New Pregnane Glycosides from *Sinomarsdenia incisa*

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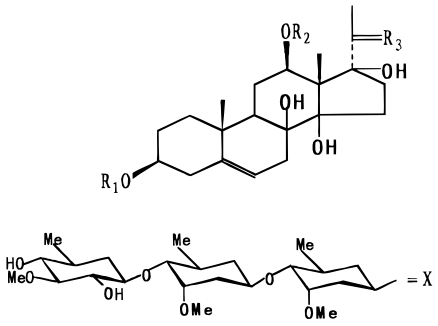
Five new pregnane glycosides, sinomarinosides A (**1**), B (**2**), C (**3**), D (**4**), and E (**5**), have been isolated from *Sinomarsdenia incisa* (Asclepiadaceae). The structures of these compounds were elucidated by NMR and mass spectroscopic methods and chemical evidence.

Sinomarsdenia incisa (P. T. Li et Y. H. Li) P. T. Li et J. J. Chen[1] (Asclepiadaceae) is a relatively new species found in Xishuangbanna, Yunnan Province in southwest of China and first identified as *Marsdenia incisa* P. T. Li et Y. H. Li.[2] Incisagenin and some related aglycones have been isolated from the acidic hydrolyzate of crude glycosides[3] from this plant along with neomarinoside, a pregnane glycoside with a B-nor (7)-6β-formyl-pregnane skeleton.[4] As a continuation of chemical and taxonomic studies on this plant, the crude glycoside mixture was subjected to repeated silica gel chromatography with various solvent systems to afford five novel pregane glycosides and a known glycoside, sarcostin 3-*O*-β-D-cymaropyranoside.[5] All of these compounds exhibited positive Liebermann−Burchard and Keller−Kiliani reactions indicating that there were steroidal glycosides containing a 2-deoxy sugar moiety. This paper deals with the isolation and structural elucidation of these glycosides (**1**−**5**) based on spectroscopic and chemical evidence.

Results and Discussion

Sinomarinoside A (**1**) had molecular formula $C_{42}H_{70}O_{16}$ based on elemental analysis. The negative FABMS of **1** showed a quasi-molecular ion peak at *m*/*z* 829 [M-($C_{42}H_{70}O_{16}$) − H]$^-$. The β-linkages of the sugars were assigned from the coupling constants of three anomeric proton signals at δ 4.77 (1H, d, J = 7.8 Hz), 5.17 (1H, dd, J = 9.6, 1.6 Hz), and 5.29 (1H, dd, J = 10.2, 1.6 Hz) in the ^{1}H NMR spectrum of **1**. The ^{13}C NMR spectrum of **1** in C_5D_5N (Table 1) indicated sarcostin (**6**)[3] as the aglycone moiety along with two cymarose and one thevetose units. This was confirmed by acidic hydrolysis of **1** which yielded **7**, cymarose, and thevetose by comparison with authentic samples. The terminal thevetopyranosyl signals were easily distinguished from other sugar signals because in the ^{13}C NMR spectrum of **1**, the thevetopyranosyl group has the longest dipole−dipole relaxation times by PR-FT measurement.[4] On mild acidic hydrolysis, **1** afforded a degraded glycoside and two sugar fragments. The degraded glycoside was identified as sarcostin 3-*O*-β-D-cymaropyranoside[5] by ^{1}H NMR and FABMS comparison. The ^{13}C and ^{1}H NMR data of the sugar fragments (Table 2) identified these as dresibiose and methyl β-dresibioside.[6] The ^{13}C NMR chemical shifts due to the sugar moiety of **1** were identical to those of stephanoside M.[7] The ^{13}C NMR chemical shifts of the sugar moiety of the other four glycosides (**2**, **3**, **4**, and **5**) coincided exactly with those of **1**, thus they contain the same sugar sequence as **2**. Shifts for C-2 (−2.2 ppm), C-3 (+6.1 ppm), and C-4 (−4.4 ppm) in the ^{13}C NMR spectrum relative to the aglycone moiety of **1**,[3] indicated that the sugar chain is linked to the C-3 hydroxyl group of aglycone. Similar glycosidation shifts of the aglycone carbon for the other glycosides (**2**−**5**) were also observed at C-2, C-3, and C-4; thus, the sugar moiety was linked to the C-3 hydroxyl group in each case. Consequently, **2** was characterized as sarcostin 3-*O*-β-D-thevetopyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside.



