Lancifodilactones B−E, New Nortriterpenes from *Schisandra lancifolia*

Rong-Tao Li, Wei Xiang, Sheng-Hong Li, Zhong-Wen Lin, and Han-Dong Sun*

State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, People's Republic of China

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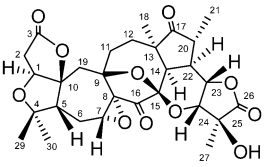
Four new nortriterpenes, lancifodilactones B−E (**1**−**4**), were isolated from the leaves and stems of *Schisandra lancifolia*. Their structures were determined by analysis of 1D and 2D NMR spectroscopic data. These compounds are members of a new highly oxygenated cycloartane skeletal class with a biosynthetically modified eight-membered ring D.

Plants belonging to the family Schisandraceae have proved to be a rich source of dibenzocyclooctadiene lignans, as well as lanostane and cycloartane triterpenes, which have been found to possess many beneficial pharmacological effects. A few examples of biological activities for triterpenoids have been reported, including anti-HIV, antitumor, and antihepatitis activities and inhibitory activity on cholesterol biosynthesis.[1−7]

Our previous phytochemical study on *Schisandra sphaerandra* (Rehd. et Wils.) A. C. Smith resulted in the isolation of a new compound, nigranoic acid, which showed inhibitory activity in anti-HIV reverse transcriptase and polymerase assays.[8] As a continuation of our investigation on plants in the Schisandraceae, we have examined the chemical constituents of *Schisandra lancifolia*. In a preceding paper, we have described the isolation of a unique bisnortriterpenoid, lancifodilactone A, from the EtOAc extract of the leaves and stems of this plant.[9] We report herein on the isolation and structural elucidation of four additional nortriterpene lactones, lancifodilactones B−E (**1**−**4**), from the same extract. Lancifodilactones B−E are cycloartane derivatives structurally related to micrandilactone A (**5**),[10] which was originally isolated as a new compound with an unusual highly oxygenated cycloartane skeleton from *S. micrantha*.

A 70% aqueous acetone extract of the leaves and stems of *S. lancifolia* was partitioned successively with petroleum ether and EtOAc. The EtOAc layer was dried and subjected to several chromatographic purification steps to afford **1**−**4**.

Lancifodilactone B (**1**) analyzed for $C_{29}H_{34}O_{11}$ by HRE-IMS (found 558.2119, calcd 558.2101), an elemental formula indicating 13 degrees of unsaturation. The IR spectrum showed that hydroxyl (3560−3250 cm^{-1}), carbonyl (1734 cm^{-1}), and γ-lactone (1785 cm^{-1}) functionalities are present in **1**. The ^1H NMR spectrum of **1** (Table 1) exhibited signals due to four tertiary methyls (δ 0.93, 0.96, 1.23, and 2.12) and a secondary methyl (δ 1.13, d, J = 7.0 Hz). The ^{13}C NMR spectrum (Table 2) showed signals for 29 carbons, while the DEPT NMR spectrum indicated the presence of five methyl groups, five methylene carbons, eight methine carbons (including four oxygenated ones), and 11 quaternary carbons (including two ester groups, two carbonyl groups, and six oxygenated carbons). The presence of these features revealed that a total of 33 protons were attached to carbons, implying the presence of only one hydroxyl group in the molecule of **1**. This also suggested that compound **1** is a highly oxygenated nortriterpene containing nine rings. On careful investigation, the ^{13}C NMR spectral data of **1** [C-1 (δ 80.7, d), C-2 (δ 35.3, t), C-3 (δ 175.1, s), C-4 (δ 83.5, s), C-10 (δ 95.5, s), C-15 (δ 98.4, s), C-16 (δ 208.0, s), C-17 (δ 220.0, s), and C-26 (δ 177.6, s)] were found to be in close agreement with those of micrandilactone A (**5**),[10] suggesting that two compounds are closely related.



