Four Novel Nortriterpenoids Isolated from *Schisandra henryi* var. *yunnanensis*

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Four novel nortriterpenoids, henridilactones A–D (**1**–**4**), members of a very rare highly oxidized cycloartane skeletal class with a biosynthetically modified eight-membered ring D, were isolated from the leaves and stems of *Schisandra henryi* var. *yunnanensis*. Their structures were elucidated using extensive spectroscopic techniques including 1D and 2D NMR spectra. Eight known triterpenoids were also isolated from the same source.

Introduction

Plants of the genus *Schisandra* belong to the economically and medicinally important family Schisandraceae. In China, over 19 species are widely used in traditional medicine.[1] In our previous research on this genus, we reported the isolation and characterization of several new triterpenoids.[2−6] In continuation of our work on this genus, we have examined the leaves and stems of *S. henryi* var. *yunnanensis* A. C. Smith, a plant indigenous to Yunnan Province of China. In this paper we describe the isolation of four novel nortriterpenoids, henridilactones A−D (**1**−**4**), together with eight known triterpenoids, schiprolactone A (**7**),[7] schisanlactone A (**8**),[8] schisanlactone B (**9**),[9] juncoside I (**10**),[10] nigranoic acid (**11**),[11] schizandronic acid (**12**),[12] changnic acid (**13**)[13] and kadsuric acid (**14**),[14] and elucidation of the structures of the new compounds by spectroscopic analysis. Henridilactones A−D are members of a unique unusual highly oxidized cycloartane skeletal class, structurally related to micrandilactone A (**5**),[5] which was firstly isolated from *S. micrantha*.

Results and Discussion

Henridilactone A (**1**) was isolated as a UV-active ($\lambda_{max.}$ 245 nm) substance and the molecular formula of $C_{29}H_{34}O_{10}$ was established by HRESI MS (found $[M + Na]^+$ 565.2043, calcd. 565.2049) and ^{13}C NMR spectroscopy, indicating 13 degrees of unsaturation. The IR spectrum indicated that the hydroxy (3469 cm^{-1}, br), carbonyl (1735 cm^{-1}) and γ-lactone (1774 cm^{-1}) functionalities were present in **1**. The ^1H NMR spectrum of **1** (Table 1) displayed signals of five methyl groups at δ = 0.94 (s), 1.01 (s), 1.19 (s), 1.56 (s) and 1.60 (d, J = 5.6 Hz) ppm; of one hydroxy group at δ = 6.19 (s) ppm; and of a further three resonances appearing as an ABX spin system at δ = 4.09 (d, J = 5.3 Hz), 2.65 (d, J = 15.0 Hz) and 2.76 (dd, J = 5.3, 15.0 Hz) ppm. The ^{13}C NMR spectrum (Table 2) of **1** showed signals for 28 carbon atoms: five methyl groups (δ = 8.5, 20.4, 25.3, 27.5, 27.5 ppm), five methylene groups (δ = 23.7, 31.0, 35.3, 39.1, 42.5 ppm), three oxygen-bearing methines (δ = 71.7, 73.6, 80.3 ppm), four non-oxygenated methine groups (δ = 41.7, 42.2, 45.9, 57.7 ppm), an olefinic methine (δ = 135.3 ppm), two ketone carbonyl groups (δ = 198.4, 220.2 ppm), two ester carbonyl groups (δ = 174.9, 178.1 ppm), an olefinic quaternary carbon atom (δ = 137.8 ppm), five oxygen-bearing quaternary carbon atoms (δ = 74.6, 82.7, 83.2, 94.7, 98.6 ppm), and a non-oxygenated quaternary carbon atom (δ = 49.6 ppm). This suggested that compound **1** was a highly oxygenated nortriterpene and contained eight rings. Careful investigation of the ^1H and ^{13}C NMR spectroscopic data of **1** revealed its structure to be very similar to that reported for micrandilactone A (**5**)[5] (Table 1 and 2, respectively), except that **1** contains a methine (δ = 42.2 ppm) in lieu of an oxygen-bearing quaternary carbon atom (C-22, δ = 75.5 ppm, in **5**), along with an additional double bond [δ = 135.3 (d) and 137.8 (s) ppm] and the absence of a hydroxy at C-22. These observations strongly suggested that compound **1** was the 22-dehydroxy derivative of **5**. The HMBC correlations observed between the hydroxy proton at δ = 6.19 (s) ppm with C-20 (δ = 74.6 ppm, s), C-22 (δ = 42.2 ppm, d) and Me-21 (δ = 25.3 ppm, q), in conjunction with the ^1H-^1H COSY spin system of 14-H/22-H/23-H/24-H/25-H further confirmed that the only hydroxy location should be assigned to C-20.

