Chinese Chemical Letters Vol. 12, No. 2, pp. 147–150, 2001

New Diterpenoid Alkaloids from *Spiraea japonica* var. *ovalifolia*

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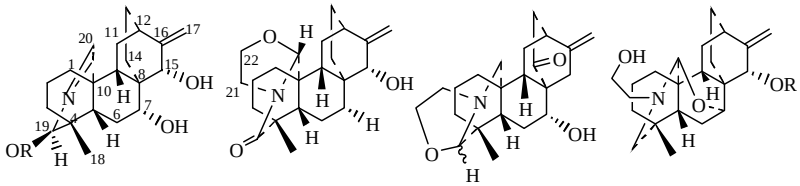
Abstract: Five new diterpenoid alkaloids, 19-*O*-deethylspiramine **N** (**1**), deacetylspiramine **S** (**2**), spiramidine **A** (**3**), spiramidine **B** (**4**) and deacetylspiramine **F** (**5**) were isolated from the aerial parts of *Spireae japonica* L. f. var. *ovalifolia*. Their structures were charaterized mainly based on spectral analysis.

Keywords: Rosaceae, *Spireae japonica* L. f. var. *ovalifolia*, diterpenoid alkaloids.

In the investigation of the chemical constituents of *Spireae japonica* L. f. var. *ovalifolia* (Rosaceae), a shrub originated in Songming, Yunnan, five new diterpenoid alkaloids, 19-*O*-deethylspiramine **N** (**1**), deacetylspiramine **S** (**2**), spiramidine **A** (**3**), spiramidine **B** (**4**) and deacetylspiramine **F** (**5**), were isolated from aerial parts of the plant and structurally elucidated.



1 R=H
7 R=CH_2CH_3

2 R=H
8 R=OAc

3 H=α
4 H=β

5 R=H
6 R=OAc

Compound **1**, a white amorphous powder with $[\alpha]_D^{23}$ +17.99 (c, 0.26, MeOH), was determined to have the molecular formula of $C_{20}H_{29}NO_3$ by HREIMS (331.2161, calcd. 331.2147). In the ^1H and ^{13}C NMR spectra, three oxygen-substituted methines were demonstrated by δ_C 88.9 (d, C-19) and δ_H 5.30 (1H, s, H-19), δ_C 80.1 (d, C-15) and δ_H 4.26 (1H, d, J 7.3Hz, H-15β), as well as δ_C 77.6 (d, C-7) and δ_H 3.90 (1H, dd, J 4.1, 7.4Hz, H-7β). The signal at δ_C163.2 (d) was attributed to the imine (C=N, 1647 cm^{-1} in IR) of C-20. The ^1H and ^{13}C NMR spectra of **1** were similar to spiramine **N** (**7**)[1]. The difference between the ^{13}C NMR spectra of **1** and **7** was the missing of the ethyl signals in **1**. Furthermore, the absence of ethyl group was also supported by its EIMS (M^+ *m/z*

331). Hence, **1** was determined to be 19-*O*-deethylspiramine **N**. The NMR assignments were thoroughly carried out on the basis of 2D NMR experiments (**Table 1** and **2**).

Compound **2** was obtained as colorless prisms ($CHCl_3$-MeOH), mp 113-115°C, $[\alpha]_D^{21}$ -74.4 (c, 0.27, MeOH). HREIMS showed its molecular ion at *m/z* 373.2237 (calcd. for $C_{22}H_{31}NO_4$, 373.2253). The ^{13}C NMR (DEPT) spectra gave 22 carbon signals including one carbonyl group at δ_C 173.2 (s) which was 1626 cm^{-1} in IR (KBr), two oxygen-substituted methines at δ_C 77.3 (d, C-7) and 80.7 (d, C-15) which were the same as **1**, and the HMQC spectra showed the corresponding ^1H NMR signals at δ_H 3.73 (1H, dd, J 5.3, 8.8Hz, H-7β) and 3.93 (1H, d, J 7.8Hz , H-15β), respectively. In the HMBC spectrum of **2**, one set of ^1H-^{13}C long-range correlations between H-20, H-21, H-22 and related carbons such as C-19, C-20, C-21 and C-22 (**Table 2**) indicated the presence of an oxazolidine ring which was the same as that of Spiramine **S** (**8**)[2,3]. The existence of a C-19 carbonyl group was confirmed by the long-range correlations between the proton signals of H-3, H-5, H-18, H-20, H-21 and the carbonyl carbon signal at δ_C173.2 (s, C-19) in the HMBC spectrum. In the ^{13}C NMR the difference between **2** and **8** was the missing of the acetyl signals in **2**, indicating **2** was the 15-deacetylspiramine S.