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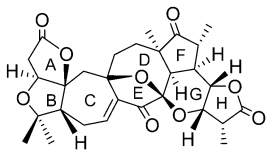

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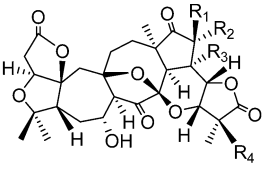

2 $R_1 = R_3 = R_4 = H$ $R_2 = CH_3$
4 $R_1 = CH_3$ $R_2 = R_3 = H$ $R_4 = OH$
5 $R_1 = R_3 = OH$ $R_2 = CH_3$ $R_4 = H$

The structure elucidation of compound **1** was mainly restricted to the differences with respect to **5** and analysis of its HMBC spectral data. The Me-21 signals in the ^1H and ^{13}C NMR spectra were shifted upfield from **5** (δ_H 1.77, s; δ_C 18.9) to **1** (δ_H 1.13, d, J = 7.0 Hz; δ_C 14.6). Moreover, a methine resonance corresponding to H-14 was shifted upfield to δ_H 2.72 (d, J = 7.3 Hz) in **1** from that of δ_H 3.31 (s) in the case of **5**. This information, along with the lack of two hydroxyl group signals (OH-20, δ 5.90; OH-22, δ 7.56), as found in **5**, suggested that **1** is a 20,22-dideoxy derivative of **5**. The oxygenated quaternary carbon resonances of C-20 (δ_C 80.2) and C-22 (δ_C 75.5) in compound **5** were absent and replaced in the case of **1** by two methines (δ_C 44.6 and 40.0), agreeing with the above assignments. This was also confirmed by HMBC correlations (Figure 1) observed from Me-21 (δ_H 1.13) to C-17, C-20, and C-22, from H-22 (δ_H 2.91) to C-15 and Me-21 (δ_C 14.6), and from H-14 (δ_H 2.72) to Me-18 (δ_C 26.5) and C-20. In addition, a methyl singlet resonance at δ 2.12, corresponding to Me-27, showed HMBC cross-peaks with an oxygenated quaternary carbon (δ_C 77.0, C-25), a lactone carbonyl (δ_C 177.6, C-26), and an

* To whom correspondence should be addressed. Tel: (86) 871-5223251. Fax: (86) 871-5216343. E-mail: hdsun@mail.kib.ac.cn.

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Table 1. ^{1}H NMR Spectroscopic Data of Compounds **1**−**4**[a]

