New C_{20}-Diterpenoid Alkaloids from *Delphinium anthriscifolium* var. *savatieri*

by **Xiao-Yu Liu**, **Qiao-Hong Chen**, and **Feng-Peng Wang***

Department of Chemistry of Medicinal Natural Products, West China College of Pharmacy, Sichuan University; No. 17, Duan 3, Renmin Nan Road, Chengdu 610041, P. R. China (phone/fax: +86-28-5501368; e-mail: wfp@scu.edu.cn)

Five new vakognavine-type C_{20}-diterpenoid alkaloids, anthriscifolmines D–H (**1**–**5**, resp.), were isolated from the whole herb of *Delphinium anthriscifolium* var. *savatieri*. The structures of these new alkaloids were determined by spectroscopic techniques, including HR-ESI-MS, 1D-, and 2D-NMR experiments.

Introduction. – Plants of genera *Aconitum* and *Delphinium* remain targets of vigorous phytochemical investigations, and a series of new diterpenoid alkaloids have recently been discovered in these plants by our group [1–3]. *Delphinium anthriscifolium* var. *savatieri* (FRANCHET) MUNZ [4], a kind of herbaceous plants with an underdeveloped root system, is one of the four plants in the section *Anthriscifolium* of the genus *Delphinium* and is native to China. As a result of our earlier study, five C_{18}-diterpenoid alkaloids and a C_{19}-diterpenoid alkaloid had been obtained from *D. anthriscifolium* var. *savatieri* [5]. This study has presented a chemotaxonomical merit for the genus *Delphinium* plants, which stimulated our interest in the further phytochemical studies of this species.

The present investigation on a re-collection of this plant led to the isolation of five new C_{20}-diterpenoid alkaloids, designated as anthriscifolmines D–H (**1**–**5**, resp.). Structurally, these vakognavine-type C_{20}-diterpenoid alkaloids are the first examples of the isolation of C_{20}-diterpenoid alkaloids with formyl ester groups [6]. Generally, these alkaloids seldom have a C(15)=C(16) bond [6], but anthriscifolmines G and H (**4** and **5**, resp.) represent exceptions to this statement. Here, we report the isolation and structure elucidation of these new alkaloids.

Results and Discussion. – Anthriscifolmine D (**1**) was obtained as a white amorphous powder with the molecular formula $C_{33}H_{41}NO_9$ as derived from its HR-ESI-MS ($[M+H]^+$ at m/z 596.2844). The ^{1}H-NMR data (*Table 1*) of **1** indicated the presence one BzO group, one 2-methylbutanoyloxy group (MbO), and two Me groups at δ(H) 1.20 (*s*) and δ(H) 2.59 (*s*). The ^{13}C-NMR and DEPT spectra (*Table 2*) displayed one exocyclic C=C bond (δ(C) 148.1 (*s*), 111.6 (*t*)), two CH_2 groups (δ(C) 27.0, 29.8) and two ester CO groups (δ(C) 165.9, 176.4), together with three additional quaternary C-atoms (δ(C) 44.4, 53.8, 59.9). In addition, an aldehyde group (δ(H) 9.87 (*s*); δ(C) 196.5) was indicated by the NMR data. It was evident that compound **1** was a vakognavine-type C_{20}-diterpenoid alkaloid [6].

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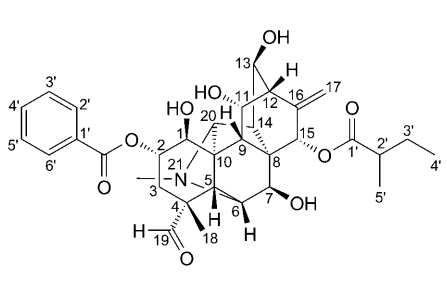

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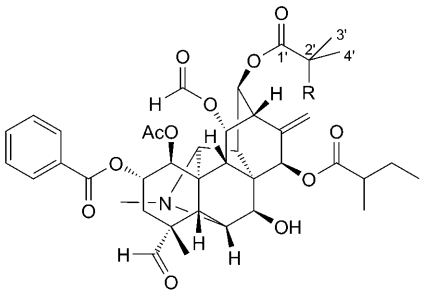

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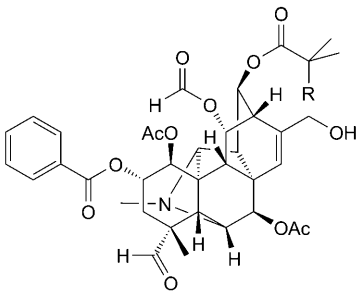
3 R = H



