Terpenoids from the Aerial Parts of *Parasenecio deltophylla*

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Five new modified eremophilane-type sesquiterpenes (**1**−**5**), including three norsesquiterpenes (**1**−**3**), and one new monoterpene (**6**) were isolated from the aerial parts of *Parasenecio deltophylla*. Their structures were established on the basis of HRMS and NMR methods. The cytotoxicity of compounds **1**−**4** and **6** against selected cancer cell lines, including human promyelocytic leukemia (HL-60) and human hepatoma (Hep-G2), was evaluated. Antioxidant activities of these compounds were assessed by ABTS and DPPH methods.

The genus *Parasenecio* (Asteraceae), which used to be named *Cacalia*, contains more than 60 species distributed mainly over the mountain areas in the northwestern and southwestern regions in the People's Republic of China.[1] Approximately 26 species have been used as Chinese traditional folk herbs for invigorating the circulation of blood, curing rheumatismal aches and injuries from falls, etc.[2,3] Previous reports have shown that a furanoeremophilane-type sesquiterpene and a modified eremophilane-type norsesquiterpene were isolated from *Parasenecio deltophylla* (Maxim) Mattf (Asteraceae).[4] In this study, we report the isolation of five new cacalol derivatives, modified eremophilane-type sesquiterpenes (**1**−**5**) that include three norsesquiterpenes (**1**−**3**) and a new monoterpene (**6**), from this plant, which is distributed in the mountain areas of the Himalayas at altitudes of 2000−3000 m in the People's Republic of China. Structures of the new compounds were evaluated by spectroscopic methods, including HRMS and 1D and 2D NMR. Compounds **1**−**4** and **6** were assessed for their cytotoxic activities against two human tumor cell lines, human promyelocytic leukemia HL-60 and human hepatoma Hep-G2, as well as for their antioxidant activities by scavenging ABTS and DPPH free radicals.

Compound **1** gave a molecular formula of $C_{20}H_{24}O_5$, as determined by HRESIMS, *m*/*z* 345.1694 $[M + H]^+$, indicating nine degrees of unsaturation. Its EIMS gave the characteristic ion fragments at *m*/*z* 244 $[M - AngOH]^+$ and 83 $[Ang]^+$. The IR spectrum indicated the presence of OH (3387 cm^{-1}), conjugated carbonyl (1699 cm^{-1}), and conjugated ester (1647 cm^{-1}) groups. The ^1H and ^{13}C NMR data of **1** (Tables 1 and 2) were similar to the published values for deltonorcacalol.[4] The most obvious distinction was the chemical shift value of C-14, which appeared as an oxygen-bearing methylene carbon at δ_C 59.4 for **1** instead of a methyl at δ_C 16.3 for deltonorcacalol. In accordance, the ^1H NMR showed two protons [δ_H 5.24 (d, J = 12.8 Hz, H-14a) and 5.19 (d, J = 12.8 Hz, H-14b)] for **1** instead of a methyl singlet at δ_H 2.30 for deltonorcacalol. The above indicated the presence of an angeloyloxy unit, which was supported by characteristic chemical shifts of five carbon resonances [δ_C 167.5 (qC), 127.4 (qC), 138.7 (CH), 15.8 (CH_3), and 20.6 (CH_3)].[5] The angeloyloxy group was placed at C-14 by the observed HMBC correlations from H-14 (δ_H 5.24 and 5.19) to C-1′ (δ_C 167.5). The above signals revealed that **1** was a cacalol derivative, a rearranged eremophilane-type norsesquiterpene possessing an angeloyloxy group. The β-configuration was assigned to Me-15 on the basis of ^1H NMR signals of H-4 and H-15 (δ_H 3.21, J = 6.8, 6.4 Hz and 1.07, J = 6.8 Hz) and ^{13}C NMR signals of C-4 and C-15 (δ_C 27.4 and 20.1) by comparing those with the literature data of cacalol derivatives.[4−7] Comparison of the specific rotation observed for **1** ($[\alpha]_D^{20}$ +21; *c* 1.00, $CHCl_3$) with that reported for deltonorcacalol ($[\alpha]_D^{20}$ +84.6; *c* 0.39, $CHCl_3$)[4] and cacalol ($[\alpha]_D$ +10)[8] supported the configuration of CH_3-15. Consequently, compound **1** was named 14-angeloyloxydeltonorcacalol.

