Four New Schisanartane-Type Nortriterpenoids from *Schisandra propinqua* var. *propinqua*

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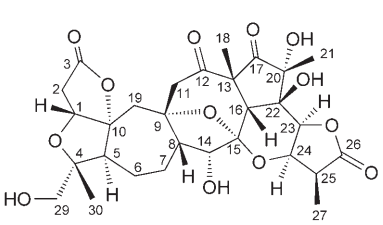
Four new, highly oxygenated nortriterpenoids with the unique schisanartane skeleton, propindilactones A–D (**1**–**4**), were isolated from the aerial parts of *Schisandra propinqua* var. *propinqua*, together with four known schisanartane-type compounds. The structures of the new plant constituents were established on the basis of extensive spectroscopic methods.

Introduction. – Plants of the genus *Schisandra* belong to the economically and medicinally important Schisandraceae family. More than 19 *Schisandra* species are widely used in traditional Chinese medicine (TCM) [1]. The medicinal relevant part are mostly fruits, which were found to be a rich source of lignans, especially of dibenzocyclooctadiene, with various biological activities [2][3]. In western China, aerial parts of this genus are also used for the treatment of rheumatic lumbago, traumatic injury, and related diseases.

In 2003, a highly oxygenated nortriterpenoid, micrandilactone A, with a unique schisanartane skeleton was isolated from the stems of *S. micrantha* [4]. Since then, a series of phytochemical studies on the aerial parts of *Schisandra* plants have been carried out in our group, and more than 60 compounds derived from three basic skeletons – schisanartane, schiartane, and 18-norschiartane – were reported [4–6]. Some of them were even found to exhibit potent anti-HIV-1 activity [5]. These discoveries triggered great interest among phytochemists, synthetic chemists, and pharmacologists.

With the aim of identifying new natural compounds with interesting biological activities as promising leads for drug development, another *Schisandra* species, *Schisandra propinqua* var. *propinqua*, indigenous to Yunnan Province, was phytochemically investigated. Herein we report the isolation and structural elucidation of four new schisanartane-type triterpenoids, propindilactones A–D (**1**–**4**), together with four known triterpenoids, micrandilactone A (**5**) [4], micrandilactones E (**6**) and D (**7**) [6], and henridilactone B (**8**) [7].

Results and Discussion. – Propindilactone A (**1**), obtained as an amorphous powder, showed the $[M-H]^-$ quasi-molecular ion peak at *m/z* 591 in its negative FAB mass spectrum. The molecular formula of **1** was established as $C_{29}H_{36}O_{13}$ by HR-ESI-



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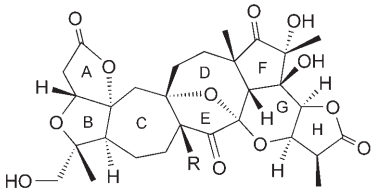

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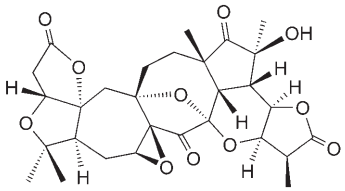

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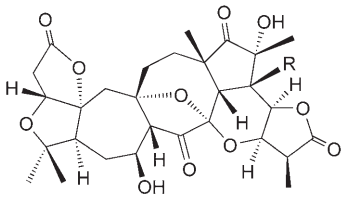

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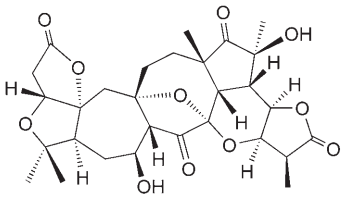

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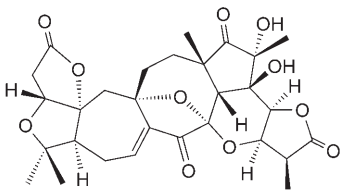