4 R = OH
5 R = H

The correlations from H–C(2) to C(4), C(10), and the CO C-atom of the BzO group; from H–C(15) to C(7), C(14), C(17), and the CO C-atom of the MbO group in the HMBC experiment (*Fig. 1*) showed that the two ester groups are positioned at C(2) and C(15), respectively. Apart from the CH_2 group in the MbO group, the remaining one was assigned to C(3), which was established by the HMBC correlations from H–C(5), Me(18) and H–C(19) to C(3). Besides the two ester groups, there were four OH groups in the molecule, which were placed at C(1), C(7), C(11), and C(13), respectively, according to the HMBC displayed in *Fig. 1*.

The relative configuration of anthriscifolmine D was deduced from the vicinal coupling constants (*Table 1*) and a NOESY experiment (*Fig. 1*). The coupling constant between H–C(11) with H_β–C(9) ($J = 8.8$ Hz) indicated a 1,2-diaxial relationship between them, implying that H–C(11) was β-oriented. Similarly, the large coupling constant of H–C(13) ($J = 8.8$ Hz) with H_α–C(14) revealed that the dihedral angle between these two H-atoms was *ca.* 0°, which implied that H–C(13) was in an α-orientation. However, the coupling constant of H–C(2) ($J = 2.8$ Hz) with H–C(3) indicated that H–C(2) was in an equatorial position, which indicated a β-orientation. The cross-peaks between H–C(1) and H_α–C(20), H–C(7) and H_α–(14), and H–C(15) and H_β–C(9) in the NOESY experiment revealed that H–C(1) and H–C(7) were α-oriented and H–C(15) was in β-orientation. Hence, the structure of **1** was established as (1β,2α,7β,11α,13β,15α)-2-(benzoyloxy)-1,7,11,13-tetrahydroxy-21-

Table 1. *^{1}H-NMR Data of* **1**–**5** (400 MHz). δ in ppm, J in Hz.

