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Scuteflorins A and B, Dihydropyranocoumarins from *Scutellaria lateriflora*

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Two new dihydropyranocoumarins, scuteflorins A (**1**) and B (**2**), together with the known compounds decursin (**3**), chrysin (**4**), oroxylin A (**5**), wogonin (**6**), 5,7-dihydroxy-8,2′-dimethoxyflavone, dihydrochrysin, dihydrooroxylin A, lupenol, scutellaric acid, pomolic acid, ursolic acid, β-sitosterol, daucosterol, and palmitic acid, were isolated from the aerial parts of *Scutellaria lateriflora*, commonly used as a dietary supplement. The structures of **1** and **2** were established by means of 1D and 2D NMR spectra as well as HRMS data. The absolute configuration of coumarins **1** and **2** was determined by comparison of experimental and theoretical calculated CD spectra. The cytotoxicity and antioxidant effects of the methanol extract of this plant and some of the constituent flavonoids were evaluated in vitro.

Scutellaria lateriflora L. (Lamiaceae), commonly named American skullcap, has been used for over 200 years as a mild relaxant and has long been hailed as an effective therapy for anxiety, nervous tension, and convulsions in Europe and North America.[1] In vivo animal behavior trials have revealed that an aqueous extract of *S. lateriflora* showed demonstrable effects on anxiety levels in rats.[2] Significant anxiolytic effects have been demonstrated in a double blind, placebo-controlled study of healthy volunteers.[3] There are mixed opinions as to the safety of *S. lateriflora* because of reports of hepatotoxic reactions after skullcap-containing preparations were ingested.[4,5] American skullcap has also been commonly adulterated with germander (e.g., *Teucrium chamaedrys* and *T. canadense*),[6,7] a group of plants known to cause liver problems when used as a weight-control supplement in France.[8] The liver toxicity of germander is reportedly due to furan ring-containing diterpenoids,[9] which have not been reported from American skullcap. In the United States, American skullcap has been classified as an "Herb of Undefined Safety" by the FDA.

In an effort to develop reliable analytical method(s) to differentiate between *S. lateriflora* and its potential adulterant germanders, and to evaluate the bioactivities of individual compounds to provide solid scientific support for the traditional usages of this plant, the present chemical investigation was undertaken. Limited data exist regarding the chemical constituents of *S. lateriflora*. Sesquiterpenes were reported as the main components of the essential oil of *S. lateriflora*.[10] Five neo-clerodane diterpenoids were isolated.[11] Three flavone glucuronides and a flavanone glucuronide were also identified along with five flavones characterized by HPLC-UV/MS.[12] Herein, we report the isolation and structure elucidation of two new coumarins, scuteflorins A (**1**) and B (**2**), and evaluation of the bioactivity of flavonoids isolated from the aerial parts of this plant. All of the known compounds except chrysin (**4**) and wogonin (**6**)[12] are reported for the first time from this plant.

Results and Discussion

The MeOH extract of the aerial parts of *S. lateriflora* was subjected to chromatography on Diaion HP-20 resin followed by repeated chromatography on silica gel, Sephadex LH-20, reversed-phase silica gel columns, and HPLC to yield three minor coumarins, scuteflorins A (**1**) and B (**2**) and decursin (**3**), along with six flavonoids, chrysin (**4**),[13] oroxylin A (**5**),[14] wogonin (**6**),[14] dihydrooroxylin A,[14] dihydrochrysin,[15] and 5,7-dihydroxy-8,2′-dimethoxyflavone,[16] four triterpenes, lupenol,[17] scutellaric acid,[18] pomolic acid,[19] and ursolic acid,[19] two steroids, β-sitosterol and daucosterol,[20] and palmitic acid.[21] The structures of known compounds were elucidated by comparison of their NMR data with those reported. The absolute configuration of the two flavanones dihy-