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MS (*m*/*z* 591.2087 ([*M* − H]$^-$; calc. 591.2078)) and ^{13}C-NMR spectroscopic data, requiring 12 degrees of unsaturation. The IR spectrum indicated OH (broad, 3431 cm^{-1}), C=O (1744 cm^{-1}), and γ-lactone (1776 cm^{-1}) functionalities. The ^{1}H-NMR spectrum of **1** (*Table 1*) exhibited three Me *singlet*s (δ(H) 1.92, 1.78, 1.17) and a Me *doublet* (δ(H) 1.42 (J = 7.0 Hz)). Characteristic signals of two *AB*-type *doublet*s at δ(H) 2.56 and 2.28, with a large coupling constant (J = 15.5 Hz), were attributed to CH$_2$(19)[1]). Further, a typical *ABX* spin-system at δ(H) 4.31 (*d*, J = 6.0 Hz, H−C(1)), 2.66 (*d*, J = 18.5 Hz, H$_\alpha$−C(2)), and 2.96 (*dd*, J = 6.0, 18.5 Hz, H$_\beta$−C(2)) was observed in the ^{1}H-NMR spectrum.

The ^{13}C-NMR spectrum of **1** (*Table 2*) showed signals for 29 C-atoms. From DEPT and HMQC data, the presence of four Me, six CH$_2$, and eight CH groups, as well as of eleven quaternary C-atoms (including two ester and two keto moieties, as well as six oxygenated C-atoms) was evident. All these signals suggested that compound **1** possessed the same skeleton as micrandilactone A (**5**).

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[1]) Arbitrary atom numbering.

Table 1. *^{1}H-NMR Data of* **1**–**4**. At 500 MHz in C_5D_5N; δ in ppm, J in Hz. Assignments were confirmed by ^{1}H,^{1}H-COSY, HMQC, and HMBC experiments. Asterisks (*) denote overlapping signals.

Position	**1**	**2**	**3**	**4**
1	4.31 (d, J = 6.0)	4.36 (d, J = 6.5)	4.30 (d, J = 6.5)	4.27 (d, J = 6.0)
2α	2.66 (d, J = 18.5)	2.70 (d, J = 18.5)	2.63 (d, J = 18.0)	2.83 (d, J = 18.5)
2β	2.90 (dd, J = 6.0, 18.5)	2.98 (dd, J = 6.5, 18.5)	2.96 (dd, J = 6.5, 18.0)	3.17 (dd, J = 6.0, 18.5)
5	2.96 (dd, J = 4.5, 12.5)	3.03 (dd, J = 4.0, 13.5)	2.90 (dd, J = 4.5, 13.0)	2.44 (dd, J = 2.5, 14.5)
6α	1.82–1.88 (m)	2.22–2.25*	2.01–2.08 (m)	2.18–2.21*
6β	1.36–1.41 (m)	1.67–1.73 (m)	1.94–1.98*	1.42–1.50 (m)
7α	1.94–1.99 (m)	2.41–2.44*	1.84–1.90 (m)	3.90 (dd, J = 6.0, 7.5)
7β	2.33–2.37 (m)	1.93–1.96*	1.45–1.51 (m)	
8	2.38–2.44 (m)		2.72 (dd, J = 5.5, 12.5)	
11α	3.20 (d, J = 14.5)	2.38–2.42*	1.88–1.92*	1.85–1.88 (m)
11β	2.90–2.92*	1.83 (dd, J = 3.5, 14.5)	1.9–1.73 (m)	1.93–1.96 (m)
12α		1.96–1.99*	1.88–1.92*	1.70–1.72*
12β		2.41–2.44 (m)	1.59–1.62 (m)	2.02–2.06 (m)
14	4.55 (d, J = 7.0)			
16	2.90*	3.32 (s)	3.18 (s)	2.86 (br. s)
18	1.92 (s)	1.60 (s)	1.57 (s)	1.22 (s)
19α	2.56 (AB, J = 15.5)	2.67 (br. s)	2.51 (AB, J = 16.0)	2.20 (AB, J = 16.0)
19β	2.28 (AB, J = 15.5)	2.22–2.25*	2.23 (AB, J = 16.0)	2.25 (AB, J = 16.0)
21	1.78 (s)	1.78 (s)	1.74 (s)	1.71 (s)
22				3.55 (d, J = 9.0)
23	5.04 (br. s)	5.05 (d, J = 1.5)	4.96 (br. s)	5.13 (br. s)
24	5.55 (br. s)	5.51–5.52 (m)	5.38–5.39 (m)	5.02–5.03 (m)
25	3.28 (dd, J = 4.0, 7.0)	3.28–3.30 (m)	3.22–3.27 (s)	3.30–3.35 (m)
27	1.42 (d, J = 7.0)	1.24 (d, J = 7.5)	1.30 (d, J = 6.5)	1.64 (d, J = 7.0)
29	3.84 (d, J = 11.5), 3.68 (d, J = 11.5)	3.85 (d, J = 12.0), 3.69 (d, J = 12.0)	3.83 (d, J = 11.5), 3.67 (d, J = 11.5)	1.24 (s)
30	1.17 (s)	1.20 (s)	1.14 (s)	0.97 (s)