	1[a])	**2**[b])	**3**[b])	**4**[b])	**5**[b])
H–C(1)	5.47 (*s*)	5.81 (*d*, *J* = 4.0)	5.83 (*d*, *J* = 4.0)	5.81 (*d*, *J* = 3.6)	5.84 (*d*, *J* = 3.6)
H–C(2)	5.92–5.99 (*m*)	5.64 (*q*, *J* = 3.2)	5.64 (*q*, *J* = 3.2)	5.62 (*q*, *J* = 3.2)	5.63 (*q*, *J* = 3.2)
H_α–C(3)	2.44 (*dd*, *J* = 14.8, 2.8)	2.29 (*dd*, *J* = 15.6, 2.8)	2.25 (*dd*, *J* = 15.2, 2.8)	2.29 (*dd*, *J* = 15.6, 3.2)	2.29 (*dd*, *J* = 15.6, 3.2)
H_β–C(3)	2.36 (*dd*, *J* = 14.8, 2.8)	1.70–1.80 (*m*)	1.70–1.80 (*m*)	1.75 (*dd*, *J* = 15.6, 3.2)	1.75 (*dd*, *J* = 15.6, 3.2)
H–C(5)	2.96 (*s*)	2.44 (*s*)	2.42 (*s*)	2.24 (*s*)	2.24 (*s*)
H–C(6)	3.54 (*d*, *J* = 2.8)	3.22 (*d*, *J* = 4.0)	3.16 (*d*, *J* = 4.0)	3.26 (*d*, *J* = 3.6)	3.22 (*d*, *J* = 2.8)
H–C(7)	4.48 (*d*, *J* = 3.6)	3.74 (*d*, *J* = 4.0)	3.70 (*d*, *J* = 3.2)	5.39 (*d*, *J* = 3.6)	5.38 (*d*, *J* = 3.6)
H–C(9)	3.36 (*d*, *J* = 8.8)	2.93 (*d*, *J* = 9.6)	2.89 (*d*, *J* = 9.2)	2.48 (*d*, *J* = 9.6)	2.45 (*d*, *J* = 9.6)
H–C(11)	4.61 (*d*, *J* = 8.8)	5.31 (*d*, *J* = 9.6)	5.28 (*d*, *J* = 9.6)	5.07 (*d*, *J* = 9.6)	5.03 (*d*, *J* = 9.6)
H–C(12)	2.91 (*d*, *J* = 2.0)	2.68 (*s*)	2.67 (*s*)	2.81 (*s*)	2.79 (*s*)
H–C(13)	4.67 (*d*, *J* = 8.8)	5.24 (*d*, *J* = 9.6)	5.12 (*d*, *J* = 9.6)	4.93 (*d*, *J* = 9.6)	4.83 (*d*, *J* = 9.6)
H–C(14)	3.21 (*d*, *J* = 9.2)	2.96 (*d*, *J* = 9.6)	2.91 (*d*, *J* = 9.2)	2.68 (*d*, *J* = 8.4)	2.64 (*d*, *J* = 8.4)
H–C(15)	6.43 (*s*)	5.72 (*s*)	5.69 (*s*)	5.77 (*s*)	5.76 (*s*)
CH_2(17)	5.20 (*s*), 5.11 (*s*)	5.37 (*s*), 5.13 (*s*)	5.33 (*s*), 5.09 (*s*)	4.21 (*s*)	4.20 (*s*)
Me(18)	1.20 (*s*)	1.12 (*s*)	1.12 (*s*)	1.08 (*s*)	1.08 (*s*)
H–C(19)	9.87 (*s*)	9.27 (*s*)	9.30 (*s*)	9.36 (*s*)	9.34 (*s*)
H–C(20)	4.53 (*s*)	4.03 (*s*)	3.89 (*s*)	3.89 (*s*)	3.78 (*s*)
Me(21)	2.59 (*s*)	2.39 (*s*)	2.32 (*s*)	2.45 (*s*)	2.43 (*s*)
HCOO–C(11)		7.84 (*s*)	7.86 (*s*)	7.87 (*s*)	7.89 (*s*)
AcO–C(1)		2.03 (*s*)	2.03 (*s*)	2.04 (*s*)	2.04 (*s*)
AcO–C(7)				2.17 (*s*)	2.16 (s)
BzO–C(2):					
H–C(2′,6′)	8.24 (*d*, *J* = 8.0)	7.90 (*d*, *J* = 8.0)	7.91 (*d*, *J* = 8.0)	7.90 (*d*, *J* = 7.2)	7.92 (*d*, *J* = 7.2)
H–C(3′,5′)	7.33 (*t*, *J* = 8.0)	7.42 (*t*, *J* = 8.0)	7.44 (*t*, *J* = 8.0)	7.43 (*t*, *J* = 7.2)	7.45 (*t*, *J* = 7.2)
H–C(4′)	7.44 (*t*, *J* = 8.0)	7.56 (*t*, *J* = 8.0)	7.57 (*t*, *J* = 8.0)	7.57 (*t*, *J* = 7.2)	7.58 (*t*, *J* = 7.2)
HmpO–C(13):					
H–C(3′)		1.00 (*s*)		1.03 (*s*)	
H–C(4′)		1.24 (*s*)		1.25 (*s*)	
MpO–C(13):					
H–C(2′)			2.18–2.22 (*m*)		2.23–2.27 (*m*)
H–C(3′)			0.75 (*d*, *J* = 7.2)		0.80 (*d*, *J* = 7.2)
H–C(4′)			0.97 (*d*, *J* = 7.2)		0.97 (*d*, *J* = 7.2)
MbO–C(15):					
H–C(2′)	2.47–2.54 (*m*)	2.48–2.53 (*m*)	2.47–2.53 (*m*)		
CH_2(3′)	1.71–1.81 (*m*), 1.43–1.54 (*m*)	1.70–1.80 (*m*), 1.50–1.58 (*m*)	1.70–1.80 (*m*), 1.50–1.57 (*m*)		
H–C(4′)	0.92 (*t*, *J* = 7.2)	0.97 (*t*, *J* = 7.2)	0.96 (*t*, *J* = 7.2)		
H–C(5′)	1.18 (*d*, *J* = 7.2)	1.23 (*d*, *J* = 7.2)	1.23 (*d*, *J* = 7.2)		

[a]) Measured in (D_5)pyridine. [b]) Measured in $CDCl_3$.

methyl-15-[(2-methylbutanoyl)oxy]-19,21-secohetisan-19-al, and the compound was given the trivial name anthriscifolmine D.

Anthriscifolmine E (**2**) was isolated as a white amorphous powder. The molecular formula $C_{40}H_{49}NO_{13}$ was deduced on the basis of its HR-ESI-MS data at *m*/*z* 752.3285 ($[M+H]^+$; calc. 752.3282). It was readily recognized that **2** was a vakognavine-type

Table 2. *^{13}C-NMR Data of* **1**–**5** (100 MHz). δ in ppm.

