Bis-spirolabdane-Type Diterpenoids from *Leonurus sibiricus*

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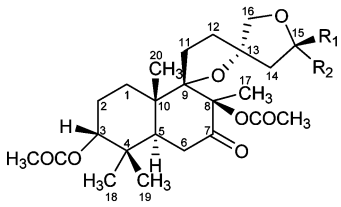
Six new bis-spirolabdane-type diterpenoids, leosibirinone A (**1**), 3α-acetoxyleoheteronone C (**2**), leosibirinone B (**3**), 3α-hydroxyleoheteronone A (**4**), 3α-acetoxyleoheteronone E (**5**), and 3α-acetoxy-15-epileoheteronone E (**6**), were isolated from the aerial parts of *Leonurus sibiricus*. Their structures were identified on the basis of 1D and 2D NMR, including ^{1}H−^{1}H COSY, HSQC, HMBC, and NOESY spectroscopic analyses.

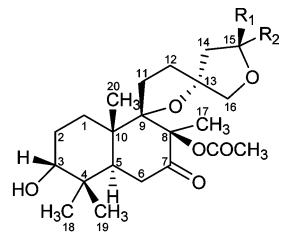
Leonurus sibiricus L. (Labiatae), commonly referred to as "motherwort" in Korea, is used in Korean traditional medicine for the treatment of menstrual irregularities, child delivery in gynecology, high blood pressure, blood stasis, heart disorders, and dysentery.[1−4] Furthermore, the juice of fresh plants is used to treat hemoptysis, edema, gout, and arthritis.[5,6] Previous phytochemical investigations resulted in the isolation of alkaloids, flavonoids, iridoids, and phenylpropanoid glycosides.[3,4,7,8] In addition, there are three reports of labdane diterpenoids from *L. sibiricus*.[9−11] Herein, we report the isolation and structural elucidation of six new bis-spirolabdane-type diterpenoids, leosibirinone A (**1**), 3α-acetoxyleoheteronone C (**2**), leosibirinone B (**3**), 3α-hydroxyleoheteronone A (**4**), 3α-acetoxyleoheteronone E (**5**), and 3α-acetoxy-15-epileoheteronone E (**6**), from *L. sibiricus*.

Results and Discussion

The MeOH extract of the aerial parts of *L. sibiricus* was partitioned into CH_2Cl_2-, EtOAc-, and *n*-BuOH-soluble fractions. Separation of the CH_2Cl_2-soluble fraction with silica gel CC, MCI gel filtration CC, and repeated RP-18 CC led to the isolation of compounds **1**−**6**.



