Acylated-oxypregnane Glycosides from the Roots of *Araujia sericifera*

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Twenty-three new acylated-oxypregnane glycosides were obtained from the roots of *Araujia sericifera*. (Asclepiadaceae). These glycosides were confirmed to be tetraglycosides possessing twelve known compounds, 12-*O*-benzoyllineolon, 12-*O*-benzoyldeacylmetaplexigenin, ikemagenin, kidjolanin, cynanchogenin, caudatin, rostratamine, penupogenin, 12-*O*-benzoylisolineolon, 12-*O*-tigloyldecylmetaplexigenin (incisagenin), 12-*O*-benzoyl-20-*O*-acetylsarcostin, 20-*O*-benzoyl-12-*O*-(*E*)-cinnamoyl-3β,5α,8β,12β,14β,17β,20-heptahydroxy-(20*S*)-pregn-6-ene and ten new acylated-oxypregnanes, 12-*O*-benzoyl-20*S*-hydroxyisolineolon, 12-*O*-tigloyllineolon, 12-*O*-salicyloyllineolon, 12-*O*-salicyloyldeacylmetplexigenin, 12-*O*-benzoyl-3β,5α,8β,12β,14β,17β-hexahydroxypregn-6-en-20-one, 12-*O*-benzoyl-19-benzoyloxydeacylmetapleligenin, 12-*O*-benzoyl-19-benzoyloxy-20-*O*-acetylsarcostin, 12-*O*-benzoyl-19-salicyloyloxy-20-*O*-acetylsarcostin, 12-*O*-benzoyl-5α,6α-epoxydeacylmetaplexigenin, and 12-*O*-benzoyl-5α,6α-epoxylineolon as their aglycones, using both spectroscopic and chemical methods.

Key words *Araujia sericifera*; Asclepiadaceae; pregnane glycosides; 2,6-dideoxyhexopyranose

Araujia sericifera is distributed through out southeast Latin America.[1] In the course of our research on phytochemicals, especially steroidal glycosides, in Asclepiadaceaus plants, we have investigated the constituents of the roots of *A. sericifera*. The present paper describes the isolation and structural determination of 23 new pregnane glycosides.

The MeOH extract from the dried roots of *A. sericifera* was suspended in water. The suspension was extracted with diethyl ether and partitioned into an ether-soluble fraction and a water-soluble fraction. The residue of the ether-soluble fraction was chromatographed on a silica gel column to give a fraction of acylated-oxypregnane glycosides from which 23 new compounds were obtained.

In order to acquire the component aglycones and sugars, the fraction containing the pregnane glycosides from silica gel column chromatography was subjected to acid hydrolysis. The obtained known aglycones were identified as 12-*O*-benzoyllineolon (**1a**),[2] 12-*O*-benzoyldeacylmetaplexigenin (**2a**),[3] kidjolanin (**5a**),[4] gagaminin (**24a**)[5] and 20-*O*-benzoyl-12-*O*-(*E*)-cinnamoyl-3β,5α,8β,12β,14β,17β,20-heptahydroxy-(20*S*)-pregn-6-ene (**16a**)[6,7] in view of the ^{1}H- and ^{13}C-NMR spectral data. In addition, two new acylated-oxypregnanes (**11a**, **18a**) were obtained.

Compound **11a** was suggested to have the molecular formula $C_{28}H_{38}O_6$ based on high resolution (HR)-FAB-MS [*m/z* 471.2747 $[M+H]^+$, 493.2545 $[M+Na]^+$]. On comparing the ^{1}H- and ^{13}C-NMR spectra of **11a** with those of 12-*O*-benzoyllineolon (**1a**), signals of the benzoyl group were also observed. But, a set of hydroxyl methine proton and carbon signals were seen at δ 3.96 (1H, br q, J=6.0 Hz) and δ 65.5 instead of the carbonyl carbon signal at C-20. Thus, **11a** was considered to be 12-*O*-benzoyl-20-hydroxylineolon or 12-*O*-benzoyl-20-hydroxyisolineolon. On the basis of ^{1}H–^{1}H correlation spectroscopy (COSY) and ^{1}H-detected heteronuclear multiple quantum coherency (HMQC) spectra, assignments of the proton signals were shown as presented in the Experimental section. In the nuclear Overhauser effect (NOE) difference experiment, irradiation at the H-12 signal (δ 4.89) showed an NOE on the H-17 signal (δ 1.84). This finding suggested that the orientation of H-17 was α, so that the side chain at C-17 had a β-orientation. In comparing the ^{13}C-NMR spectral data of 12-*O*-acetyl-20*S*-hydroxyisolineolon[8] and 12-*O*-acetyl-20*R*-hydroxyisolineolon,[8] the ^{13}C-NMR spectral data around C-20 of **11a** were consistent with those of 12-*O*-acetyl-20*S*-hydroxyisolineolon. Thus, **11a** was determined to be 12-*O*-benzoyl-20*S*-hydroxyisolineolon.