	R_1	R_2	R_3
1	X	H	H, OH
2	X	Cin	H, OH
3	X	H	H, Olsoval
4	X	H	O
5	X	Tig	O
6	H	H	H, OH
7	H	Cin	H, OH
8	H	H	H, Olsoval
9	H	H	O
10	H	Tig	O

Sinomarinoside B (**2**) had molecular formula $C_{51}H_{76}O_{17}$ by elemental analysis and an ion peak at *m*/*z* 959 [M($C_{51}H_{76}O_{17}$) − H]$^-$ in the negative FABMS. From the ^{1}H and ^{13}C NMR data in $CDCl_3$ (Tables l and 2), **2** possessed penupogenin (**7**)[8] as the aglycone moiety and two cymarose and one thevetose units. The ^{1}H NMR spectrum of **2** showed three anomeric proton signals at δ 4.25 (1H, d, J = 7.7 Hz), 4.70 (1H, dd, J = 10.4, 1.8 Hz), and 4.80 (IH, dd, J = 9.2, 1.5 Hz) indicating the existence of three

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Table 1. ^{13}C NMR Data for the Aglycone Moieties of **1**−**5**[a]

carbon	1	2	3	4	5
1	39.4	38.7	39.4	39.4	39.5
2	30.0	29.0	30.0	30.0	30.0
3	77.8	76.7	77.9	77.8	78.0
4	39.1	38.7	39.0	39.0	39.2
5	139.2	139.7	139.2	139.5	139.6
6	119.1	117.5	119.7	119.4	119.2
7	34.2	34.4	34.2	34.3	34.1
8	74.1	73.9	74.4	74.3	74.5
9	44.7	43.5	44.7	45.0	44.6
10	37.4	37.0	37.3	37.4	37.6
11	29.1	24.6	30.0	29.4	25.1
12	78.1	74.3	70.2	69.4	73.3
13	58.6	56.1	58.7	60.5	58.5
14	88.9	87.8	88.2	88.3	88.8
15	34.6	34.4	33.8	32.8	33.2
16	35.4	33.3	35.2	35.1	35.0
17	89.0	87.9	88.7	92.6	92.6
18	11.3	11.0	11.2	9.4	10.8
19	18.6	17.7	18.8	18.9	19.6
20	73.1	71.2	75.4	209.6	209.9
21	17.8	18.3	15.4	27.8	28.0
		Cin	Isoval		Tig
1′		166.1	172.0		166.7
2′		118.2	43.9		129.6
3′		146.0	25.5		137.1
4′		134.9	22.6		14.5
5′		129.3	22.5		12.5
6′		128.2			
7′		130.5			
8′		128.2			
9′		129.3			

[a] ^{13}C NMR spectra were measured in C_5D_5N except for glycoside **2** in $CDCl_3$; assignments on the basis of $^1H-^1H$ and $^{13}C-^1H$ correlated 2D spectroscopy (COSY) and distortionless enhancement by polarization transfer (DEPT).

Table 2. ^{13}C NMR Data for the Sugar Moieties of **1**−**5**[a]

carbon	1	2	3	4	5
Cym-C-1′	96.4	95.6	96.4	96.4	96.6
2′	37.0	35.2	37.0	37.0	37.1
3′	78.0	76.8	78.0	78.0	78.2
4′	83.1	82.5	83.1	83.1	83.4
5′	69.0	68.3	69.0	69.0	69.2
6′	18.4	18.1	18.4	18.4	18.4
3′-OMe	58.8	57.9	58.3	58.8	59.1
Cym C-1″	100.4	99.5	100.4	100.4	100.5
2″	37.3	35.6	37.3	37.3	37.4
3″	78.2	77.8	78.1	78.2	78.3
4″	83.4	82.5	83.4	83.4	83.5
5″	69.3	68.5	69.3	69.0	69.5
6″	18.6	18.1	18.5	18.5	18.7
3″-OMe	58.9	57.9	58.8	58.8	59.1
Thev C-1‴	*106.2	104.3	106.2	106.2	106.2
2‴	*75.1	74.5	75.1	75.1	75.2
3‴	*87.9	85.4	87.9	87.9	87.8
4‴	*75.9	74.6	75.9	75.9	76.0
5‴	*72.8	71.6	72.7	72.8	72.8
6‴	*18.5	18.5	18.6	18.6	18.8
3‴-OMe	*60.8	60.5	60.9	61.0	61.1

[a] ^{13}C NMR spectra were measured in C_5D_5N except for glycoside **3** ($CDCl_3$); assignments on the basis of $^1H-^1H$ and $^{13}C-^1H$ correlated 2D spectroscopy (COSY) and distortionless enhancement by polarization transfer (DEPT). Chemical shifts with asterisks have the longest dipole−dipole relaxation times by PRFT measurement.