	R_1	R_2
1	OCH_3	H
2	H	OCH_3
5	OH	H
6	H	OH



	R_1	R_2
3	OCH_3	H
4	H	OCH_3

Leosibirinone A (**1**) was obtained as a white, amorphous powder, $[\alpha]^{25}_D$ +14.1. Its molecular formula was determined to be $C_{25}H_{38}O_8$ by HREIMS (*m*/*z* 466.2566 $[M]^+$). In the IR spectrum, the absorption band for an ester (1739 cm^{-1}) group was observed. The ^{1}H NMR (Table 1), ^{13}C NMR (Table 2), and HSQC spectroscopic data of **1** showed the presence of 25 carbons, which were assignable to four tertiary methyl groups [δ_H 0.88 (s), 0.90 (s), 1.19 (s), 1.40 (s); δ_C 27.4, 21.4, 18.1, 15.8, respectively], a ketone group (δ_C 205.7), an acetal methine group [δ_H 5.00 (d, J = 5.5 Hz); δ_C 104.8], an isolated oxygenated methylene group [δ_H 3.77 and 3.89 (d, J = 8.5 Hz); δ_C 77.7], three oxygenated quaternary carbons (δ_C 87.6, 90.9, 96.5), two acetyl groups [δ_H 2.04 (s), 2.08 (s); δ_C 170.5, 169.1, respectively], six methylene groups (δ_C 22.2, 26.6, 28.5, 35.4, 39.4, 46.4), two methine group [δ_H 2.24 (m), 4.64 (br s); δ_C 44.1, 77.5, respectively], one *O*-methyl group [δ_H 3.30 (s); δ_C 54.8], and two quaternary carbons (δ_C 37.6, 43.3). On the basis of the ^{1}H and ^{13}C NMR data, the structure of **1** was closely related to leoheteronone C, which was isolated from *L. heterophyllus*,[12] except for the presence of an additional acetoxy group (δ_C 170.5 and 21.2, δ_H 2.04) and the different configuration of C-15 in **1**. Compared with the chemical shifts of C-3 and C-16 of leoheteronone C, downfield shifts at C-3 (δ_C 77.5; $\Delta\delta_C$ +36.2) and C-16 (δ_C 77.7; $\Delta\delta_C$ +3.3) were observed in **1**, implying that **1** might be a leoheteronone C derivative having an acetoxy substituent at C-3 and the opposite C-15 configuration. Furthermore, in the HMBC spectrum, correlations between H-3 (δ_H 4.64), −OCOC<u>H</u>$_3$ (δ_H 2.04) and −O<u>C</u>OCH$_3$ (δ_C 170.5) and between H-2 (δ_H 1.68) and −OCO<u>C</u>H$_3$ (δ_C 21.2) suggested that the additional acetoxy group could reside at C-3. Correlations between H-15 (δ_H 5.00) and C-13 (δ_C 90.9), H-12 (δ_H 2.27) and C-9 (δ_C 96.5), H-5 (δ_H 2.24) and C-4 (δ_C 37.6)/C-6 (δ_C 35.4)/C-10 (δ_C 43.3), 20-Me (δ_H 1.19) and C-8 (δ_C 87.6), and 17-Me (δ_H 1.40) and C-9 (δ_C 96.5) also supported the proposed structure of **1**. The relative configuration of **1** was proposed from the 2D NOESY experiments and the comparison of the observed and reported NMR data.[10,12,15] In the NOESY spectrum, correlations between H-5 (δ_H 2.24), tentatively assigned an α-orientation, and Me-18 (δ_H 0.88), H-5α, and H-6α (δ_H 2.27) and between H-6α and Me-17 (δ_H 1.40) indicated that these are on the same side (α), while correlations between Me-20 (δ_H 1.19) and axial 8-OAc (δ_H 2.08), Me-20 and H-11 (δ_H 2.17, 2.26), and Me-20 and Me-19 (δ_H 0.90) indicated that these are on the opposite side (β).[12,15] In addition, correlations between Me-17 and H_2-14 (δ_H 1.98, 2.42) suggested the relative configuration at C-13 as shown in **1**.[14,15] The methoxy group at C-15 appeared to be β-oriented in **1** by the comparison of the chemical shift of C-16 in (*rel*-5*S*,6*R*,8*R*,9*R*,10*S*,13*S*,15*R*)-6-acetoxy-9,13;15,16-diepoxy-15-methoxylabdane reported by Ono et al.[15] In addition, the distinct NOE between H-3 (δ_H 4.64) and axial Me-19 (δ_H 0.90) and the coupling pattern of H-3 (δ_H 4.64, br s) supported the β-orientation of H-3.[13] On the basis of the above results, the structure of **1** is proposed to be 3α,8β-diacetoxy-9,13;15,16-diepoxy-15β-methoxylabdan-7-one, named leosibirinone A.

3α-Acetoxyleoheteronone C (**2**) was obtained as a white, amorphous powder, $[\alpha]^{25}_D$ +31.4, and has the same molecular formula ($C_{25}H_{38}O_8$) as **1** by HRFABMS (*m*/*z* 489.2835 $[M + Na]^+$). The ^{1}H and ^{13}C NMR data showed differences at H_2-16 (upfield shifts: δ_H 3.49; $\Delta\delta_H$ −0.28 and δ_H 3.74; $\Delta\delta_H$ −0.15) and C-16 (δ_C