Seriatim comparison was carried out between the spectroscopic information of compounds **1** and **5**. The signals due to rings *A* and *F*–*H* were nearly the same, the main differences being restricted to rings *B*–*E*. In rings *B* and *C*, the Me(29) signal of **5** (δ(H) 1.24 (s); δ(C) 27.7) changed into a CH_2 moiety in **1** (δ(H) 3.84, 3.68 (AB-type d, J = 11.5 Hz); δ(C) 67.5), and the oxygen-bearing H–C(7) in **5** (δ(H) 4.51 (dd, J = 9.3, 10.1 Hz); δ(C) 67.8) turned into another CH_2 group in **1** (δ(H) 1.94–1.99, 2.33–2.37 (2m); δ(C) 22.6). The ^{1}H-NMR signal for Me(30) was shifted downfield from δ(H) 1.04 in **5** to 1.17 in **1**, whereas the corresponding ^{13}C-NMR signal was shifted upfield from δ(C) 20.8 to 17.2; this is a result of the space effect to the H-atoms of Me(30) in combination with γ-compression due to the O-atom at C(29) in **1**.

The HMBC correlations (*Fig. 1*) from CH_2(29) to C(4), C(5), and C(30), from Me(30) to C(4), C(5), and C(29), from H–C(5) to C(7), and from CH_2(7) to C(5), C(6), and C(8), as well as the ^{1}H,^{1}H-COSY spin system H–C(5)/CH_2(6)/CH_2(7)/H–C(8), confirmed the structure assignment of rings *B* and *C* in **1** (*Fig. 1*).

Some C-atom in rings *D* and *E* of **1** had to carry an O-atom or an OH group, since the molecular formula of **1** had one O-atom more than that of **5**, while the degree of unsaturation remained unchanged. Careful analysis on the NMR signals of rings *D* and

Table 2. *^{13}C-NMR Data of* **1**–**4**. At 125 MHz in C_5D_5N; δ in ppm. Assignments were confirmed by ^{1}H,^{1}H-COSY, HMQC, and HMBC experiments.

Position	**1**	**2**	**3**	**4**	Position	**1**	**2**	**3**	**4**
1	81.9	82.0	81.8	80.8	16	56.4	54.5	54.1	45.0
2	35.2	35.2	35.2	35.3	17	219.7	220.8	220.8	221.6
3	175.4	175.4	175.4	175.2	18	23.6	31.2	31.0	28.4
4	87.2	87.2	87.0	83.7	19	43.0	41.7	42.6	39.1
5	56.4	56.3	56.2	54.1	20	81.3	80.3	80.3	76.3
6	24.1	19.8	26.9	28.1	21	20.3	18.7	18.7	20.8
7	22.6	33.1	24.1	64.0	22	76.5	75.7	75.6	43.7
8	50.8	78.2	52.1	61.3	23	77.0	76.7	76.7	74.1
9	83.3	85.4	83.8	80.2	24	74.1	75.3	75.2	70.7
10	97.2	97.0	96.4	95.7	25	43.0	42.5	42.5	42.6
11	57.7	37.2	41.6	35.9	26	178.1	177.6	177.7	175.9
12	206.3	33.8	32.6	31.6	27	8.5	8.2	8.2	8.4
13	64.8	49.3	49.4	49.3	29	67.5	67.5	67.3	27.6
14	76.7	213.2	210.0	207.9	30	17.2	17.2	17.1	20.5
15	103.1	98.5	99.7	97.7					