position	1	2	3	4
1	4.22 (d, 6.0)	4.23 (d, 6.3)	4.24 (d, 6.5)	4.25 (d, 6.1)
2α	2.77 (d, 18.4)	2.73 (d, 18.6)	2.78 (d, 18.6)	2.76 (d, 18.7)
2β	3.15 (dd, 6.0, 18.4)	3.04 (dd, 6.3, 18.6)	3.14 (dd, 6.5, 18.6)	3.05 (dd, 6.1, 18.7)
5	2.42 (dd, 2.8, 14.6)	2.45 (dd, 4.6, 13.4)	2.16 (overlap)	2.50 (dd, 4.4, 13.3)
6α	1.42 (m)	2.05 (m)	2.14 (m)	2.10 (m)
6β	2.22 (m)	2.17 (m)	2.14 (m)	2.23 (m)
7	3.92 (dd, 6.0, 7.3)	4.49 (dd, 9.3, 9.6)	7.03 (m)	4.56 (dd, 9.2, 9.6)
8		2.87 (d, 9.6)		2.87 (d, 9.6)
11α	1.92 (m)	1.66 (m)	1.65 (m)	1.55 (m)
11β	1.92 (m)	1.92 (m)	2.03 (m)	2.15 (overlap)
12α	1.68 (m)	1.56 (m)	1.41 (m)	1.64 (m)
12β	1.99 (m)	1.82 (m)	1.85 (m)	1.79 (m)
14	2.72 (d, 7.3)	2.79 (overlap)	2.71 (d, 5.8)	2.85 (d, 8.2)
18	0.93 (s)	0.91 (s)	0.93 (s)	0.96 (s)
19α[b]	2.29 (ABd, 16.1)	2.39 (ABd, 15.8)	2.33 (ABd, 15.8)	2.45 (ABd, 16.0)
19β[b]	2.17 (ABd, 16.1)	2.27 (ABd, 15.8)	2.24 (ABd, 15.8)	2.17 (ABd, 16.0)
20	2.52 (m)	2.62 (m)	2.52 (m)	2.81 (m)
21	1.13 (d, 7.0)	1.10 (d, 7.0)	1.23 (d, 6.8)	1.48 (d, 7.8)
22	2.91 (dd, 7.3, 13.3)	2.80 (m)	2.83 (dd, 5.8, 10.3)	3.46 (dd, 8.2, 11.6)
23	5.24 (br s)	4.63 (br s)	4.49 (br s)	5.40 (br s)
24	4.94 (d, 1.5)	5.25 (dd, 1.5, 2.0)	4.69 (dd, 1.8, 2.0)	4.98 (d, 1.4)
25		3.19 (m)	3.08 (m)	
27	2.12 (s)	1.21 (d, 7.3)	1.60 (d, 7.0)	1.60 (s)
29	1.23 (s)	1.23 (s)	1.22 (s)	1.22 (s)
30	0.96 (s)	1.05 (s)	1.01 (s)	1.06 (s)
OH-7				5.11 (overlap)
OH-25				8.79 (s)

[a] Data were determined at 500 MHz in pyridine-d_5 with chemical shifts in ppm and coupling constants in Hz. [b] Two-proton AB doublets.

Table 2. ^{13}C NMR Spectroscopic Data of Compounds **1**−**4**[a]

carbon	1	2	3	4
1	80.7 d	81.4 d	80.6 d	81.5 d
2	35.3 t	35.3 t	35.7 t	35.1 t
3	175.1 s	175.6 s	175.5 s	175.3 s
4	83.5 s	83.7 s	83.5 s	84.0 s
5	54.2 d	58.4 d	57.8 d	58.2 d
6	28.0 t	36.2 t	23.8 t	36.6 t
7	63.9 d	67.6 d	135.5 d	68.0 d
8	61.1 s	56.0 d	138.2 s	60.5 d
9	80.1 s	81.2 s	82.2 s	81.4 s
10	95.5 s	95.7 s	95.1 s	96.0 s
11	36.0 t	41.8 t	39.4 t	40.9 t
12	31.7 t	30.9 t	31.5 t	30.3 t
13	50.7 s	50.2 s	50.7 s	49.8 s
14	46.2 d	45.0 d	45.8 d	45.5 d
15	98.4 s	98.7 s	99.2 s	98.3 s
16	208.0 s	209.5 s	198.7 s	209.1 s
17	220.0 s	220.3 s	220.5 s	221.6 s
18	26.5 q	26.0 q	26.5 q	25.9 q
19	38.9 t	42.4 t	42.3 t	42.5 t
20	44.6 d	44.7 d	45.0 d	41.1 d
21	14.6 q	14.9 q	15.0 q	12.4 q
22	40.0 d	40.1 d	40.3 d	33.2 d
23	74.5 d	75.4 d	75.4 d	74.6 d
24	72.4 d	69.2 d	68.6 d	75.6 d
25	77.0 s	42.0 d	42.5 d	76.9 s
26	177.6 s	177.9 s	178.3 s	177.1 s
27	17.7 q	7.9 q	8.6 q	17.5 q
29	27.5 q	27.7 q	27.7 q	27.8 q
30	20.4 q	20.8 q	20.6 q	21.0 q

[a] Data were determined at 125 MHz in pyridine-d_5, and chemical shifts are in ppm.

oxygenated methine (δ_C 72.4, C-24), suggesting that the hydroxyl group is located at C-25. This placement was consistent with the downfield shift of the neighboring carbon signal at δ_C 17.7 (Me-27).