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Table 1. ^{1}H NMR Data of Compounds **1**−**6** (δ in ppm, J in Hz, 500 MHz, in $CDCl_3$)[a]

position	1	2	3	4	5	6
1	1.14(m)	1.14(m)	1.12(m)	1.09(m)	1.14(m)	1.17(m)
		1.62(m)	1.93(m)	1.93(m)	1.59(m)	1.70(m)
2	1.68(m)	1.69(m)	1.65(m)	1.65(m)	1.70(m)	1.70(m)
		1.90(m)	1.95(m)	1.95(m)	1.96(m)	1.91(m)
3	4.64(br s)	4.64(t, 2.5)	3.43(br s)	3.40(br s)	4.64(m)	4.64(m)
5	2.24(m)	2.19(m)	2.18(m)	2.19(m)	2.20(m)	2.16(m)
6	2.27(m)	2.26(m)	2.22(m)	2.24(m)	2.26(m)	2.29(m)
	2.52(dd, 14, 12)	2.51(dd, 14, 12)	2.51(dd, 14, 12)	2.51(dd, 14.5, 12)	2.50(m)	2.55(m)
11	2.17(m)	2.18(m)	2.22(m)	2.18(m)	2.32(m)	2.18(m)
	2.26(m)	2.28(m)		2.24(m)		
12	2.17(m)	1.97(m)	2.16(m)	1.96(m)	2.26(m)	2.05(m)
	2.27(m)	2.17(m)	2.35(m)	2.15(m)	2.30(m)	2.14(m)
14	1.98(d, 13)	2.21((m)	1.96(m)	2.19(m)	2.01(m)	2.16(m)
	2.42(dd, 12.5, 5.5)	2.31(m)	2.33(m)	2.28(m)	2.45(m)	2.33(m)
15	5.00(d, 5.5)	4.94(dd, 6, 4)	4.99(d, 5)	4.93(dd, 5.5, 4)	5.53(d, 5)	5.42(dd, 5, 2.5)
16	3.77(d, 8.5)	3.49(d, 8)	3.83(d, 9)	3.58(d, 8)	3.53(d, 8.5)	3.55(d, 8.5)
	3.89(d, 8.5)	3.74(d, 8)	4.06(d, 9)	3.92(d, 8)	3.85(d, 8.5)	4.06(d, 8.5)
17	1.40(s)	1.39(s)	1.31(s)	1.33(s)	1.41(s)	1.44(s)
18	0.88(s)	0.88(s)	0.96(s)	0.96(s)	0.87(s)	0.88(s)
19	0.90(s)	0.90(s)	0.86(s)	0.85(s)	0.91(s)	0.91(s)
20	1.19(s)	1.17(s)	1.17(s)	1.19(s)	1.20(s)	1.20(s)
3-OCOC$\underline{H_3}$	2.04(s)	2.06(s)			2.07(s)	2.03(s)
8-OCOC$\underline{H_3}$	2.08(s)	2.08(s)	2.07(s)	2.06(s)	2.08(s)	2.09(s)
15-OC$\underline{H_3}$	3.30(s)	3.34(s)	3.28(s)	3.34(s)		

[a] The assignments were based on HMQC, ^{1}H−^{1}H-COSY, and HMBC experiments.

Table 2. ^{13}C NMR Data of Compounds **1**−**6** (δ in ppm, 125 MHz, in $CDCl_3$)