Compound **18a** was confirmed to have the molecular formula $C_{35}H_{40}O_9$ based on HR-FAB-MS [*m/z* 627.2552 $[M+Na]^+$]. Comparison of the ^{1}H- and ^{13}C-NMR spectral data of **18a** with those of 12-*O*-benzoyldeacylmetaplexigenin (**2a**) suggested that **18a** has two benzoyl groups. The results of the one dimensional (1D)- and 2D-NMR (^{1}H–^{1}H COSY, HMQC and ^{1}H-detected heteronuclear multiple-bond connectivity (HMBC)) spectra of **18a** exhibited oxygenated methylene signals at δ 5.21 (1H, d, J=12.0 Hz), 5.50 (1H, d, J=12.0 Hz) and δ 64.4, which were assigned at the H-19 and C-19 positions. Additionally, the HMBC experiment showed long-range correlations between δ 166.4 (C″-1 of the benzoyl group) and δ 5.21 (1H, d, J=12.0 Hz, H-19), 5.50 (1H, d, J=12.0 Hz, H-19), δ 165.4 (C′-1 of the benzoyl group) and δ 5.41 (1H, dd, J=11.5, 4.5 Hz, H-12). These findings suggested that two benzoyl groups were attached at C-12-OH and C-19-OH of 19-hydroxydeacylmetaplexigenin, respectively. Thus, **18a** was concluded to be 12-*O*-benzoyl-19-benzoyloxydeacylmetaplexigenin.

The acquired sugar mixtures were fractionated to cymarose and to a disaccharide by silica gel column chromatography. The absolute configuration of this cymarose was believed to be a D-form on the basis of its optical rotation value. The absolute configuration of thevetose was also determined to be a D-form based on GC analysis following its reaction with D-cysteine methyl ester hydrochloride (see Experimental).

Compound **1** was suggested to have the molecular formula $C_{56}H_{84}O_{19}$ based on HR-FAB-MS. In ^{1}H- and ^{13}C-NMR spectra of **1**, four anomeric proton and carbon signals were observed at δ 5.27, 5.10, 5.09, 4.77 and δ 96.4, 100.4×2, 106.2, in addition to signals due to the aglycone which was identified as 12-*O*-benzoyllineolon (**1a**) by acid hydrolysis with 0.05 M HCl. The ^{13}C-NMR spectral comparison of **1** with **1a** showed that glycosylation shifts were presented at the C-2, -3 and -4 positions [C-2 (−2.2 ppm), C-3

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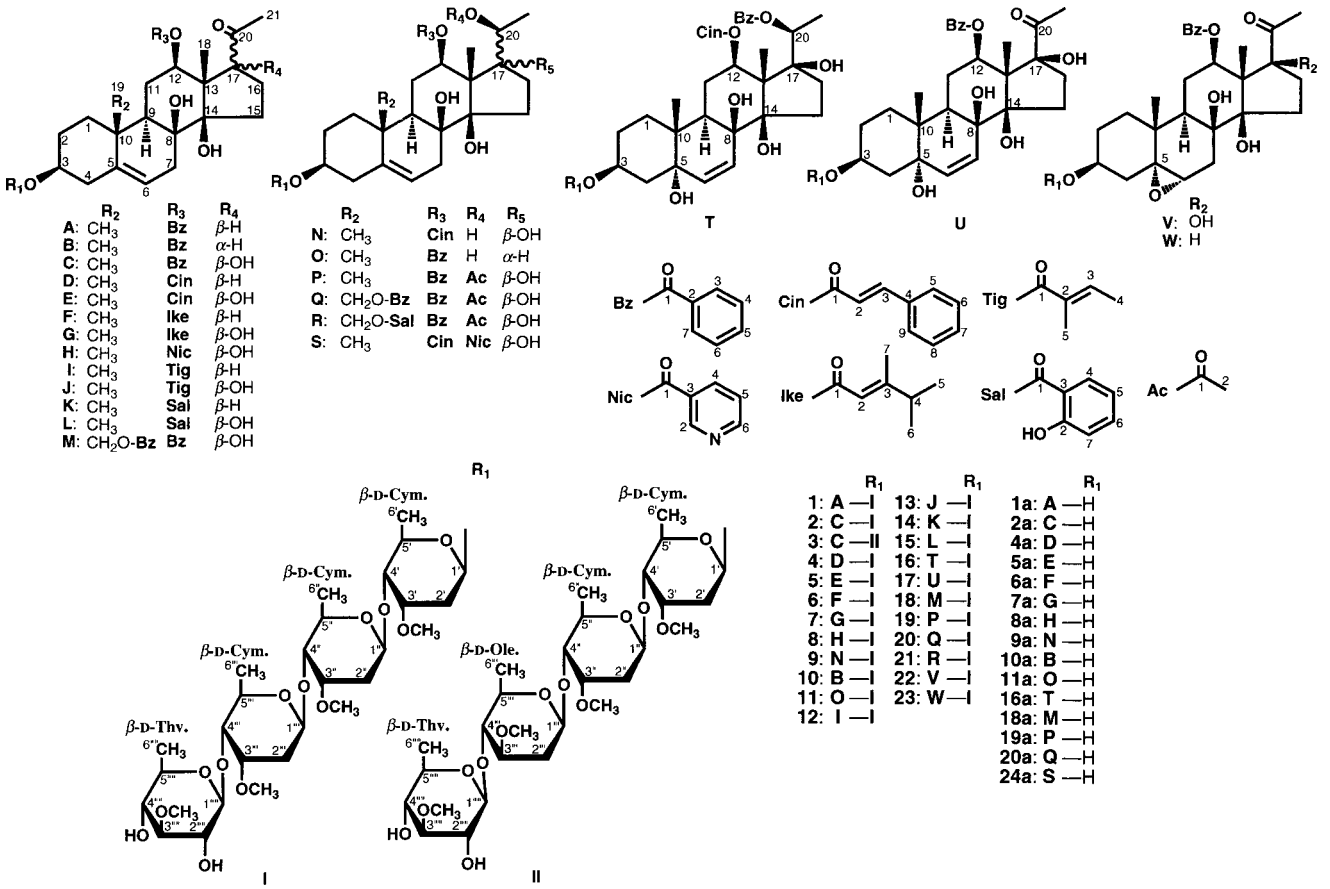