Table 1 ^1H and ^{13}C NMR data for **1** and **2**

	1 [a]		**2** [b]	
No	^1H	^{13}C	^1H	^{13}C
1	2.46 (m, αH), 1.04 (m, βH)	35.4t	2.37(m, αH), 0.89 (m, βH)	33.6t
2	1.41 (m, αH), 1.76 (m, βH)	20.1t	1.45 (m, αH), 1.30 (m, βH)	20.4t
3	1.61 (m, αH), 0.99 (m, βH)	34.3t	1.42 (m, αH), 1.84 (m, βH)	40.0t
4	/	36.8s	/	41.2s
5	1.21 (d, 14.0)	49.8d	1.52 (d, 9.6)	49.7d
6	1.65 (m, αH), 2.34 (m, βH)	14.6t	1.95 (m, αH), 1.75 (m, βH)	15.3t
7	3.90 (dd, 4.1, 7.4)	77.6d	3.73 (dd, 5.3, 8.8)	77.3d
8	/	41.6s	/	41.1s
9	1.27 (d, 5.4)	44.8d	1.12 (dd, 5.9, 8.6)	45.7d
10	/	43.2s	/	39.5s
11	2.02 (d, 13.0, αH), 1.56(m, βH)	28.6t	1.69 (m, αH), 1.42 (m, βH)	26.0t
12	2.31 (d, 16.0)	36.3d	2.36 (m)	35.5d
13	1.15 (m, αH), 1.62 (m, βH)	27.5t	1.30 (m, αH), 1.41 (m, βH)	27.2t
14	1.18 (m, αH), 1.76 (m, βH)	26.3t	1.42 (m, αH), 1.68 (m, βH)	27.6t
15	4.26 (d, 4.1)	80.1d	3.93 (d, 7.8)	80.7d
16	/	156.0s	/	147.1s
17	5.11 (s), 5.33 (s)	108.7t	5.09 (s), 5.06 (s)	109.0t
18	1.10 (s)	25.7q	1.21 (s)	21.8q
19	5.30 (s)	88.9d	/	173.2s
20	7.99 (s)	163.2d	5.11 (s)	88.7d
21	/	/	3.28 (m, αH), 3.90 (m, βH)	42.2t
22	/	/	3.87 (m, αH), 4.18 (m, βH)	64.4t

[a] ^1H (^{13}C NMR) spectra were obtained at 400 (100) MHz and recorded in C_5D_5N.
[b] ^1H (^{13}C NMR) spectra were obtained at 400 (100) MHz and recorded in $CDCl_3$.

Compounds **3** and **4**, colorless crystals (acetone), were obtained as mixture. HREIMS indicated both possessed the same molecular formula $C_{22}H_{31}NO_3$, M^+ *m/z*

357.2289 (calcd. 357.2304). The NMR signals were in pairs, particularly those at δ_C 97.7/95.5 (d, C-19R/S), indicating that **3** and **4** were C-19 epimers. The signals at δ_C 97.7/95.5 and δ_H 3.70/ 3.89 (1H, br.s, H-19α/β), together with δ_C 54.7/54.6 (d, C-20) and δ_H 3.02/2.85 (m, H-20) (**Table 3**) revealed the presence of an oxazolidine-ring, the same as in spiramines **A** and **B**[4]. Inspections of the HMBC (**Table 2**) spectrum revealed that H-20~22 were all correlated with C-19, which added evidences to the deduction. The assignments of the R- and S-configuration for C-19 of **3** and **4** were carried out on the basis of the ^{13}C NMR data, repectively[5]. The signal at δ_C 219.4 (s) and 76.5 (d) , δ_H (3.03,1H, d, J 2.5Hz) were assigned to C-14 carbonyl group which was 1708 cm^{-1} in IR (KBr) and C-7α OH, the same ones as in spiramine **G**[6], which was confirmed by the HMBC correlation of C-14 to H-7, 9, 12, 13, 15 and H-7β to C-5, 6, 8, 9, 14, 15, respectively. All the H and C assignments of **3** and **4** were made by the DEPT and HMQC technique.