carbon	1	2	3	4	5	6
1	26.6	26.4	26.1	26.2	26.5	26.8
2	22.2	22.3	24.7	24.6	22.2	22.2
3	77.5	77.2	75.3	75.2	77.1	77.1
4	37.6	37.6	38.6	38.5	37.6	37.6
5	44.1	44.5	43.6	42.9	43.3	44.6
6	35.4	35.2	35.4	35.5	35.3	35.3
7	205.7	205.1	205.6	205.3	205.7	205.6
8	87.6	87.4	87.6	87.6	87.5	87.5
9	96.5	96.4	96.7	96.6	96.4	97.2
10	43.3	43.1	43.2	43.4	43.2	43.2
11	28.5	28.0	28.5	28.1	28.5	28.0
12	39.4	39.7	39.9	39.3	39.3	36.8
13	90.9	90.6	91.3	90.8	90.6	91.2
14	46.4	46.0	47.3	46.4	46.7	46.3
15	104.8	104.3	105.1	104.4	98.2	98.2
16	77.7	74.3	77.9	74.8	77.9	75.4
17	15.8	15.8	15.7	15.6	15.7	16.1
18	27.4	27.4	27.7	27.8	27.3	27.4
19	21.4	21.4	21.8	21.8	21.3	21.3
20	18.1	17.8	17.9	18.0	18.0	18.0
3-O$\underline{C}$OCH$_3$	170.5	170.5			170.5	170.4
3-OC$\underline{O}$CH$_3$	21.2	21.3			21.3	21.1
8-O$\underline{C}$OCH$_3$	169.1	169.0	169.0	169.0	169.1	169.0
8-OC$\underline{O}$CH$_3$	21.3	21.4	21.4	21.4	21.3	21.3
15-O$\underline{C}$H$_3$	54.8	55.0	54.6	55.0		

74.3; upfield shift: $\Delta\delta_C$ −3.4), suggesting that **2** was the 15-epimer of **1**. The relative configurations at C-5, -8, -9, -10, and -13 of **2** appeared to be the same as those of **1**, on the basis of NOESY data. The methoxy group at C-15 was likely to be α-oriented in **2** on the basis of an NOE association between H-15 (δ_H 4.94) and H_2-12 (δ_H 1.97, 2.17) and the comparison of NMR data with those of (*rel*-5*S*,6*R*,8*R*,9*R*,10*S*,13*S*,15*S*)-6-acetoxy-9,13;15,16-diepoxy-15-methoxylabdane.[15] The NOE between H-3 (δ_H 4.64) and axial Me-19 (δ_H 0.90) and the coupling pattern of H-3 (δ_H 4.64, br s) both supported the β-orientation of H-3.[12−15] Thus, the structure of **2** is proposed to be 3α,8β-diacetoxy-9,13;15,16-diepoxy-15α-methoxylabdan-7-one, named 3α-acetoxyleoheteronone C.

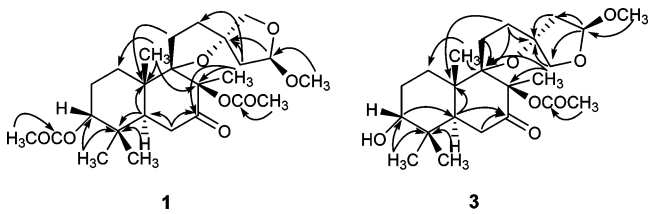

Figure 1. Selected HMBC correlations of compounds **1** and **3**.

Leosibirinone B (**3**) was obtained as a yellowish oil, $[\alpha]^{25}_D$ +19.9. Its molecular formula was found to be $C_{23}H_{36}O_7$ by HREIMS (m/z 424.2459 $[M]^+$). In the IR spectrum, the absorption bands for hydroxy (3446 cm^{-1}) and ester (1738 cm^{-1}) groups were observed. The ^{1}H and ^{13}C NMR data of **3** were similar to those of leoheteronone A[12] except for the presence of a hydroxy group and the different configuration of C-15 in **3**. In comparison with the chemical shifts of C-3 and C-16 of leoheteronone A, downfield shifts at C-3 (δ_C 75.3; $\Delta\delta_C$ +34.2) and C-16 (δ_C 77.7; $\Delta\delta_C$ +3.5) were observed in **3**, implying that **3** might be a leoheteronone A derivative having a C-3 hydroxy substituent and the opposite C-15 configuration. The relative configuration at C-5, -8, -9, and -10 was the same as assigned in **1**, on the basis of NOESY data. The NOESY cross-peak between Me-17 and H_2-16 (δ_H 3.83, 4.06) indicated the relative configuration at C-13 as shown in **3**. The methoxy group at C-15 appeared to be β-oriented on the basis of no NOE between H-15 (δ_H 4.99) and H_2-12 (δ_H 2.16, 2.35), which was also comparable to the reported NMR data.[15] The NOE between H-3 (δ_H 4.64) and axial Me-19 (δ_H 0.90) and the coupling pattern of H-3 (δ_H 3.43, br s) supported the β-orientation of H-3.[13−16] Accordingly, the structure of **3** is proposed to be 3α-hydroxy-8β-acetoxy-9,13;15,16-diepoxy-15β-methoxylabdan-7-one, named leosibirinone B.

