

New Diterpenoid Alkaloids from *Spiraea fritschiana* var. *parvifolia*

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Abstract: Two new C₂₀ hetisine-type diterpenoid alkaloids, spirafine III (**1**) and spirafine II (**2**), were isolated from the roots of *Spiraea fritschiana* var. *parvifolia*. Their structures were elucidated based on HRMS, IR and NMR spectral data, and chemical reaction.

Keywords: *Spiraea fritschiana*, C₂₀ diterpenoid alkaloid, hetisine, NMR.

Spiraea fritschiana var. *parvifolia* distributed in the north of China is one of the three varieties of *S. fritschiana*¹. Recently three C₂₀ hetisine-type diterpenoid alkaloids, spiradine D (**3**)², spirafine III (**1**) and spirafine II (**2**) were isolated from its roots. Preliminary pharmaceutical investigation revealed that spiradine D had anti-PAF activity.

Compound **1** is obtained in form of colorless needle crystals, m.p. 192-193°C; $[\alpha]_D^{22.3} - 46.07$ (c 2.0, C₅H₅N). Its molecular formula was determined as C₂₂H₃₁NO₂ by HRMS (341.2279, calc.: 341.2355). Its IR (KBr) spectrum exhibited the absorption at ν 1680 cm⁻¹ for the keto group, whose ¹³C signal appeared at 206.00 ppm in the ¹³C NMR spectrum. Twenty two signals in the ¹³C NMR (DEPT) spectrum were recognized (1 × CH₃, 11 × CH₂, 5 × CH, 5 × C), including two carbons of the exocyclic double bond [C-16: δ_C 151.49 (s), C-17: δ_C 103.06 (t), δ_H 4.66 (d, 1H, J = 1.8), δ_H 4.492 (d, 1H, J = 1.8). The ion peak at m/z 296 [M⁺ - 45] in EI and the IR absorption at 3495cm⁻¹ (OH) showed the group of HOCH₂CH₂-, and their ¹H and ¹³C NMR data supported this suggestion [C-22: δ_C 59.63 (t), δ_H 3.725 (m, 2H); C-21: δ_C 55.81 (t), δ_H 3.050 (m, 2H)]. Comparison of the ¹H and ¹³C NMR data (Table 1) with those of **3**² suggested that **1** was the opened oxazolidine ring product of **3**, and this suggestion had been confirmed by the chemical transformation: spirafine III was acquired when **3** was reduced with KBH₄ in MeOH at room temperature (yield: 96%). Compound **1** was named as spirafine III in comparison with spirafine I, previously isolated from the roots of *Spiraea fritschiana*³.

Compound (**2**), named as spirafine II, another colorless needle crystals, m.p. 155-156°C; $[\alpha]_D^{22.3} - 33.16$ (c 2.0, C₅H₅N), has the same molecular formula as **1**: C₂₂H₃₁NO₂, by means of HRMS (341.2327, calc.: 341.2355). The determination of