Chart 1

(+6.1 ppm), C-4 (−4.1 ppm)].[9] Thus, **1** was glycosylated at the C-3 position, and is considered to be 12-*O*-benzoyllineolon 3-*O*-tetraglycoside. Acid hydrolysis of **1** showed that the sugar moiety consisted of cymarose and thevetose, and these sugars were identified as *β*-D-cymaropyranose and *β*-D-thevetopyranose, as judged from the *J* value of each anomeric proton signal [*J*=9.5, 2.0 Hz (cymarose), *J*=8.0 Hz (thevetose)]. For the sugar sequence of **1**, NOE difference spectra were measured on irradiation of the anomeric proton or H-4 signals of each sugar, and NOEs were observed as follows, *δ* 5.27 (1H, dd, *J*=9.5, 2.0 Hz, H′-1 of *β*-D-cymaropyranose) and *δ* 3.84 (1H, m, H-3 of the aglycone), *δ* 5.10 (1H, dd, *J*=9.5, 2.0 Hz, H″-1 of *β*-D-cymaropyranose) and *δ* 3.50 (1H, dd, *J*=9.5, 3.0 Hz, H′-4 of *β*-D-cymaropyranose), *δ* 5.09 (1H, dd, *J*=9.5, 2.0 Hz, H‴-1 of *β*-D-cymaropyranose) and *δ* 3.42 (1H, dd, *J*=9.5, 3.0 Hz, H″-4 of *β*-D-cymaropyranose), *δ* 4.77 (1H, d, *J*=8.0 Hz, H⁗-1 of *β*-D-thevetopyranose) and *δ* 3.59 (overlapping, H‴-4 of *β*-D-cymaropyranose). Hence, the structure of **1** was established as 12-*O*-benzoyllineolon 3-*O*-*β*-D-thevetopyranosyl-(1→4)-*β*-D-cymaropyranosyl-(1→4)-*β*-D-cymaropyranosyl-(1→4)-*β*-D-cymaropyranoside.

The following compounds **2**—**22** and **23** were also glycosylated at the C-3 position of each aglycone based on observations of glycosylation shifts in the ^{13}C-NMR spectra. Moreover, the sugar sequences of compounds **2**, **4**—**22** and **23** were identical with that of **1**, because of ^{1}H- and ^{13}C-NMR spectral consistency on the signals due to the sugar moieties.

The molecular formulae of compounds **2** and **3** were deduced to be $C_{56}H_{84}O_{20}$ as determined by HR-FAB-MS. Acid hydrolysis of these compounds yielded cymarose, thevetose from **2** and cymarose, oleandrose, thevetose from **3** as the sugar moieties, in addition to 12-*O*-benzoyldeacylmetaplexigenin (**2a**). The ^{1}H- and ^{13}C-NMR spectral data of the sugar moiety in **3** were consistent with those of 15*β*-hydroxylineolon 3-*O*-*β*-D-thevetopyranosyl-(1→4)-*β*-D-oleandropyranosyl-(1→4)-*β*-D-cymaropyranosyl-(1→4)-*β*-D-cymaropyranoside.[10] On the basis of the above evidence, the structures of **2** and **3** were shown as presented in Chart 1.

Compounds **4**—**10** and **11** were presumed to be 12-*O*-acylated-pregnane 3-*O*-*β*-D-thevetopyranosyl-(1→4)-*β*-D-cymaropyranosyl-(1→4)-*β*-D-cymaropyranosyl-(1→4)-*β*-D-cymaropyranoside. Acid hydrolysis of these compounds yielded ikemagenin (**4a**),[11] kidjolanin (**5a**), cynanchogenin (**6a**),[12—14] caudatin (**7a**),[14,15] rostratamine (**8a**),[16] penupogenin (**9a**),[17] 12-*O*-benzoylisolineolon (**10a**)[18] and 12-*O*-benzoyl-20*S*-hydroxyisolineolon (**11a**), respectively, together with cymarose and thevetose as their sugar moieties. Thus, their structures were determined to be as shown in Chart 1.

Compounds **12**—**14** and **15** had the molecular formulae, $C_{54}H_{86}O_{19}$, $C_{54}H_{86}O_{20}$, $C_{56}H_{84}O_{20}$ and $C_{56}H_{84}O_{21}$, respectively, by the results of HR-FAB-MS. The ^{1}H- and ^{13}C-NMR spectra of the aglycones in **12**, **14** and **13**, **15** were similar to those of 12-*O*-benzoyllineolon (**1a**) and 12-*O*-benzoyldeacymetaplexigenin (**2a**), except for the ester moieties. Therefore, the aglycones of **12**, **14** and **13**, **15** were considered to be 12-*O*-acylated-lineolon and 12-*O*-acylated-deacylmetaplexigenin. Alkaline hydrolysis following acid hydrolysis

Table 1. ^{13}C-NMR Spectral Data of the Aglycone Moiety and Anomeric Carbon of the First Cymaropyranose of Compounds **1**—**23**