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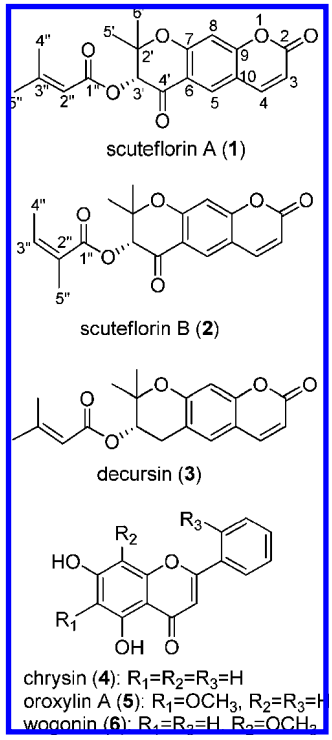

drochrysin and dihydrooroxylin A was confirmed on the basis of their specific rotation data.

Scuteflorin A (**1**) was obtained as a white powder, $[\alpha]_D$ +25.2 (*c* 0.032, MeOH). The HRESITOFMS of compound **1** gave an $[M + Na]^+$ ion at *m*/*z* 365.1013 and a $[2M + Na]^+$ ion at 707.2011 consistent with the pseudomolecular formula $C_{19}H_{18}O_6Na$ (calcd for $[M + Na]^+$ 365.1001 and calcd for $[2M + Na]^+$ 707.2105, respectively). The characteristic bright blue fluorescence under UV light at 254 nm and the UV absorptions at λ 255 and 330 nm (α,β-unsaturated C═O) along with an IR absorption band at 1732 cm^{-1} (C═O of α-pyrone and ester) indicated a coumarin skeleton for this compound. The ^1H NMR spectrum of **1** (see Table 1) showed a pair of doublets at δ_H 8.04 and 6.36 ascribable to H-3 and H-4 of a coumarin moiety. The two singlets at δ_H 8.11 and 6.90 were assigned to H-5 and H-8 and suggested 6,7-disubstitution of the aromatic ring. This 6,7-disubstitution was determined as resulting from a dihydro-γ-pyranone ring on the basis of the ^1H and ^{13}C NMR data and the HMBC correlations as depicted in Figure 1. The H-5 (δ_H 8.11) signal correlated with a carbonyl carbon at C-4′ (δ_C 187.8); H-3′ (δ_H 5.71) with C-2′ (δ_C 83.6), C-5′ (δ_C 26.2), C-6′ (δ_C 20.1), and C-4′ (δ_C 187.8); H-5′ (δ_H 1.58) with C-2′, C-3′, and C-6′; and H-6′ (δ_H 1.39) with C-2′, C-3′, and C-5′ (see Figure 1). The 4′-carbonyl substitution explained the downfield shift of H-5. The remaining resonances in the ^1H and ^{13}C NMR spectra corresponded to those of a senecioyloxy group,[22] which was located at C-3′ according to the HMBC correlation of H-3′ with C-1″ (δ_C 165.2). Thus, the planar structure of compound **1** was deduced as 3′-senecioyloxy-4′-oxo-3′,4′-dihydroxanthyletin, and this substance was given the trivial name scuteflorin A.

Compound **1** gave a positive specific rotation (+25.2), as compared to +135 of (+)-decursin (**3**), with a C-3′*S* absolute configuration.[23] However, due to the considerable structural differences between compounds **1** and **3**, one may expect significant changes in specific rotation value. Recourse was thus taken to electronic circular dichroism (ECD) to determine its absolute configuration by comparing the experimentally observed and theoretically calculated ECD spectra. Using this approach, our group has defined successfully the absolute configuration of several natural products.[24] The potential energy surface of compound **1** in the gas phase was scanned at the AM1 level by rotating about the C-3′−O, C-1″−O (C-3′), and C-1″−C-2″ bonds. Six conformers were found and redefined at the B3LYP/6-31G** level. Conformational analysis indicated that conformer **1a** is predominant [95.6% at the B3LYP/6-31G** level in the gas phase by Gibbs free energies and 95.9% at the B3LYP-SCRF/6-31G**//B3LYP/6-31G** level in MeOH with the "conductor-like continuum screening model" (COSMO) by total energies] (see Supporting Information for detailed information). Theoretical calculation of the ECD of conformer **1a** was performed by the time-dependent density functional theory (TDDFT) method at the B3LYP/6-31G** and B3LYP/AUG-cc-pVDZ//B3LYP/6-31G** levels in the gas phase and at the B3LYP-SCRF/6-31G**//B3LYP/6-31G** level in MeOH. The calculated ECD spectra of **1a** in the gas phase and in MeOH, together with the experimental ECD of **1** in MeOH, are shown in Figure 2. The overall patterns of the calculated ECD spectra were consistent with that of the experimental one, i.e., a positive Cotton effect (CE) in the 250−300 nm region and a negative CE in the 300−350 nm region. Considering the extended π-system of the dihydro-γ-pyranone containing a coumarin chromophore in **1**, the positive CE near 260 nm and the shoulder near 290 nm in the experimental