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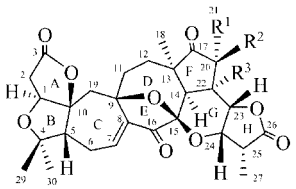
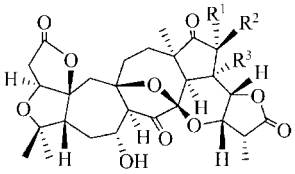
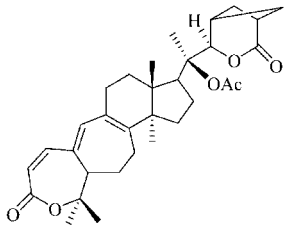


1 $R^1 = -CH_3$ $R^2 = OH$ $R^3 = H$
2 $R^1 = -CH_3$ $R^2 = R^3 = OH$
3 $R^2 = -CH_3$ $R^1 = R^3 = H$
6 $R^1 = -CH_3$ $R^2 = R^3 = H$



4 $R^1 = R^3 = H$ $R^2 = -CH_3$
5 $R^1 = -CH_3$ $R^2 = R^3 = OH$



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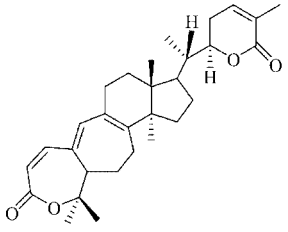

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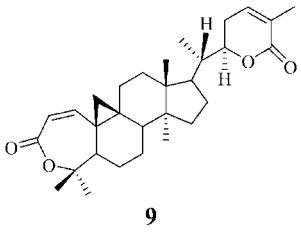

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Table 1. ^1H NMR spectroscopic data (500 MHz) of compounds **1**−**5** in C_5D_5N.