Compound **2** was formulated as $C_{20}H_{24}O_6$ with nine degrees of unsaturation (HREIMS). The ^1H and ^{13}C NMR data of **2** (Tables 1 and 2) were very similar to those of **1**. The only difference was the presence of one more OH group in **2**. An oxygenated methine resonance at δ_C 68.4 was assigned to C-3 bearing an OH group by the HMBC correlations from H-1 (δ_H 6.95) and H-15 (δ_H 1.04) to C-3 (δ_C 68.4). The coupling constants for H-2 (6.30, dd, J = 9.6, 6.0 Hz) and H-3 (4.12, dd, J = 6.0 Hz) suggested that H-3 had an α-orientation. In the 1D NOE difference spectrum, the enhancement of H-3 (+2.13%) by irradiation of H-4 further supported the α-orientation of H-3. Consequently, compound **2** was assigned as 14-angeloyloxy-3β-hydroxydeltonorcacalol.[9]

Compound **3** was formulated as $C_{20}H_{24}O_7$ with nine degrees of unsaturation (HREIMS). The ^1H and ^{13}C NMR data of **3** (Tables 1 and 2) were very similar to those of **1**. They differed mainly in the presence of proton signals at δ_H 3.43 (t, J = 3.2 Hz), 3.54 (t, J = 3.2 Hz), and 5.51 (brs) and carbon signals at δ_C 51.7, 55.0, and 62.7, which were attributable to an epoxide ring and one more OH group, respectively.[9] The OH group was assigned to C-1, the epoxide ring was assigned between C-2 and C-3, and the angeloyloxy unit was attached to C-14 as indicated by HMBC correlations from H-2 (δ_H 3.54) to C-1 (δ_C 62.7); from H-3 (δ_H 3.43) and H-4 (δ_H 3.66) to C-2 (δ_C 51.7); from H-4 and H-15 (δ_H 1.34) to C-3 (δ_C 55.0); from H-3 and H-15 to C-4 (δ_C 30.3); and from H-14 (δ_H 5.23) to C-1′ (δ_C 167.3). Both the ^1H and ^{13}C NMR spectra (Tables 1 and 2) of **3** were similar to the published values for angulifolin B.[9] Five carbons in the A ring of both compounds, C-1, C-2, C-3, C-4, and C-15, showed nearly the same chemical shifts, δ_C 62.7, 51.7, 55.0, 30.3, and 20.5 for **3** and δ_C 62.5, 51.7, 55.0, 30.3, and 21.3 for angulifolin B. The above evidence suggested that the configuration of compound **3** was the same as angulifolin B; namely, H-1 and H-4 are α-oriented and H-2 and H-3 are β-oriented. Furthermore, the α-configuration of the epoxy of **3** caused positive specific rotation as in angulifolin B ($[\alpha]_D^{25}$ +61.8; *c* 0.22, $CHCl_3$) by comparing the specific rotation observed for **3** ($[\alpha]_D^{20}$ −17 (*c* 1.00, $CHCl_3$) and with that reported for **2** ($[\alpha]_D^{20}$ −130 (*c* 1.00, $CHCl_3$). The collected data indicate the structure of **3** to be 14-angeloyloxy-2α,3α-epoxy-1β-hydroxydeltonorcacalol.[9]

Compound **4** had the molecular formula $C_{21}H_{22}O_6$ (HREIMS), indicating 11 degrees of unsaturation. In the ^1H NMR spectrum (Table 1), a characteristic signal of a furan ring (H-12) proton appeared at δ_H 7.49 (s). Comparison of the NMR data of **4** with those of **3** suggested that **4** was a modified eremophilane cacalol

