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Nortriterpenoids from *Schisandra lancifolia*

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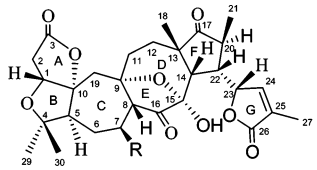
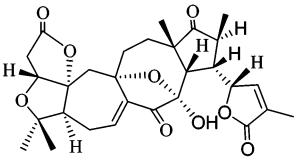
Six new nortriterpenoids, lancifodilactones I−N (**1**−**6**), as well as nine known ones, were isolated from the leaves and stems of *Schisandra lancifolia*. Their structures were elucidated on the basis of spectroscopic methods including 2D NMR analysis, and the structures of compounds **1** and **4** were further confirmed by single-crystal X-ray crystallography. In addition, all new compounds were tested for anti-HIV-1 activity.

Plants of the genus *Schisandra* are known to contain dibenzocyclooctadiene lignans and lanostane and cycloartane triterpenes, and some of them possess antihepatitis, antitumor, and anti-HIV activities.[1−6] Our group has reported a series of highly oxygenated nortriterpenoids from plants of this genus.[7−15] As part of our continuing work to discover more novel compounds from this genus, we reinvestigated the leaves and stems of *Schisandra lancifolia* (Rehd. et Wils) A. C. Smith (Schisandraceae), which led to the isolation of six new nortriterpenoids, lancifodilactones I−N (**1**−**6**), together with nine known compounds including lancifodilactones C−E (**7**−**9**),[7] micrandilactones A and D (**10**, **11**),[8−9] and henridilactones A−D (**12**−**15**).[10] In the present paper, we report the structural characterization of **1**−**6** and their anti-HIV-1 activities.

Chart 1



1 R = OH
2 R = OAc



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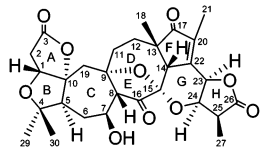

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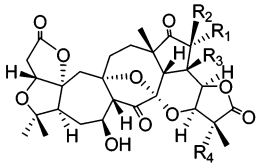
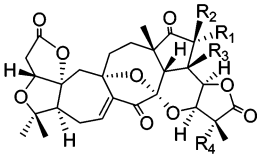


	R_1	R_2	R_3	R_4
4	H	Me	H	OH
7	H	Me	H	H
9	Me	H	H	OH
10	OH	Me	OH	H
11	OH	Me	H	H
15	Me	H	H	H



	R_1	R_2	R_3	R_4
6	H	Me	H	OH
8	H	Me	H	H
12	OH	Me	H	H
13	OH	Me	OH	H
14	Me	H	H	H

Results and Discussion

Compound **1** gave a quasi-molecular ion peak at *m*/*z* 567 [M + Na]$^+$ in its positive ESIMS spectrum and was assigned a molecular formula of $C_{29}H_{36}O_{10}$, which was confirmed by HRESIMS (found [M + Na]$^+$ 567.2395, calcd 567.2368) and NMR data. Obvious in the ^{1}H NMR spectrum were five methyl signals due to four tertiary methyls and a secondary methyl. The ^{13}C NMR and DEPT spectra of **1** exhibited signals for 29 carbons, including two ester groups, two ketone groups, six quaternary carbons (four oxygenated ones and an olefinic one), nine methines (three oxygenated ones and an olefinic one), five methylenes, and five methyls. This suggested that compound **1** was a highly oxygenated nortriterpene and contained seven rings. Careful investigation of the ^{1}H and ^{13}C NMR data of **1** revealed it was similar to that reported for lancifodilactone C (**7**),[7] which was also isolated in our present studies. Comparison of 1D NMR data, together with detailed HMBC and ^{1}H−^{1}H COSY analyses, identified the presence of rings A−F, which led to the establishment of partial structure **1a** (Figure 1). The NMR data for the remaining portion of the structure of **1** were quite distinctive from that of **7**. HMBC correlations from both H-23 and Me-27 to C-24, C-25, and C-26, along with the critical MS fragment at *m*/*z* 453 [M + Na − $C_5H_4O_2$]$^+$ and a base peak at *m*/*z* 119 [$C_5H_4O_2$ + Na]$^+$, indicated the presence of a five-membered α-methyl-α,*β*-unsaturated-*γ*-lactone ring (G), which established the partial structure **1b** (Figure 1). The additional HMBC correlation from H-24 to C-22, along with the ^{1}H−^{1}H COSY correlations, H-22/H-23/H-24, required direct connection of C-22 to C-23 and permitted fragments **1a** and **1b** to be joined together as shown (Figure 1).