Table 1. NMR Data for Compounds **1** and **2** in MeOH-d_4

	compound **1**			compound **2**	
position	δ_C	δ_H (*J* in Hz)	HMBC	δ_C	δ_H (*J* in Hz)
2	159.9				[a]
3	115.6	6.36, d (9.6)		115.6	6.35, d (9.6)
4	144.5	8.04, d (9.6)		144.4	8.04, d (9.6)
5	128.7	8.11, s	C-4,7,9, 4′	128.7	8.11, s
6	118.2			118.1	
7	162.2			162.1	
8	106.0	6.90, s	C-6,7,9,10	106.0	6.91, s
9	160.6			160.4	
10	115.1			115.1	
2′	83.6			83.5	
3′	76.5	5.71, s	C-2′,4′,5′,6′,1″	77.2	5.78, s
4′	187.8			187.6	
5′	26.2	1.58, s	C-2′,3′,6′	26.4	1.59, s
6′	20.1	1.39, s	C-2′,3′,5′	20.1	1.41, s
1″	165.2			166.6	
2″	115.5	5.85, br	C-1″,3″,4″,5″	127.9	
3″	160.5			140.4	6.27, qq (8.4, 1.5)
4″	27.5	1.97, d (1.2)	C-2″,3-,5″	20.7	1.95, p (1.5)
5″	20.5	2.20, d (1.1)	C-2″,3″,4″	16.1	2.00, dq (7.2, 1.5)

[a] Not observed.

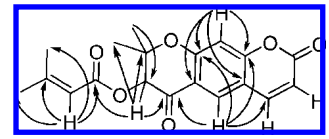

Figure 1. Key HMBC correlations of compound **1**.

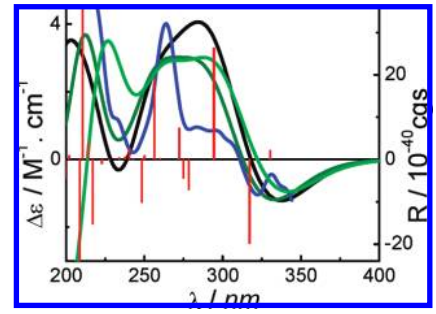

Figure 2. Calculated ECD spectra of conformer **1a** and the experimental ECD of compound **1** (red and olive lines, in the gas phase at the B3LYP/6-31G** level; black, in MeOH solvent at the B3LYP-SCRF/6-31G**//B3LYP/6-31G** level with COSMO; green, in the gas phase at the B3LYP/AUG-cc-pVDZ//B3LYP/6-31G** level; blue, experimental ECD in MeOH).

Table 2. Key Transitions and Oscillator and Rotatory Strengths of Conformer **1a** of Compound **1** at the B3LYP/6-31G** Level in the Gas Phase

excited state	ΔE [a] (eV)	λ [b] (nm)	f [c]	R_{vel} [d]	R_{len} [e]
90→91	3.91	317	0.180	−21.8	−19.8
90→92	4.21	294	0.162	25.8	26.4
88→91	4.55	272	0.039	7.9	7.4
86→93	4.83	257	0.011	18.6	19.2
87→93	5.89	211	0.431	84.8	84.1

[a] Excitation energy. [b] Wavelength. [c] Oscillator strength. [d] Rotatory strength in velocity form (10^{-40} cgs). [e] Rotatory strength in length form (10^{-40} cgs).