β-glycosidic linkages. On acidic hydrolysis, **2** gave cymarose, thevetose, dresibiose, and methyl-β-D-dresibioside. The thevetopyranosyl group was proposed to be the terminal sugar on the basis of an ion peak at m/z 799 $[(C_{51}H_{76}O_{17}) - 161]^-$ in the negative FABMS. Thus, **2** was established to be penupogenin 3-*O*-β-D-thevetopyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside.

Sinomarinoside C (**3**) had molecular formula $C_{47}H_{78}O_{17}$ by elemental analysis. Compound **3** gave a quasi-molecular ion peak at m/z 913 $[M(C_{47}H_{78}O_{17}) - H]^-$ in the negative FABMS. On mild acidic hydrolysis, **3** afforded cymarose, thevetose, dresibiose, and methyl-β-1-D-dresibioside and **8** by TLC comparison. The ^1H NMR spectrum showed three anomeric proton signals at δ 4.77 (1H, d, $J = 7.7$ Hz), 5.11 (1H, dd, $J = 9.0$, 2.0 Hz), and 5.28 (^1H, dd, $J = 9.2$, 2.0 Hz) indicating three β-glycosidic linkages. In the ^{13}C NMR spectrum of **3**, the portion due to the sugar moiety (Table 2) was identical with that of **1**, thus **3** had the same sugar sequence as **2**. The ^{13}C NMR spectrum of **3** (Table 1) was also similar to that of **1** except for signals due to the isovaleryl group. The ^1H NMR spectrum of the aglycone of **3** also gave two methyl group signals due to an isolvalery group.[9] The ^1H NMR comparison of **1** and **3** showed that the signal due to the 20-hydroxyl methine of the aglycone moved downfield from δ 4.45 in **1** to δ 5.76 in **3**, but there was no change of chemical shift for the 12-hydroxyl methine. Therefore, the isovaleryl group of **3** was inferred to be linked at the 20-hydroxyl methine. This aglycone of **3** was an unknown compound (**8**) and named incisagenin A. Compound **8** was not obtained from **3** due to the small amount available. Compound **3** was concluded to be incisagenin A 3-*O*-β-D-thevetopyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside.

Sinomarinoside D (**4**) had molecular formula $C_{42}H_{68}O_{16}$ by elemental analysis. The negative FABMS of **4** exhibited a quasi-molecular ion peak at m/z 827 $[M(C_{42}H_{68}O_{16}) - H]^-$. The ^1H NMR spectrum contained anomeric proton signals at δ 4.79 (1H, d, $J = 7.8$ Hz), 5.18 (1H, dd, $J = 9.5$, 2.0 Hz), and 5.30 (1H, dd, $J = 9.2$, 1.8 Hz), which suggested three β-linkages in the sugar sequence. The ^{13}C NMR spectrum of **4** implied deacylmetaplexigein (**9**)[10] as the aglycone moiety and two cymarose and one thevetose units. On acidic hydrolysis, **4** gave **9**, cymarose, thevetose, dresibiose, and methyl-β-D-dresibioside. Thus, **4** was determined to be deacylmetaplexigenin 3-*O*-β-D-thevetopyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside.

Sinomarinoside E (**5**) had molecular formula $C_{47}H_{74}O_{17}$ as determined by elemental analysis. The negative FABMS of **5** gave a quasi-molecular ion peak at m/z 909 $[(C_{47}H_{74}O_{17}) - H]^-$. The ^1H NMR, IR, and UV spectra of **5** indicated that there was a tigloyl group in the molecule. Three β-linkages of sugars were indicated by the coupling constants of three anomeric proton signals at δ 4.76 (1H, dd, $J = 7.6$ Hz), 5.09 (1H, dd, $J = 8.0$ 1.6 Hz), and 5.24 (1H, dd, $J = 9.1$, 2.0 Hz) in the ^1H NMR spectrum of **5**. The ^{13}C NMR spectrum of **5** implied that incisagenin (**10**)[3] was the aglycone moiety and, that there were two cymarose and one thevetose units. On acidic hydrolysis, **5** gave **10**, cymarose, thevetose, dresibiose, and methyl-β-D-dresibioside. Thus, **6** was elucidated to be incisagenin 3-*O*-β-D-thevetopyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside.

