

New C₁₉- and C₁₈-Diterpenoid Alkaloids from *Delphinium anthriscifolium* var. *savatieri*

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Three new C₁₉-diterpenoid alkaloids, anthriscifoldines A—C (1—3), and two new C₁₈-diterpenoid alkaloids, anthriscifolcines F and G (5, 6), were obtained from the whole herbs of *Delphinium anthriscifolium* var. *savatieri* during our further investigation on a larger scale of recollected plants. Their structures were elucidated based on the interpretation of NMR and high-resolution ESI-MS data, and chemical transformation. In addition, five known C₁₉-diterpenoid alkaloids were also isolated and identified as nudicaulamine (4), delbruninol (7), blacknine (8), winkleriline (9), and deltaline (10).

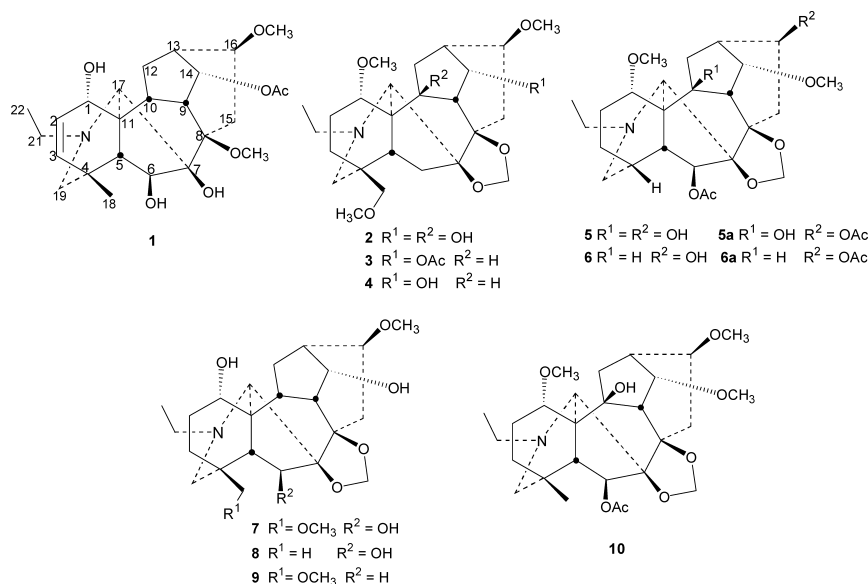
Key words *Delphinium*; *anthriscifolium*; diterpenoid alkaloid; anthriscifoldine; anthriscifolcine

In a continuation of our phytochemical studies on the pharmacologically interesting plants *Aconitum* and *Delphinium*, we obtained a series of structurally and chemotaxonomically interesting diterpenoid alkaloids.^{1–3} It was very intriguing that we also discovered a novel diterpene from one of these plants.⁴ *Delphinium anthriscifolium* var. *savatieri* (FRANCHET) MUNZ⁵ belongs to the Sect. *Anthriscifolium* (which consists of only 4 plants) of the genus *Delphinium*. Our earlier chemical investigation of a small batch of specimens of this plant led to the discovery of some new C₁₈-diterpenoid alkaloids, which presented a chemotaxonomical advantage for the genus *Delphinium*.⁶ Further investigation of a large batch of recollected samples resulted in the isolation of three new C₁₉-diterpenoid alkaloids, anthriscifoldines A—C (1—3), and two new C₁₈-diterpenoid alkaloids anthriscifolcines F and G (5, 6), together with five known alkaloids. In this paper, we report the isolation and structural elucidation of these new alkaloids.