ECD would be characteristic for this molecule. This was supported by analysis of the molecular orbitals involved in key transitions generating the ECD spectrum of **1a** at the B3LYP/6-31G** level in the gas phase. The calculated positive rotatory strength at 272 nm (Table 2), which likely contributes to the positive CE near 260 nm in the experimental ECD, originates via the transitions from MO88 to MO91 (Figure 3). Another calculated positive rotatory strength at 294 nm, indicative of the shoulder near 290 nm in the experimental ECD, is derived from the transition from MO90 to MO92. The calculated negative rotatory strength at 317 nm, which may be associated with the negative CE beyond 300 nm in the experimental ECD, is generated by the transition from MO90 to MO91. All four MOs involve the π-electrons in the dihydro-γ-pyranone containing a coumarin chromophore. The calculated positive rotatory value at 257 nm (Table 2), which originates via the transition from MO86 to MO93, also contributed to the positive CE near 260 nm in the experimental ECD spectrum (Figure 3). The strong calculated positive rotatory value at 210 nm results from the transition from MO87 to MO93. Since these three MOs involve the electrons of the α,β-unsatuated ester system that may rotate along the C-3′−O (C-1″), C-1″−O (C-3′), and C-1″−C-2″ bonds in solution, caution should be exercised in using the CEs near these wavelengths to predict absolute configuration. Based on the above evidence, we concluded that compound **1** retains the same absolute configuration at C-3′ as in (+)-decursin (**3**), but was assigned as *R* in **1** due to the reversal of the Cahn–Ingold–Prelog priorities.

Scuteflorin B (**2**) was obtained as a white powder, $[\alpha]_D$ +5.8 (*c* 0.017, MeOH). Its molecular formula, $C_{19}H_{18}O_6$, was determined to be the same as compound **1** from the HRESITOFMS data at *m*/*z* 365.1011 (calcd $[M + Na]^+$ for 365.1001) and *m*/*z* 707.2085 (calcd $[2M + Na]^+$ for 707.2105). Analysis of the NMR data (^{1}H, ^{13}C, HSQC, and COSY) of **2** showed that most values were similar to those of compound **1**, except that the senecioyloxy group in **1** was replaced by an angeloyloxy group in **2** by comparison with literature[22] and 2D NMR data. Thus, compound **2** was assigned as 3′-angeloyloxy-4′-oxo-3′,4′-dihydroxanthyletin and given the trivial name scuteflorin B. Since compound **2** is also dextrorotatory, the 3′*R* absolute configuration of **2** should be the same as in compound **1**.

The cytotoxicities of the methanol extract of *S. lateriflora* and several flavonoid constituents were evaluated against a panel of normal cell lines (Vero: monkey kidney fibroblasts and LLC-PK$_{11}$: pig kidney epithelial cells) and solid tumor cell lines (HepG2: human hepatocellular carcinoma, SK-MEL: human malignant melanoma, KB: human epidermal carcinoma (oral), BT-549: human breast carcinoma, and SK-OV-3: human ovary carcinoma). No cytotoxicity was observed for any of the samples up to a highest concentration of 50 μM for purified compounds and 50 μg/mL for the extract in any of the cell lines tested (data not shown). A potent antioxidant activity (inhibition of intracellular reactive oxygen species generation in HL-60 cells) was observed for the methanol extract (IC_{50} value 1.5 μg/mL), which could be correlated with the presence of wogonin (**6**, IC_{50} value of 0.7 μM) (see Table 2). This result is consistent with published data.[25,26] The antioxidant effect of wogonin (**6**) may be compared with the positive control, vitamin C (IC_{50} of 0.01 μM). No cytotoxicity up to 62.5 μM observed for HL-60 cells in the antioxidant assay (data not shown) ruled out that the antioxidant effect was due to this possibility. Potential anti-inflammatory activity was determined in terms of inhibition of NF-κB-mediated transcription in SW1353 cells induced by phorbol myristate acetate (PMA). Moderate activity was observed for chrysin (**4**) and wogonin (**6**) with IC_{50} values of 33 and 39 μM, respectively, in comparison with the positive control, parthenolide (IC_{50} of 4.1 μM) (see Table 3). None of the samples tested inhibited control plasmid Sp-1-dependent luciferase expression (data not shown), indicating that their effects on NF-κB were specific and were not due to cytotoxicity to SW1353 cells.