	1	**2**, **3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Carbon No.											
C- 1	39.0	38.9	39.1	39.0	39.0	39.0	38.9	39.0	39.0	39.1	39.0
- 2	29.9	29.9	29.9	29.9	29.9	29.9	29.9	29.9	29.9	30.0	29.9
- 3	77.7	77.6	77.7	77.7	77.7	77.7	77.6	77.7	77.7	77.8	77.7
- 4	39.3	39.3	39.3	39.4	39.4	39.3	39.3	39.4	39.3	39.4	39.3
- 5	139.5	139.5	139.5	139.5	139.5	139.5	139.4	139.2	139.2	139.1	139.5
- 6	119.1	119.1	119.2[a)]	119.1[a)]	119.2	119.1	119.1	119.5[a)]	119.4	119.7	119.1
- 7	35.2	34.8	35.2	34.8	35.2	34.8	34.7	35.1	35.9	36.2[a)]	35.2
- 8	74.6	74.4	74.6	74.3	74.6	74.3	74.3	74.2	74.4	74.1	74.6
- 9	44.7	44.5	44.8	44.6	44.9	44.6	44.5	44.2	45.2	45.1	44.7
-10	37.6	37.4	37.6	37.4	37.6	37.4	37.4	37.3	37.7	37.6	37.5
-11	25.0	25.1	25.0	25.0	25.1	25.1	25.1	25.7	24.8[a)]	24.8	24.9
-12	73.7	74.1	73.4	73.6	72.4	74.8	74.7	74.8	78.6	78.8	72.9
-13	56.1	58.4	55.9	58.1	55.8	58.0	58.3	57.0	55.1	54.0	56.1
-14	87.5	89.5	87.5	89.5	87.5	89.5	89.5	88.9	86.6	85.7	87.9
-15	34.2	33.9	34.2	33.8	34.2	33.8	33.8	34.3	36.7	36.1[a)]	34.2
-16	22.2	33.2	22.0	33.1	21.9	33.0	33.3	33.0	24.7[a)]	19.0	22.1
-17	60.3	92.5	60.6	92.4	60.7	92.4	92.5	88.6	59.3	52.3	60.3
-18	15.9	10.8	15.8	10.7	15.9	10.7	10.7	11.7	12.7	12.1	15.8
-19	18.2	18.2	18.2	18.2	18.2	18.2	18.2	19.3	18.4	18.3	18.2
-20	209.4	210.6	209.3	209.7	209.1	209.3	210.5	70.1	214.1	65.5	209.2
-21	32.2	27.8	32.2	27.7	32.1	27.5	27.9	18.3	31.7	22.5	32.2
Ester moiety linked to the C-12 position											
	Bz	Bz	Cin	Cin	Ike	Ike	Nic	Cin	Bz	Bz	Tig
C-1′	165.5	165.3	165.9	165.8	166.1	166.0	164.3	166.9	166.6	166.7	166.7
-2′	131.4	131.3	119.3[a)]	119.2[a)]	114.3	114.2	153.9	119.7[a)]	131.2	131.5	129.6
-3′	129.9	129.9	144.9	144.9	165.2	165.3	126.9	145.3	130.0	129.9	136.8
-4′	128.9	128.9	135.1	135.1	38.1	38.2	137.1	135.1	129.1	129.1	14.2
-5′	133.2	133.2	128.6	128.6	20.9	20.9[a)]	123.7	128.6	133.6	133.4	12.3
-6′	128.9	128.9	129.3	129.3	20.9	21.0[a)]	151.1	129.2	129.1	129.1	—
-7′	129.9	129.9	130.6	130.6	16.5	16.5	—	130.4	130.0	129.9	—
-8′	—	—	129.3	129.3	—	—	—	129.2	—	—	—
-9′	—	—	128.6	128.6	—	—	—	128.6	—	—	—
Ester moiety linked to the C-19 position											
C-1″	—	—	—	—	—	—	—	—	—	—	—
-2″	—	—	—	—	—	—	—	—	—	—	—
-3″	—	—	—	—	—	—	—	—	—	—	—
-4″	—	—	—	—	—	—	—	—	—	—	—
-5″	—	—	—	—	—	—	—	—	—	—	—
-6″	—	—	—	—	—	—	—	—	—	—	—
-7″	—	—	—	—	—	—	—	—	—	—	—
Ester moiety linked to the C-20 position											
C-1‴	—	—	—	—	—	—	—	—	—	—	—
-2‴	—	—	—	—	—	—	—	—	—	—	—
-3‴	—	—	—	—	—	—	—	—	—	—	—
-4‴	—	—	—	—	—	—	—	—	—	—	—
-5‴	—	—	—	—	—	—	—	—	—	—	—
-6‴	—	—	—	—	—	—	—	—	—	—	—
-7‴	—	—	—	—	—	—	—	—	—	—	—
Anomeric signal of the first cymaropyranose											
C-1′	96.4	96.4	96.4	96.4	96.5	96.4	96.4	96.4	96.4	96.5	96.4

produced tiglic acid, lineolon from **12**, tiglic acid, deacylmetaplexigenin from **13**, salicylic acid, lineolon from **14** and salicylic acid, deacylmetaplexigenin from **15** (see Experimental). The above evidence led us to conclude that the aglycones of **12**—**14** and **15** were 12-*O*-tigloyllineolon, 12-*O*-tigloyldeacylmetaplexigenin (incisagenin),[19] 12-*O*-salicyloyllineolon and 12-*O*-salicyloyldeacylmetaplexigenin, so the structures of these compounds were elucidated as shown in Chart 1.