Experimental Section

General Experimental Procedures. Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Optical rotations were measured with a J-20 C digital polarimeter at room temperature. UV spectra were obtained in EtOH with a Shimadzu UV-210 spectrometer and absorption maxima are given in nm. IR spectra were recorded in KBr on a Perkin-Elmer 577 spectrometer. FABMS was performed on a VG AUTOSPEC 3000 mass spectrometer. The NMR were run on a Bruker AM-400 instrument at 400 MHz for ^1H and 100.6 MHz for ^{13}C in C_5D_5N or $CDCl_3$, and chemical shifts were given as δ (ppm) with TMS as an internal standard. Column

chromatography was carried out on Qingdao silica gel (200−300 mesh), MCI CHP-20 gel, FUJI (ODS-Q_3) gel (Mitsubishi Chemical Co.), and Lobar RP-18 gel (Merck). TLC was performed on Merck precoated plates (Kieselgel 60 254 and RP-18 254) with the following solvent systems: A, MeOH−$CHCl_3$ (5:95 and 10:90 v/v); B, Me_2CO−petrol (2:3); and C, H_2O−MeOH (2:8 and 3:7).

Plant Material. The plant used in this work was collected in September, 1988, July, 1990, and September, 1991, in Xishuangbanna, Yunnan, China, and identified as *Sinomarsdenia incisa* (P. T. Li et Y. H. Li) P. T. Li et J. J. Chen by Professor Guo-da Tao and Mr. Jing-yun Cui of Xishuangbanna Tropical Botanic Garden, Kunming Institute of Botany, Chinese Academy of Sciences. The voucher specimen (No. Cui 9009) is deposited in the herbarium of the Garden.

Extraction and Isolation of Glycosides. The whole plant of *S. incisa* was air-dried, powdered (30 kg), and extracted with 95% EtOH heated under reflux. The green-blue tar (1.1 kg) obtained by concentration of the extract was suspended in 5 L H_2O and chromatographed on a D_{101} macroreticular resin with solvents of H_2O, 95% EtOH, and Me_2CO, respectively. The 95% EtOH eluent was evaporated *in vacuo* to afford crude glycosides (310 g). Column chromatography on silica gel eluting stepwise with mixed solvents of increasing polarity from $CHCl_3$ to MeOH−$CHCl_3$ (15:85, v/v) yielded fraction A (35 g), fraction B (180 g), and fraction C (78 g). Fraction B was subjected to silica gel chromatography using CH_3OH−$CHCl_3$ (5:95 to 10:90) to give fraction B-I (18 g, a mixture of **3**, **4**, and **5**), fraction B-II (18 g, a mixture of sarcostin 3-*O*-*β*-cymaropyranoside, **1** and **2**), and fractions B-III and B-IV (13 g). Fractions B-I and B-II were submitted to MCI CHP-20, Rp-18, and FUJI (ODS-Q_3) gel chromatography with H_2O−MeOH (30:70 to 10:90), and silica gel chromatography with Me_2CO−petrol and MeOH−$CHCl_3$ (2:98), respectively, to give pure sarcostin 3-*O*-*β*-cymaropyranoside[7] (160 mg), **1** (860 mg), **2** (180 mg), **3** (30 mng), **4** (180 mg), and **5** (560 mg).