	1[a])	**2**[b])	**3**[b])	**4**[b])	**5**[b])[c])
C(1)	65.7 (*d*)	69.4 (*d*)	69.4 (*d*)	69.1 (*d*)	69.1 (*d*)
C(2)	73.7 (*d*)	67.7 (*d*)	67.8 (*d*)	67.6 (*d*)	67.9 (*d*)
C(3)	29.8 (*t*)	29.2 (*t*)	29.5 (*t*)	29.2 (*t*)	29.5 (*t*)
C(4)	44.4 (*s*)	43.8 (*s*)	43.8 (*s*)	43.7 (*s*)	43.6 (*s*)
C(5)	56.3 (*d*)	55.5 (*d*)	55.6 (*d*)	57.0 (*d*)	57.1 (*d*)
C(6)	62.9 (*d*)	60.7 (*d*)	60.6 (*d*)	59.4 (*d*)	59.4 (*d*)
C(7)	63.3 (*d*)	62.4 (*d*)	62.5 (*d*)	68.6 (*d*)	68.6 (*d*)
C(8)	53.8 (*s*)	53.7 (*s*)	53.5 (*s*)	51.4 (*s*)	51.2 (*s*)
C(9)	51.0 (*d*)	47.6 (*d*)	47.5 (*d*)	46.4 (*d*)	46.2 (*d*)
C(10)	59.9 (*s*)	56.9 (*s*)	56.7 (*s*)	56.7 (*s*)	56.5 (*s*)
C(11)	74.1 (*d*)	72.4 (*d*)	71.6 (*d*)	75.5 (*d*)	75.8 (*d*)
C(12)	51.5 (*d*)	44.4 (*d*)	44.3 (*d*)	40.8 (*d*)	40.6 (*d*)
C(13)	71.4 (*d*)	73.3 (*d*)	72.5 (*d*)	74.0 (*d*)	72.2 (*d*)
C(14)	40.6 (*d*)	37.3 (*d*)	37.4 (*d*)	42.5 (*d*)	42.8 (*d*)
C(15)	68.5 (*d*)	67.8 (*d*)	67.9 (*d*)	124.4 (*d*)	124.1 (*d*)
C(16)	148.1 (*s*)	141.1 (*s*)	141.3 (*s*)	142.9 (*s*)	143.1 (*s*)
C(17)	111.6 (*t*)	116.6 (*t*)	116.2 (*t*)	62.4 (*t*)	62.5 (*t*)
C(18)	26.9 (*q*)	26.4 (*q*)	26.3 (*q*)	26.5 (*q*)	26.3 (*q*)
C(19)	196.5 (*d*)	196.9 (*d*)	195.3 (*d*)	197.2 (*d*)	196.5 (*d*)
C(20)	63.4 (*d*)	62.9 (*d*)	63.0 (*d*)	63.4 (*d*)	63.4 (*d*)
C(21)	33.5 (*q*)	33.5 (*q*)	33.8 (*q*)	33.7 (*q*)	33.9 (*q*)
H*C*OO–C(11)		159.5 (*d*)	159.6 (*d*)	159.9 (*d*)	160.0 (*d*)
*Ac*O–C(1)		169.6 (*s*)	169.6 (*s*)	169.5 (*s*)	169.7 (*s*)
		21.4 (*q*)	21.3 (*q*)	21.3 (*q*)	21.3 (*q*)
*Ac*O–C(7)				170.1 (*s*)	170.1 (*s*)
				21.1 (*q*)	21.1 (*q*)
BzO–C(2):					
C=O	165.9 (*s*)	165.2 (*s*)	165.1 (*s*)	165.1 (*s*)	165.1 (*s*)
C(1′)	131.4 (*s*)	129.9 (*s*)	129.9 (*s*)	129.8 (*s*)	129.8 (*s*)
C(2′,6′)	130.0 (*d*)	129.6 (*d*)	129.6 (*d*)	129.6 (*d*)	129.6 (*d*)
C(3′,5′)	128.7 (*d*)	128.5 (*d*)	128.6 (*d*)	128.6 (*d*)	128.6 (*d*)
C(4′)	133.1 (*d*)	133.3 (*d*)	133.4 (*d*)	133.4 (*d*)	133.4 (*d*)
HmpO–C(13):					
C(1′)		176.8 (*s*)		176.9 (*s*)	
C(2′)		71.9 (*s*)		71.9 (*s*)	
C(3′)		26.5 (*q*)		26.6 (*q*)	
C(4′)		27.1 (*q*)		27.1 (*q*)	
MpO–C(13):					
C(1′)			176.2 (*s*)		176.3 (*s*)
C(2′)			33.3 (*d*)		33.5 (*d*)
C(3′)			18.2 (*q*)		18.3 (*q*)
C(4′)			18.7 (*q*)		18.6 (*q*)
MbO–C(15):					
C(1′)	176.4 (*s*)	178.4 (*s*)	178.5 (*s*)		
C(2′)	41.7 (*d*)	41.6 (*d*)	41.6 (*d*)		
C(3′)	27.0 (*t*)	26.6 (*t*)	26.6 (*t*)		
C(4′)	11.7 (*q*)	11.8 (*q*)	11.8 (*q*)		
C(5′)	16.8 (*q*)	16.7 (*q*)	16.8 (*q*)		