The molecular formulae of compounds **16** and **17** were considered to be $C_{65}H_{92}O_{22}$ and $C_{56}H_{84}O_{21}$ on the basis of HR-FAB-MS. The ^{1}H- and ^{13}C-NMR spectra suggested that the aglycone of **16** was 20-*O*-benzoyl-12-*O*-(*E*)-cinnamoyl-3β,5α,8β,12β,14β,17β,20-heptahydroxy-(20*S*)-pregn-6-ene (**16a**), and that was supported by mild acid hydrolysis with 0.1 M H_2SO_4. Thus, the structure of **16** was concluded to be as shown in Chart 1. In the ^{1}H-NMR spectrum, the aglycone of **17** showed two *cis*-olefinic proton signals [δ 5.92 (1H, d, J=10.0 Hz), 6.21 (1H, d, J=10.0 Hz)], two methyl proton signals [δ 1.52 (3H, s), 2.07 (3H, s)], and one acetyl methyl

Table 1. (continued)

	13	14	15	16	17	18	19	20	21	22	23
Carbon No.											
C- 1	38.9	39.0	38.9	27.7	27.8	33.4	39.3	32.9	32.8	38.1	38.1
- 2	29.8	29.9	29.9	26.6	26.6	30.0	29.9	29.9	29.8	29.0	29.0
- 3	77.6	77.7	77.6	74.9[a)]	74.9[a)]	76.9	77.6	76.9	76.9	74.9	74.9
- 4	39.3	39.3	39.3	39.2	39.2	39.6	38.7	39.6	39.6	38.8	38.8
- 5	139.4	139.5	139.5	74.8[a)]	74.8[a)]	135.2	139.2	134.8	134.4	64.6	64.6
- 6	119.1	119.1	119.1	136.8	137.2	123.6	119.4	124.1	124.4	65.5	65.6
- 7	34.8	35.1	34.7	127.3	127.0	35.1	35.0[a)]	35.3	35.3	30.9	31.3
- 8	74.3	74.6	74.3	74.1	74.1	74.2	74.3	74.2	74.1	75.9	76.1
- 9	44.4	44.7	44.5	36.8	36.9	44.2	44.0	43.7	43.7	44.7	45.0
-10	37.4	37.6	37.4	39.7	39.7	41.6	37.3	41.5	41.3	36.2	36.3
-11	25.0	25.0	25.1	23.7	23.2	26.5	25.9	27.5	27.4	25.5	25.4
-12	73.3	74.5	74.9	75.8	75.4	74.0	75.0	75.0	74.9	73.6	73.4
-13	58.3	56.1	58.4	58.2	59.5	58.2	57.1	57.0	57.0	58.2	55.8
-14	89.5	87.6	89.6	88.3	88.7	89.5	88.9	88.8	88.7	88.8	86.8
-15	33.8	34.2	33.8	33.2	33.0	34.1[a)]	33.8[a)]	34.0	34.1	32.7	33.3
-16	33.1	22.2	33.4	34.3	34.0	33.2[a)]	33.8[a)]	33.6	33.5	33.7	22.6
-17	92.4	60.2	92.5	87.8	92.5	92.5	87.5	87.6	87.6	92.2	60.1
-18	10.7	15.8	10.8	12.4	11.8	10.9	11.6	11.6	11.6	10.7	15.8
-19	18.2	18.2	18.2	21.5	21.5	64.3	18.1	64.0	64.5	17.4	17.5
-20	209.7	209.8	210.7	75.4	210.3	210.0	74.7	74.6	74.7	210.0	209.4
-21	27.8	32.4	27.8	15.6	27.8	27.7	15.2	15.2	15.2	27.8	32.2
Ester moiety linked to the C-12 position											
	Tig	Sal	Sal	Cin	Bz	Bz	Bz	Bz	Bz	Bz	Bz
C-1′	166.5	169.7	169.6	166.8	165.4	165.4	166.5	166.6	166.6	165.2	165.4
-2′	129.5	162.5	162.5	120.3	131.2	131.2	132.4	132.3	132.2	131.1	131.2
-3′	136.8	113.5	113.5	144.0	129.9	129.8	130.1	130.0	130.0	129.9	129.9
-4′	14.2	130.2	130.2	135.0	128.9	128.9	128.7	128.8	128.7	128.9	128.9
-5′	12.3	119.5	119.5	128.6	133.3	133.3	133.2	133.1	133.1	133.3	133.3
-6′	—	136.0	136.1	129.1	128.9	128.9	128.7	128.8	128.7	128.9	128.9
-7′	—	118.2	118.2	130.4	129.9	129.8	130.1	130.0	130.0	129.9	129.9
-8′	—	—	—	129.1	—	—	—	—	—	—	—
-9′	—	—	—	128.6	—	—	—	—	—	—	—
Ester moiety linked to the C-19 position											
						Bz		Bz	Sal		
C-1″	—	—	—	—	—	166.4	—	166.4	170.3	—	—
-2″	—	—	—	—	—	131.1	—	131.0	162.0	—	—
-3″	—	—	—	—	—	129.6	—	129.5	113.2	—	—
-4″	—	—	—	—	—	128.6	—	128.6	129.8	—	—
-5″	—	—	—	—	—	133.0	—	132.9	119.3	—	—
-6″	—	—	—	—	—	128.6	—	128.6	135.7	—	—
-7″	—	—	—	—	—	129.6	—	129.5	117.8	—	—
Ester moiety linked to the C-20 position											
				Bz			Ac	Ac	Ac		
C-1‴	—	—	—	165.9	—	—	ND	ND	169.2	—	—
-2‴	—	—	—	131.3	—	—	21.3	21.2	21.2	—	—
-3‴	—	—	—	130.2	—	—	—	—	—	—	—
-4‴	—	—	—	128.7	—	—	—	—	—	—	—
-5‴	—	—	—	133.1	—	—	—	—	—	—	—
-6‴	—	—	—	128.7	—	—	—	—	—	—	—
-7‴	—	—	—	130.2	—	—	—	—	—	—	—
Anomeric signal of the first cymaropyranose											
C-1′	96.4	96.5	96.4	97.8	97.8	96.4	96.4	96.4	96.5	96.7	96.7

