Hz), a tertiary methyl ( $\delta_H$ 0.76,  $\delta$ C26.3), two methoxyl groups ( $\delta_H$  3.27 and 3.18, each 3H, s) and a benzoyl group [ $\delta$  166.5 (C=O), 132.5 (4'), 130.6 (1'), 129.4 (2',6'), 128.3 (3',5')]. The triplet at  $\delta$  5.13 (J=5Hz) can be assigned to the 14  $\beta$ -H, indicating location of the benzoyl group at C-14. The presence of a methoxy at C-1 was proven by the strong

[M-31]<sup>+</sup> peak in the EIMS as well as from the <sup>13</sup>CNMR signals at  $\delta$  26.63 and  $\delta$  37.76 for C-2 and C-3, respectively<sup>7</sup>. The <sup>13</sup>CNMR data of **2** were quite similar to those of sachacontine, except for the extra benzoyl group at C-14; but the <sup>1</sup>HNMR spectrum of **2**, 14  $\beta$ -H signal appeared at  $\delta$  5.13 for **2** instead of  $\delta$  4.07 as in sachacontine. Thus, the structure of 14-benzoyl-sachacontine was assigned as **2**.

**Table 1.** <sup>13</sup>CNMR data of **1** and **2** (400MHz, CDCl<sub>3</sub>)

carbon	1	2	carbon	1	2
1	84.7 (d)	85.7 (d)	16	82.1 (d)	81.7 (d)
2	25.6 (t)	26.6 (t)	17	62.8 (d)	61.7 (d)
3	27.8 (t)	37.8 (t)	18	75.7 (t)	26.3 (q)
4	47.8 (s)	34.4 (s)	19	164.9 (d)	56.7 (t)
5	46.3 (d)	50.7 (d)	N-CH <sub>2</sub> CH <sub>3</sub>		49.2
6	25.5 (t)	25.4 (t)	N-CH <sub>2</sub> CH <sub>3</sub>		13.5
7	42.7 (d)	45.1 (d)	1-OMe		55.9
8	72.3 (s)	73.8 (s)	16-OMe	55.9	56.1
9	52.3 (d)	46.6 (d)	18-OMe	56.5	166.5
10	46.3 (d)	36.4 (d)	14-CO	59.5	130.6
11	50.4 (s)	48.9 (s)	1'		129.4
12	27.3 (t)	28.5 (t)	2',6'		128.3
13	37.6 (d)	45.1 (d)	3',5'		132.5
14	75.5 (d)	76.8 (d)	4'		
15	37.8 (t)	40.8 (t)			



## References

1. H. C. Wang, D. Z. Zhu, Z. Y. Zhao, R. H. Zhu, *Huaxue Xuebao*, **1980**, 38, 475.
2. H. C. Wang, Y. L. Gao, Z. S. Xu, R. H. Zhu, *Huaxue Xuebao*, **1981**, 39, 869.
3. S. Y. Chen, S. H. Li, X. J. Hao, *Acta. Bot. Sin.*, **1986**, 28, 86.
4. X. Y. Wei, S. Y. Chen, *Acta. Bot. Yunnan*, **1989**, 11, 453.
5. V. Boido, O. E. Edwards, K. Handa, R. J. Kolt, K. K. Purushothaman, *Can. J. Chem.*, **1984**, 62, 778.
6. M. S. Yunusov, S. Y. Yunusov, *Khim. Prir. Soedin.*, **1969**, 515.
7. S. W. Pelletier, M. M. Badavi, *Heterocycles*, **1985**, 23, 2873

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