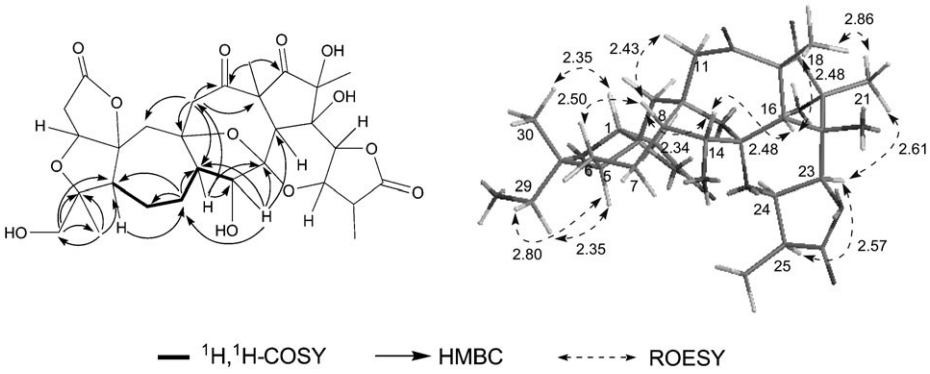

Fig. 1. *^{1}H,^{1}H-COSY, Key HMBC, and selected ROESY correlations for* **1**. Calculated interatomic distances are given in Å.

E of both **1** and **5**, in combination with ^{1}H,^{1}H-COSY correlations (*Fig. 1*), showed that the CH_2(11)/CH_2(12) spin system in **5** had disappeared, just leaving a CH_2(11) group in **1**, which was shifted downfield from δ(H) 1.98/1.79 (2*m*) (δ(C) 42.3) in **5** to δ(H) 3.20 (*d*, *J* = 14.5 Hz)/2.90–2.92 (*m*) (δ(C) 57.7) in **1**. At the same time, another ^{1}H,^{1}H-COSY spin system, H–C(8)/H–C(14), occurred in **1**. This information indicated that C(11) was part of a C=O group, and C(8) was linked with an oxygenated methine (H–C(14)). This was further confirmed by HMBC correlations (*Fig. 1*) from CH_2(11) to C(8), C(9), C(12), C(13), and C(19), from Me(18) to C(12), C(13), C(16), and C(17), from H–C(8) to C(11), C(14), and C(15), and from H–C(14) to C(7), C(8), C(15), and C(16).

The relative configuration of **1** was elucidated by analysis of ^{1}H-NMR coupling constants and ROESY data (*Fig. 1*), and by the analogy with micrandilactone A (**5**).

The signal for H–C(5) showed a ROESY correlation with CH_2(29), indicating α-orientation of CH_2(29) and β-orientation of Me(30). ROESY Correlations for Me(18)/H–C(16) and H–C(16)/H–C(14) indicated that H–C(14) was in β-orientation. Correlations for H–C(8)/H–C(14), CH_2(7), H_β–C(6), and, especially, with H_β–C(11), indicated that H–C(8) was β-oriented. Moreover, the ^{1}H-NMR signal of H–C(14) displayed a small coupling [δ(H) 4.55 (*d*, J = 7.0 Hz)] with H–C(8), which implied a small dihedral angle between H–C(14) and H–C(8), further confirming the β-orientation of both H–C(14) and H–C(8). Finally, ROESY correlations for Me(18)/Me(21), Me(21)/H–C(23), H–C(23)/H–C(24), H–C(23)/H–C(25), and Me(30)/H–C(1) indicated that Me(21) and H–C(1) were in β-orientation, whereas H–C(23), H–C(24), and H–C(25) were in α-orientation, just as in **5**. These ROESY correlations were further supported by calculation of the pertinent interatomic distances, which were all $<$3 Å (*Fig. 1*). From these data, the structure and relative configuration of **1** was elucidated, and the compound named *propindilactone A*[2]).