3α-Hydroxyleoheteronone A (**4**) was obtained as a yellowish oil, $[\alpha]^{25}_D$ +19.2, and has the same molecular formula ($C_{23}H_{36}O_7$) as **3** by HRFABMS (m/z 447.2915 $[M + Na]^+$). Comparison of the ^{1}H and ^{13}C NMR data of **4** with those of **3** revealed one significant difference at C-16 (δ_C 74.8; upfield shift: $\Delta\delta_C$ −3.1), suggesting that **4** should be the 15-epimer of **3**. The relative configurations at C-5, -8, -9, -10, and -13 appeared to be the same as those of **3** on the basis of NOESY data. The methoxy group at C-15 (δ_H 3.34) could be assigned an α-orientation from the observation of NOESY correlations between H-15 (δ_H 4.93) and H_2-12 (δ_H 1.96, 2.15) and also on the basis of the reported NMR data.[15] The NOE between H-3 (δ_H 3.40 br s) and axial Me-19 (δ_H 0.85) and the coupling pattern of H-3 (δ_H 3.43, br s) suggested the

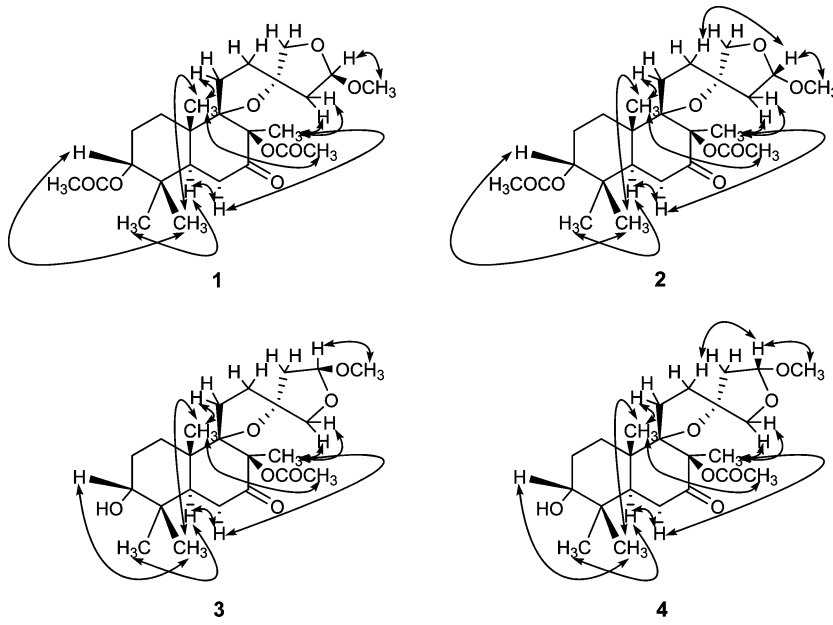

Figure 2. Key NOESY correlations of compounds **1**−**4**.

β-orientation of H-3.[12,13,17,18] Thus, the structure of **4** is proposed to be 3α-hydroxy-8β-acetoxy-9,13;15,16-diepoxy-15α-methoxy-labdan-7-one, named 3α-hydroxyleoheteronone A.