H atom[a]	**1**	**2**	**3**	**4**	**5**
1	4.09 (d, J = 5.3)	4.13 (d, J = 5.3)	4.24 (d, J = 5.0)	4.25 (d, J = 6.3)	4.22 (d, J = 6.3)
2α	2.65 (d, J = 15.0)	2.68 (d, J = 15.3)	2.77 (d, J = 16.1)	2.79 (d, J = 18.6)	2.74 (d, J = 18.6)
2β	2.76 (dd, J = 5.3, 15.0)	2.87 (dd, J = 5.3, 15.3)	3.09 (dd, J = 5.0, 16.1)	3.06 (dd, J = 6.3, 18.6)	2.93 (dd, J = 6.3, 18.6)
5	2.12 (overlap)	2.11 (overlap)	2.16 (overlap)	2.48 (dd, J = 4.8, 13.3)	2.47 (dd, J = 4.2, 13.4)
6α	1.58 (overlap)	2.15 (m)	2.14 (m)	2.06 (m)	2.09 (m)
6β				2.19 (m)	2.21 (overlap)
7	7.07 (t, J = 5.9)	7.09 (d, J = 6.2)	7.02 (t, J = 5.0)	4.50 (dd, J = 9.3, 9.8)	4.51 (dd, J = 9.3, 10.1)
8	−	−	−	2.84 (d, J = 9.8)	2.99 (d, J = 10.1)
11α	1.72 (m)	1.78 (overlap)	1.62 (m)	1.57 (m)	1.79 (m)
11β	2.19 (m)	2.11(m)	2.21 (m)	2.28 (m)	1.98 (m)
12α	1.50 (m)	1.56 (m)	1.41 (m)	1.78 (m)	1.67 (m)
12β	1.93 (m)	2.05 (m)	1.83 (m)		1.98 (overlap)
14	2.84 (d, J = 6.7)	3.23 (s)	2.75 (d, J = 6.5)	2.80 (overlap)	3.31 (s)
18	1.01 (s)	1.61(s)	0.94 (s)	0.92 (s)	1.58 (s)
19α	2.24 (d, J = 5.6)	2.30 (s)	2.26 (s)	2.42 (AB d, J = 16.1)	2.52 (AB d, J = 15.8)
19β				2.13 (AB d, J = 16.1)	2.23 (AB d, J = 15.8)
20	−	−	2.81 (m)	2.79 (overlap)	−
21	1.56 (s)	1.79 (s)	1.29 (d, J = 6.4)	1.45 (d, J = 7.8)	1.77 (s)
22	3.16 (d, J = 6.7)	−	3.38 (dd, J = 6.5, 9.1)	3.38 (dd, J = 8.3, 11.1)	−
23	4.99 (br. s)	4.99 (overlap)	4.65 (br. s)	4.79 (br. s)	4.99 (d, J = 1.5)
24	4.89 (dd, J = 1.8, 3.2)	4.98 (overlap)	4.58 (dd, J = 1.5, 1.8)	5.27 (overlap)	5.42 (dd, J = 1.5, 2.0)
25	3.14 (m)	3.22 (m)	3.12 (m)	3.13 (m)	3.26 (m)
27	1.60 (d, J = 5.6)	1.62 (d, J = 5.8)	1.60 (d, J = 5.6)	1.12 (d, J = 7.3)	1.17 (d, J = 7.1)
29	1.19 (s)	1.18 (s)	1.21 (s)	1.22 (s)	1.24 (s)
30	0.94 (s)	0.97 (s)	1.01 (s)	1.05 (s)	1.04 (s)
20-OH	6.19 (s)	6.20 (s)	−	−	5.90 (s)
22-OH	−	8.03 (s)	−	−	7.56 (s)

[a] Data were recorded with a Bruker DRX-500 MHz spectrometer, chemical shifts (δ) are in ppm, J in Hz.

Table 2. ^{13}C NMR spectral data (125 MHz) of compounds **1**, **2**, **5** in C_5D_5N.

C-atom[a]	1	2	5	C-atom	1	2	5
1	80.3	80.3	81.4	16	198.4	197.3	207.4
2	35.3	35.3	35.0	17	220.2	220.5	220.7
3	174.9	175.0	175.2	18	27.5	31.6	30.8
4	83.2	83.2	83.9	19	42.5	42.5	41.8
5	57.7	57.6	58.3	20	74.6	80.1	80.2
6	23.7	23.8	36.4	21	25.3	18.9	18.9
7	135.3	136.5	67.8	22	42.2	75.6	75.5
8	137.8	137.2	59.7	23	73.6	76.6	76.8
9	82.7	83.0	82.2	24	71.7	74.4	75.2
10	94.7	94.7	95.6	25	41.7	42.9	42.5
11	39.1	39.6	42.3	26	178.1	177.9	177.5
12	31.0	33.2	32.6	27	8.5	8.5	7.8
13	49.6	49.6	49.3	29	27.5	27.5	27.7
14	45.9	55.4	54.1	30	20.4	20.4	20.8
15	98.6	100.3	99.7				

[a] Data were recorded with a Bruker DRX-500 MHz spectrometer, chemical shifts (δ) are in ppm; assignments were confirmed by ^1H-^1H COSY, HMQC and HMBC.