The relative stereochemistry of **1** was established by single-crystal X-ray crystallography (Figure 3), together with analysis of ROESY NMR data (Figure 2). Biogenetically, H-5 was α- and C-18 was *β*-oriented.[9] The H-5 signal showed ROESY correlation with H-7, indicating α-orientation of H-7. ROESY correlations of Me-18 with H-14 and H-22 and of H-14 with Me-21 indicated that H-14, H-22, and Me-21 were *β*-oriented. The relative configurations of C-15 and C-23 were deduced as *S** and *R**, respectively, by X-ray diffraction experiment.

The molecular formula of **2** was deduced as $C_{31}H_{38}O_{11}$ from its HRESIMS and ^{13}C NMR data. Its ^{1}H NMR spectrum was very similar to that of **1**, except for a signal for an additional acetate group as a singlet at *δ* 2.07 and by the presence of additional carbon signals at *δ* 170.0 and 21.1. HMBC correlation of the signal at *δ* 5.80 (t, 1H, *J* = 8.3 Hz, H-7) with the carbonyl carbon of the acetate group indicated that the acetate group was located at C-7. The downfield chemical shift of H-7 from *δ* 4.72 in **1** to *δ* 5.80 in **2** also supported the above deduction. In addition, the ROESY

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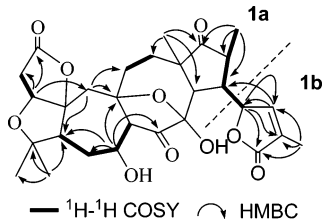


Figure 1. Selected HMBC and ^{1}H−^{1}H COSY correlations of **1**.

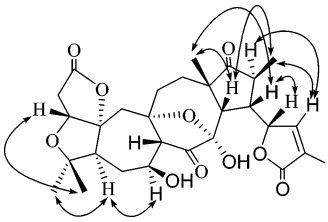
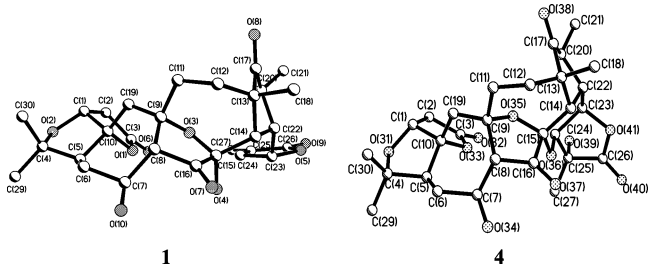


Figure 2. Selected ROESY correlations of **1**.



1 **4**

Figure 3. ORTEP drawings of **1** and **4**.

Table 1. ^{13}C NMR Assignments of **1**−**6**[a]