Propindilactone B (**2**) had the molecular formula $C_{29}H_{36}O_{13}$, as derived from HR-ESI-MS (*m*/*z* 591.2072 ([M – H]$^-$; calc. 591.2078)) and ^{13}C-NMR data, which is 16 mass units higher than in the case of **5**. The ^{1}H- and ^{13}C-NMR spectroscopic data (*Tables 1 and 2*) of **2**, regarding rings *A* and *F*–*H*, were almost the same as those of **5**. In ring *B*, the Me *singlet* in **5** was changed into an oxygenated CH_2 group in **2**, just as for **1**, as confirmed by ^{1}H- and ^{13}C-NMR data, and by HMBC correlations. The signals for rings *C*–*E* of **2** *vs.* **5** showed that the 7-OH group of **5** was transferred to an 8-OH moiety in **2**, H–C(7) of **5** (δ(H) 4.51 (*dd*, J = 9.3, 10.1); δ(C) 67.8) being replaced by CH_2(7) in **2** (δ(H) 2.41–2.44, 1.93–1.96; δ(C) 33.1), and H–C(8) in **5** (δ(H) 2.99 (*d*, J = 10.1 Hz); δ(C) 59.7) being replaced by a tertiary C-atom in **2** (δ(C) 78.2). Accordingly, the signals in the vicinity of C(7) and the oxygenated C(8) in **2** changed a lot: C(6) and C(11) at δ(C) 36.4 and 42.3 in **5** were shifted upfield to δ(C) 19.8 and 37.2 in **2**, and C(9) and C(14) at δ(C) 82.2 and 207.4 in **5** were shifted downfield to δ(C) 85.4 and 213.2 in **2**, respectively. HMBC correlations from CH_2(6) to C(8), from CH_2(7) to C(8), C(9), and C(14), from CH_2(11) to C(8) and C(9), and from both CH_2(12) and CH_2(19) to C(9) (*Fig. 2*), together with the ^{1}H,^{1}H-COSY spin system H–C(5)/CH_2(6)/CH_2(7), fully corroborated the proposed structure of **2**.

Propindilactone C (**3**) had the molecular formula $C_{29}H_{36}O_{12}$ according to HR-ESI-MS (*m*/*z* 575.2111 ([M – H]$^-$; calc. 575.2129)) and ^{13}C-NMR spectroscopic data, which

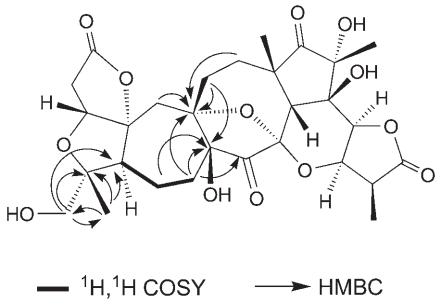

Fig. 2. *^{1}H,^{1}H-COSY and Key HMBC correlations for* **2**

[2]) For systematic names, see *Exper. Part.*

is 16 mass units less than that of **2**. By carefully comparison of the NMR spectra of **3** and **2**, we found that **3** was also a 29-hydroxylated derivative of **5**, just as **2**. The main difference between them were a lacking 8-OH group in **3** compared to **2**. Thus, the oxygenated tertiary C(8) atom in **2** (δ(C) 78.2) was replaced with a methine in **3** (δ(H) 2.72 (*dd*, J = 5.5, 12.5 Hz); δ(C) 52.1). The HMBC correlations from CH_2(6) to C(5), C(7), and C(8), and from CH_2(7) to C(5), C(6), and C(8), as well as the ^{1}H,^{1}H-COSY spin system H–C(5)/CH_2(6)/CH_2(7)/H–C(8), confirmed the gross structure of **3**.