Carbon signals observed at δ_C 63.9 (d) and 61.1 (s) and a proton signal at δ_H 3.92 (1H, dd, J = 6.0, 7.3 Hz) indicated a trisubstituted epoxide in **1**. The epoxide group was positioned between C-7 and C-8 on the basis of HMBC correlations, which showed that the H-5 (δ_H 2.42) and H_2-6 (δ_H 1.42/2.22) resonances were correlated with C-7 (δ_C 63.9), and H-7 (δ_H 3.92) was correlated with C-6 (δ_C 28.0) and C-8 (δ_C 61.1), while H_2-11 (δ_H 1.92) and H_2-19 (δ_H 2.17/2.29) both correlated with C-8. These assignments were in agreement with the observation that the signals for C-5, C-6, C-7, and C-9 in **1** were shifted upfield to δ_C 54.2, 28.0, 63.9, and 80.1 from those of δ_C 58.3, 36.4, 67.8, and 82.2 in **5**.

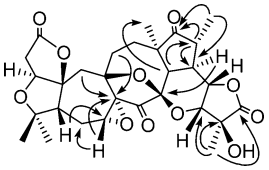

Figure 1. Key HMBC correlations for lancifodilactone B (**1**).

The relative stereochemistry of compound **1** was elucidated by analysis of ^{1}H NMR J values and ROESY data and by analogy with micrandilactone A (**5**).[10] The H-5 signal showed ROESY correlations with H-7, indicating a β-orientation of H-7. ROESY correlations for Me-18/H-14 and H-22, H-23/H-20, and H-24/H-20 indicated that H-14 and H-22 were α-oriented and H-23 and H-24 were β-oriented. Moreover, the ^{1}H NMR signal of H-24 displayed a small coupling (δ_H 4.94, d, J = 1.5 Hz) with H-23 and implied a small dihedral angle between H-23 and H-24, further confirming the β-orientations of both H-23 and H-24. From these results, it was concluded that **1** has the same relative configuration as shown in **5**. Accordingly, on the basis of all the above evidence, the structure of **1** was established as the 7,8-epoxy-20,22-dideoxy derivative of micrandilactone A (**5**), named lancifodilactone B.

The molecular formula of lancifodilactone C (**2**) was determined to be $C_{29}H_{36}O_{10}$ (12 unsaturations), from its HRESIMS (found $[M + Na]^+$ 567.2203, calcd 567.2206) and NMR data. The IR spectrum exhibited absorptions due to hydroxyl (3530−3210 cm^{-1}), γ-lactone (1770 cm^{-1}), and ketone carbonyl (1712 cm^{-1}) groups. The ^{13}C NMR spectrum (Table 2) exhibited signals for nine quaternary

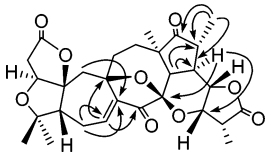

Figure 2. Key HMBC correlations for lancifodilactone D (**3**).

carbons (including two ester groups, two carbonyl groups, and four oxygenated carbons), 10 methines, five methylenes, and five methyls. The ^{1}H NMR spectrum (Table 1) of **2** showed signals for three tertiary methyls (δ_H 0.91, 1.05, and 1.23) and two secondary methyls (δ_H 1.10, d, J = 7.0 Hz, and 1.21, d, J = 7.3 Hz). In addition, typical signals of two proton AB doublets at δ_H 2.39 and 2.27 (d, J = 15.8 Hz) were assigned to H-19α and H-19β. A further three resonances, appearing as an ABX spin system at δ_H 4.23 (1H, d, J = 6.3 Hz), δ_H 2.73 (1H, d, J = 18.6 Hz), and δ_H 3.04 (1H, dd, J = 6.3, 18.6 Hz), were assigned to H-1, H-2α, and H-2β, respectively. Moreover, a diagnostic oxymethine signal at δ_H 4.49 (dd, J = 9.3, 9.6 Hz) was the H-7 resonance. All these data revealed that compound **2** possesses the same skeleton as **1** and **5**.