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Chart 1

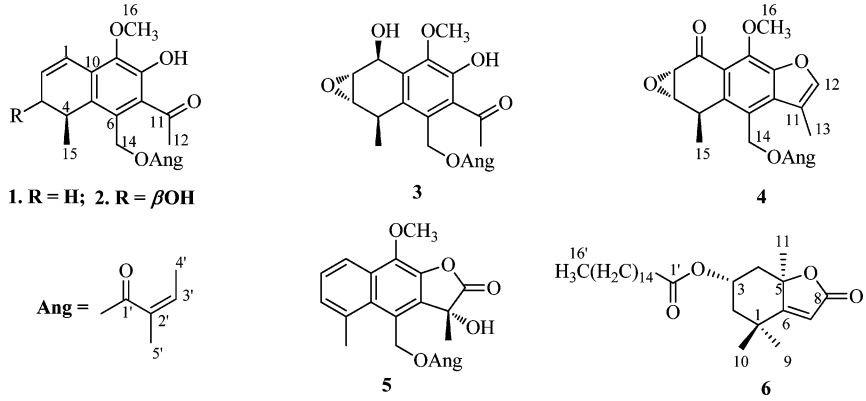

Table 1. ^{1}H NMR Spectroscopic Data (400 MHz, $CDCl_3$) for **1**−**5** [δ_H, mult. (*J* in Hz)]

position	1	2	3	4	5
1	6.76 dd (9.8, 2.8)	6.96 d (9.6)	α, 5.51 brs		8.21 brd (8.4)
2	6.09 m	6.30 dd (9.6, 6.0)	α, 3.54 t (3.2)	α, 3.72 d (4.4)	7.42 dd (8.4, 6.8)
3	*β*, 2.51 ddd (17.6, 6.4, 2.8) α, 2.25 dd (17.6, 6.4)	α, 4.12 d (6.0)	α, 3.43 t (3.2)	α, 3.78 dd (4.4, 2.4)	7.34 brd (6.8)
4	α, 3.21 tq (6.8, 6.4)	α, 3.43 q (7.2)	α, 3.66 dq (6.8, 3.2)	α, 4.08 dq (6.8, 2.4)	
12	2.61 s	2.62 s	2.58 s	7.49 s	
13				2.35 s	*β*, 1.86 s
14	5.24 d (12.8) 5.19 d (12.8)	5.28 d (12.8) 5.24 d (12.8)	5.23 brs 5.23 brs	5.50 d (12.8) 5.44 d (12.8)	5.97 d (12.8) 5.83 d (12.8)
15	1.07 d (6.8)	1.04 d (7.2)	1.34 d (6.8)	1.22 d (6.8)	2.93 s
16	3.82 s	3.87 s	3.93 s	4.23 s	4.22 s
OH	8.26 brs	8.14 brs	8.13 brs		
OAng3′	6.09 m	6.09 qq (7.2, 1.2)	6.11 qq (7.2, 1.2)	6.08 q (7.2)	6.08 qq (7.2, 1.2)
OAng4′	1.97 dq (7.2, 1.2)	1.98 dq (7.2, 1.2)	1.98 dq (7.2, 1.2)	1.94 d (7.2)	1.90 dq (7.2, 1.2)
OAng5′	1.87 brs	1.87 brs	1.86 brs	1.84 brs	1.80 brs

Table 2. ^{13}C NMR Spectroscopic Data (100 MHz, $CDCl_3$) for **1**−**5** (δ_C, mult.)