Propindilactone D (**4**) had the molecular formula $C_{29}H_{34}O_{11}$, as established by HR-ESI-MS (*m*/*z* 557.2015 ($[M-H]^-$; calc. 557.2023)), requiring 13 degrees of unsaturation. Investigation on the ^{1}H- and ^{13}C-NMR data of **4** (*Tables 1* and *2*) revealed that it was a member of the schisanartane family. By comparing the spectroscopic data of **4** and **7**, many similarities were found, except that the molecular weight of **4** was two mass units lower than that of **7**, having one degree of unsaturation less than **7**. Minor changes were found in ring *B* of **4**, which indicated that **4** was the 7,8-epoxy derivative of **7**. HMBC Correlations from H–C(5) to C(7), from H–C(7) to C(6) and C(8), and from CH_2(19) to C(8) for **4** confirmed this assumption (*Fig. 3*). The relative configurations at C(7) and C(20) were evident from key ROESY correlations for H–C(5)/H–C(7), Me(21)/H–C(23), and Me(21)/H–C(24), as shown in *Fig. 3*.

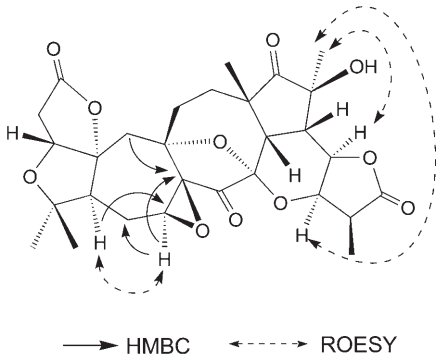

Fig. 3. *Key HMBC and selected ROESY correlations for* **4**

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Experimental Part

General. Petroleum ether (PE) for chromatography had a b.p. range of 60–90°. Column chromatography (CC) was performed on silica gel (200–300 mesh; *Qingdao Marine Chemical, Inc.*, China) and silica gel *H* (10–40 μm; *Qingdao*); fractions were monitored by TLC, and spots were visualized by spraying with 8% H_2SO_4 in EtOH, followed by heating. Semi-preparative HPLC was performed on an *Agilent 1100* apparatus equipped with a UV detector and *Zorbax SB-C-18* (*Agilent*, 9.4 mm × 25 cm) column. Optical rotations: *Horiba SEPA-300* spectropolarimeter. IR Spectra: *BioRad FTS-135* spectrophotometer, with KBr discs; in cm^{-1}. 1D- and 2D-NMR Spectra: *Bruker AM-400* and *DRX-500* instruments; chemical shifts δ in ppm rel. to residual solvent signals, *J* in Hz. HR-ESI-MS: *VG AutoSpec-3000* mass spectrometer; in *m*/*z*.

Plant Material. Plants of *Schisadra propinqua* var. *propinqua* were collected in Tengchong County, Yunnan Province, P. R. China, in July 2006, and identified by Prof. *Xi-Wen Li*, Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen (No. 20050823) was deposited at the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, P. R. China.

Extraction and Isolation. The air-dried leaves and stems of *S. propinqua* var. *propinqua* (8 kg) were extracted with 70% aq. acetone (4 × 15 l, 3 d each) at r.t. The solvent was removed *in vacuo* to afford a crude extract (560 g), which was dissolved in H_2O, and then extracted successively with PE and AcOEt. The AcOEt-soluble part (250 g) was purified by CC (SiO_2; $CHCl_3$/acetone 1:0, 9:1, 8:2, 2:1, 1:1, 0:1) to afford six main fractions (*Fr. A–F*). *Fr. D* (45 g) was purified by repeated CC, first on SiO_2, then on *Sephadex LH-20*, followed by recrystallization, which yielded **2** (50 mg), **5** (70 mg), **7** (200 mg), and **8** (7 mg). *Fr. E* was purified first by CC on *RP-18* gel and then silica gel *H*, eluting with PE/i-PrOH 9:1, followed by semi-prep. HPLC (40% MeOH in H_2O) to yield **1** (28 mg), **3** (30 mg), **4** (3 mg), and **6** (10 mg).

