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A New Norditerpene from *Miliusa balansae* Finet *et* Gagnep

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Abstract: A novel norditerpene, miliusate (**1**), was isolated from *Miliusa balansae* Finet et Gagnep. Its structure was elucidated by spectral analysis.

Keywords: *Miliusa balansae* Finet *et* Gagnep., miliusate.

The plant *Miliusa balansae* Finet *et* Gagnep. is used in Chinese folk medicine for different symptom such as gastropathy and glomerulonephropathy. There is no report about its chemical investigation. In this study a new norditerpene with novel skeleton, named miliusate (**1**) was isolated, and its structure was established by spectral evidence.

Compound **1** was obtained as white flaky crystal, mp 89-91°C; Its molecular formula $C_{20}H_{26}O_5$ was provided by quasi-molecular ion $[M+H]^+$ at *m/z* 347.17970 (calcd. 347.18585) in HRFAB-MS spectrum. The IR spectrum revealed γ-lactone (1779 cm^{-1}), acetoxyl (1749, 1031 cm^{-1}) and ketone carbonyl (1675 cm^{-1}) groups. The fragment ions at *m/z* 303 $[M-CH_3CO]^+$ and 287 $[M-CH_3COO]^+$ in the EI-MS spectrum, ^{13}C NMR signals at 170.4 (-COO-) and 21.0, ^1H NMR signal at δ 2.12 (s, 3H) suggested the presence of CH_3COO-. The resonances at δ_H 6.04 dd (H-7), 6.97 dd (H-8), and at δ_C 197.1 (s, C-6), 130.6 (d, C-7) and 147.5 (d, C-8) provided an α,β-unsaturated ketone. Three other methyl groups appearing at δ_H 1.65 (s, 3H, 7'-H), 1.59 (s, 3H, 6'-Me) and 1.77 (d, 3H, 2'-Me) were recognized.

From HMQC and HMBC correlation, two substructures in the molecular could be concluded (**A** and **B** in **Figure 1**). The double bond between C-1' and C-2' was determined as *trans*, because 2'-Me resonates at δ_C 16.9 instead of δ_C 23 for those *cis* analogues[1]. The HMBC correlation between C-6 (at δ_C 197.1) and H-4 [at δ_H 3.02 (d), 2.65(d), J = 17.2 Hz], C-6 and H-10 [at δ_H 2.51 (dd), 2.25 (dd)] suggested C-6 carbon is adjacent to a quarternary carbon (C-5). The following correlation supported the spiro rings of C-1 to C-10: H-1/C-3, C-4, C-5, C-6 and C-10, H-7/C-8 and C-9, H-8/C-6 and C-10, H-9/C-1, C-5, C-7, C-8 and C-10. The acetoxyl group could be located to C-9 in view of the HMBC correlation δ5.63 (H-9)/174.0 ($CH_3\underline{C}OO$) (**Table 1**). Accordingly, the structure of compound **1** could be deduced as 9-acetoxyl-1-(2,6-dimethyl-1,5 -heptadiene)-3,6-dioxo-2-oxaspiro[4.5]deca-7-ene, named miliusate. It possesses a novel skeleton.

Figure 1 Structure of **1** and HMBC Correlation

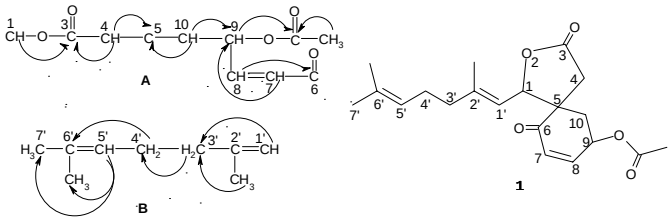

Table 1 NMR Data of Compound **1**

Carbon	δ_C*	δ_H	*J* (Hz)	HMBC Correlation
1	82.2	5.39	d, 9.9	H-1/C-6, C-3, C-2', C-1', C-5, C-4, C-10
3	174.9	--	--	
4a	38.6	3.02	d, 17.2	H-4/C-6, C-3, C-1, C-5, C-10
b		2.65	d, 17.2	
5	53.2	--	--	
6	197.1	--	--	
7	130.6	6.04	dd, 10.2, 1.6	H-7/C-9, C-5
8	147.5	6.97	dd, 10.2, 3.2	H-8/C-6, C-10
9	66.6	5.63	m	H-9/$CH_3\underline{C}OO$, C-8, C-7, C-1, C-5, C-10
10a	36.8	2.51	dd, 13.9, 5.4	H-10/C-6, C-8, C-1, C-9, C-5, C-4
b		2.25	dd, 13.9, 6.7	
1'	119.8	5.25	dd, 9.9, 1.1	H-1'/C-1, C-5, C-3', $C_{2'}$-$\underline{C}H_3$
2'	144.7	--	--	
3'	40.3	2.06	m	H-3'/C-2', C-5', C-1', C-4', $C_{2'}$-$\underline{C}H_3$
4'	26.7	2.09	m	H-4'/C-6', C-5', C-3', C-2'
5'	124.4	5.03	m	H-5'C-6', C-3', C-4', C-7', $C_{6'}$-$\underline{C}H_3$
6'	132.3	--	--	
7'	25.9	1.65	s	H-7'/C-6', C-5', $C_{6'}$-$\underline{C}H_3$
$C_{2'}$-$\underline{C}H_3$	16.9	1.77	d, 1.3	2'-CH_3/C-2', C-1', C-3'
$C_{6'}$-$\underline{C}H_3$	17.8	1.59	s	6'-CH_3/C-6', C-5', C-7'
CO-$\underline{C}H_3$	21.0	2.12	s	
$CH_3\underline{C}O$	170.4	--	--	

*The assignment were based on HMQC diagram.

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Reference

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