Since many species of the genus *Scutellaria* have important uses as medicinal plants in traditional medicine, comprehensive chemical studies on the secondary metabolites have been conducted, especially on several species including *S. baicalensis,*[27] *S. discolor*,[28] *S. rivularis,*[29] and *S. galericulata*.[30] Several hundred compounds have been identified including flavonoids[31] and diterpenoids.[32] However, this is the first report of coumarins from the genus *Scutellaria*. Similar prenylated dihyropyranocoumarins have been reported from traditional Chinese medicine (e.g., *Angelica gigas* and *Peucedanum* spp.) with cytotoxicity,[33] neuroprotective,[34,35] and protein kinase C (PKC)[33] activating activities. All the known compounds described herein except chrysin (**4**) and wogonin (**6**) are reported for the first time from *S. lateriflora*. The major compounds, including the flavonoids and triterpenoids, may be used as chemical markers for quality control of this plant's raw materials and botanical products claiming to contain *S. lateriflora.*

Experimental Section

General Experimental Procedures. Optical rotations were measured in MeOH using a Rudolph Research Auto Pol IV polarimeter with a sodium lamp (589 nm) and a 1 dm microcell. UV spectra were acquired on a Varian 50 Bio UV spectrophotometer. Circular dichroism (CD) spectra were measured using an Olis DSM 20 CD instrument. IR spectra were obtained on a Perkin Elmer 100 FT-IR spectrometer. NMR spectra were recorded in pyridine-d_5 or methanol-d_4 on either a Varian 600 or Bruker Avance 400 NMR. All chemical shifts (δ) are given in ppm with reference to solvents, and coupling constants (*J*) are given in Hz. HRESIMS were acquired on a Bruker MicroTOF mass spectrometer. A highly porous synthetic resin (Diaion HP-20) was purchased from Mitsubishi Kagaku, Ltd. (Tokyo, Japan). Column chromatography (CC) was carried out on silica gel (40 μm for flash chromatography, J. T. Baker), 100 C_{18} reversed-phase silica gel (Sigma-Aldrich, 230−400 mesh), and Sephadex LH-20 (Mitsubishi Kagaku, Tokyo, Japan). The fractions were monitored by TLC on normal-phase silica gel 60 F_{254} plates (Merck, Germany) and reversed-phase C_{18} F254s plates (Merck, Darmstadt, Germany). Spots were visualized under UV light or by heating at 105 °C for 1−2 min after spraying with anisaldehyde/H_2SO_4 reagent. HPLC was performed on an ODS column (Phenomenex Luna C_{18}, 10 × 250 mm, 5 μm) as well as a silica NP-column (Phenomenex Luna Silica, 10 × 250 mm, 5 μm), and the elution was monitored at 240 nm.

Plant Material. The aerial parts of *S. lateriflora* were purchased from Starwest Botanicals (http://www.starwest-botanicals.com) and authenticated by Dr. V. Joshi at the National Center for Natural Products Research, University of Mississippi, where a voucher specimen (voucher no. 2120) has been deposited.