A side-by-side comparison of the ^{1}H and ^{13}C NMR spectral data of **2** and **5** showed that the hydrogen and carbon atom shifts of the rings A−E in **2** are highly comparable with those of **5**. This strongly suggested the similarity of the moiety of rings A−E for **2** and **5** and the differences in the substitution nature of the rings F and G. HMBC correlations were observed between Me-21 (δ 1.10) and C-20 (δ 44.7), C-22 (δ 40.1), and C-17 (δ 220.3) and between H-14 (δ 2.79) and C-20 and C-22, in conjunction with the ^{1}H−^{1}H COSY spin system of H-14/H-22/H-23/H-24, establishing the structure of compound **2** as 20,22-dideoxylmicrandilactone A. The relative stereochemistry of compound **2** was assumed to be the same as that of **5** due to the similarity of proton−proton coupling constants and from the following significant ROESY correlations: H-5/H-7, Me-18/H-14, H-14/Me-21, H-20/H-23, H-20/H-24, H-23/H-25, Me-29/H-5, and Me-30/H-1.

Compound **3**, which was named lancifodilactone D, was isolated as a UV-active (λ_{max} 243 nm) substance, and the molecular formula of $C_{29}H_{34}O_9$ was established by HRES-IMS (found $[M + Na]^+$ 549.2098, calcd 549.2100) and from its ^{13}C NMR spectrum, which indicated 18 mass units less than compound **2**. Comparison of the IR spectrum of **3** with that of **2** indicated the presence of γ-lactone (1776 cm^{-1}), ketone carbonyl (1738 cm^{-1}), α,β-unsaturated ketone (1662 cm^{-1}), and olefin groups (1635 cm^{-1}), but with the absence of a hydroxyl group. The ^{1}H and ^{13}C NMR spectral data of **3** (Tables 1 and 2) were closely comparable to those of **2**, except for the presence of two low-field signals at δ_C 135.5 (d) and δ_C 138.2 (s) and the absence of two methines due to C-7 and C-8 (δ_C 67.6 and 56.0). On the basis of these observations, it was reasonable to assume that **3** is a 7-dehydrated derivative of **2**. HMBC cross-peaks (Figure 2) observed between the olefinic proton signal at δ_H 7.03 (H-7) and C-16 (δ_C 198.7) and C-9 (δ_C 82.2), between H_2-19 (δ_H 2.24/2.33) and C-8 (δ_C 138.2), and between H_2-6 (δ_H 2.14) and C-7 (δ_C 135.5) and C-8 fully corroborated the proposed structure of **3**. This assignment was in accord with the observation of the C-6 signal being shifted upfield by 12.4 ppm and the C-9 signal being shifted downfield by 1.0 ppm. Therefore, lancifodilactone D (**3**) was established similarly as 20,22-dideoxy-7(8)-ene micrandilactone A.

HRFABMS analysis of lancifodilactone E (**4**) demonstrated that it has the molecular formula $C_{29}H_{36}O_{11}$, differing from **2** by the addition of one oxygen atom. The

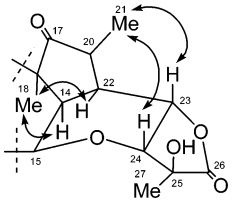

Figure 3. Selected ROESY correlations for lancifolilactone E (**4**).