Results and Discussion

Anthriscifoldine A (1) was obtained as a white amorphous powder. Its molecular formula was deduced to be C₂₅H₃₇NO₇

from a pseudomolecular ion at m/z 464.2661 [M+H]⁺ in its HR-ESI-MS. The ¹H-NMR spectrum (Table 1) showed the presence of an *N*-ethyl group (δ_{H} 1.06, 3H, t, $J=7.2$ Hz; δ_{H} 2.90, 2H, m), two methoxy groups (δ_{H} 3.34, 3.49, each 3H, s), an acetyl group (δ_{H} 2.05, 3H, s), a disubstituted double bond (δ_{H} 5.77, 1H, dd, $J=9.2, 4.8$ Hz; δ_{H} 5.66, 1H, $J=9.6$ Hz), and a methyl group attached to a quaternary carbon (δ_{H} 1.09, 3H, s). The ¹³C-NMR and distortionless enhancement by polarization transfer (DEPT) data demonstrated the existence of four methylene carbons (δ_{C} 27.5, 26.7, 56.2, 50.3) and five quaternary carbons (δ_{C} 89.1, 84.6, 33.7, 49.2, 170.1). The aforementioned NMR features suggested that compound 1 is a lycotonine-type C₁₉-diterpenoid alkaloid.⁷ A triplet signal at δ_{H} 4.81 (t, $J=4.4$ Hz) was attributed to H-14 β ,⁷ implying the presence of the only acetoxy group at the C-14 position. The two methoxy groups were attributed to C-8 and C-16 based on the long-range correlations between 8-OCH₃ and C-8, and 16-OCH₃ and C-16 in its heteronuclear multiple bonding connectivity (HMBC) spectrum. Along with the above-mentioned signals, its ¹³C-NMR spectrum (Table 2) displayed six oxygenated carbon signals, suggesting that this compound possesses three additional hy-



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Table 1. ¹H-NMR Data for Compounds **1**, **2**, **5** and **6** (400 MHz, δ_{H} Mult., J =Hz in CDCl₃)

Position	1	2	5	6
1	3.72 d (4.4)	3.63 dd (10.4, 7.2)	3.58 t (8.4)	3.03 dd (10.4, 7.2)
2	5.77 dd (9.2, 4.8)	2.07 m	2.80 m (β) 2.08 m (α)	2.01 overlapped
3	5.66 d (9.6)	1.44 m	1.35 m	1.78 overlapped
4	—	—	2.11 overlapped	2.16 m
5	1.65 s	1.78 m	1.86 m	1.53 m
6	4.28 s	2.18 overlapped	5.32 s	5.23 s
9	2.17 m	2.30 overlapped	3.49 m	3.62 t (5.2)
10	2.56 m	—	—	1.87 overlapped
12	2.28 m	2.41 overlapped	2.63 m	2.10 overlapped
	2.24 m	1.70 m	1.68 m	1.93 m
13	3.26 m	2.55 m	2.50 m	2.37 m
14	4.81 t (4.4)	4.63 q (5.6)	4.30 t (4.4)	3.79 t (4.8)
15	2.58 m (β) 1.88 m (α)	1.79 m (β) 1.77 m (α)	2.59 m (β) 1.75 m (α)	2.57 m (β) 1.73 m (α)
16	3.38 d (5.2)	3.46 br d (7.6)	3.66 m	3.70 t (10.0)
17	2.78 br s	3.18 s	3.28 br s	3.39 br s
18	1.09 s	3.13, 3.01 ABq (8.8)	—	—
19	2.43 m	2.66 m 2.44 m	2.88 m	2.85 m
21	2.90 m	2.83 m 2.73 m	2.77 m	2.77 m
22	1.06 t (7.2)	1.06 t (7.2)	1.07 t (7.2)	1.06 t (7.2)
1-OCH ₃	—	3.26 s	3.26 s	3.26 s
8-OCH ₃	3.49 s	—	—	—
14-OCH ₃	—	—	3.51 s	3.51 s
16-OCH ₃	3.34 s	3.30 s	—	—
18-OCH ₃	—	3.35 s	—	—
OCH ₂ O	—	5.05 s, 4.97 s	4.97 s, 4.94 s	4.97 s, 4.96 s
OAc	2.05 s	—	2.08 s	2.07 s

droxyl groups in addition to an ester group and two methoxy groups. The one-proton doublet signal at δ_{H} 3.72 ($J=4.4$ Hz) in the ¹H-NMR spectrum was assigned to H-1 β , and the singlet at δ_{H} 4.28 to H-6 α . In addition, the location of the three hydroxyl groups at C-1, C-6, and C-7 was further confirmed by the corresponding correlation spectroscopy (COSY) and HMBC correlations (Fig. 1). Also, the presence of a $\Delta^{2,3}$ double bond could be corroborated by the critical HMBC correlations (Fig. 1) from H-2 (δ_{H} 5.77) to C-4 and C-11, and from H-3 (δ_{H} 5.66) to C-5, C-18, and C-19. The structure of anthriscifoldine A was thus established.