3α-Acetoxyleoheteronone E (**5**) and 3α-acetoxy-15-epileoheteronone E (**6**) were white, amorphous powders, $[\alpha]^{25}_{D}$ −5.7, and isolated as an inseparable epimeric mixture. The molecular formulas were found to be $C_{24}H_{36}O_8$ by HREIMS (*m*/*z* 452.2408 $[M]^+$). In the IR spectrum, the absorption bands for hydroxy (3442 cm^{-1}) and ester (1737 cm^{-1}) groups were observed. Closer examination of the ^1H and ^{13}C NMR data revealed the structure of **5/6** to be quite similar to those of leoheteronone E and 15-epileoheteronone E[12] except for the presence of an additional acetoxy group in **5/6**. In the ^{13}C NMR spectrum, a downfield shift at C-3 (δ_C 77.1; $\Delta\delta_C$ +35.3) was observed. In addition, chemical shifts at δ_H 2.07/2.03 (s, 3H), δ_C 170.5/170.4, and δ_C 21.3/21.1 indicated the presence of a C-3 acetoxy group in **5/6**. In the HMBC spectrum, correlations between H-3 (δ_H 4.64), −OCOC<u>H</u>$_3$ (δ_H 2.07) and −O<u>C</u>OCH$_3$ (δ_C 170.5) and between H-2 (δ_H 1.70, 1.96) and −OCO<u>C</u>H$_3$ (δ_C 21.3) suggested that the additional acetoxy group resides at C-3. The relative configurations of **5/6** were assigned on the basis of the NOESY spectrum. The relative configurations at C-5, -8, -9, -10, and -13 appeared to be the same as those of **1**−**4** on the basis of NOESY data. The hydroxy group at C-15 was likely β-oriented in compound **5** and α-oriented in compound **6** on the basis of the NOE between H-15 (δ_H 5.42) and H-12 (δ_H 2.14) of compound **6** and the reported NMR data.[13−19] The NOE between H-3 (δ_H 4.64 × 2) and the axial Me-19 (δ_H 0.91 × 2) supported the β-orientation of H-3. The structures of **5/6** are therefore proposed as 3α,8β-diacetoxy-9,13;15,16-diepoxy-15β-hydroxylabdan-7-one, named 3α-acetoxyleoheteronone E (**5**), and 3α,8β-diacetoxy-9,13;15,16-diepoxy-15α-hydroxylabdan-7-one, named 3α-acetoxy-15-epileoheteronone E (**6**), respectively. This is the first report of naturally occurring 3-acetoxy and 3-hydroxy bis-spirolabdane-type diterpenoids from *Leonurus sibiricus*.

Experimental Section

General Experimental Procedures. Optical rotations were measured on an Autopol-IV polarimeter (Rudolph Research Flangers). FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. NMR spectra were recorded on a Varian Unity Inova 500 spectrometer. $^1H-^1H$ COSY, HMQC, HMBC, and NOESY NMR spectra were obtained with the usual pulse sequences. HRFABMS and HREIMS were measured on a JEOL JMS 700 mass spectrometer. Open column chromatography was performed on silica gel 60 (40−63 and 63−200 μm, Merck), LiChroprep RP-18 (40−63 μm, Merck), MCI gel CHP 20P (70−150 μm, Mitsubishi Chemical Co.), and Sephadex LH-20 (25−100 μm, Sigma). TLC was carried out on precoated Kieselgel 60 F_{254} (art. 5715, Merck) and RP-18 F_{254s} (art. 15389, Merck) plates and detected by spraying with 10% H_2SO_4 in EtOH and heating on a hot plate.

Plant Materials. The aerial parts of *L. sibiricus* were collected from the herbarium of the College of Pharmacy, Chosun University, Korea, in May 2003. Plants were identified by Professor Emeritus Young Hee Moon of College of Pharmacy, Chosun University, Korea. A voucher specimen was deposited in the Herbarium of the College of Pharmacy, Chosun University (CSU-1005-17).

Extraction and Isolation. The air-dried aerial parts of *L. sibiricus* (1.0 kg) were extracted with MeOH three times at room temperature, and 151 g of residue was produced. The MeOH extract was suspended in H_2O and partitioned sequentially in CH_2Cl_2, EtOAc, and *n*-BuOH. The CH_2Cl_2 fraction (7.6 g) was chromatographed over a silica gel column using a gradient solvent system of *n*-hexane−acetone (1:2 → 0:100) to give subfractions D1 (4 g), D2 (2.2 g), and D3 (1.3 g). Subfraction D1 (4 g) was subjected to silica gel CC eluting with a gradient solvent system of *n*-hexane−acetone (4:1 → 1:3) to yield six subfractions, D11−D16. Subfraction D12 (300 mg) was subjected to silica gel CC eluting with *n*-hexane−acetone (4:1) to give two subfractions (D121 and D122). Subfraction D121 (73.6 mg) was purified by repeated RP-18 CC eluting with CH_3CN-H_2O (2:3) and $CH_3CN-MeOH-H_2O$ (3:1:6) to give compound **1** (6.2 mg).

