Chinese Chemical Letters Vol. 12, No. 1, pp. 67–68, 2001 

# Two New Diterpene Alkaloids from the Roots of *Spiraea japonica* var. *acuta*

Hong Ping HE,[1] Yue Mao SHEN,[1] Xiao Sheng YANG,[1,2] Bin Gui WANG,[1]
Ling LI,[1] Xiao Jiang HAO [1,2]*

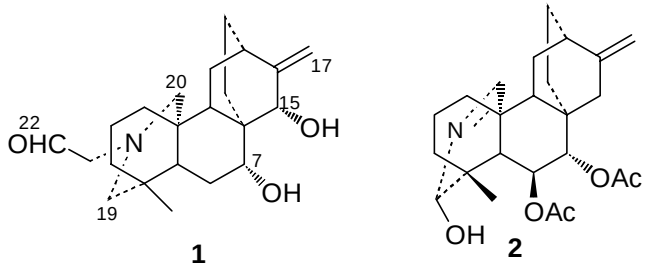
[1]Laboratory of Phytochemistry, Kunming Institute of Botany, the Chinese Academy of Sciences, Kunming 650204.
[2]The Key Laboratory of Chemistry for Natural Products of Guizhou Provence and the Chinese Academy of Sciences, Guiyang 550002.

**Abstract:** Chemical investigation on the ethanol extract from the roots of *Spiraea japonica* var. *acuta* resulted in the isolation of two new diterpene alkaloids named spiratines A and B (**1**-**2**), respectively.

**Keywords:** *Spiraea japonica* var. *acuta*, diterpene alkaloids, spiratine A, spiratine B.

*Spiraea japonica* L. (Rosaceae) is widely distributed in Yunnan Provence, P. R. China. Previous chemical investigations on *S. japonica* and its varieties have led to the report of 7 new atisane-type diterpenoids and 38 new diterpene alkaloids of atisine- and hetisine-type[1-11]. This paper describes the isolation and structure elucidation of two new diterpene alkaloids named spiratines A and B (**1**-**2**). Their structures were elucidated on the basis of 1D and 2D NMR experiments (HMQC, HMBC, $^1$H-$^1$H COSY).

**Figure 1** The Structure of spiratines A (**1**) and B (**2**)




Compound **1** was determined to have the molecular formula $C_{22}H_{33}NO_3$ based on high resolution EIMS (at *m*/*z* 359.2448 $[M]^+$, calcd: 359.2460). The inspection of the NMR data (proton, carbon, DEPT, HMQC, HMBC and $^1$H - $^1$H COSY) revealed an atisine-type alkaloid[1-6]. The $^{13}$C NMR and DEPT spectra of **1** showed twenty-two carbon signals including one methyl, eleven methylene, six methine, and four quaternary carbons. The $^{13}$C NMR signal at $\delta_C$ 110.2 (t) revealed a double bond methylene. In the

HMBC, this methylene $\delta_H$ 5.05, 4.04 showed correlations with $\delta_C$ 36.5 (C-12), 80.1 (C-15) and 154.8 (C-16), suggesting a hydroxyl at C-15. The $^1H$ - $^{13}C$ long-range correlations between $\delta_H$ 8.73 (H-22) and $\delta_C$ 60.5 (C-19) and 65.0 (C-21), and between $\delta_H$ 3.81 (H-19) and $\delta_C$ 24.8 (C-18), 34.2 (C-4), 41.6 (C-3), 65.0 (C-21), 182.9 (C-22) indicated an aldehyde at C-22, which also was supported by its IR data (1746 $cm^{-1}$). Based on those analyses, the structure of **1** was identified as shown in (**Figure 1**), and named spiratine A.

The HREIMS determined the formula of compound **2** to be $C_{24}H_{33}NO_5$ (at *m/z* 415.2359 $[M]^+$, calcd: 415.2359). Its $^1H$ and $^{13}C$ NMR spectra were similar to those of spiramine Z[11], suggesting **2** an atisine-type alkaloid[1-6]. The difference between the $^{13}C$ NMR spectra of **2** and spiramine Z was the missing of the hydroxyethyl signals in **2**, indicating that **2** was an analogue of spiramine Z. The assignment of the R-configuration for C-19 of **2** was carried out on the base of the $^{13}C$ NMR signal at $\delta_C$ 87.8 ($\delta_C$ 95 for C-19 in S-form and $\delta_C$ 91 for C-19 in R-form)[1]. Thus **2** was characterized to be spiratine B.