Anthriscifoldine B (**2**) has the molecular formula as C₂₅H₃₉NO₇, which was determined by HR-ESI-MS (m/z 466.2801 [M+H]⁺). Compound **2** also exhibited characteristic NMR features (Tables 1, 2) of a lycocotinine-type C₁₉-diterpenoid alkaloid⁷⁾ bearing an *N*-ethyl group (δ_{H} 1.06, 3H, t, $J=7.2$ Hz; δ_{H} 2.73, 2.83, each 1H, m; δ_{C} 14.0 q, 50.6 t), three methoxy groups (δ_{H} 3.26, 3.30, 3.35, each 3H, s; δ_{C} 55.7 q, 59.5 q, 56.4 q), and a methylenedioxy group (δ_{H} 4.97, 5.05, each 1H, s; δ_{C} 93.8 t), as well as five quaternary carbons at δ_{C} 38.2, 55.7, 78.1, 82.6, and 91.7. The three methoxy groups could be readily assigned to C-1, C-16, and C-18 based on the cross-peaks (between 1-OCH₃ and C-1, 16-OCH₃ and C-16, and 18-OCH₃ and C-18) observed in its HMBC spectrum (Fig. 1). The methylenedioxy was located at C-7 and C-8 due to the long-range correlations of the methylene group with C-7 and C-8. The existence of seven oxygenated carbons deduced from its ¹³C-NMR spectrum suggested that **2** had two hydroxyl groups in addition to three methoxy groups and a methylenedioxy group. The H-14 β

Table 2. ¹³C-NMR Data for Compounds **1**–**3**, **5**, and **6** (100 MHz, CDCl₃)

Position	1	2	3	5	6
1	70.9 d	77.9d	83.7d	77.1 d	83.8 d
2	130.1 d	26.0 t	26.5 t	25.9 t	25.8 t
3	137.4 d	32.1 t	32.3 t	28.6 t	28.9 t
4	33.7 s	38.2 s	38.1 s	33.7 d	33.9 d
5	57.5 d	39.3 d	43.3 d	44.5 d	49.6 d
6	81.7 d	32.3 t	32.0 t	81.4 d	80.8 d
7	89.1 s	91.7 s	90.8 s	92.8 s	93.6 s
8	84.6 s	82.6 s	81.3 s	80.4 s	81.6 s
9	44.5 d	55.4 d	47.0 d	47.9 d	38.6 d
10	37.0 d	78.1 s	36.5 d	83.1 s	47.9 d
11	49.2 s	55.7 s	50.7 s	54.6 s	49.3 s
12	27.5 t	36.9 t	27.3 t	37.8 t	27.1 t
13	42.1 d	36.3 d	44.2 d	40.1 d	40.1 d
14	75.4 d	72.8 d	75.2 d	82.4 d	83.7 d
15	26.7 t	32.8 t	33.5 t	37.8 t	37.0 t
16	82.4 d	81.1 d	81.3 d	71.7 d	72.1 d
17	65.0 d	62.6 d	62.1 d	64.7 d	64.8 d
18	23.7 q	78.8 t	78.9 t	—	—
19	56.2 t	52.3 t	52.4 t	50.6 t	50.7 t
21	50.3 t	50.6 t	50.7 t	50.3 t	50.6 t
22	13.7 q	14.0 q	14.0 q	13.9 q	13.9 q
1-OCH ₃	—	55.7 q	55.8 q	55.7 q	55.9 q
8-OCH ₃	57.6 q	—	—	—	—
14-OCH ₃	—	—	—	58.0 q	57.9 q
16-OCH ₃	56.2 q	56.4 q	56.2 q	—	—
18-OCH ₃	—	59.5 q	59.5 q	—	—
OCH ₂ O	—	93.8 t	93.3 t	93.9 t	93.7 t
OAc	170.1 s 21.1 q	—	171.7 s 21.4 q	170.2 s 21.7 q	170.3 s 21.6 q