Another major difference between structures **1** and **5** was established by combined analysis of NMR, HMBC and COSY data. The chemical shift of the ketocarbonyl group (C-16, δ = 198.4 ppm, s) suggested that it was α,β-unsaturated, and the olefinic methine was consequently assigned to the β-position of an α,β-unsaturated ketone moiety, after the observations of HMBC correlations (Figure 1) from the olefinic proton at δ = 7.07 (t, *J* = 5.9 Hz, 7-H) ppm to C-5 (δ = 57.7 ppm, d), C-6 (δ = 23.7 ppm, t), C-9 (δ = 82.7 ppm, s) and C-16 (δ = 198.4 ppm, s), from 5-H (δ = 2.12 ppm) to C-7 (δ = 135.3 ppm, d) and C-8 (δ = 137.8 ppm, s), and from 19-H (δ = 2.24 ppm, d, *J* = 5.6 Hz) to C-8. The assignment of the double bond to between C-7 and C-8 of compound **1** was in agreement with the observation of the C-6 signal being shifted upfield by 12.7 ppm compared to the signal from compound **5**.

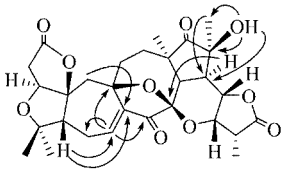

Figure 1. Selected HMBC (from H to C) correlations for **1**

The relative configuration of the stereocenters in **1** were assumed to be the same as those of **5** because of the similarity of the proton−proton coupling constants and from the following significant ROESY correlations: 18-Me/22-H, 18-Me/14-H, 21-Me/14-H, 14-H/22-H, 27-Me/24-H, 23-H/25-H, 29-Me/5-H and 30-Me/1-H.

HRESI MS of henridilactone B (**2**) gave a molecular ion at *m*/*z* = 581.2019 ([M + Na]$^+$) corresponding to the molecular formula $C_{29}H_{34}O_{11}$, indicating 16 mass units more than compound **1**. The signals in its ^1H and ^{13}C NMR spectra strikingly matched those of **1** (Table 1 and 2, respectively). The only significant differences included the obvious presence of a new hydroxy group at δ = 8.03 (s) ppm, and the lack of a 22-H signal in the ^1H NMR spectrum. This implied that the new hydroxy group is present at C-22 in compound **2**. In the ^{13}C NMR spectrum, the non-oxygenated methine (δ = 42.2 ppm, C-22) in **1** was invisible and was replaced in the case of **2** by an oxygenated quaternary carbon atom at δ = 75.6 (C-22) ppm, agreeing with the presence of 22-OH. This was further confirmed by the observation of HMBC correlations between the new hydroxy with C-20 (δ = 80.1 ppm, s) and C-22 (δ = 75.6 ppm, s).

Henridilactone C (**3**), was obtained as a white powder. Its molecular formula was determined to be $C_{29}H_{34}O_9$ by analysis of ^1H and ^{13}C NMR spectroscopic data, and was verified by HRESI MS ([M + Na]$^+$ found 549.2124, calcd. 549.2100). The ^1H NMR spectrum of **3** (Table 1) showed the presence of five methyl groups at δ = 0.94 (s), 1.01 (s), 1.21 (s), 1.29 (d, *J* = 6.4 Hz), and 1.60 (d, *J* = 5.6 Hz) ppm. In addition, the characteristic ABX spin system at δ_H = 4.24 (d, *J* = 5.0 Hz, 1 H), 2.77 (d, *J* = 16.1 Hz, 1 H) and 3.09 (dd, *J* = 5.0, 16.1 Hz, 1 H) ppm, which were assigned to 1-H, 2α-H and 2β-H, respectively, revealed that compound **3** possessed the same skeleton as **1** and **2**.