Measured in pyridine-d_5 at 35 °C. *a*) Interchangeable in each column. ND: A signal was not detected. Bz: benzoyl, Cin: cinnamoyl, Ike: ikemaoyl, Nic: nicotinoyl, Tig: tigloyl, Sal: salicyloyl, Ac: acetyl.

proton signal [δ 2.34 (3H, s)]. And the ^{13}C-NMR spectrum of **17** exhibited two hydroxyl methine carbon signals (δ 74.9, 75.4), four hydroxyl quaternary carbon signals (δ 74.8, 74.1, 88.7, 92.5), two sp^2 carbon signals (δ 127.0, 137.2), one carbonyl carbon signal (δ 210.3), two methyl carbon signals (δ 11.8, 21.5) and one acetyl methyl carbon signal (δ 27.8) in addition to the signals due to the benzoyl group. Based on the results of the 2D-NMR (HMQC, HMBC and ^{1}H–^{1}H COSY) experiments, the assignments of these ^{1}H- and ^{13}C-NMR spectral data are presented in Tables 1—3. Moreover, comparison of the 1D-NMR signals of **17** with those of **2a** and **16a** suggested that the aglycone of **17** was 12-*O*-benzoyl-3β,5α,8β,12β,14β,17β-hexahydroxy-pregn-6-ene-20-one. Therefore, **17** was determined to be as presented in Chart 1.

Compound **18** had the molecular formula, $C_{63}H_{88}O_{22}$ by HR-FAB-MS. By acid hydrolysis, **18** produced 12-*O*-benzoyl-19-benzoyloxydeacylmetaplexigenin (**18a**) as the agly-

Table 2. ^{1}H-NMR Spectral Data of the Aglycones and First Cymaropyranose in Compounds **1**—**23**

	1	**2**, **3**	**4**	**5**	**6**	**7**	**8**
Proton No.							
- 3	3.84 (m)	3.84 (m)	3.84 (m)	3.85 (m)	3.83 (m)	3.84 (m)	3.85 (m)
- 6	5.30 (br s)	5.30 (br s)	5.30 (br s)	5.30 (br s)	5.29 (br s)	5.29 (br s)	5.30 (br s)
- 7							
-12	5.41 (dd, 12.0, 4.0)	5.36 (dd, 12.0, 4.0)	5.25 (dd, 11.5, 4.0)	5.18 (dd, 12.0, 4.0)	5.10*	5.03 (dd, 11.5, 4.5)	5.37 (dd, 12.0, 4.5)
-17	3.53 (t, 9.5)	—	3.51 (t, 9.5)	—	3.47 (t, 9.5)	—	—
-18	2.00 (s)	2.06 (s)	2.00 (s)	2.03 (s)	1.95 (s)	1.97 (s)	2.03 (s)
-19	1.32 (s)	1.32 (s)	1.34 (s)	1.35 (s)	1.32 (s)	1.33 (s)	1.35 (s)
	—	—	—	—	—	—	—
-20	—	—	—	—	—	—	—
-21	2.11 (s)	2.35 (s)	2.27 (s)	2.49 (s)	2.28 (s)	2.50 (s)	2.33 (s)
Ester moiety linked to the C-12 position							
	Bz	Bz	Cin	Cin	Ike	Ike	Nic
-2′	—	—	6.78 (d, 16.0)	6.80 (d, 16.0)	5.84 (t, 0.5)	5.86 (br s)	9.58 (d, 2.0)
-3′	8.27 (br d, 8.0)	8.28 (br d, 8.0)	7.97 (d, 16.0)	8.00 (d, 16.0)	—	—	—
-4′	7.46 (br t, 8.0)	7.47 (br t, 8.0)			2.25*	2.28*	8.44 (dt, 8.0, 2.0)
-5′	7.53 (br t, 8.0)	7.54 (br t, 8.0)			0.95 (d, 6.5)	0.96 (d, 6.5)	7.37 (dd, 8.0, 4.5)
-6′	7.46 (br t, 8.0)	7.47 (br t, 8.0)			0.97 (d, 6.5)	0.98 (d, 6.5)	8.87 (dd, 4.5, 2.0)
-7′	8.27 (br d, 8.0)	8.28 (br d, 8.0)			2.26 (d, 0.5)	2.28 (br s)	—
-8′	—	—			—	—	—
-9′	—	—			—	—	—
Ester moiety linked to the C-19 position							
-2″	—	—	—	—	—	—	—
-3″	—	—	—	—	—	—	—
-4″	—	—	—	—	—	—	—
-5″	—	—	—	—	—	—	—
-6″	—	—	—	—	—	—	—
-7″	—	—	—	—	—	—	—
Ester moiety linked to the C-20 position							
-2‴	—	—	—	—	—	—	—
-3‴	—	—	—	—	—	—	—
-4‴	—	—	—	—	—	—	—
-5‴	—	—	—	—	—	—	—
-6‴	—	—	—	—	—	—	—
-7‴	—	—	—	—	—	—	—
Anomeric signal of the first cymaropyranose							
	5.27 (dd, 9.5, 2.0)	5.27 (dd, 9.5, 2.0)	5.26 (dd, 9.5, 2.0)	5.27 (d, 9.5, 2.0)	5.26 (dd, 9.5, 2.0)	5.26 (dd, 9.5, 2.0)	5.27 (dd, 9.5, 2.0)

cone moiety along with cymarose and thevetose. Thus, compound **18** was determined to be 12-*O*-benzoyl-19-benzoyloxydeacylmetaplexigenin 3-*O*-β-D-thevetopyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside.