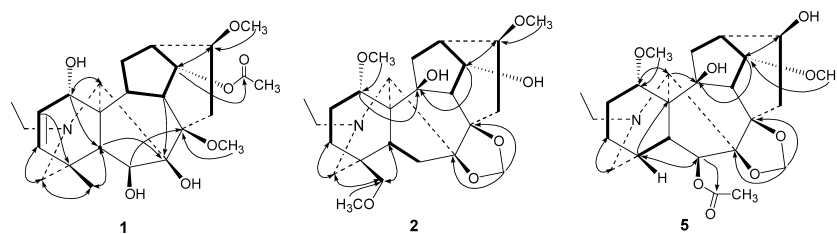


Fig. 1. Key ^1H - ^1H COSY Correlations (—) and Selected HMBC Correlations ($\text{H} \cdots \text{C}$) of **1**, **2** and **5**

signal appeared at a lower field [δ_{H} 4.63 (q, $J=5.6$ Hz)], indicating the location of the two hydroxyl groups at C-10 and C-14, which was supported by the key correlations in its HMBC spectrum (Fig. 1). Notably, the chemical shift value of C-1 and C-14 appeared at a higher field due to the γ -gauch effect of a 10-OH group. All available evidence indicated the structure of anthriscifoldine B to be **2**.

Anthriscifoldine C (**3**), a white amorphous powder, $\text{C}_{27}\text{H}_{41}\text{NO}_7$ (HR-ESI-MS), was also a lycotonine-type C_{19} -diterpenoid alkaloid.⁷⁾ Its NMR data showed distinctive signals at δ_{H} 1.06 (3H, t, $J=7.2$ Hz) and δ_{C} 14.0 q for an *N*-ethyl group; δ_{H} 3.26, 3.28, 3.29 (each 3H, s) for three methoxy groups; δ_{H} 4.93, 5.01 (each 1H, s) and δ_{C} 93.3 t for a methylenedioxy group; and δ_{H} 2.07 (3H, s) with δ_{C} 21.4 q, 171.7 s for an acetoxy group. Comparison of the NMR data of **3** with those of the known nudicaulamine⁸⁾ (**4**) revealed that they were structurally similar except for the existence of an additional acetyl group in **3**. Notably, the H-14 β signal in **3** appeared at δ_{H} 4.82 (t, $J=4.8$ Hz) instead of at δ_{H} 4.04 (t, $J=4.8$ Hz) in **4**. The acetyl group was therefore attached to C-14 in **3**. This assignment was further supported by hydrolysis of **3** with 5% NaOH/ CH_3OH to yield a product that was identical to an authentic sample of **4**.

Anthriscifolcine F (**5**) was obtained as a white amorphous powder, and its molecular formula $\text{C}_{25}\text{H}_{37}\text{NO}_8$ was determined based on a pseudomolecular ion peak at m/z 480.2573 $[\text{M}+\text{H}]^+$ in its HR-ESI-MS spectrum. The NMR spectra (Tables 1, 2) indicated the presence of an *N*-ethyl group (δ_{H} 1.07, 3H, t, $J=7.2$ Hz; δ_{C} 13.9 q, 50.3 t), two methoxy groups (δ_{H} 3.26, 3.51, each 3H, s; δ_{C} 55.7 q, 58.0 q), an acetoxy group (δ_{H} 2.08, 3H, s; δ_{C} 170.2 s, 21.7 q), and a methylenedioxy group (δ_{H} 4.94, 4.97, each 1H, s; δ_{C} 93.9 t), as well as five quaternary carbons (δ_{C} 54.6, 80.4, 83.1, 92.8, 170.2). The presence of only one nonoxygenated quaternary carbon at δ_{C} 54.6 suggested that compound **5** is a C_{18} -diterpenoid alkaloid.⁹⁾ The key HMBC correlations (Fig. 1) of H-1 β (δ_{H} 3.58, t, $J=8.4$ Hz) with 1-OCH₃, and of H-14 β (δ_{H} 4.30, t, $J=4.4$ Hz) with 14-OCH₃, confirmed the attachment of two methoxy groups at C-1 and C-14. The HMBC cross-peak between H-6 (δ_{H} 5.32, s) and the carbonyl carbon of OAc indicated the location of the acetoxy group at C-6. The methylenedioxy group was located at C-7 and C-8 based on the long-range correlations of the methylene group with C-7 and C-8. Along with the above-mentioned signals, its ^{13}C -NMR spectrum displayed seven oxygenated carbon signals, suggesting that this compound possesses two additional hydroxyl groups, which could be located at C-10 and C-16 due to the HMBC correlations shown in Fig. 1. The above findings led to the assignment of anthriscifolcine F as **5**.