position	1	2	3	4	5	6
1	82.0 d	81.8 d	80.7 d	81.5 d	81.5 d	80.5 d
2	35.7 t	35.5 t	35.5 t	35.4 t	35.4 t	35.6 t
3	175.0 s	174.5 s	175.5 s	175.5 s	175.4 s	175.3 s
4	84.2 s	83.9 s	83.4 s	83.9 s	83.8 s	83.3 s
5	58.5 d	55.4 d	57.6 d	58.5 d	58.3 d	57.7 d
6	36.9 t	32.4 t	23.6 t	36.4 t	36.3 t	23.7 t
7	69.0 d	71.6 d	133.3 d	67.9 d	67.7 d	135.5 d
8	59.8 d	57.6 d	139.3 s	60.2 d	60.0 d	138.0 s
9	80.0 s	79.6 s	79.9 s	81.4 s	81.0 s	82.2 s
10	96.4 s	95.9 s	95.4 s	95.8 s	95.7 s	94.9 s
11	43.2 t	42.7 t	40.2 t	41.9 t	42.6 t	39.2 t
12	32.7 t	33.3 t	32.1 t	31.3 t	30.6 t	31.3 t
13	50.7 s	50.4 s	50.7 s	50.2 s	46.3 s	50.6 s
14	53.9 d	53.7 d	54.6 d	45.0 d	54.4 d	45.6 d
15	101.2 s	101.1 s	101.7 s	99.1 s	100.4 s	99.4 s
16	214.8 s	213.3 s	203.9 s	209.5 s	208.2 s	198.5 s
17	222.2 s	221.7 s	221.6 s	220.4 s	210.2 s	220.3 s
18	28.1 q	30.1 q	28.0 q	26.0 q	27.8 q	26.3 q
19	42.1 t	41.8 t	41.7 t	42.6 t	42.0 t	42.3 t
20	46.4 d	46.1 d	45.5 d	40.3 d	140.2 s	44.7 d
21	15.7 q	15.6 q	15.8 q	14.9 q	8.2 q	14.7 q
22	46.6 d	46.3 d	47.1 d	44.6 d	156.2 s	40.2 d
23	83.7 d	83.4 d	83.8 d	73.2 d	72.4 d	74.8 d
24	151.7 d	151.2 d	151.6 d	75.1 d	75.7 d	72.5 d
25	131.7 s	131.5 s	130.6 s	76.8 s	41.5 d	76.9 s
26	176.1 s	175.7 s	174.2 s	177.5 s	178.2 s	177.7 s
27	10.9 q	10.8 q	11.0 q	17.5 q	8.2 q	18.0 q
29	28.1 q	27.9 q	27.7 q	27.8 q	27.8 q	27.5 q
30	21.2 q	20.9 q	20.6 q	20.9 q	20.9 q	20.4 q
OAc		170.0 s				
		21.1 q				

[a] Spectra were recorded in C_5D_5N; chemical shifts (δ) are in ppm.

correlation of H-5 (δ 2.47) with H-7 suggested that the orientation of H-7 was α. Accordingly, the acetate group was assigned as β-oriented.

Compound **3** was isolated as white crystals and was determined to have the molecular formula $C_{29}H_{34}O_9$ by HRESIMS and ^{13}C NMR spectra, which indicated 18 mass units less than compound **1**. The ^{1}H and ^{13}C NMR data of **3** were closely comparable to those of **1**, except for the presence of two low-field signals at δ 133.3 and 139.3 and the absence of two methines due to C-7 and C-8 (δ 69.0 and 59.8). On the basis of these observations, it was reasonable to assume that **3** is a 7-dehydrated derivative of **1**, which was also supported by the abnormal upfield shift of C-6 by 13.3 ppm. HMBC correlations observed from the olefinic proton signal at δ 6.82 (H-7) to C-16 (δ 203.9) and C-9 (δ 79.9), from H_2-19 (δ 2.22/2.38) to C-8 (δ 139.3), and from H_2-6 (δ 2.02/2.12) to C-7 (δ 133.3) and C-8 (δ 139.3) corroborated the proposed structure of **3**.

Compound **4** crystallized as colorless prisms and has the molecular formula $C_{29}H_{36}O_{11}$ as deduced by HRESIMS (found $[M + Na]^+$ 583.2159, calcd 583.2155), which was the same as that of lancifodilactone E (**9**).[7] The NMR data of **4** were very similar to that of **9**. Analysis of HMBC and ^{1}H−^{1}H COSY spectra showed that the two compounds have an identical planar structure. Comparison of ^{1}H and ^{13}C NMR spectra revealed that the differences observed were in fact consistent with a change in the relative stereochemical orientation of the methyl group at C-20. The change at C-20 from *R** in **9** to *S** in **4** was hinted by the obvious differences of ^{1}H and ^{13}C NMR data as follows: H-20 (δ 2.87, m), Me-21 (δ 1.02, d, J = 7.1 Hz), and H-22 (δ 2.66, m) in **4** versus H-20 (δ 2.81, m), Me-21 (δ 1.48, d, J = 7.8 Hz), and H-22 (δ 3.46, m) in **9**; Me-21 (δ 14.9) and C-22 (δ 44.6) in **4** versus Me-21 (δ 12.4) and C-22 (δ 33.2) in **9**. The relative C-20 (*S**) stereochemistry in **4** was also supported by ROESY correlation of H-14/Me-21 and finally confirmed by an X-ray diffraction experiment (Figure 3).