NMR data of **4** revealed a close relationship to compound **2** (Tables 1 and 2), in particular in rings A−E. However, the secondary methyl resonance at δ_H 1.21 (d, J = 7.3 Hz) corresponding to Me-27 in **2** was shifted downfield to δ_H 1.60 (s) in **4**. This observation, along with the appearance of an additional hydroxyl signal at δ_H 8.79 (s), indicated the presence of a 25-hydroxyl group. The HMBC correlations from the hydroxyl to the oxygenated quaternary carbon at δ_C 76.9 (C-25) and the ketone carbon at δ_C 177.1 (C-26) and from Me-27 to C-24 (δ_C 75.6), C-25, and C-26 further supported the above assignment. A detailed comparison of the ^{1}H and ^{13}C NMR spectra of **2** and **4** revealed that other differences observed between these compounds 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 **2** to *S* in **4** was clearly indicated by the following differences in the ^{1}H NMR spectra data: H-20 (δ_H 2.81, m), Me-21 (δ_H 1.48, d, J = 7.8 Hz), and H-22 (δ_H 3.46, dd, J = 8.2, 11.6 Hz) in **4** versus δ_H 2.62 (m), δ_H 1.10 (d, J = 7.0 Hz), and δ_H 2.80 (m) in **2**. The relative C-20 (*S*) stereochemistry was also evident from the key ROESY correlations of Me-21/H-23, Me-21/H-24 as shown in Figure 3. The ^{1}H and ^{13}C NMR spectra for **4**, together with the analysis of J values and COSY and ROESY experiments, showed that all other common stereochemical elements remained unchanged. Thus, compound **4** was assigned as 21β-methyl-20,22-dideoxy-25-hydroxymicrandilactone A.

Experimental Section

General Experimental Procedures. Melting points were recorded on an XRC-1 micro melting point apparatus and are uncorrected. Optical rotations were measured in a Horiba SEPA-300 polarimeter. UV spectra were measured using a Shimadzu UV-2401PC spectrophotometer. IR spectra were obtained on a Bio-Rad Win infrared spectrophotometer. 1D and 2D NMR experiments were performed on Bruker AM-400 and DRX-500 instruments with TMS as internal standard. Chemical shifts (δ) were expressed in ppm with reference to the solvent signals. EI (70 eV) mass spectra were obtained on a VG Auto Spec-3000 spectrometer. Column chromatography was performed on silica gel (200−300 mesh, Qingdao Marine Chemical Inc., Qingdao, People's Republic of China) or on silica gel H (10−40 μm, Qingdao Marine Chemical Inc.) and over porous resin D101 (Chemical Factory of Tianjin University, Tianjin, People's Republic of China). Fractions were monitored by TLC, and spots were visualized by heating silica gel plates sprayed with 10% H_2SO_4 in EtOH.

Plant Material. The leaves and stems of *Schisandra lancifolia* were collected in Dali, Yunnan, People's Republic of China, in May 1999. A voucher specimen (No. KIB 99-5-20) was deposited in the Herbarium of the Department of Taxonomy, Kunming Institute of Botany, the Chinese Academy of Sciences, and was identified by Su-Gong Wu.

Extraction and Isolation. The air-dried and powdered stems and leaves (1.9 kg) of *S. lancifolia* were extracted three times with 70% aqueous Me_2CO at room temperature and filtered. The filtrate was concentrated and partitioned successively with petroleum ether and EtOAc. The EtOAc layer (31 g) was solubilized, absorbed on 50 g of silica gel, and chro-

matographed on a prepacked (200 g) silica gel column. Gradient elution was accomplished with $CHCl_3$−Me_2CO (1:0−0:1) to give fractions 1−6. Fraction 2 (1.5 g) was chromatographed over porous resin D-101 by elution with 90% aqueous ethanol to afford two fractions: 2a and 2b. Fraction 2a was subjected to column chromatography on silica gel, eluting with petroleum ether−Me_2CO (8:2) and $CHCl_3$−MeOH (100:1), respectively, to give **2** (18 mg) and **3** (35 mg). Fraction 3 (4.5 g) was chromatographed on MCI-gel CHP 20P (50%−90% MeOH−H_2O) to afforded three main fractions, 3a−c. Fraction 3a was subjected to column chromatography on silica gel using $CHCl_3$−MeOH (100:1) as eluent to give **4** (14 mg). Fraction 3b was further purified using column chromatography on RP-18 by eluting with 55% MeOH−H_2O to yield **1** (13 mg).