The ^1H and ^{13}C NMR spectroscopic data of compounds **2** and **3** (Tables 1−3) showed that they have identical constituting rings A−H and differ only in the substitution nature of rings F and G. HMBC correlations from 21-Me (δ_H = 1.29 ppm, d, *J* = 6.4 Hz) to C-20 (δ = 41.2 ppm, d), C-22 (δ = 33.3 ppm, d) and C-17 (δ = 221.6 ppm, s), and from 14-H (δ = 2.75 ppm, d, *J* = 6.5 Hz) to C-20 and C-22, established the structure of compound **3** as 20, 22-didehydroxy-henridilactone B (**2**). The ^1H-^1H COSY spin system of 21-Me/20-H/22-H/14-H further supported the above assignment. Moreover, the ^{13}C NMR spectroscopic data of **3** lacked two oxygenated quaternary carbon atom signals

Table 3. ^{13}C NMR spectral data (125 MHz) of compounds **3**, **4**, **6** in C_5D_5N

C atom[a]	3	4	6	C atom	3	4	6
1	80.4	81.6	80.6	16	198.7	209.1	198.7
2	35.4	35.2	35.7	17	221.6	221.6	220.5
3	175.2	175.5	175.5	18	26.6	26.0	26.5
4	83.3	84.0	83.5	19	42.5	42.5	42.3
5	57.6	58.3	57.8	20	41.2	41.2	45.0
6	23.6	36.6	23.8	21	12.7	12.4	15.0
7	135.3	67.9	135.5	22	33.3	33.3	40.3
8	138.2	60.6	138.2	23	74.6	75.0	75.4
9	82.3	81.4	82.2	24	71.0	71.7	68.6
10	95.0	96.1	95.1	25	42.6	42.2	42.5
11	38.8	41.0	39.4	26	177.9	177.8	178.3
12	30.5	30.3	31.5	27	8.5	7.9	8.6
13	50.3	49.9	50.7	29	27.6	27.8	27.7
14	46.6	45.8	45.8	30	20.4	21.0	20.6
15	98.3	98.0	99.2				

[a] Data were recorded with a Bruker DRX-500 MHz spectrometer, chemical shifts (δ) are in ppm; assignments were confirmed by ^1H-^1H COSY, HMQC and HMBC.

[C-20 (δ = 80.1 ppm, s); C-22 (δ = 75.6 ppm, s) in **2**], showing instead two methine signals at δ = 41.2 and 33.3 ppm, in agreement with the absence of 20-OH and 22-OH groups.

Interestingly, the structure of **3** proved strikingly similar to that of landifodilactone C (**6**), a new compound also belonging to this unusual novel highly oxidized cycloartane skeletal class, which we recently obtained from *S. lancifolia*.[15] A close comparison of the ^{13}C NMR spectra of **3** and **6** (Table 3) revealed only a change in the relative stereochemical orientation of the 21-Me group. Thus, compound **3** was an epimer at 21-Me with **6**. The α-orientation of 21-Me in **6** to β-orientation in **3** was clearly indicated by the differences in the ^{13}C NMR spectroscopic data: C-20 (δ = 41.2 ppm, d), 21-Me (δ = 12.7 ppm, q) and C-22 (δ = 33.3 ppm, d) in **3** vs. δ = 45.0, 15.0 and 40.3 ppm in **6**. The β-orientation of 21-Me was also evident from the key ROESY correlations of 21-Me/23-H, 21-Me/24-H as shown in Figure 2.

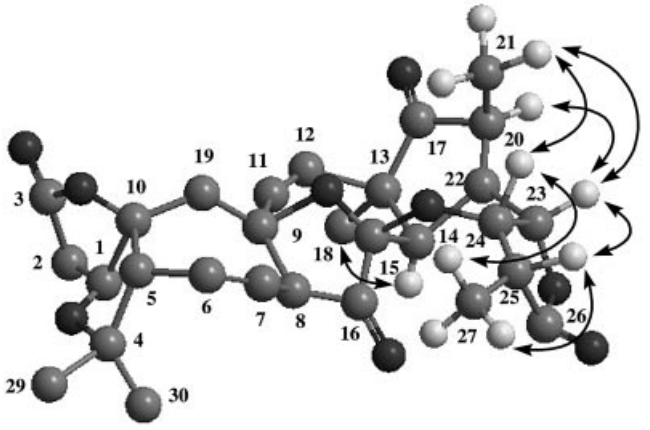

Figure 2. Selected ROESY (from H to H) correlations for **3**; only key hydrogen atoms are shown