Compound **5** was isolated as white crystals. HRESIMS analysis demonstrated that it has the molecular formula $C_{29}H_{34}O_{10}$, 18 mass units less than micrandilactone D (**11**).[9] From ^{1}H and ^{13}C NMR data, it was clear that **5** was closely related to **11**, as the chemical shifts of rings A−E, G, and H were very similar. Comparison of ^{1}H and ^{13}C NMR data of **5** with those of **11** showed that the differences can be rationalized by the replacement of an oxygenated quaternary carbon (C-20) and a methine (C-22) in **11** by two tetrasubstituted olefin carbons at δ 140.2 (C-20) and 156.2 (C-22) in **5**. This was confirmed by HMBC cross-peaks from Me-21 (δ 1.71) and H-24 (δ 5.26) to C-22 and from H-14 (δ 3.49) and H-23 (δ 5.64) to C-20.

HRESIMS analysis of compound **6** showed that it has the molecular formula $C_{29}H_{34}O_{10}$, indicating 18 mass units less than **4**. This suggested that **6** may be a dehydrated derivative of **4**. A side-by-side comparison of the ^{1}H and ^{13}C NMR data of **4** and **6** showed that the differences were two methines due to C-7 and C-8 (δ 67.9 and 60.2) in **4** replaced by two olefin carbon signals at δ 135.5 (C-7) and 138.0 (C-8) in **6**. This was confirmed by HMBC correlations from the olefinic proton signal at δ 7.08 (H-7) to C-16 (δ 198.5) and C-9 (δ 82.2), from H_2-19 (δ 2.24/2.38) to C-8, and from H_2-6 (δ 2.19) to C-7 and C-8. The observed upfield chemical shift of C-16 from δ 220.4 in **4** to δ 198.5 in **6** also supported this assignment.

The anti-HIV-1 activities of compounds **1**−**6** were evaluated in preventing the cytopathic effects of HIV-1 in C8166, and cytotoxicity was measured in parallel with the determination of antiviral activity using AZT as a positive control (EC_{50} = 0.0033 μg/mL and CC_{50} > 200 μg/mL). Compounds **1**−**6** showed anti-HIV-1 activities with EC_{50} in the range 76.6−100.0 μg/mL, and compounds **1**−**5** exerted minimal cytotoxicity against C8166 cells (CC50 > 200 μg /mL) (Table 3).

Experimental Section

General Experimental Procedures. Melting points were obtained on a XRC-1 micro melting point apparatus and are uncorrected. Optical rotations were measured with a Horiba SEPA-300 polarimeter. UV spectra were obtained using a Shimadzu UV-2401A spectrophotometer.

Table 2. ^{1}H NMR Assignments of Compounds **1**−**6**[a]