position	1	2	3	4	5
1	120.6 CH	122.8 CH	62.7 CH	195.1 qC	121.4 CH
2	129.4 CH	128.8CH	51.7 CH	55.4 CH	126.4 CH
3	30.6 CH_2	68.4 CH	55.0 CH	56.1 CH	130.9 CH
4	27.4 CH	36.7 CH	30.3 CH	31.5 CH	130.8 qC
5	133.7 qC	131.4 qC	130.3 qC	138.6 qC	135.0 qC
6	126.5 qC	127.4 qC	127.0 qC	119.6 qC	124.2 qC
7	125.6 qC	127.5 qC	129.4 qC	134.7 qC	131.9 qC
8	147.8 qC	147.8 qC	147.3 qC	145.4 qC	136.1 qC
9	143.6 qC	144.4 qC	147.1 qC	145.5 qC	138.6 qC
10	128.6 qC	126.6 qC	130.2 qC	118.6 qC	130.8 qC
11	204.6 qC	204.6 qC	205.0 qC	116.2 qC	73.3 qC
12	31.9 CH_3	31.9 CH_3	31.8 CH_3	145.0 CH	176.3 qC
13				10.0 CH_3	27.8 CH_3
14	59.4 CH_2	59.2 CH_2	59.0 CH_2	58.7 CH_2	60.6 CH_2
15	20.1 CH_3	18.9 CH_3	20.5 CH_3	20.8 CH_3	24.0 CH_3
16	61.4 CH_3	61.9 CH_3	61.8 CH_3	61.5 CH_3	61.0 CH_3
OAng1′	167.5 qC	167.4 qC	167.3 qC	167.6 qC	167.9 qC
OAng2′	127.4 qC	127.2 qC	127.3 qC	127.2 qC	127.1 qC
OAng3′	138.7 CH	139.4 CH	139.6 CH	139.0 CH	140.1 CH
OAng4′	15.8 CH_3	15.9 CH_3	15.8 CH_3	15.8 CH_3	15.8 CH_3
OAng5′	20.6 CH_3	20.6 CH_3	20.3 CH_3	20.5 CH_3	20.5 CH_3

bearing an angeloyloxy group.[5,10] A noted difference between the compounds was that **4** had a C-1 ketone instead of the C-1 OH group of **3**. On the other hand, the missing signals of the phenolic OH and acetyl groups of **3** suggested that the furan ring of **4** was attached between C-7 and C-8. The assignments were confirmed by the observed HMBC correlations from H-2 (δ_H 3.72) to C-1(δ_C 195.1), C-3 (δ_C 56.1), and C-10 (δ_C 118.6) and from H-13 (δ_H 2.35) to C-11 (δ_C 116.2), C-12 (δ_C 145.0), and C-7 (δ_C 134.7). Consequently, compound **4** was assigned as 14-angeloyloxy-2α,3α-epoxy-1-oxo-*O*-methylcacalol.[9]

Compound **5** had the molecular formula $C_{21}H_{22}O_6$ (HREIMS), indicating 11 degrees of unsaturation. The UV spectrum revealed absorptions at 203 and 236 nm. EIMS showed an important fragment ion at *m*/*z* 271 $[M - AngO]^+$ and 83 $[Ang]^+$. Analysis of the ^{13}C and DEPT NMR spectra of **5** (Table 2) indicated the presence of one lactone carbonyl carbon and three tetrasubstituted double bonds. The ^{1}H NMR spectrum (Table 1) suggested three *ortho*-benzenoid proton signals. Consequently, this required an aromatic tricyclic sesquiterpene. Comparison of the NMR data of **5** with those of **4** suggested that **5** was a cacalolide bearing an angeloyloxy group.[6,7,11] HMBC correlations observed between CH_3-13 (δ_H 1.86) and C-11 (δ_C 73.3), C-12 (δ_C 176.3), and C-7 (δ_C 131.9), in addition to a correlation observed from H-14a and H-14b (δ_H 5.97 and 5.83) to C-7, provided the basis for assignments of C-11, C-12, and C-7 in the lactone ring. The ^{1}H, ^{13}C, and 2D NMR data of **5** were similar to those of 3-hydroxycacalolide,[6] except that the A ring in **5** appeared as a benzene ring instead of a cyclohexene ring in 3-hydroxycacalolide and that the C-14 methyl was substituted by an angeloyloxy group. These conclusions were verified by the observed HMBC correlations from H-14a and H-14b to C-1′ at δ_C 167.9. The OH group at C-11 was confirmed as α-oriented by comparing the specific rotation of **5**, $[\alpha]_D^{20}$ −33 (*c* 0.05, $CHCl_3$), with that of 3-hydroxycacalolide, $[\alpha]_D$ −18 (*c* 0.59, CH_2Cl_2) and *epi*-3-hydroxycacalolide, $[\alpha]_D$ +35 (*c*1.00, CH_2Cl_2).[6] Consequently, compound **5** was elucidated as 14-angeloyloxy-11α-hydroxy-*O*-methyl-1,2,3,4-tetrahydrocacalolide.