Compound **19** would be expected to have the molecular formula $C_{58}H_{88}O_{21}$ based on HR-FAB-MS. Acid hydrolysis of **19** yielded aglycone **19a**, whose molecular formula was $C_{30}H_{40}O_8$ by HR-FAB-MS [*m/z* 551.2646 $[M+Na]^+$], together with cymarose and thevetose. Moreover, by alkaline hydrolysis, **19a** was decomposed into sarcostin and benzoic acid, which were detected using the HPLC analysis with authentic samples. Because the molecular formulae of sarcostin and a benzoyl group were $C_{21}H_{34}O_6$ and C_7H_5O, respectively, the molecular formula of the remaining residue was presumed to be C_2H_3O, which was suitable for an acetyl group. These findings suggested that **19a** consisted of sarcostin, a benzoyl group and an acetyl group. In the ^{13}C-NMR spectra, **19a** showed carbonyl carbon signals of the benzoyl and acetyl groups at δ 167.8 and 171.4, and in the HMBC experiment, the carbonyl carbon signal of the benzoyl group (δ 167.8) showed a $^3J_{COCH}$ to the H-12 signal of sarcostin [δ 4.99 (1H, dd, J=11.5, 4.5 Hz)], but a $^3J_{COCH}$ between the carbonyl carbon signal of the acetyl group (δ 171.4) and the H-20 signal of sarcostin [δ 4.56 (1H, br q, J=6.0 Hz)] was not observed, contrary to our expectation. 1D-NMR spectral comparison of **19a** with 12-*O*-acetylsarcostin[20] showed downfield movement of the C-20 and H-20 signals (C-20: +3.8 ppm, H-20: +0.68 ppm). Thus, the benzoyl and acetyl groups were bounded to C-12-OH and C-20-OH, respectively. So, the structure of **19a** was concluded to be 12-*O*-benzoyl-20-*O*-acetylsarcostin. This compound had been previously detected from the dried roots of *Asclepias lilacina* W.[21,22] On the basis of the above arguments, compound **19** was established to be 12-*O*-benzoyl-20-*O*-acetylsarcostin 3-*O*-β-D-thevetopyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside.

Based on the results of the ^{1}H-, ^{13}C-NMR spectra and HR-FAB-MS, compound **20** had one more benzoyl group in its structure than **19** did. The ^{1}H- and ^{13}C-NMR spectra of **20** exhibited the H-19 and C-19 signals at δ 5.10 (overlapping), 5.51 (1H, d, J=12.0 Hz) and δ 64.0, the same as with **18**.

Table 2. (continued)

	9	10	11	12	13	14	15
Proton No.							
- 3	3.85 (m)	3.85 (m)	3.86 (m)	3.83 (m)	3.83 (m)	3.86 (m)	3.86 (m)
- 6	5.37 (br s)	5.35 (br s)	5.39 (br s)	5.29 (br s)	5.29 (br s)	5.31 (br s)	5.31 (br s)
- 7							
-12	5.28*	5.24 (dd, 12.0, 4.0)	5.28*	5.21 (dd, 11.0, 4.0)	5.13 (dd, 12.0, 4.0)	5.44 (dd, 12.0, 4.0)	5.37 (dd, 12.0, 4.0)
-17	—	3.26 (dd, 9.5, 5.5)	2.14*	3.48 (t, 9.5)	—	3.55 (t, 9.5)	—
-18	2.15 (s)	1.63 (s)	1.80 (s)	1.93 (s)	1.95 (s)	2.01 (s)	2.04 (s)
-19	1.38 (s)	1.34 (s)	1.40 (s)	1.31 (s)	1.31 (s)	1.35 (s)	1.35 (s)
	—	—	—	—	—	—	—
-20	4.13 (q, 6.0)	—	4.24*	—	—	—	—
-21	1.35 (d, 6.0)	2.19 (s)	1.13 (d, 6.0)	2.20 (s)	2.43 (s)	2.13 (s)	2.36 (s)
Ester moiety linked to the C-12 position							
	Cin	Bz	Bz	Tig	Tig	Sal	Sal
-2′	6.94 (d, 16.0)	—	—	—	—	—	—
-3′	8.17 (d, 16.0)	8.35 (br d, 8.0)	8.33 (br d, 8.0)	6.97 (br q, 7.5)	6.98 (br q, 7.0)	—	—
-4′		7.52 (br t, 8.0)	7.49 (br t, 8.0)	1.67 (br d, 7.5)	1.68 (br d, 7.0)	8.01 (dd, 8.0, 1.5)	8.01 (dd, 8.0, 1.5)
-5′		7.59 (br t, 8.0)	7.57 (br t, 8.0)	1.93 (br s)	1.94 (br s)	6.97 (ddd, 8.0, 6.5, 1.0)	6.97 (ddd, 8.0, 6.5, 1.0)
-6′		7.52 (br t, 8.0)	7.49 (br t, 8.0)	—	—	7.48 (ddd, 8.0, 6.5, 1.5)	7.48 (ddd, 8.0, 6.5, 1.5)
-7′		8.35 (br d, 8.0)	8.33 (br d, 8.0)	—	—	7.13 (dd, 8.0, 1.0)	7.13 (dd, 8.0, 1.0)
-8′		—	—	—	—	—	—
-9′		—	—	—	—	—	—
Ester moiety linked to the C-19 position							
-2″	—	—	—	—	—	—	—
-3″	—	—	—	—	—	—	—
-4″	—	—	—	—	—	—	—
-5″	—	—	—	—	—	—	—
-6″	—	—	—	—	—	—	—
-7″	—	—	—	—	—	—	—
Ester moiety linked to the C-20 position							
-2‴	—	—	—	—	—	—	—
-3‴	—	—	—	—	—	—	—
-4‴	—	—	—	—	—	—	—
-5‴	—	—	—	—	—	—	—
-6‴	—	—	—	—	—	—	—
-7‴	—	—	—	—	—	—	—
Anomeric signal of the first cymaropyranose							
	5.28*	5.27 (dd, 9.5, 2.0)	5.28 (dd, 9.5, 2.0)	5.26 (dd, 9.5, 2.0)	5.26 (dd, 9.5, 2.0)	5.28 (dd, 9.5, 2.0)	5.27 (dd, 9.5, 2.0)