The molecular formula of anthriscifolcine G (**6**) was de-

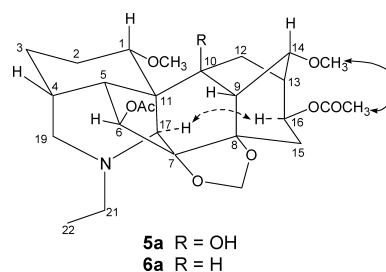


Fig. 2. Key NOE Correlations ($\text{H} \cdots \text{H}$) of **5a** and **6a**

duced to be $\text{C}_{25}\text{H}_{37}\text{NO}_7$ from its HR-ESI-MS at m/z 464.2650 $[\text{M}+\text{H}]^+$. From its NMR data (Tables 1, 2), an *N*-ethyl group, two methoxy groups, an acetoxy group, and a methylenedioxy group could be easily recognized. Compound **6** shared highly similar ^1H - and ^{13}C -NMR spectral patterns with those of **5**. The only difference is that the C-10 oxygenated quaternary carbon (δ_{C} 83.1 s) in **5** was replaced with a methine carbon (δ_{C} 47.9 d) in **6**. The structure of anthriscifolcine G was further confirmed by extensive analyses of its 1D NMR and 2D NMR spectra.

The configurations at C-6 and C-16 in all new alkaloids were determined based on NMR data and selective NOE difference spectra. As mentioned in our previous report,⁶⁾ the configuration of 6-OH in **1** or 6-OAc in **5** and **6** has a β -orientation due to the singlet signal corresponding to H-6 α in their ^1H -NMR spectra.⁷⁾ The configuration of 16-OCH₃ in compounds **1**—**3** was also determined to have a β -orientation according to the δ values (81—83 ppm) of C-16 in their ^{13}C -NMR spectra.¹⁰⁾

The orientation of the 16-OH group in **5** and **6** was ambiguous at first since no evident NOE correlation could be found when H-16 was irradiated. Fortunately, from the derivatives (**5a**, **6a**) prepared by acetylation of 16-OH in compounds **5** and **6**, NOE correlations (Fig. 2) could be observed between 16-OAc and 14-OCH₃, and H-16 and H-17 in both **5a** and **6a**. The configuration of the 16-OH group in **5** and **6** therefore was unambiguously established to have a β -orientation. The conformation of the D ring in **5a** and **6a** was suggested to be a boat one, which would enable the 16-OAc substituent to remain in an equatorial position.

The five known C_{19} -diterpenoid alkaloids isolated from this plant were identified as nudicaulamine (**4**),⁸⁾ delbruninol (**7**),¹¹⁾ blacknine (**8**),¹²⁾ winkleriline (**9**),¹³⁾ and deltaline (**10**)¹⁰⁾ by comparing their spectroscopic data with those reported in the literature. The abundant chemical components found in this plant should be very helpful in further chemotaxonomic research on the *Delphinium* genus.

Experimental

General Experimental Procedures Optical rotations were measured on a Perkin-Elmer 341 polarimeter. IR spectra were obtained on a Nicolet FT-IR 200 SXV spectrophotometer. NMR spectra were recorded on a Varian Unity INOVA 400/45 NMR spectrometer. Mass spectra were carried out on Finnigan LCQ and Micromass Auto Ultima-ToF spectrometers. Silica gel H (Qindao Sea Chemical Factory, P. R. China) was used for column chromatography. Spots on TLC plates (silica gel G, Qindao Sea Chemical Factory) were visualized with modified Dragendorff's reagent.