Lancifodilactone B (1): colorless needles from acetone; mp 222−224 °C; $[\alpha]_D$ +55.12° (*c* 0.25, C_5H_5N); UV (MeOH), end absorption; IR (KBr) ν_{max} 3560−3250, 2930, 1785, 1734, 1457, 1214, 1185, 1112, 1009 cm^{-1}; ^1H and ^{13}C NMR spectral data, see Tables 1 and 2; EIMS (70 eV) *m*/*z* 558 $[M]^+$ (1), 540 (10), 526 (10), 514 (91), 498 (12), 470 (20), 438 (8), 411 (42), 263 (14), 189 (14), 175 (25), 149 (22), 121 (23), 109 (37), 95 (47); HREIMS *m*/*z* 558.2119 (calcd for $C_{29}H_{34}O_{11}$ 558.2101).

Lancifodilactone C (2): colorless prisms from MeOH; mp 209−211 °C; $[\alpha]_D$ +47.74° (*c* 0.20, C_5H_5N); UV (MeOH), end absorption; IR (KBr) ν_{max} 3530−3210, 2974, 2922, 1770, 1712, 1457, 1378, 1234, 1093, 1008, 985, 927 cm^{-1}; ^1H and ^{13}C NMR spectral data, see Tables 1 and 2; EIMS (70 eV) *m*/*z* 544 $[M]^+$ (3), 516 (30), 498 (42), 483 (26), 456 (62), 438 (45), 265 (36), 247 (55), 205 (45), 189 (20), 149 (25), 110 (38), 95 (50); HRESIMS *m*/*z* 567.2203 $[M + Na]^+$ (calcd for $C_{29}H_{36}O_{10}Na$ 567.2206).

Lancifodilactone D (3): colorless prisms from MeOH; mp 230−232 °C; $[\alpha]_D$ +80.77° (*c* 0.26, C_5H_5N); UV (MeOH) λ_{max} (log ϵ) 243 nm (3.89); IR (KBr) ν_{max} 2971, 2940, 1776, 1738, 1662, 1635, 1177, 1155, 1111, 1071 cm^{-1}; ^1H and ^{13}C NMR spectral data, see Tables 1 and 2; EIMS (70 eV) *m*/*z* 526 $[M]^+$ (84), 511 (25), 498 (30), 483 (18), 466 (22), 438 (52), 275 (35), 187 (32), 155 (40), 109 (42), 95 (58); HRESIMS *m*/*z* 549.2098 $[M + Na]^+$ (calcd for $C_{29}H_{34}O_9Na$ 549.2100).

Lancifodilactone E (4): colorless prisms from acetone; mp 200 °C; $[\alpha]_D$ +70.42° (*c* 0.21, MeOH); UV (MeOH), end absorption; IR (KBr) ν_{max} 3580−3440, 2935, 1778, 1734, 1634, 1457, 1379, 1204, 1114, 1098, 1009 cm^{-1}; ^1H and ^{13}C NMR spectral data, see Tables 1 and 2; EIMS (70 eV) *m*/*z* 542 $[M - H_2O]^+$ (30), 524 (10), 514 (35), 498 (30), 472 (20), 454 (47), 413 (22), 395 (16), 275 (17), 247 (20), 205 (20), 187 (30), 149 (35), 119 (30), 109 (42), 95 (60); positive FABMS *m*/*z* 561 $[M + 1]^+$ (92), 501 (100); HRFABMS *m*/*z* 583.2142 $[M + Na]^+$ (calcd for $C_{29}H_{36}O_{11}Na$ 583.2155).

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