[a]) Recorded in (D_5)pyridine. [b]) Recorded in $CDCl_3$. [c]) Recorded at 50 MHz.

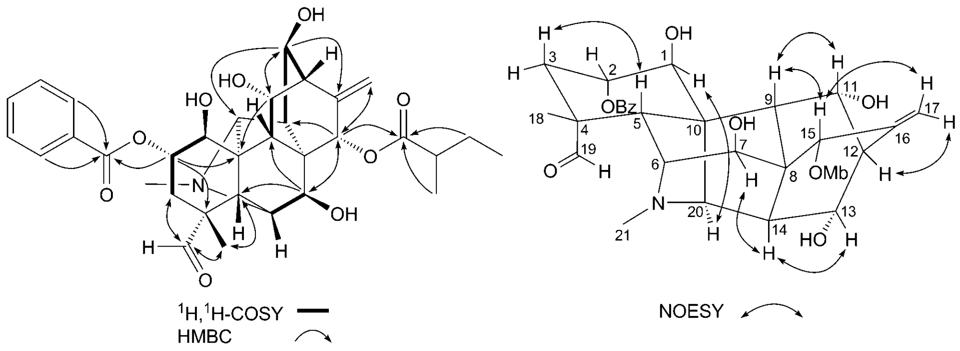


Fig. 1. *Key $^1H,^1H$-COSY, HMBC, and NOESY correlations of anthriscifolmine D* (**1**)

C_{20}-diterpenoid alkaloid [6] according to the NMR spectra (*Tables 1* and *2*), which showed the presence of an aldehyde group (δ(H) 9.27 (*s*); δ(C) 196.9), one exocyclic C=C bond (δ(C) 141.1 (*s*), 116.6 (*t*)), and five ester groups including one AcO group, one BzO group, one formyloxy group (HCOO), one MbO group and one 2-hydroxy-2-(methylpropanoyl)oxy group (HmpO) (δ(H) 1.00 (*s*), 1.24 (*s*), each 3 H; δ(C) 176.8 (*s*), 71.9 (*s*), 26.5 (*q*), 27.1 (*q*)), as well as two Me groups at δ(H) 1.12 (*s*, Me(18)) and δ(H) 2.39 (*s*, MeN).

The ester groups were positioned at C(1), C(2), C(11), C(13), and C(15) as a result of HMQC and HMBC data (*Fig. 2*) of H−C(1), H−C(2), H−C(11), H−C(13), and H−C(15) with their adjoining ester CO C-atoms AcO (δ(C) 169.7), BzO (δ(C) 165.2), HCOO (δ(C) 159.5), HmpO (δ(C) 176.8), and MbO (δ(C) 178.4), respectively. The remaining O-atom was present as a OH group in this molecule according to the molecular formula and the NMR data. The HMBC cross-peaks between H−C(7) (δ(H) 3.74) and C(5), C(9), and C(15) led to the location of the OH at C(7).

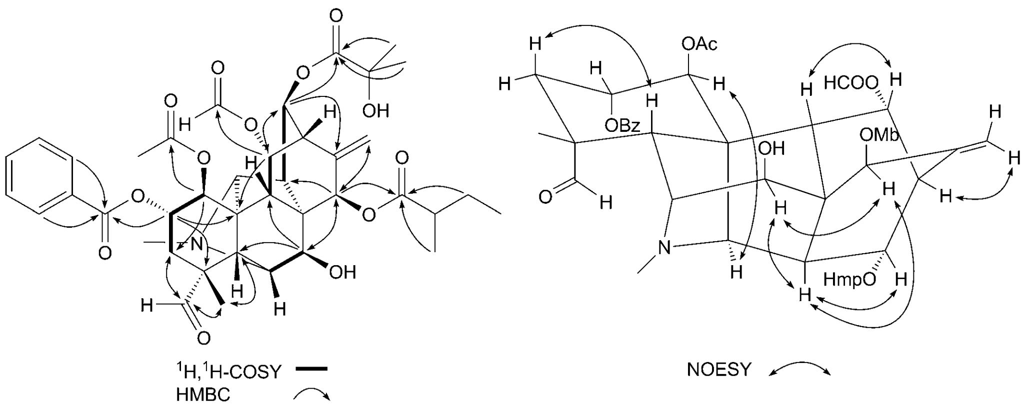


Fig. 2. *Key $^1H,^1H$-COSY, HMBC, and NOESY correlations of anthriscifolmine E* (**2**)