Plant Material *D. anthriscifolium* var. *savatieri* was collected from Pengzhou, Sichuan Province, P. R. China, in June 2006 and authenticated by Wen-Jin Zhang of Pengzhou County Centre of Disease Prevention and Control. A voucher specimen (No. 20060918-1) was deposited in the West China College of Pharmacy, Sichuan University.

Extraction and Isolation The dried and powdered whole herbs (4.0 kg) of *D. anthriscifolium* var. *savatieri* were percolated with 0.1 mol/l HCl (40 l). The filtrate was then alkalinized with 25% aqueous NH_4OH (1.5 l) to pH >9 and extracted with ethyl acetate (20 l × 3). Removal of the solvent under reduced pressure gave a residue of 10.0 g. Four extractions in total were performed in the same procedure to produce 42.5 g of crude alkaloids, which were then subjected to silica gel column chromatography eluted with chloroform-methanol (100:1→95:5) to give 10 fractions (A–J). Fraction B (1.1 g) was further chromatographed on a silica gel column eluted with chloroform-methanol (400:1) to give four subfractions. Compound **3** (5 mg) was obtained by purification of subfraction B-4 (79 mg) on a silica gel column using cyclohexane-ethyl acetate (10:1) as the eluent. Fraction C (1.9 g) was subjected to silica gel column chromatography eluted with cyclohexane-ethyl acetate (15:1) to give **6** (15 mg). Fraction E (2.0 g) was chromatographed on a silica gel column and eluted with cyclohexane-acetone (10:1) to yield three subfractions (E-1–E-3). E-2 was further chromatographed on a silica gel column eluted with chloroform-methanol (400:1) to provide compound **1** (47 mg) and nudicaulamine (**4**, 15 mg). E-3 was subjected to silica gel column chromatography eluted with cyclohexane-acetone (10:1) to give deltaline (**10**, 5 mg). Fraction G (1.2 g) was chromatographed on a silica gel column using cyclohexane-acetone (8:1) as the eluent to give three subfractions. Subfraction G-1 was purified on a silica gel column eluted with chloroform-methanol (300:1) to afford compound **5** (52 mg). Chromatography of fraction H (5.5 g) on a silica gel column eluted with cyclohexane-acetone (8:1) produced six subfractions (H-1–H-6). Delbruninol (**7**, 19 mg) was recrystallized from fraction H-4 with acetone. Winkleriline (**9**, 23 mg) and blacknine (**8**, 30 mg) were obtained from column chromatography of H-5 using chloroform-methanol (200:1) as the eluent. Fraction H-6 (180 mg) was further purified on a silica gel column using cyclohexane-acetone (10:1) as the eluent to yield compound **2** (10 mg).

Anthriscifoldine A (**1**): White amorphous powder; $[\alpha]_D^{20} +66.7^\circ$ ($c=0.50$, CHCl_3); IR (KBr) cm^{-1} : 3488, 3477, 1738; $^1\text{H-NMR}$ (400 MHz, CDCl_3), see Table 1; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3), see Table 2; HR-ESI-MS m/z : 464.2661 $[\text{M}+\text{H}]^+$, Calcd for $\text{C}_{25}\text{H}_{38}\text{NO}_7$, 464.2643.

Anthriscifoldine B (**2**): White amorphous powder; $[\alpha]_D^{20} -22.5^\circ$ ($c=0.40$, CHCl_3); IR (KBr) cm^{-1} : 3430, 2929, 1090; $^1\text{H-NMR}$ (400 MHz, CDCl_3), see Table 1; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3), see Table 2; HR-ESI-MS m/z : 466.2801 $[\text{M}+\text{H}]^+$, Calcd for $\text{C}_{25}\text{H}_{40}\text{NO}_7$, 466.2805.