Extraction and Isolation. The dried powder of the aerial parts (850 g) of *S. lateriflora* was extracted by immersing in MeOH (3 × 3 L) at room temperature for two days each time, and the MeOH extracts were combined. A brown crude viscous residue (127.6 g) was obtained after evaporation of the solvent in vacuo. This MeOH extract (126.0 g) was subjected to passage over a Diaion HP-20 column (1.65 kg) eluting with 95% EtOH (7 L), MeOH−Me_2CO (1:1, 8 L), Me_2CO (6 L), EtOAc (5 L), and $CHCl_3$ (5 L), successively, to give seven fractions (A−G). Fraction D (9 g) was subjected to normal-phase silica gel CC (288 g) eluting with cyclohexane−EtOAc−MeOH mixtures of increasing polarity, to afford scutellaric acid (11.2 mg) and a mixture of 1-triacontanol and 1-dotriacontanol in the ratio of 2:1 (32.1 mg).

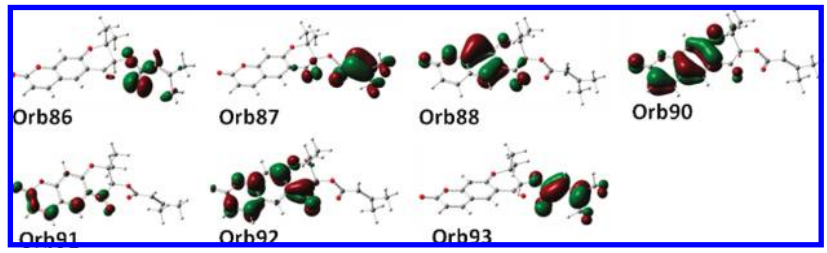

Figure 3. Molecular orbitals involved in key transitions in the ECD spectra of **1** at the B3LYP/6-31G** level in the gas phase.

Table 3. Antioxidant and Anti-inflammatory Activities of Selective Constituents from *S. lateriflora*

sample	antioxidant activity (IC_{50})	anti-inflammatory activity (IC_{50})
MeOH extract	1.5 μg/mL	>50 μg/mL
chrysin (**4**)	NA[a]	33 μM
oroxylin A (**5**)	NA[a]	>50 μM
wogonin (**6**)	0.7 μM	39 μM
vitamin C[b]	0.01 μM	
parthenolide[b]		4.1 μM

[a] Not active. [b] Positive control.

Fraction E (21.45 g) was chromatographed on silica gel (556 g) and eluted with a gradient of $CHCl_3$−MeOH (99:1 to 7:3) to give 52 fractions. Fraction E-6 (128.1 mg) was subjected to reversed-phase silica gel chromatography (Biotage RP-18, 40 g), eluted with MeOH−H_2O (92:8), to afford lupenol (42.1 mg). Fraction E-8 (407.7 mg) afforded β-sitosterol (213.2 mg) after crystallization from MeOH. Fraction E-9 (103.2 mg) was purified by preparative TLC using hexanes−EtOAc (9:1) to give a mixture of arachidic acid, behenic acid, and lignoceric acid in the ratio of 2:1:0.3 (42.7 mg). Fraction E-10 was separated by Sephadex LH-20 CC eluting with MeOH to afford two main subfractions. Subfraction 1 was repeatedly purified by HPLC on RP-18 using a MeOH−H_2O gradient as well as on a silica NP column using a hexanes−EtOAc gradient to afford decursin (0.37 mg, **3**) and scutellorins A (0.95 mg, **1**) and B (0.51 mg, **2**). Fraction F (55 g) was subjected to flash CC on silica gel (761 g) [cyclohexane−EtOAc (83:17 to 4:6), $CHCl_3$−MeOH (94:6 to 87:13), MeOH] to give six main fractions. Subfraction F-1 was purified further by crystallization from MeOH to furnish palmitic acid (21.3 mg). Subfraction F-2 (612.7 mg) was subjected to normal-phase silica gel chromatography with a gradient of cyclohexane−EtOAc (1:1 to 1:9) to give four fractions F2-1−F2−4. Oroxylin A (**5**) (13.2 mg) was obtained by crystallization (MeOH) from fraction F2-2. Fraction F2-1 and F2-3 were purified on Sephadex LH-20 eluted with MeOH to afford dihydrooroxylin A (4.6 mg) and dihydrochrysin (3.2 mg), respectively. The MeOH-soluble part of subfraction F-3 (748 mg) was subjected to Sephadex LH-20 CC eluted with MeOH to afford oroxylin A (**5**) (21.5 mg), wogonin (**6**) (27.9 mg), and chrysin (**4**) (42.1 mg). The MeOH-insoluble part of subfraction F-3 was crystallized from MeOH to furnish ursolic acid (57.9 mg). Subfraction F-4 (1.0223 g) was subjected to Sephadex LH-20 CC eluted with MeOH followed by normal-phase silica gel chromatography with a gradient of cyclohexane−EtOAc (93:7 to 4:6) to give oroxylin A (**5**) (12.9 mg), wogonin (**6**) (12.7 mg), and pomolic acid (17.9 mg). Subfractions F-5 and F-6 were purified by crystallization from MeOH to afford 5,7-dihydroxy-8,2′-dimethoxyflavone (7.8 mg) and daucosterol (89.9 mg), respectively.