Subfraction D122 (78.5 mg) was purified by RP-18 CC eluting with $CH_3CN-MeOH-H_2O$ (3:1:6) followed by MCI gel filtration CC eluting with $CH_3CN-MeOH-H_2O$ (2:1:7) to yield compound **2** (1 mg). Fraction D14 (476 mg) was subjected to silica gel CC eluting with *n*-hexane−acetone (4:1), repeated RP-18 CC eluting with $CH_3CN-MeOH-H_2O$ (3:1:6), and MCI gel CC eluting with $CH_3CN-MeOH-H_2O$ (2:1:7) to produce compound **3** (4.5 mg) and compound **4** (4 mg). Fraction D15 (260 mg) was purified by repeated RP-18 CC eluting with $MeOH-H_2O$ (1:1) and $CH_3CN-MeOH-H_2O$ (3:1:6) to give an inseparable mixture of compounds **5** and **6** (33.6 mg).

Leosibirinone A (1): white, amorphous powder; $[\alpha]^{25}_{D}$ +14.1 (*c* 1.2, MeOH); IR (KBr) ν_{max} 2959, 2873, 1739, 1463, 1244 cm^{-1}; ^1H and ^{13}C NMR data, Tables 1 and 2; HREIMS *m*/*z* 466.2566 $[M]^+$ (calcd for $C_{25}H_{38}O_8$, 466.2567).

3α-Acetoxyleoheteronone C (2): white, amorphous powder; $[\alpha]^{25}_{D}$ +31.4 (*c* 0.5, MeOH); IR (KBr) ν_{max} 2954, 2897, 1740, 1463, 1215 cm^{-1}; ^1H and ^{13}C NMR, Tables 1 and 2; HRFABMS *m*/*z* 489.2835 $[M + Na]^+$ (calcd for $C_{25}H_{38}O_8Na$, 489.2836).

Leosibirinone B (3): yellowish oil; $[\alpha]^{25}_{D}$ +19.9 (*c* 1.0, MeOH); IR (KBr) ν_{max} 3446, 2956, 2873, 1738, 1470, 1369, 1246 cm^{-1}; ^{1}H and ^{13}C NMR data, Tables 1 and 2; HREIMS *m*/*z* 424.2459 $[M]^+$ (calcd for $C_{23}H_{36}O_7$, 424.2461).

3α-Hydroxyleoheteronone A (4): yellowish oil; $[\alpha]^{25}_{D}$ +19.2 (*c* 1.0, MeOH); IR (KBr) ν_{max} 3442, 2945, 2832, 1746, 1470, 1369, 1245 cm^{-1}; ^{1}H and ^{13}C NMR data, Tables 1 and 2; HRFABMS *m*/*z* 447.2915 $[M + Na]^+$ (calcd for $C_{23}H_{36}O_7Na$, 447.2917).

3α-Acetoxyleoheteronone E (5) and 3α-acetoxy-15-epileoheteronone E (6): white, amorphous powder; $[\alpha]^{25}_{D}$ −5.7 (*c* 1.25, MeOH); IR (KBr) ν_{max} 3442, 2959, 2873, 1737, 1466, 1373, 1244 cm^{-1}; ^{1}H and ^{13}C NMR data, Tables 1 and 2; HREIMS *m*/*z* 452.2408 $[M]^+$ (calcd for $C_{24}H_{36}O_8$, 452.2410).

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Note Added after ASAP Publication: This paper was published on the Web on Jan 8, 2010, with errors in the last sentence of the Results and Discussion section and in refs 14, 16, and 18. The corrected version was reposted on Jan 26, 2010.

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

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