Compound **6** had a molecular formula of $C_{27}H_{46}O_4$ (HREIMS). The ^{1}H and ^{13}C NMR data (see Experimental Section) resembled those of loliolide,[12−14] except that it displayed signals of another methyl group at δ_H 0.87 (3H, t, J = 6.8 Hz) and long-chain methylenes at δ_H 2.33 (2H, t, J = 7.2 Hz), 1.62−1.67 (2H, m), and 1.25 (24H, m). Deshielding of the H-3 methine (δ_H 5.26) in relation to that of loliolide (δ_H 4.31) indicated that **6** was a loliolide derivative in which the OH group at C-3 was esterified by a long-chain fatty acid. The EIMS showed fragment ions at *m*/*z* 239, 211, 183, 127, 113, 99, 85, 71, 57, and 43, consistent a palmitoyl group.

Loliolide, also isolated from *P. deltophylla*, had physical and spectroscopic features identical to those reported for (−)-loliolide,[12–14] especially the specific rotation for observed loliolide ($[\alpha]_D^{20}$ −90.0; *c* 0.10, $CHCl_3$) and for reported (−)-loliolide ($[\alpha]_D^{23}$ −87; *c* 0.66, $CHCl_3$).[12] Its esterified derivative at C-3, compound **6**, also showed a negative specific rotation ($[\alpha]_D^{20}$ −34; *c* 1.00, $CHCl_3$). Therefore, compound **6** was elucidated as (−)-3-*O*-palmitoylloliolide.

It was reported that sesquiterpenoids, especially eremophilane-type sesquiterpenes, are common constituents of members of the genus *Parasenecio*.[15] In this investigation, compounds **1**−**5** isolated from *P. deltophylla* provided additional support for this observation.

Five compounds, **1**−**4** and **6**, were evaluated for their cytotoxic activities against two human tumor cell lines, promyelocytic leukemia (HL-60) and hepatoma (Hep-G2). They were also tested for their antioxidant potential by scavenging ABTS and DPPH free radicals. Compound **4** gave an IC_{50} of 27.8 μM against HepG2. Compounds **4** and **6** showed IC_{50}'s of 49.8 and 47.5 μM against HL-60. Mitomycin was used as a positive control, with IC_{50} values of 1.5 μM against HL-60 cells and 5.4 μM against Hep-G2 cells, respectively. The tested compounds had no free radical scavenging capacity for $ABTS^{\bullet+}$ and $DPPH^{\bullet}$, and the IC_{50} values were all over 200 μM. Trolox was used as a positive control, with IC_{50} values of 13.2 μM.

Experimental Section

General Experimental Procedures. Melting points were measured using an uncorrected X-4 Digital Display micromelting point apparatus. Optical rotations were obtained on a Perkin-Elmer 341 digital polarimeter in $CHCl_3$. UV spectra were collected in MeOH using a Shimadzu UV-260 spectrophotometer. IR spectra were obtained with a Nicolet NEXUS-670 FT-IR spectrometer. 1D and 2D NMR spectra were recorded in $CDCl_3$ with Bruker AM-400 and Varian Mercury-300 NMR spectrometers, and the chemical shifts are given as δ values with TMS as the internal standard. HRESIMS were recorded on a Bruker Daltonics APEX II mass spectrometer. EIMS was measured on a HP 5988A GC-MS instrument at 70 eV. Column chromatography was carried out on silica gel (200−300 mesh and Type 60), and TLC was also performed on silica gel (GF_{254}, 10−40 μm), with both materials supplied by Qingdao Marine Chemical Co.