Sinomarinoside A (1): prisms (Me_2CO); mp 185−189 °C, $[\alpha]_D^{20}$ −10.0° (*c* 0.30; $CHCl_3$); IR (KBr, cm^{-1}) 3480−3400 (OH), 2980, 2940, 1635 (C═C), 1110−1050 (C−O−C); ^{1}H NMR (C_5D_5N, 400 MHz) *δ* 1.37 (3H, d, *J* = 6.2 Hz, Me-6′), 1.40 (3H, s, Me-18), 1.51 (3H, d, *J* = 6.3 Hz, Me-21), 1.58 (3H, d, *J* = 6.0 Hz, Me-6″), 1.60 (3H, d, *J* = 6.1 Hz, Me-6‴), 1.94 (3H, s, Me-19), 3.48 (1H, dd, *J* = 9.5, 2.8 Hz, H-4′), 3.56 (3H, s, OMe-3′), 3.58 (1H, dd, *J* = 10.8, 3.2 Hz, H-4″), 3.59 (1H, dd, *J* = 9.2, 6.0 Hz, H-4‴), 3.60 (1H, dd, *J* = 8.4, 6.0 Hz, H-3‴), 3.62 (3H, s, OMe-3″), 3.73 (1H, dq, *J* = 9.2, 6.1 Hz, H-5‴), 3.87 (1H, m, H-3), 3.90 (3H, s, OMe-3‴), 3.91 (1H, dd, *J* = 8.4, 7.5 Hz, H-2‴), 3.92 (1H, dd, *J* = 7.8, 4.5 Hz, H-12α), 4.06 (2H, ddd, *J* = 3.6, 3.0, 2.8 Hz, H-3′ and 3″), 4.22 (2H, dq, *J* = 9.4, 6.2 Hz, H-5′ and 5″), 4.45 (1H *J* = 5.5 Hz, H-20), 4.77 (1H, d, *J* = 7.8 Hz, H-1‴), 5.17 (1H, dd, *J* = 9.6, 1.6 Hz, H-1″), 5.29 (1H, dd, *J* = 10.2, 1.6 Hz, H-1′), 5.38 (1H, br, H-6); ^{13}C NMR, see Tables 1 and 2; negative ion FABMS *m*/*z* 829 $(M - H)^-$, 669 $(M - 161)^-$, 525 $(M - 305)^-$, 381 $(M - 449)^-$; *anal.* C 59.02%, H 8.51%, calcd for $C_{42}H_{70},O_{16}\cdot{}^3/_2H_2O$, C 58.81%, H 8.52%.

Mild Acidic Hydrolysis of 1. A solution of 200 mg of **1** in 25 mL of MeOH was treated with 25 mL of 0.02 M H_2SO_4, and the mixture was kept at 60 °C for 20 min; 25 mL of H_2O was added, and the whole was concentrated to 50 mL. The solution was warmed and heated at 60 °C for another 20 min and then extracted with EtOAc (50 mL × 3). The organic phase was evaporated *in vacuo* to give a residue which was purified by silica gel column chromatography with MeOH−$CHCl_3$ (5:95) to afford sarcostin 3-*O*-*β*-cymaropyranoside[7] (70 mg). The aqueous layer was neutralized with saturated $Ba(OH)_2$. The precipitate was filtered off, and the filtrate was concentrated to a syrup which was then chromatographed on silica gel using MeOH−$CHCl_3$ (2:98) to give dresibiose[6] (15 mg) and methyl-*β*-D-dresibioside[6] (18 mg).

Sinomarinoside B (2): amorphous colorless powder; mp 153−158 °C; $[\alpha]_D^{25}$ +37.5° (*c* 0.52, MeOH); IR (KBr, cm^{-1}) 3440 (OH), 2960, 1700 (C═O), 1625 (C═C), 1570, 1460, 1275, 1170, 1100−1050 (C−O−C), 940, 910, 860, 765; ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 1.05 (3H, d, *J* = 6.0 Hz, Me-21), 1.12 (3H, s, Me-19), 1.15, 1.21, 1.25 (each 3H, d, *J* = 6 Hz, Me-6′, 6″, and 6‴), 1.19 (3H, s, Me-18), 3.43 (1H, q, *J* = 6.0 Hz, H-20), 3.37, 3.34, 3.60 (each 3H, s, OMe-3′, 3″, and 3‴), 3.74 (1H, dd, *J* = 9.4, 3.5 Hz, H-12α), 4.11 (1H, q, *J* = 6.1 Hz, H-20), 4.25 (1H, d, *J* = 7.7 Hz, H-1‴), 4.70 (1H, dd, *J* = 10.4, 1.8 Hz, H-1″), 4.80 (1H, dd, *J* = 9.2, 1.5 Hz, H-1′), 5.33 (1H, br, H-6), 6.41 (1H, d, *J* = 15.9 Hz, Cin-H-2), 7.35 (3H, br t, *J* = 8.0 Hz, Cin-H-6, 7, 8), 7.50 (2H, brd, *J* = 7.0 Hz, Cin-H-5, 9), 7.70 (1H, d, *J* = 15.9 Hz, Cin-H-3); ^{13}C NMR, Tables 1 and 2; negative ion FABMS *m*/*z* 959 $(M - H)^-$, 799 $(M - 161)^-$, 655 $(M - 305)^-$, 511 $(M - 449)^-$; *anal.* C 62.31%, H 7.83%, calcd for $C_{51}H_{76}O_{17}\cdot H_2O$, C 62.58%, H 7.98%.