Propindilactone A (= rel-*(1*S*,3a*S*,3b*R*,4*R*,5a*R*,7a*R*,8a*R*,11a*R*,13*R*,13a*S*,15a*S*,16*R*,16a*S*,16b*R*,17a*R*)-Tetradecahydro-3b,4,16-trihydroxy-13-(hydroxymethyl)-1,4,5a,13-tetramethyl-2*H*,10*H*-7a,16a-epoxy-3,9,12,17-tetraoxacyclopent[3′,3a′]azuleno[6′,5′:5,6]cyclooct[1,2,3*-cd*]-as-indacene-2,5,6,10(1*H*,7*H*,8*H*)-tetrone*; **1**). Amorphous powder. $[\alpha]_D^{24.5} = +24.3$ ($c = 0.23$, MeOH). IR (KBr): 3431, 2975, 2939, 1776, 1774, 1690, 1241, 1076, 1027, 926. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESI-MS (neg.): 591.2087 ($[M-H]^-$, $C_{29}H_{35}O_{13}^-$; calc.591.2078).

Propindilactone B (= rel-*(1*S*,3a*S*,3b*R*,4*R*,5a*S*,7a*S*,8a*R*,11a*R*,13*R*,13a*S*,15a*S*,16a*S*,16b*R*,17a*R*)-Tetradecahydro-3b,4,15a-trihydroxy-13-(hydroxymethyl)-1,4,5a,13-tetramethyl-2*H*,10*H*-7a,16a-epoxy-3,9,12,17-tetraoxacyclopent[3′,3a′]azuleno[6′,5′:5,6]cyclooct[1,2,3*-cd*]-as-indacene-2,5,10,16(1*H*,8*H*,13*H*)-tetrone*; **2**). Colorless solid. $[\alpha]_D^{24.4} = +58.6$ ($c = 0.46$, MeOH). IR (KBr): 3377, 2937, 1765, 1770, 1629, 1190, 1175, 1040, 994. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESI-MS (neg.): 591.2072 ($[M-H]^-$, $C_{29}H_{35}O_{13}^-$; calc. 591.2078).

Propindilactone C (= rel-*(1*S*,3a*S*,3b*R*,4*R*,5a*S*,7a*S*,8a*R*,11a*R*,13*R*,13a*S*,15a*R*,16a*S*,16b*R*,17a*R*)-Tetradecahydro-3b,4-dihydroxy-13-(hydroxymethyl)-1,4,5a,13-tetramethyl-2*H*,10*H*-7a,16a-epoxy-3,9,12,17-tetraoxacyclopent[3′,3a′]azuleno[6′,5′:5,6]cyclooct[1,2,3*-cd*]-as-indacene-2,5,10,16(1*H*,8*H*,13*H*)-tetrone*; **3**). Colorless solid. $[\alpha]_D^{24.5} = +61.20$ ($c = 0.38$, MeOH). IR (KBr): 3428, 2938, 1775, 1744, 1632, 1454, 1381, 1170, 1104. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESI-MS (neg.): 575.2111 ($[M-H]^-$, $C_{29}H_{35}O_{12}^-$; calc. 575.2129).

Propindilactone D (= rel-*(1*S*,3a*R*,3b*S*,4*S*,5a*S*,7a*S*,8a*R*,11a*R*,13a*S*,14a*S*,15a*S*,16a*S*,16b*S*,17a*R*)-Tetradecahydro-4-hydroxy-1,4,5a,13,13-pentamethyl-2*H*,10*H*-7a,16a-epoxy-3,9,12,15,17-pentaoxacyclopenta[3′,3a′]cycloprop[6′,7′]azuleno[6′,5′:5,6]cyclooct[1,2,3*-cd*]-as-indacene-2,5,10,16(1*H*,8*H*)-tetrone*; **4**). Colorless solid. $[\alpha]_D^{24.2} = +34.5$ ($c = 0.09$, MeOH). IR (KBr): 3468, 2974, 2927, 1784, 1739, 1437, 1230, 1185, 1042, 955. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESI-MS (neg.): 557.2015 ($[M-H]^-$, $C_{29}H_{33}O_{11}^-$; calc. 557.2023).

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