The configuration of H−C(2), H−C(11), H−C(13) was β, β, and α, respectively, consistent with those of anthriscifolmine D (**1**), since the corresponding coupling

constants (*Table 1*) were almost identical to the ones in **1**. The correlations between H–C(1) and H_α–C(20), and of H–C(7), H–C(15), and H_α–C(14) in the NOESY spectrum (*Fig. 2*) revealed that H–C(1), H–C(7), and H–C(15) were all α-oriented. Accordingly, the structure of anthriscifolmine E (**2**) was established as (1β,2α,7β,11α, 13β,15β)-1-(acetyloxy)-2-(benzoyloxy)-11-(formyloxy)-7-hydroxy-13-[(2-hydroxy-2-methylpropanoyl)oxy]-21-methyl-15-[(2-methylbutanoyl)oxy]-19,21-secohetisan-19-al.

Anthriscifolmine F (**3**) exhibited a *pseudo*-molecular-ion peak at *m*/*z* 736.3332 ($[M+H]^+$) in the HR-ESI-MS, corresponding to the molecular formula $C_{40}H_{49}NO_{12}$. The NMR data of **3** (*Tables 1* and *2*) were very similar to those of **2** except for the presence of a CH group (δ(H) 2.18–2.22 (*m*); δ(C) 33.3(*d*)) instead of the quaternary C-atom at δ(C) 71.9 (*s*) in **2**. In addition, two secondary Me groups (δ(H) 0.75 (*d*), 0.97 (*d*), $J = 7.2$ Hz) were in place of the two tertiary Me groups (δ(H) 1.00 (*s*), 1.24 (*s*)) observed in **2**. As a result, it was evident that a 2-methylpropanoyloxy group (MpO) took the place of the 2-hydroxy-2-methylpropanoyloxy group (HmpO) of **2**. The configuration of **3** was determined to be identical to that of **2** by comparing their NMR data. The structure of **3** was therefore elucidated as (1β,2α,7β,11α,13β,15β)-1-(acetyloxy)-2-(benzoyloxy)-11-(formyloxy)-7-hydroxy-21-methyl-15-[(2-methylbutanoyl)oxy]-13-[(2-methylpropanoyl)oxy]-19,21-secohetisan-19-al.

Anthriscifolmine G (**4**), $C_{37}H_{43}NO_{13}$ (according to the HR-ESI-MS), and anthriscifolmine H (**5**), $C_{37}H_{43}NO_{12}$ (according to its HR-ESI-MS), were also deduced to represent vakognavine-type C_{20}-diterpenoids [6]. An aldehyde group, five ester groups including two AcO groups, a BzO group, a HCOO group, and a HmpO group for **4** or a MpO group for **5**, a tertiary Me group and a MeN group were present in both compounds. They feature a trisubstituted C=C bond (δ(C) 124.4 (*d*), 142.9 (*s*)) and an O-bearing CH_2 group (δ(H) 4.21; δ(C) 62.4) instead of the typical exocyclic C=C bond of C_{20}-diterpenoid alkaloids. It was thus concluded that the classical allyl alcohol moiety from C(15) to C(17), exocyclic C=C bond with a OH (or its ester) group at C(15), was isomerized to a C(15)=C(16) bond with a OH group at C(17). This assumption was confirmed by the correlations from H–C(7) and CH_2(17) to C(15), from H–C(11) and H–C(13) to C(16), and from H–C(15) to C(17) in the HMBC spectrum of **4** (*Fig. 3*). The ester moieties in **4** were readily assigned at C(1), C(2), C(7), C(11), and C(13) respectively, on the basis of the key correlations for H–C(1)/AcO (δ(C) 169.6), H–C(2)/BzO (δ(C) 165.1), H–C(7)/AcO (δ(C) 170.1), H–C(11)/HCOO (δ(C) 159.9), and H–C(13)/HmpO (δ(C) 176.9). Compound **4** possessed a similar configuration to that of **3** according to the deduction from its NOESY experiment (*Fig. 3*) and the coupling constants of vicinal H-atoms (*Table 1*). A closer look at the NMR data of **4** and **5** (*Tables 1* and *2*) indicated that the only difference between them was the presence of a 2-methylpropanoyloxy (MpO) group in **5** instead of the 2-hydroxy-2-methylpropanoyloxy (HmpO) group in **4**. The structures of anthriscifolmines G and H were thus established as (1β,2α,7β,11α,13β)-1,7-bis(acetyloxy)-2-(benzoyloxy)-11-(formyloxy)-17-hydroxy-13-[(2-hydroxy-2-methylpropanoyl)oxy]-21-methyl-19,21-secohetisan-15-en-19-al (**4**) and (1β,2α,7β,11α,13β)-1,7-bis(acetyloxy)-2-(benzoyloxy)-11-(formyloxy)-17-hydroxy-21-methyl-13-[(2-methylpropanoyl)oxy]-19,21-secohetisan-15-en-19-al (**5**).