All proton and carbon resonances of **1** and **2** were assigned by analyzing the $^1H$ - $^1H$ COSY, HMQC and HMBC data.

**Acknowledgment**

This work was financially supported by the National Foundation for Outstanding Young Scientists to X. J. Hao (No. 39525025).

**References and Nots**

1. M. Node, X. J. Hao, J. Zhou, S. Y. Chen, T. Taga, Y. Miwa, K. Fuji, *Heterocycles*, **1990**, *30*, 635.
2. X. J. Hao, J. Zhou, K. Fuji, M. Node, *Chin. Chem. Lett.*, **1992**, *3*, 427.
3. X. J. Hao, M. Node, J. Zhou, S. Y. Chen, T. Taga, Y. Miwa, K. Fuji, *Heterocycles*, **1993**, *36*, 825.
4. X. J. Hao, M. Node, J. Zhou, S. Y. Chen, K. Fuji, *Acta Bot. Yunnan.*, **1994**, *16*, 301.
5. X. J. Hao, X. Hong, X. S. Yang, B. T. Zhao, *Phytochemistry*, **1995**, *38* (2), 545.
6. X. Y. Hao, X. J. Hao, *Guizhou Kexue*, **1995**, *13*, 25.
7. J. L. Nie, X. J. Hao, *Acta Bot. Yunnan.*, **1996**, *18*, 226.
8. X. Hong, J. L. Nie, X. J. Hao, *Chin. Chem. Lett.*, **1996**, *7*, 133.
9. J. L. Nie, X. J. Hao, *Acta Bot. Yunnan.*, **1997**, *19*, 429.
10. J. L. Nie, X. J. Hao, Phyotchemistry, **1998**, *48*, 1213.
11. B. G. Wang, L. Lin, X. S. Yang, Z. H. Chen, X. J. Hao, *Heterocycles*, **2000**, *53* (6), 1343.
12. The $^1H$ and $^{13}C$ NMR data of Compounds **1**-**2**. Compound **1**, $[\alpha]_D^{24.4}$ -6.25 (c 1.0, $CH_3OH$), EIMS (*m/z*, %): 359 ($M^+$, 11), 328 (100), 300 (9). $^1H$ NMR ($CD_3OD$, $\delta$): 8.73 (s, H-22), 5.05 and 4.04 (br s, 2H, H-17), 4.19 and 4.16 (m, 2H, H-21), 1.08 (s, 3H, H-18); $^{13}C$ NMR ($CD_3OD$, $\delta$): 35.2 (C-1), 20.0 (C-2), 41.6 (C-3), 34.2 (C-4), 43.9 (C-5), 28.7 (C-6), 77.2 (C-7), 41.9 (C-8), 45.8 (C-9), 47.0 (C-10), 28.2 (C-11), 36.5 (C-12), 26.1 (C-13), 14.8 (C-14), 80.1 (C-15), 154.8 (C-16), 110.2 (C-17), 24.8 (C-18), 60.5 (C-19), 58.6(C-20), 65.0 (C-21), 182.9 (C-22). Compound **2**, $[\alpha]_D^{25.2}$ +129.48 (c 5.0, $CHCl_3$), EIMS (*m/z*, %): 415 ($M^+$, 32), 355 (35), 312 (14), 296 (100). $^1H$ NMR ($CDCl_3$, $\delta$): 7.76 (br s, H-20), 5.20 (t, 8.0, H-6), 5.11 (s, H-19), 4.79 and 4.62 (br s, 2H, H-17), 4.74 (d, 8.0, H-7), 2.0 (s, 3H, OAc of C-7), 1.96 (s, 3H, OAc of C-6), 0.98 (s, 3H, H-18); $^{13}C$ NMR ($CDCl_3$, $\delta$): 34.4 (C-1), 19.4 (C-2), 35.9 (C-3), 36.9 (C-4), 51.8 (C-5), 69.1(C-6), 79.5 (C-7), 38.0 (C-8), 45.7 (C-9), 43.8 (C-10), 27.8 (C-11), 35.7 (C-12), 25.7 (C-13), 21.6 (C-14), 41.4 (C-15), 149.4 (C-16); 105.9 (C-17), 26.6 (C-18), 87.8 (C-19), 163.4 (C-20), 170.5 and 21.4 (OAc of C-7), 170.3 and 20.7 (OAc of C-6).

Received June 23, 2000