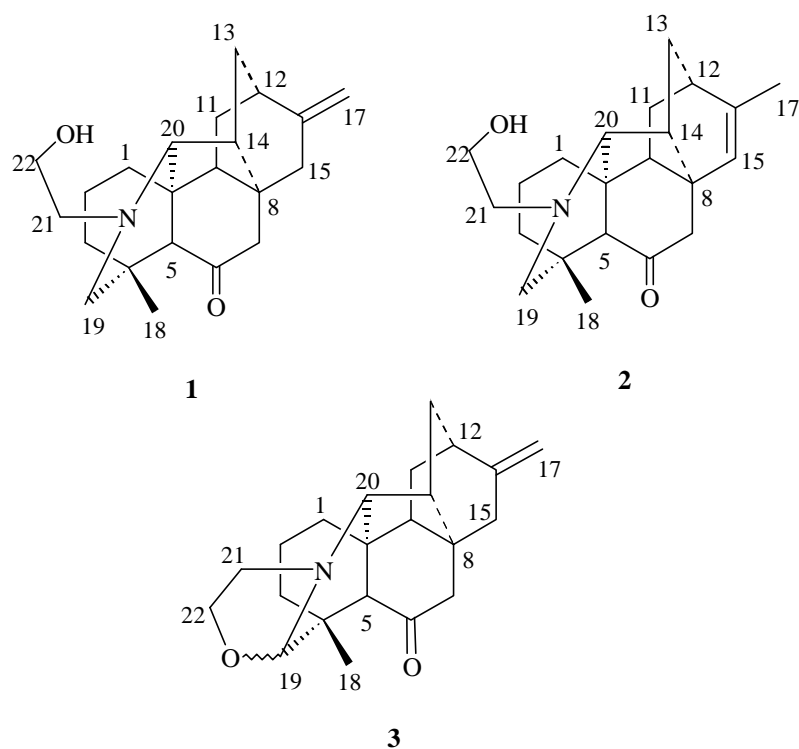
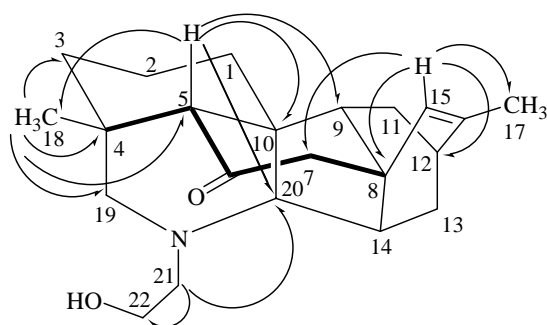
the endocyclic methine group was based on the ^1H and ^{13}C NMR [C-15: δ_{C} 125.72 (d), δ_{H} 5.25 (s); C-16: δ_{C} 146.32 (s)], and the chemical shift of C-17 at ^{13}C NMR varied greatly from 103.06 ppm: =CH₂ in **1** to 19.52 ppm -CH₃ in **2**, while other data of **2** (**Table 1**) were close to those of the **1** [v (KBr) 1680 cm⁻¹ (C=O), 3495 cm⁻¹ (OH)]. From the information above, the structure of spirafine II was established, and the NMR assignments were carried out on the basis of ^1H – ^1H cosy, HMQC and HMBC experiments. Some selected HMBC correlations are shown in **Figure 2** and the full HMBC data of spirafine II were listed in **Table 1**.

Table 1. 1-D data* for spirafine III, spirafine II and the HMBC data for spirafine II

Atom No.	Spirafine III		Spirafine II		
	^{13}C	^1H	^{13}C	^1H	HMBC
1	35.46	1.717 (m, 2H)	36.44	1.633 (m, 2H)	C2, C3
2	18.87	1.573 (m, 2H)	18.86	1.523 (m, 2H)	C10, C20
3	40.42	1.252 (m, 2H)	40.69	1.257 (m, 2H)	C2, C18, C19
4	37.53		37.41		
5	60.41	1.573 (s)	60.62	1.523 (s)	C18, C10, C9, C20
6	206.00		206.00		
7	52.64	2.661 (dd, 11.9, 71.55, 2H)	51.04	2.843 (dd, 18.39, 82.06, 2H)	C8, C14, C9, C5, C6
8	40.30		44.07		
9	50.16	1.573 (s)	52.00	1.531 (s)	C10, C20
10	46.99		46.20		
11	29.62	2.023 (m, 2H)	29.02	1.856 (m, 2H)	C12, C8, C10, C9
12	34.02	2.134 (m)	34.50	2.194 (m)	
13	31.99	1.620 (m, 2H)	33.19	1.853 (m, 2H)	
14	45.84	1.620 (m, 2H)	47.69	1.853 (m)	C12, C10
15	35.34	2.197 (s, 2H)	125.72	5.251 (s)	C17, C12, C8, C7
16	151.49		146.32		
17	103.06	4.660 (br.s) 4.492 (br.s)	19.52	1.762 (s, 3H)	C12, C15, C16
18	30.77	1.492 (s, 3H)	30.87	1.508 (s, 3H)	C4, C3, C19, C5, C6
19	56.84	2.661 (dd, 11.92, 2H)	56.99	2.679 (dd, 11.92, 314.58, 2H)	C18, C4, C3, C21, C20
20	77.51	2.202 (s)	75.74	2.332 (s)	C13, C1, C8, C21, C5
21	55.81	3.050 (m, 2H)	56.04	3.050 (m, 2H)	C22, C20
22	59.63	3.729 (m, 2H)	59.52	3.734 (m, 2H)	

* 1. ^1H and ^{13}C NMR spectral data were obtained at a Bruker AM-400 NMR spectrometer at 400 MHz and 100 MHz, respectively, with C₅D₅N as solvent. Chemical shifts were in ppm referenced from TMS.

2. All the data of ^1H should be regarded as to one proton except special appointment.

Figure 1 Chemical structures of the diterpenoid alkaloids from *Spiraea fritschiana* var. *parvifolia***Figure 2** Selected HMBC correlations of spirafine II (from H to C)

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