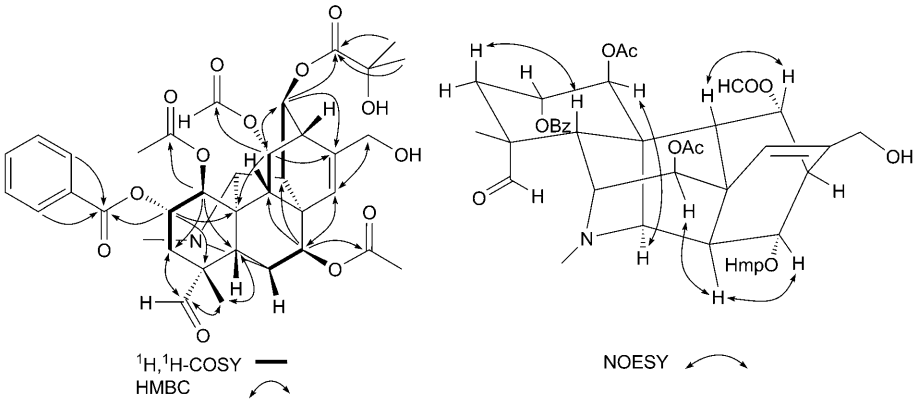


Fig. 3. *Key ^{1}H,^{1}H-COSY, HMBC, and NOESY correlations of anthriscifolmine G* (**4**)

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Experimental Part

General. TLC: Silica-gel plates; detection by spraying with *Dragendorff* reagent. Column chromatography (CC): silica gel (SiO_2; 300–400 mesh, 10–40 μm; *Qindao Sea Chemical, Inc.*). Optical rotations: *Perkin-Elmer 341* polarimeter. IR Spectra: *Nicolet FT-IR 200S* spectrometer; KBr pellets; in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Varian Unity-INOVA-400/54* spectrometers: at 400/100 or 200/50 MHz, resp.; δ in ppm rel. to Me_4Si, *J* in Hz. ESI-MS: *Finnigan LCQ*; in *m/z* (rel.%). HR-ESI-MS: *Micromass Auto-Ultima-Tof* spectrometer.

Plant Material. The sample of *D. anthriscifolium* var. *savatieri* was collected from Pengzhou City in Sichuan Province in China in June 2006, and authenticated by *Wen-Jing Zhang* of the Pengzhou County Centre of Disease Prevention and Control. Voucher specimens (No. 20060918-1) were deposited with the West China College of Pharmacy at the Sichuan University.

Extraction and Isolation. Dried whole herbs (4.0 kg) of *D. anthriscifolium* var. *savatieri* were milled and percolated with 0.1M HCl (40 l). The filtrate was then alkalized with 25% aq. NH_4OH (1.5 l) to pH > 9, and the subsequent mixture was extracted with AcOEt (20 l × 3), and the solvents were removed to furnish a residue (10.0 g). Four extraction batches were processed by the same procedure to yield 42.5 g of crude alkaloids, which were subjected to SiO_2 CC eluting with $CHCl_3$/MeOH (100 : 1 → 95 : 5) to give ten fractions (*Frs. A–J*). *Fr. H* (5.0 g) was subjected to CC (SiO_2; cyclohexane/Me_2CO 8:1): *anthriscifolmine E* (**2**, 15 mg), and a mixture (260 mg) which was repurified through CC (SiO_2, cyclohexane/AcOEt 1 : 1) to give *anthriscifolmine F* (**3**, 15 mg). *Fr. I* (5.5 g) was purified repeatedly by CC (SiO_2, $CHCl_3$/MeOH 200 : 1 → cyclohexane/Me_2CO 8 : 1): *anthriscifolmine G* (**4**, 10 mg) and *anthriscifolmine H* (**5**, 5 mg). *Fr. J* (4.0 g) was subjected to CC (SiO_2, $CHCl_3$/MeOH 100 : 1): *anthriscifolmine D* (**1**, 19 mg).