Compound 1: white powder; $[\alpha]^{25}_D$ +25.2 (*c* 0.032, MeOH); UV (MeOH) λ_{max} (log ε) 260 (1.31), 330 (0.58) nm; IR ν_{max} 2924, 1732 (C=O), 1623 (aromatic −C=C−) cm^{-1}; for ^1H (600 MHz) and ^{13}C NMR (125 MHz, methanol-d_4) data, see Table 1; HRESIMS *m/z* 365.1013 (M + Na, calcd for 365.1001) and 707.2011 (2M + Na, calcd for 707.2105).

Compound 2: white powder; $[\alpha]^{25}_D$ +5.8 (*c* 0.017, MeOH); UV λ_{max} (log ε) 255 (3.31), 330 (1.17) nm; IR ν_{max} 1728 (C=O), 1570 (aromatic −C=C−) cm^{-1}; for ^1H (600 MHz) and ^{13}C NMR (125 MHz, methanol-d_4) data, see Table 1; HRESIMS *m/z* 365.1011 (M + Na, calcd for 365.1001) and 707.2085 (2M + Na, calcd for 707.2105).

Methods of Calculation Used in Electronic Circular Dichroism. All calculations were performed at 298 K by the Gaussian03 program package.[36] The AM1 method was employed to scan the potential energy surface (PES) to identify conformers of compound **1**. Ground-state geometries were optimized at the B3LYP/6-31G** level, total energies of individual conformers were obtained, and vibrational analysis was done to confirm these minima. Single-point energies of conformers of compound **1** were calculated at the B3LYP-SCRF/6-31G**//B3LYP/6-31G** level with the COSMO model in MeOH. Conformational distributions were calculated at the B3LYP/6-31G** and B3LYP-SCRF/6-31G**//B3LYP/6-31G** levels. TDDFT was employed to calculate excitation energy (in nm) and rotatory strength *R* in dipole velocity (R_{vel}) and dipole length (R_{len}) forms, at the B3LYP/6-31G** and B3LYP/AUG-cc-pVDZ//B3LYP/6-31G** levels in the gas phase and at the B3LYP-SCRF/6-31G**//B3LYP/6-31G** level in MeOH. The calculated rotatory strengths were simulated into an ECD curve by using the Gaussian function

$$\Delta\epsilon(E) = \frac{1}{2.297 \times 10^{-39}} \frac{1}{\sqrt{2\pi}\sigma} \sum_i^A \Delta E_i R_i e^{-[(E - \Delta E_i)/(2\sigma)]^2}$$

where σ is the width of the band at 1/*e* height and ΔE_i and R_i are the excitation energies and rotatory strength for transition *i*, respectively. σ = 0.20 eV and R_{len} were used.

Assays for Biological Activity. Cytotoxicity was determined by the neutral red assay procedure as described earlier.[37] Antioxidant activity was determined by the DCFH-DA method in myelomonocytic HL-60 cells and the anti-inflammatory effect in SW1353 cells as reported earlier.[38,39]

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Supporting Information Available: ^1H and ^{13}C NMR and 2D NMR spectra for **1** and **2**, the structures of triterpenes reported in this paper, and detailed information on the ECD calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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