Plant Material. The aerial parts of *P. deltophylla* were collected in Huzhu County, Qinghai Province, People's Republic of China, in August 2006, and identified by Prof. Guo-Liang Zhang, School of Life Science, Lanzhou University. A voucher specimen (no. Pd20060803) was deposited at the State Key Laboratory of Applied Organic Chemistry, Lanzhou University.

Extraction and Isolation. The air-dried aerial parts of *P. deltophylla* (5.5 kg) were powdered and extracted with petroleum ether−Et_2O−MeOH (v/v/v = 5:5:5 L) four times at room temperature. The extract was evaporated under reduced pressure to afford a dried residue (308 g). A portion (300 g) of this residue was chromatographed over a silica gel column, using petroleum ether (60−90 °C)−acetone mixtures of increasing polarity (100:0 to 0:100), and finally washed with MeOH, to give 22 fractions. Fraction 7 (petroleum ether−acetone, 15:1) was subjected to further chromatography with $CHCl_3$−acetone (100:1) and petroleum ether−acetone (5:1), followed by $CHCl_3$−EtOAc (80:1), to yield **1** (17 mg). Fraction 9 (petroleum ether−acetone, 10:1) was subjected to chromatography with petroleum ether−acetone (10:1), followed by petroleum ether−EtOAc (5:1) and $CHCl_3$−EtOAc (6:1), to give **4** (40 mg) and **6** (19 mg). Fraction 13 (petroleum ether−acetone, 8:1) was subjected to chromatography with $CHCl_3$−acetone (20:1), petroleum ether−acetone (3:1), and $CHCl_3$−EtOAc (3:1), to give **2** (3 mg) and **5** (1.8 mg). Fraction 15 (petroleum ether−acetone, 5:1) was subjected to chromatography with $CHCl_3$−acetone (5:1), further $CHCl_3$−EtOAc (2:1), followed by petroleum ether−acetone (2:1), to yield **3** (7 mg).

Compound 1: yellow oil; $[\alpha]_D^{20}$ +21 (*c* 1.00, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 231 (4.1), 280 (3.8), 320 (3.4) nm; IR ν_{max} (film) 3387, 2960, 2929, 1699, 1647, 1592, 1458, 1428, 1351, 1271, 1231, 1153, 1044, 972, 851 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; EIMS *m/z* 344 $[M]^+$ (4), 261 (10), 244 (21), 229 (34), 115 (15), 83 (63), 55 (100), 43 (91); HRESIMS *m/z* 345.1694 $[M + H]^+$ (calcd for $C_{20}H_{25}O_5$, 345.1697).

Compound 2: colorless oil; $[\alpha]_D^{20}$ −130 (*c* 1.00, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 229 (4.4), 275 (4.0) nm; IR ν_{max} (film) 3374, 2962, 2928, 1698, 1646, 1591, 1459, 1429, 1351, 1273, 1231, 1153, 1045, 1014, 975, 850 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; EIMS *m/z* 360 $[M]^+$ (0.5), 342 (0.6), 277 (1), 260 (12), 242 (29), 277 (1), 83 (61), 55 (100), 43 (96); HRESIMS *m/z* 383.1471 $[M + Na]^+$ (calcd for $C_{20}H_{24}O_6Na$, 383.1465).

Compound 3: colorless oil; $[\alpha]_D^{20}$ −17 (*c* 1.00, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 222 (4.4), 285 (3.7) nm; IR ν_{max} (film) 3391, 2964, 2929, 1703, 1595, 1464, 1433, 1352, 1272, 1231, 1149, 1043, 838 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; EIMS *m/z* 376 $[M]^+$ (3), 293 (3), 276 (16), 261 (14), 247 (52), 83 (59), 55 (80), 43 (100); HRESIMS *m/z* 394.1867 $[M + NH_4]^+$ (calcd for $C_{20}H_{28}O_7N$, 394.1860).