no.	1	2	3	4	5	6
1	4.29 (d, 5.6)	4.26 (d, 5.9)	4.21 (d, 6.0)	4.22 (d, 6.4)	4.15 (d, 6.0)	4.23 (d, 6.4)
2 α	3.15 (dd, 5.5,18.4)	3.09 (dd, 5.5, 18.3)	3.09 (dd, 5.5,18.6)	3.03 (dd, 6.0,18.1)	2.72 (d, 18.4)	3.13 (dd, 6.5, 18.6)
2 *β*	2.79 (d, 18.4)	2.76 (d, 18.3)	2.79 (d, 18.6)	2.72 (d, 18.1)	2.75 (dd, 5.8, 18.4)	2.74 (dd, 6.5, 18.6)
5	2.34 (overlapped)	2.47 (dd, 4.2, 12.8)	1.89 (overlapped)	2.48 (dd, 3.9, 13.2)	2.42 (dd, 3.8, 13.1)	2.19 (overlapped)
6 α	2.08 (m)	2.00 (m)	2.02 (m)	2.07 (m)	2.04 (overlapped)	2.19 (overlapped)
6 *β*			2.12 (m)	2.23 (m)	2.19 (m)	
7	4.72 (t, 8.0)	5.80 (t, 8.3)	6.82 (t, 7.9)	4.56 (dd, 9.4, 9.7)	4.47 (m)	7.08 (t, 6.0)
8	2.94 (d, 8.0)	2.95 (d, 8.3)		2.89 (d, 9.7)	2.95 (d, 10.1)	
11 α	1.70 (overlapped)	1.65 (m)	1.61 (m)	1.64 (m)	1.69 (m)	1.66 (m)
11 *β*	1.91 (m)	1.93 (m)	1.94 (overlapped)	1.93 (m)	2.04 (overlapped)	2.04 (m)
12 α	1.57 (m)	1.54 (m)	1.55 (m)	1.55 (m)	1.69 (m)	1.42 (m)
12 *β*	2.01 (m)	1.98 (m)	1.93 (overlapped)	1.81 (m)	1.65 (m)	1.85 (m)
14	3.22 (d, 7.9)	3.10 (d, 7.8)	3.13 (d, 7.7)	2.84 (d, 7.1)	3.49 (s)	2.74 (overlapped)
18	1.09 (s)	1.08 (s)	1.03 (s)	0.92 (s)	0.93 (s)	0.93 (s)
19 α	2.50 (AB d, 15.8)	2.50 (AB d, 15.5)	2.38 (AB d, 15.9)	2.40 (AB d, 15.4)	2.33 (AB d, 15.2)	2.38 (AB d, 15.9)
19 *β*	2.47 (AB d, 15.8)	2.40 (AB d, 15.5)	2.22 (AB d, 15.9)	2.29 (AB d, 15.4)	2.28 (AB d, 15.2)	2.24 (AB d, 15.9)
20	2.71 (m)	2.70 (m)	2.72 (m)	2.87 (m)		2.47 (m)
21	1.04 (d, 6.7)	0.96 (d, 6.8)	1.08 (d, 6.9)	1.02 (d, 7.1)	1.71 (s)	1.18 (d, 7.0)
22	3.07 (m)	3.06 (m)	3.05 (m)	2.66 (m)		2.89 (dd, 7.0, 12.6)
23	6.35 (br s)	6.26 (br s)	6.19 (br s)	5.15 (br s)	5.64 (br s)	5.18 (br s)
24	8.53 (br s)	8.49 (br s)	8.06 (br s)	5.17 (br s)	5.26 (br s)	4.68 (br s)
25					3.49 (m)	
27	2.31 (s)	2.30 (s)	1.82 (s)	1.68 (s)	1.26 (d, 7.3)	2.07 (s)
29	1.20 (s)	1.26 (s)	1.14 (s)	1.24 (s)	1.23 (s)	1.22 (s)
30	1.10 (s)	1.04 (s)	0.99 (s)	1.05 (s)	1.04 (s)	1.02 (s)
OAc		2.07 (s)				

[a] Spectra were recorded in C_5D_5N; chemical shifts (δ) are in ppm and J in Hz.

Table 3. Summary of Cytotoxicities and Anti-HIV-1 Activities of Compounds **1**−**6**

compound	cytotoxicity, CC_{50} (μg /mL)[a]	anti-HIV-1_{IIIB} activitiy, EC_{50} (μg/mL)	selectivity index, CC_{50}/EC_{50}
1	>200	96.4	>2.08
2	>200	88.3	>2.26
3	>200	78.5	>2.55
4	>200	100.0	>2.00
5	>200	76.6	>2.61
6	186.3	77.6	2.4
ATZ	>200	0.0033	>60606.1

[a] Minimal cytotoxicity against C8166 cells when CC_{50} > 200 (μg/mL).

A Tenor 27 spectrophotometer was used for scanning IR spectroscopy with KBr pellets. 1D and 2D NMR spectra were recorded on Bruker AM-400 and DRX-500 spectrometers. Unless otherwise specified, chemical shifts (δ) were expressed in ppm with reference to the solvent signals. Mass spectra were performed on a VG Autospec-3000 spectrometer at 70 eV. Column chromatography was performed using silica gel (200−300 mesh, Qing-dao Marine Chemical, Inc., Qingdao, China). Semipreparative HPLC was performed on an Agilent 1100 liquid chromatograph with a Zorbax SB-C_{18}, 9.4 mm × 25 cm, column. Preparative HPLC was performed on a Shimadzu LC-8A preparative liquid chromatograph with a Shimadzu PRC-ODS (K) column. Fractions were monitored by TLC, and spots were visualized by heating the silica gel plates sprayed with 10% H_2SO_4 in EtOH.