Table 2 HMBC (H→C) for **1-4** [c]

	Correlated No of C		
No of H	**1**	**2**	**3** (**4**)
1	2, 3, 5, 10, 20	2, 3, 5, 10, 20	2, 3, 4, 5, 10, 20
2	1, 3, 4, 10	1, 3, 4, 10	1, 3, 4, 10
3	1, 2, 4, 5, 18, 19	1, 2, 4, 5	1, 2, 4, 5
5	3, 6, 7, 10, 18, 19, 20	1, 3, 6, 9, 18, 19, 20	1, 3, 6, 9,10, 18, 19, 20
6	4, 5, 7, 8, 10,	4, 5, 7, 8, 10	4, 5, 7, 8, 10
7	5, 6, 8, 9, 15	5, 6, 8, 9, 14, 15	5, 6, 8, 9, 14, 15
9	1, 8, 10, 11	6, 7, 8, 10, 20	6, 7, 8, 10, 11, 14, 20
11	9, 12	9, 12, 13, 16	9, 12, 13, 16
12	11, 15, 16, 17	9, 11, 13, 14, 16, 17	9, 11, 13, 14, 16, 17
13	8, 11, 12, 14, 16	8, 11, 12, 16	8, 11, 12, 14, 16
14	7, 8, 12, 13, 15	7, 8, 12, 13, 15	/
15	7, 8, 9, 12, 16, 17	7, 8, 9, 10, 16, 17	7, 8, 9, 10, 14, 16, 17
17	12, 15, 16	12, 15, 16	12, 15, 16
18	3, 4, 5, 19	3, 4, 5, 19	3, 4, 5, 19
19	3, 4, 5, 18, 20	/	4, 5, 18, 20
20	9, 10, 19	1, 9, 19, 22	1, 9, 19
21	/	19, 20, 22	19, 20
22	/	19	19, 21

[c] Spectra were obtained at 500 MHz.

Compound **5**, colorless plates (acetone), mp 149-151°C, $[\alpha]_D^{22}$ -134.75 (*c*, 0.30, MeOH), HREIMS for $C_{22}H_{33}NO_3$ 359.2444 (calcd. 359.2460), The IR and NMR spectra showed it to be a deacetyl product of spiramine **F** (**6**)[6] which was primarily obtained during the structural elucidation of **6**. However, **5** was isolated as a natural component in the plant for the first time.

Table 3 ^{1}H and ^{13}C NMR data for **3** and **4**[b]

No	^{1}H[d]	^{13}C[d]
1	1.43, m, αH;1.22, m, βH	40.0t
2	2.28,m, αH;1.45, m, βH	21.6 (21.5)t
3	1.91, m, αH; 1.97, m, βH	29.8t
4	/	35.4s
5	0.89 (0.71), m	48.5 (46.9)d
6	1.43, m, αH ;1.58, m, βH	27.7t
7	3.03, d, 2.5	76.5d
8	/	51.9s
9	1.50, m	49.6 (49.5)d
10	/	39.3s
11	1.98, m, αH; 1.58, m, βH	27.7 (27.3)t
12	2.86, m	38.5 (38.4)d
13	2.16, m, αH ; 2.23, m, βH	45.5 (44.8)t
14	/	219.4s
15	2.99,s; 2.24, dd, 2.5, 8	38.2 (38.1)d
16	/	147.1(146.3)s
17	4.87, 4.69 (4.83, 4.62), br.s	107.5 (107.0)t
18	1.04 (1.01), s	24.0q
19	3.70 (3.89), br.s	97.7 (95.5)d
20	2.65, m, αH ;3.04, m, βH	54.7 (54.6)t
21	3.46, m, αH;3.41, m, βH	58.7 (58.6)t
22	3.75,m	64.5 (63.0)t

[d] Data in ( ) were different values for compound **4** , others of **3** and **4** were the same.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (NSFC) for outstanding young scientists to X. J. Hao (No. 39525025), which is gratefully acknowledged. All spectra were recorded by the analytical group of Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences.

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7. ^{13}C NMR (obtained at 500 MHz in C_5D_5N) of **5**: δ 41.7 (t, C-1), 21.5 (t, C-2), 30.4 (t, C-3), 34.9 (s, C-4), 44.8 (d, C-5), 25.7 (t, C-6), 74.5 (d, C-7), 41.7 (s, C-8), 44.8 (d, C-9), 34.9 (s, C-10), 24.1 (t, C-11), 37.9 (d, C-12), 25.4 (t, C-13), 21.2 (C-14), 70.2 (d, C-15), 156.5 (s, C-16), 111.6 (t, C-17), 26.8 (q, C-18), 53.9 (d, C-19), 88.0 (d, C-20), 58.4 (t, C-21), 59.9 (t, C-22).

Received 10 July, 2000