Anthriscifoldine C (**3**): White amorphous powder; $[\alpha]_D^{20} -15.4^\circ$ ($c=0.18$, CH_3COCH_3); IR (KBr) cm^{-1} : 3384, 2876, 1735, 1245, 1087; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ_{H} 1.06 (3H, t, $J=7.2$ Hz, H-22), 2.07 (3H, s, OAc), 3.10, 3.01 (ABq, $J=8.8$ Hz, H-18), 3.26, 3.28, 3.29 (each 3H, s, $3\times\text{OCH}_3$), 4.82 (1H, t, $J=4.8$ Hz, H-14 β), 5.01, 4.93 (each 1H, s, OCH_2O); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3), see Table 2; HR-ESI-MS m/z 492.2940 $[\text{M}+\text{H}]^+$, Calcd for $\text{C}_{27}\text{H}_{42}\text{NO}_7$, 492.2961.

Hydrolysis of Anthriscifoldine C (**3**): A solution of anthriscifoldine C (**3**) (5 mg) in 2 ml of 5% NaOH/ CH_3OH was stirred at room temperature for 1 h. The reaction mixture was extracted with CHCl_3 , the combined extracts were dried over anhydrous Na_2SO_4 , and the solvent was removed to yield the corresponding hydrolytic derivative nudicaulamine (**4**) (2 mg).

Anthriscifoldine F (**5**): White amorphous powder; $[\alpha]_D^{20} -27.8^\circ$ ($c=0.50$, CHCl_3); IR (KBr) cm^{-1} : 3421, 1736, 1090; $^1\text{H-NMR}$ (400 MHz, CDCl_3), see Table 1; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3), see Table 2; HR-ESI-MS m/z : 480.2573 $[\text{M}+\text{H}]^+$, Calcd for $\text{C}_{25}\text{H}_{38}\text{NO}_8$, 480.2592.

Acetylation of Anthriscifoldine F (**5**): 1 ml of acetic anhydride was added to a solution of anthriscifoldine F (**5**) (30 mg) in pyridine (3 ml), and the mixture was stirred at room temperature for 4 h. Then **5a** (25 mg) was obtained after the usual work-up and flash column chromatography. **5a**: white amorphous powder; $[\alpha]_D^{20} -20.6^\circ$ ($c=0.50$, CHCl_3); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ_{H} 1.07 (3H, t, $J=7.2$ Hz, H-22), 2.04, 2.08 (each 3H, s, $2\times\text{OAc}$), 3.15 (1H, s, H-17), 3.26, 3.51 (each 3H, s, $2\times\text{OCH}_3$), 4.15 (1H, t, $J=4.8$ Hz, H-14 β), 4.72 (1H, dd, $J=8.8$, 6.8 Hz, H-16 α), 4.96, 4.91 (each 1H, s, OCH_2O), 5.30 (1H, s, H-6 α).

Anthriscifoldine G (**6**): White amorphous powder; $[\alpha]_D^{20} -56.7^\circ$ ($c=0.30$, CHCl_3); IR (KBr) cm^{-1} : 3492, 2929, 1740, 1244, 1087; $^1\text{H-NMR}$ (400 MHz, CDCl_3), see Table 1; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) see Table 2; HR-ESI-MS m/z : 464.2650 $[\text{M}+\text{H}]^+$, Calcd for $\text{C}_{25}\text{H}_{38}\text{NO}_7$, 464.2648.

Acetylation of Anthriscifoldine G (**6**): 0.5 ml of acetic anhydride was added to a solution of anthriscifoldine G (**6**) (10 mg) in pyridine (2 ml), and the mixture was stirred at room temperature for 4 h. The usual work-up and flash column chromatography provided the acetylated analogue **6a** (7 mg). **6a**: white amorphous powder; $[\alpha]_D^{20} -23.5^\circ$ ($c=0.50$, CHCl_3); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ_{H} 1.06 (3H, t, $J=7.2$ Hz, H-22), 2.05, 2.07 (each 3H, s, $2\times\text{OAc}$), 3.21 (1H, s, H-17), 3.25, 3.46 (each 3H, s, $2\times\text{OCH}_3$), 3.69 (1H, t, $J=4.8$ Hz, H-14 β), 4.78 (1H, dd, $J=8.8$, 6.0 Hz, H-16 α), 4.77, 4.75 (each 1H, s, OCH_2O), 5.25 (1H, s, H-6 α).

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