Sinomarinoside C (3): amorphous colorless powder; mp 135−142 °C; $[\alpha]_D^{20}$ 16.0° (*c* 0.25; $CHCl_3$); IR (KBr, cm^{-1}) 3480−3450 (OH), 1715 (C═O), 1630 (C═C), 1190 (C−O), 1100−1050 (C−O−C); ^{1}H NMR (C_5D_5N, 400 MHz) *δ* 0.84 (3H, d, *J* = 6.1 Hz, Isoval-H-4), 0.86 (3H, d, *J* = 5.8 Hz, Isoval-H-5), 1.38 (3H, d, *J* = 6.2 Hz, H-6′), 1.41 (3H, s, Me-18), 1.54 (3H, d, *J* = 6.3 Hz, Me-21), 1.58 (3H, d, *J* = 6.3 Hz, Me-6‴), 1.61 (3H, d, J = 5.0 Hz, Me-6″), 2.01 (3H, s, Me-19), 3.47 (1H, dd, *J* = 9.5, 2.8 Hz, H-4′), 3.57 (3H, s, OMe-3′), 3.59 (1H, dd, *J* = 10.6, 3.2 Hz, H-4″), 3.61 (3H, s, OMe-3″), 3.62 (1H, dd, *J* = 9.2, 6.0 Hz, H-4‴), 3.63 (1H, dd, *J* = 9.2, 6.0 Hz, H-3‴), 3.75 (1H, dq, *J* = 9.2, 6.1 Hz, H-5‴), 3.85 (1H, m, H-3 α), 3.90 (1H, dd, *J* = 8.0, 6.0 Hz, H-2‴), 3.91 (3H, s, OMe-3‴), 3.92 (1H, dd, *J* = 8.0, 5.0 Hz, H-12 α), 4.06 (2H, ddd, *J* = 3.6, 3.0, 2.8 Hz, H-3′ and 3″), 4.21 (2H, dq, *J* = 9.4, 6.3 Hz, H-5′ and 5″), 4.77 (1H, d, *J* = 7.7 Hz, H-1‴), 5.11 (1H, dd, *J* = 9.0, 2.0 Hz, H-1″), 5.28 (1H, dd, *J* = 9.2, 2.0 Hz, H-1′), 5.34 (1H, br s, H-6), 5.74 (1H, q, *J* = 6.2 Hz, H-20); ^{13}C NMR, see Tables 1 and 2; negative ion FABMS *m*/*z* 913 $(M - 1)^-$, 753 $(M - 161)^-$, 609 $(M - 305)^-$; *anal.* C 60.02%, H 8.48%, calcd for $C_{47}H_{78}O_{17}\cdot H_2O$, C 60.05%, H 8.58%.

Sinomarinoside D (4): amorphous colorless powder; mp 125−128 °C; $[\alpha]_D^{20}$ −20.0° (*c* 0.20; $CHCl_3$); IR *ν* (KBr, cm^{-1}) 3500−3450 (OH), 1700 (C═O), 1640 (C═C), 1110−1050 (C−O−C); ^{1}H NMR (C_5D_5N, 400 MHz) *δ* 1.37 (3H, d, *J* = 6.2 Hz, Me-6′), 1.42 (3H, s, Me-18), 1.61 (3H, d, *J* = 5.6 Hz, Me-6″), 1.62 (3H, d, *J* = 5.7 Hz, Me-6‴), 2.07 (3H, s, Me-19), 2.66 (3H, s, Me-21), 3.40 (1H, dd, *J* = 9.5, 3.0 Hz, H-4′), 3.49 (1H, dd, *J* = 9.4, 2.3 Hz, H-4‴), 3.58 (1H, dd, *J* = 9.2, 6.0 Hz, H-4″), 3.57 (3H, s, OMe-3′), 3.62 (3H, s, OMe-3″), 3.88 (1H, m, H-3 α), 3.91 (1H, dd, *J* = 8.5, 4.50 Hz, H-12 α), 3.92 (3H, s, OMe-3‴), 3.95 (1H, dq, *J* = 9.2, 6.1 Hz, H-3‴), 4.08 (2H, ddd, *J* = 3.7, 3.0, 2.8, Hz, H-3′), 4.21 (2H, dq, *J* = 9.4, 6.3 Hz, H-5′ and 5″), 4.79 (1H, d, *J* = 7.8 Hz, H-1‴), 5.18 (1H, dd, *J* = 9.5, 2.0 Hz, H-l″), 5.30 (1H, dd, *J* = 9.2, 1.8 Hz, H-1′), 5.35 (1H, br s, H-6); ^{13}C NMR, Tables 1 and 2; negative ion FABMS *m*/*z* 827 $(M - H)^-$, 667 $(M - 161)^-$; *anal.* C 58.19%, H 8.47%, calcd for $C_{42}H_{68}O_{16}\cdot 2H_2O$, C 58.33%; H, 8.33%.