HRESI MS analysis of henridilactone D (**4**) revealed a molecular formula of $C_{29}H_{36}O_{10}$ ([M + Na]$^+$, found 567.2193, calcd. 567.2206), corroborated by the ^{13}C NMR spectroscopic data, and differing from **3** by the addition of one oxygen atom and two hydrogen atoms. The signals displayed in the ^1H NMR spectrum (Table 1) of compound **4** revealed the presence of the characteristic 1-H (δ = 4.25 ppm, d, *J* = 6.3 Hz), 2α-H (δ = 2.79 ppm, d, *J* = 18.6 Hz), and 2β-H (δ = 3.06 ppm, dd, *J* = 6.3, 18.6 Hz), already reported for compounds **1**−**3**. The main differences with respect to the ^1H NMR spectrum of **3** were the absence of the olefinic proton ascribed to 7-H, together with two additional signals at δ = 4.50 (dd, *J* = 9.3, 9.8 Hz) and 2.84 (d, *J* = 9.8 Hz) ppm. The ^{13}C NMR spectrum of **4** (Table 3) indicated the presence of five methyl groups, five methylene groups, ten methine groups, two ketone carbonyl groups, two ester carbonyl groups and five quaternary carbon atoms. These features revealed a total of 35 protons attached to carbon atoms, implying the presence of only one hydroxy group. The lack of olefinic resonance comparable to that found in compounds **1**−**3**, and the downfield shift of the methylene carbon (C-6) from **3** to **4** (Δ, 13.0 ppm), suggested that the hydroxy group was located at C-7. This was verified by the ^1H-^1H COSY correlations which led to connectivities from 5-H to 8-H, and HMBC cross-peaks between 7-H (δ = 4.50 ppm, dd, *J* = 9.3, 9.8 Hz) and C-5 (δ = 58.3 ppm, d) and between 6-H (δ = 2.06/2.19 ppm, m) and 8-H (δ = 2.84 ppm, d, *J* = 9.8 Hz) and C-7 (δ = 67.9 ppm, d).

Experimental Section

General Experimental Procedures: Optical rotations were measured with a Jasco DIP-370 digital polarimeter. UV spectra were obtained using a Shimadzu UV-2401PC spectrophotometer. A Bio-Rad-Fts-135 spectrophotometer was used for scanning IR spectroscopy of compounds with KBr pellets. 1D and 2D NMR spectra were recorded with a DRX-500 spectrometer; chemical shifts are referenced to the residual solvent signal and TMS as internal standard. Both high- and low-resolution MS were obtained on a VG Autospec-3000 spectrometer (70 eV). HPLC separations were performed on a HP 1100 apparatus equipped with an RI detector and Zorbax SB-C-18 (Agilent, 9.4 mm × 25 cm) column. Column chromatography was performed on silica gel (200−300 mesh, Qingdao Marine Chemical Inc., Qingdao, Peoples Republic of China) or on silica gel H (10−40 μm, Qingdao Marine Chemical Inc.).

Plant Material: The leaves and stems of *S. henryi* var. *yunnanensis* were collected in Malipo, Yunnan Province of China (1994) and identified by Prof. Zhongwen Lin; a voucher specimen (KIB-99-7-11 Lin) was deposited in the Laboratory of phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation: The powdered air-dried stems and leaves (2.5 kg) were exhaustively extracted three times with 80% aq. Me_2CO (12 L) at room temperature and filtered. The filtrate was evaporated and the resulting residue was partitioned between H_2O and EtOAc (3 L). The EtOAc layer (105 g) was subjected to silica-gel column chromatography (with $CHCl_3$/Me_2CO, 1:0 → 0:1 gradient systems) to give Fractions 1−6. After repeated column chromatography (silica gel, petroleum ether/Me_2CO, 9:1 and petroleum ether/EtOAc, 4:1), Fr.1 (20 g) afforded **7** (210 mg), **8** (352 mg), **9** (2 mg) and **10** (5 mg); Fr. 4 afforded **11** (220 mg), **12** (55 mg), **13** (210 mg), **14** (2 mg). Fr. 2 (20 g) was further purified over silica gel ($CHCl_3$/MeOH, 100:1), then by RP-HPLC with 55% MeOH/H_2O (flow rate 3.0 mL/min) to afford **1** (4 mg), **2** (16 mg), **3** (24 mg) and **4** (2 mg).