Plant Material. The leaves and stems of *S. lancifolia* were collected in Dali Prefecture, Yunnan Province, People's Republic of China, in August 2002. The specimen was identified by Prof. Su-Gong Wu, and a voucher specimen (No. KIB 2002-08-11) has been deposited at the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation. The plant material of *S. lancifolia* (5.7 kg) was ground and exhaustively extracted with 70% aqueous Me_2CO at room temperature. The solvent was evaporated in vacuo, and the crude extract (290 g) was dissolved in H_2O and partitioned with EtOAc. The EtOAc portion (101 g) was chromatographed on a silica gel column eluting with $CHCl_3$−Me_2CO (1:0, 9:1, 8:2, 2:1, 1:1, and 0:1) to afford fractions I−V. Fraction II (18.4 g) was repeatedly chromatographed on silica gel (200−300 mesh) and Sephadex LH-20 and finally by semipreparative HPLC (MeOH−H_2O, 45:55) to yield compounds **2** (7 mg), **5** (10 mg), and **11** (5 mg). Fraction III (25.9 g) was chromatographed on a silica gel column eluting with $CHCl_3$−MeOH (20:1 10:1, 5:1, 2:1, 1:1) to afford subfractions A−E. Subfraction B (5.1 g) was purified by recrystallization and repeated chromatography over silica gel, RP-18, and Sephadex LH-20 (MeOH) and followed by semipreparative and preparative HPLC (CH_3CN−H_2O, 35:65, and MeOH−CH_3CN−H_2O, 10:33:57) to yield compounds **1** (34 mg), **3** (6 mg), **4** (7 mg), **10** (16 mg), and **12** (22 mg). Similarly, subfractions C (3.6 g) and D (2.9 g) were respectively purified using the chromatography methods mentioned above, to yield compounds **6** (10 mg), **7** (23 mg), **8** (35 mg), **9** (9 mg), **13** (23 mg), **14** (14 mg), and **15** (18 mg).

Anti-HIV-1 Assay. The cytotoxicity assay against C8166 cells (CC_{50}) was assessed using the MTT method, and anti-HIV-1 activity was evaluated by the inhibition assay for the cytopathic effects of HIV-1 (EC_{50}).[16]

Lancifodilactone I (1): white crystals; mp 198−199 °C; $[\alpha]_D^{20}$ +98.8 (*c* 0.7, MeOH); UV (MeOH) λ_{max} (log ϵ) 209 (3.46) nm; IR (KBr) ν_{max} 3460, 2972, 2932, 2873, 1753, 1653, 1458, 1379, 1317, 1232, 1202, 1100, 1017, 924, 867, 758, 682 cm^{-1}; ^{1}H and ^{13}C NMR data, see Tables 1 and 2; positive ESIMS *m*/*z* $[M + Na]^+$ 567; HRESIMS *m*/*z* $[M + Na]^+$ 567.2395 (calcd 567.2386 for $C_{29}H_{36}O_{10}$-Na).

Lancifodilactone J (2): white crystals; mp 196−197 °C; $[\alpha]_D^{22}$ +88.8 (*c* 0.5, MeOH); UV (MeOH) λ_{max} (log ϵ) 210 (3.55) nm; IR (KBr) ν_{max} 3457, 2976, 2922, 2853, 1741, 1643, 1455, 1377, 1311, 1212, 1902, 1108, 1007, 929, 857 cm^{-1}; ^{1}H and ^{13}C NMR data, see Tables 1 and 2; positive ESIMS *m*/*z* $[M + Na]^+$ 609; HRESIMS *m*/*z* $[M + Na]^+$ 609.6267 (calcd 609.6262 for $C_{31}H_{38}O_{11}Na$).

Lancifodilactone K (3): white crystals; mp 186−187 °C; $[\alpha]_D^{20}$ +77.5 (*c* 0.3, MeOH); UV (MeOH) λ_{max} (log ϵ) 211 (3.89) nm; IR (KBr) ν_{max} 3441, 2979, 2912, 2833, 1744, 1633, 1458, 1387, 1321, 1215, 1912, 1101, 1007, 921, 850 cm^{-1}; ^{1}H and ^{13}C NMR data, see

Tables 1 and 2; positive ESIMS *m/z* $[M + Na]^+$ 549; HRESIMS *m/z* $[M + Na]^+$ 549.5744 (calcd 549.5738 for $C_{29}H_{34}O_9Na$).