Compound 4: colorless crystals; 111−112 °C (acetone); $[\alpha]_D^{20}$ −120 (*c* 1.00, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 236 (4.4), 287 (4.4), 320 (4.0) nm; IR ν_{max} (film) 2958, 2929, 1711, 1687, 1612, 1584, 1478, 1456, 1333, 1229, 1148, 1119, 1038, 991, 948, 860, 583 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; EIMS *m/z* 370 $[M]^+$ (11), 271 (97), 241 (34), 115 (22), 83 (35), 55 (100), 43 (26); HRESIMS *m/z* 371.1483 $[M + H]^+$ (calcd for $C_{21}H_{23}O_6$, 371.1489).

Compound 5: colorless oil; $[\alpha]_D^{20}$ −33 (*c* 0.05, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 203 (3.5), 236 (4.8) nm; ^1H and ^{13}C NMR data, see Tables 1 and 2; EIMS *m/z* 370 $[M]^+$ (12), 271 (8), 242 (32), 227 (64), 149 (38), 83 (86), 55 (100), 43 (69); HRESIMS *m/z* 388.1760 $[M + NH_4]^+$ (calcd for $C_{21}H_{26}O_6N$, 388.1755).

Compound 6: colorless gum; $[\alpha]_D^{20}$ −34 (*c* 1.00, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 217 (4.1) nm; IR ν_{max} (film) 2925, 2854, 1759, 1743, 1463, 1256, 1151, 1113, 954 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H 5.73 (1H, brs, H-7), 5.26 (1H, m, H-3α), 2.50 (1H, dt, *J* = 14.2, 2.4 Hz, H-4a), 2.33 (2H, t, *J* = 7.2 Hz, H-2′), 2.04 (4H, dt, *J* = 14.8, 2.4 Hz, H-2a), 1.81 (4H, dd, *J* = 14.2, 4.0 Hz, H-4b), 1.71 (3H, s, H-11α), 1.62−1.67 (2H, m, H-3′), 1.56 (1H, dd, *J* = 14.8, 4.0 Hz, H-2b), 1.39 (3H, s, H-10*β*), 1.28 (3H, s, H-9α), 1.25 (24H, m, H-4′−H-15′), 0.87 (3H, t, *J* = 6.8 Hz, H-16′); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 181.2 (qC, C-6), 172.5 (qC, C-1′), 171.4 (qC, C-8), 113.4 (CH, C-7), 85.9 (qC, C-5), 68.3 (CH, C-3), 44.2 (CH_2, C-2), 42.9 (CH_2, C-4), 35.7 (qC, C-1), 34.7 (CH_2, C-2′), 31.9 (CH_2, C-14′), 30.4 (CH_3, C-9), 29.1−29.6 (CH_2, C-4′−13′), 26.5 (CH_3, C-11), 25.9 (CH_3, C-10), 24.8 (CH_2, C-3′), 22.7 (CH_2, C-15′), 14.1 (CH_3, C-16′); EIMS *m/z* 434 $[M]^+$ (0.1), 406 (1), 378 (0.3), 239 (0.6), 238 (1), 211 (1), 196 (4), 183 (1), 178 (61), 150 (22), 135 (35), 127 (1), 113 (2), 107 (19), 99 (3), 85 (12), 71 (20), 57 (45), 43 (100); HRESIMS *m/z* 435.3474 $[M + H]^+$ (calcd for $C_{27}H_{47}O_4$, 435.3469).

Bioassay. Cytotoxic assays of compounds **1**−**4** and **6** against the human leukemia HL-60 and human hepatoma Hep-G2 cell lines were carried out using the MTT method, as described previously.[16] In addition, the antioxidant activities for these compounds were determined by ABTS and DPPH methods.[17,18]

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Supporting Information Available: 1D and 2D NMR and HRESIMS spectra of **1**−**6** are available free of charge via the Internet at http://pubs.acs.org.

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