Anthriscifolmine D (*=(1β,2α,7β,11α,13β,15α)-2-(Benzoyloxy)-1,7,11,13-tetrahydroxy-21-methyl-15-[(2-methylbutanoyl)oxy]-19,21-secohetisan-19-al*; **1**). White amorphous powder. $[\alpha]_D^{20} = +13.0$ ($c = 0.22$, MeOH). IR (KBr): 3422, 2935, 1717, 1275, 1117, 715. ^{1}H-NMR (400 MHz, C_5D_5N): *Table 1*. ^{13}C-NMR (100 MHz, C_5D_5N): *Table 2*. HR-ESI-MS: 596.2844 ($[M+H]^+$, $C_{33}H_{42}NO_9^+$; calc. 596.2860).

Anthriscifolmine E (*=(1β,2α,7β,11α,13β,15β)-1-(Acetyloxy)-2-(benzoyloxy)-11-(formyloxy)-7-hydroxy-13-[(2-hydroxy-2-methylpropanoyl)oxy]-21-methyl-15-[(2-methylbutanoyl)oxy]-19,21-secohetisan-19-al*; **2**). White amorphous powder. $[\alpha]_D^{20} = -24.9$ ($c = 0.55$, $CHCl_3$). IR (KBr): 3470, 2933, 1726,

1372, 1236, 1153. ^{1}H-NMR (400 MHz, $CDCl_3$): *Table 1*. ^{13}C-NMR (100 MHz, $CDCl_3$): *Table 2*. HR-ESI-MS: 752.3285 ($[M+H]^+$, $C_{40}H_{50}NO_{13}^+$; calc. 752.3282).

Anthriscifolmine F (*=(1β,2α,7β,11α,13β,15β)-1-(Acetyloxy)-2-(benzoyloxy)-11-(formyloxy)-7-hydroxy-21-methyl-15-[(2-methylbutanoyl)oxy]-13-[(2-methylpropanoyl)oxy]-19,21-secohetisan-19-al*; **3**). White amorphous powder. $[\alpha]_D^{20} = -25.0$ ($c = 0.50$, $CHCl_3$). IR (KBr): 3467, 2932, 1727, 1371, 1235, 1154. ^{1}H-NMR (400 MHz, $CDCl_3$): *Table 1*. ^{13}C-NMR (100 MHz, $CDCl_3$): *Table 2*. HR-ESI-MS: 736.3332 ($[M+H]^+$, $C_{40}H_{50}NO_{12}^+$; calc. 736.3333).

Anthriscifolmine G (*=(1β,2α,7β,11α,13β)-1,7-Bis(acetyloxy)-2-(benzoyloxy)-11-(formyloxy)-17-hydroxy-13-[(2-hydroxy-2-methylpropanoyl)oxy]-21-methyl-19,21-secohetisan-15-en-19-al*; **4**). White amorphous powder. $[\alpha]_D^{20} = +12.1$ ($c = 0.70$, $CHCl_3$). IR (KBr): 3448, 2935, 1724, 1373, 1235, 1154. ^{1}H-NMR (400 MHz, $CDCl_3$): *Table 1*. ^{13}C-NMR (100 MHz, $CDCl_3$): *Table 2*. HR-ESI-MS: 710.2815 ($[M+H]^+$, $C_{37}H_{44}NO_{13}^+$; calc. 710.2813).

Anthriscifolmine H (*=(1β,2α,7β,11α,13β)-1,7-Bis(acetyloxy)-2-(benzoyloxy)-11-(formyloxy)-17-hydroxy-21-methyl-13-[(2-methylpropanoyl)oxy]-19,21-secohetisan-15-en-19-al*; **5**). White amorphous powder. $[\alpha]_D^{20} = +8.4$ ($c = 0.25$, $CHCl_3$). IR (KBr): 3433, 2934, 1725, 1371, 1234, 1156. ^{1}H-NMR (400 MHz, $CDCl_3$): *Table 1*. ^{13}C-NMR (50 MHz, $CDCl_3$): *Table 2*. HR-ESI-MS: 694.2858 ($[M+H]^+$, $C_{37}H_{44}NO_{12}^+$; calc. 694.2864).

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