Lancifodilactone L (4): white crystals; mp 180−181 °C; $[\alpha]_D^{26}$ +46.5 (*c* 0.4, MeOH); UV (MeOH) λ_{max} (log ϵ) 204 (3.88) nm; IR (KBr) ν_{max} 3467, 2927, 2854, 1779, 1734, 1632, 1458, 1378, 1236, 1206, 1097, 1009, 926, 590 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; positive ESIMS *m/z* $[M + Na]^+$ 583; HRESIMS *m/z* $[M + Na]^+$ 583.2159 (calcd 583.2155 for $C_{29}H_{36}O_{11}Na$).

Lancifodilactone M (5): white crystals; mp 185−186 °C; $[\alpha]_D^{26}$ +104.6 (*c* 0.3, MeOH); UV (MeOH) λ_{max} (log ϵ) 200 (3.00) nm; IR (KBr) ν_{max} 3523, 3445, 2976, 2943, 1778, 1755, 1704, 1459, 1380, 1233, 1219, 1156, 1103, 1066, 982, 929, 681, 594 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; positive ESIMS *m/z* $[M + Na]^+$ 565; HRESIMS *m/z* $[M + Na]^+$ 565.2040 (calcd 565.2049 for $C_{29}H_{34}O_{10}$-Na).

Lancifodilactone N (6): white crystals; mp 203−204 °C; $[\alpha]_D^{18}$ +117.4 (*c* 0.3, MeOH); UV (MeOH) λ_{max} (log ϵ) 204 (2.98) nm; IR (KBr) ν_{max} 3546, 3499, 3448, 2925, 1786, 1742, 1665, 1458, 1382, 1232, 1212, 1108, 1068, 1007, 921, 872, 735 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; positive ESIMS *m/z* $[M + Na]^+$ 565; HRESIMS *m/z* $[M + Na]^+$ 565.2045 (calcd 565.2049 for $C_{29}H_{34}O_{10}$-Na).

X-ray crystal structure of lancifodilactone I (1): $C_{29}H_{36}O_{10}$, M = 544.60, monoclinic, space group $P2_1$, a = 12.319(1) Å, b = 18.355(1) Å, c = 14.218(1) Å, β = 73.37(4)°, V = 3080.4(2) $Å^3$, Z = 2, d = 1.209 g/cm^3, a crystal of dimensions 0.15 × 0.20 × 0.35 mm was used for measurements on a MAC DIP-2030K diffractometer with a graphite monochromator ($\omega-2\theta$ scans, $2\theta_{max}$ = 50.0°), Mo Kα radiation. The total number of independent reflections measured was 5843, of which 5639 were observed ($|F|^2 \geq 2\sigma|F|^2$). Final indices: R_1 = 0.0819, wR_2 = 0.1336, S = 1.164, $(\Delta/\sigma)_{max}$ = 0.086, $(\Delta\rho)_{min}$ = −0.283 $e/Å^3$, $(\Delta\rho)_{max}$ = 0.650 $e/Å^3$. The crystal structure of **1** was solved by direct methods using SHELX-86[17] and expanded using difference Fourier techniques, refined by the program and method NOMCSDP[18] and full-matrix least-squares calculations. The CIF file of X-ray data of **1** has been deposited in the Cambridge Crystallographic Data Centre (deposition number: 295263).

X-ray crystal structure of lancifodilactone L (4): $C_{29}H_{36}O_{11}$, M = 560.60, monoclinic, space group $P2_1$, a = 8.428(1) Å, b = 16.075-(1) Å, c = 11.381(1) Å, β = 84.144(1)°, V = 1533.8(2) $Å^3$, Z = 2, d = 1.331 g/cm^3, a crystal of dimensions 0.10 × 0.10 × 0.40 mm was used for measurements on a MAC DIP-2030K diffractometer with a graphite monochromator ($\omega-2\theta$ scans, $2\theta_{max}$ = 50.0°), Mo Kα radiation. The total number of independent reflections measured was 3236, of which 2566 were observed ($|F|^2 \geq 3\sigma|F|^2$). Final indices: R_f = 0.0798, R_w = 0.1013 ($w = 1/\sigma|F|^2$). The crystal structure of **4** was solved using the same methods as those of **1**.[17,18] The CIF file of X-ray data of **4** was deposited in the Cambridge Crystallographic Data Centre (deposition number: 295264).

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