Henridilactone A (1): White powder. $[\alpha]_D^{26.2}$ = +89.23 (*c* = 0.33, C_5H_5N). UV (MeOH): $\lambda_{max.}$ (log ε) = 245 (3.92) nm. IR (KBr): $\tilde{\nu}_{max.}$ = 3469 (br), 1774, 1735, 1665 cm^{-1}. EIMS: *m*/*z* (%) = 542 (10) [M]$^+$, 514 (36), 496 (18), 482 (7), 471 (16), 454 (30), 426 (9), 411 (8), 383 (5), 342 (22), 275 (24), 261 (25), 187 (50), 155 (72), 149 (67), 131 (48), 109 (68), 91 (90), 69 (100). HRESI MS: calcd. for $C_{29}H_{34}O_{10}$ [M + Na]$^+$ *m*/*z* = 565.2049, found *m*/*z* = 565.2043. ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2.

Henridilactone B (2): White powder. $[\alpha]_D^{24.6}$ = +84.24 (*c* = 0.18, MeOH). UV (MeOH): $\lambda_{max.}$ (log ε) = 201 (3.73), 242 (3.67) nm. IR spectrum was identical with that of **1**. EI MS: *m*/*z* (%) = 558 (20) [M]$^+$, 530 (38), 512 (6), 470 (13), 342 (100), 315 (17), 301 (20), 284 (21), 275 (23), 261 (49), 215 (35), 187 (40), 175 (37), 155 (46), 131 (43), 105 (54), 91 (75), 82 (87), 69 (96). HRESI MS: calcd. for $C_{29}H_{34}O_{11}$ [M + Na]$^+$ *m*/*z* = 581.1998, found *m*/*z* = 581.2019. ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2.

Henridilactone C (3): White powder. $[\alpha]_D^{27.4}$ = +60.30 (*c* = 0.20, MeOH). UV spectrum was identical with that of **2**. IR (KBr): $\tilde{\nu}_{max.}$ = 2976, 2941, 1772, 1736, 1662 cm^{-1}. EI MS: *m*/*z* (%) = 526 (32) $[M]^+$, 511 (15), 498 (18), 480 (15), 467 (16), 438 (32), 275 (32), 249 (55), 215 (35), 189 (93), 175 (30), 155 (45), 105 (52), 91 (83), 69 (100). HRESI MS: calcd. for $C_{29}H_{34}O_9$ $[M + Na]^+$ *m*/*z* = 549.2100, found *m*/*z* = 549.2124. ^1H and ^{13}C NMR spectroscopic data: see Tables 1 and 3.

Henridilactone D (4): White powder. $[\alpha]_D^{27.3}$ = +56.82 (*c* = 0.088, MeOH). UV: end absorption. IR (KBr): $\tilde{\nu}_{max.}$ = 3442 (br), 1774, 1735, 1630 cm^{-1}. EI MS: *m*/*z* (%) = 544 (1) $[M]^+$, 526 (36) $[M - H_2O]^+$, 511 (18), 498 (23), 467 (17), 438 (35), 275 (37), 215 (41), 187 (55), 155 (49), 105 (61), 91 (90), 69 (100). HRESIMS: calcd. for $C_{29}H_{36}O_{10}$ $[M + Na]^+$ *m*/*z* = 567.2206, found *m*/*z* = 567.2193. ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 3.

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