Sinomarinoside E (5): amorphous colorless powder; mp 138−142 °C; $[\alpha]_D^{20}$ + 41.1° (*c* 0.34, $CHCl_3$); UV (EtOH) nm (log *ϵ*) 221 (4.67); IR (KBr, cm^{-1}) 3500−3420 (OH), 1710 (C═O), 1640 (C═C), 1100−1050 (C−O−C); ^{1}H NMR (C_5D_5N, 400 MHz) *δ* 1.30 (3H, s, Me-18), 1.43 (3H, d, *J* = 5.4 Hz, Me-6′), 1.57 (3H, d, *J* = 6.1 Hz, Me-6″) 1.59 (3H, d, *J* = 6.5 Hz, Me-6‴), 1.70 (3H, d, *J* = 7.0 Hz, Tig-Me-4), 1.93 (3H, d, *J* = 4.6 Hz, Tig-Me-5), 2.16 (3H, s, Me-19), 2.43 (3H, s, Me-21), 3.47 (1H, dd, *J* = 9.5, 3.0 Hz, H-4′), 3.54 (1H, br d *J* = 12.7 Hz, H-4″), 3.56 (3H, s, OMe-3′), 3.59 (1H, br d, *J* = 12.2 Hz, H-4‴), 3.63 (3H, s, OMe-3″), 3.66 (1H, dd, *J* = 8.5, 6.0 Hz, H-3‴), 3.72 (1H, dq, *J* = 9.2, 6.0 Hz, H-5‴), 3.89 (1H, m, H-3 α), 3.90 (3H, s, OMe-3‴), 3.94 (1H, dd, *J* = 8.5, 7.5 Hz, H-2‴), 4.05 (2H, ddd, *J* = 3.7, 3.0, 2.8 Hz, H-3′), 4.19 (2H, dq, *J* = 9.4, 6.3 Hz, H-5′ and 5″), 4.76 (1H, d, *J* = 7.6 Hz, H-1‴), 5.09 (1H, dd, *J* = 8.2, 1.6 Hz, H-1″), 5.24 (1H, dd, *J* = 9.1, 2.0 Hz, H-1′), 5.30 (1H, br s, Tig-H-3), 5.36 (1H, br s, H-6); ^{13}C NMR, Tables 1 and 2; negative ion FABMS *m*/*z* 909 $(M - H)^-$, 749 $(M - 161)^-$, 605 $(M - 305)^-$; *anal.* C 60.80%, H 8.22%, calcd for $C_{47}H_{74}O_{17}\cdot H_2O$, C 60.78%, H 8.20%.

Acidic Hydrolysis of 1−5. A solution of **1** (5 mg) in MeOH (2 mL) was allowed to react with 0.2 M H_2SO_4 (2 mL) at 60 °C for 40 min, 2 mL of H_2O was added and the whole was concentrated to 4 mL. The solution was kept at 60 °C for 40

min and neutralized with saturated $Ba(OH)_2$. The precipitate was filtered off and the filtrate was evaporated. The hydrolyzate contained **7**, cymarose, thevetose, dresibiose, and methyl-β-D-dresibioside as determined by TLC comparison with authentic samples (solvent systems A, B, and C). The other glycosides were acid-hydrolyzed by the procedure described above. Glycosides **2**, **3**, **4**, and **5** respectively gave aglycones **7**, **8**, **9**, and **10** and afforded sugar residues cymarose, thevetose, dresibiose and methyl-β-D-dresibioside by TLC comparison. However, sarcostin 3-*O*-β-D-cymaropyranoside, on acid hydrolysis, gave aglycone **6** and cymarose.

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