According to 1D-NMR spectral comparison with those of **18** and **19**, compound **20** was expected to have a benzoyl group at C-12-OH, a benzoyloxy group at C-19 and an acetyl group at C-20-OH of sarcostin. The attached positions of these acyl groups were confirmed by observations of $^{3}J_{COCH}$ between δ 166.6 (C-1′ of the benzoyl group) and δ 5.43 (H-12), δ 166.4 (C-1″ of the benzoyl group) and δ 5.10 (H-19) in the HMBC experiment and movement of the C-20 and H-20 signals to downfield in the 1D-NMR spectra. Thus, the aglycone of **20** (**20a**) was determined to be 12-*O*-benzoyl-19-benzoyloxy-20-*O*-acetylsarcostion, and the structure of **20** was as shown in Chart 1.

The ^{1}H- and ^{13}C-NMR spectra of compound **21** were similar to those of **20**. But the ester moieties attached at C-12-OH and C-19-OH were considered to be a benzoyl group and a salicyloyl group. In the HMBC experiment, $^{3}J_{COCH}$s were observed between δ 170.3 (C-1″ of a salicyloyl group) and δ 5.04 (H-19), δ 166.6 (C-1′ of a benzoly group) and δ 5.42 (H-12). These findings suggested that the benzoyl and salicyloyl groups were linked to C-12-OH and C-19-OH, respectively. Thus, **21** was determined to be 12-*O*-benzoyl-19-salicyloyloxy-20-*O*-acetylsarcostin 3-*O*-β-D-theveto-pyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside.

The molecular formulae of compounds **22** and **23** were $C_{56}H_{84}O_{21}$ and $C_{56}H_{84}O_{20}$. Because the sugar sequences of these compounds were 3-*O*-β-D-thevetopyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside, the molecular formulae of the aglycones were presumed to be $C_{28}H_{36}O_{8}$ and $C_{28}H_{36}O_{7}$, respectively. The 1D-NMR spectral data of the aglycone moieties in **22** and **23** were similar to those of **2** and **1** except for the signals around the C-5 and -6 positions. Both compounds exhibited one oxygenated quaternary carbon signal (δ 64.6 in **22** and **23**), and each of one oxygenated methine carbon and proton signals [δ 65.5 and δ 3.38 (1H, d, J=2.0 Hz) in **22**; δ 65.6 and δ 3.36 (1H, d, J=2.0 Hz) in **23**], instead of the sp^2 carbon and olefinic proton signals in **2** and **1**. The above results suggested that the aglycones of **22** and **23** had epoxide rings in their structures. Its position was proposed at C-5 and C-6, which was confirmed according to the existence of $^{3}J_{CCCH}$s between δ 64.6 (C-5) and δ 1.09 (H-19), δ 75.9

Table 2. (continued)

	16	17	18	19	20	21	22	23
Proton No.								
- 3	4.16*	4.16*	3.89*	3.84 (m)	3.88*	3.88 (m)	3.91*	3.91*
- 6	5.92 (d, 10.5)	5.92 (d, 10.0)	5.53 (br s)	5.34 (br s)	5.56 (br s)	5.58 (br s)	3.38 (d, 2.0)	3.36 (d, 2.0)
- 7	6.21 (d, 10.5)	6.21 (d, 10.0)						
-12	5.34 (dd, 10.0, 4.5)	5.39 (dd, 10.0, 4.0)	5.39 (dd, 12.0, 4.0)	5.43 (dd, 11.5, 4.5)	5.43 (dd, 11.5, 4.0)	5.42 (dd, 12.5, 4.0)	5.20 (dd, 11.5, 4.5)	5.25 (dd, 11.5, 4.0)
-17	—	—	—	—	—	—	—	3.42 (t, 9.5)
-18	2.16 (s)	2.07 (s)	2.05 (s)	2.09 (s)	2.04 (s)	2.05 (s)	1.91 (s)	1.85 (s)
-19	1.50 (s)	1.52 (s)	5.11 (d, 12.0)	1.30 (s)	5.10*	5.04 (d, 12.0)	1.09 (s)	1.08 (s)
	—	—	5.46 (d, 12.0)	—	5.51 (d, 12.0)	5.51 (d, 12.0)	—	—
-20	5.27 (q, 6.0)	—	—	5.02 (br s)	5.04 (br s)	5.05*	—	—
-21	1.55 (d, 6.0)	2.34 (s)	2.34 (s)	1.37*	1.36*	1.35*	2.31 (s)	2.07 (s)
Ester moiety linked to the C-12 position								
	Cin	Bz	Bz	Bz	Bz	Bz	Bz	Bz
-2′	6.48 (d, 16.0)	—	—	—	—	—	—	—
-3′	7.89 (d, 16.0)	8.28 (br d, 8.0)	8.26 (br d, 8.0)	8.32 (br d, 8.0)	8.24 (br d, 8.0)	8.24 (br d, 8.0)	8.24 (br d, 8.0)	8.24 (br d, 8.0)
-4′		7.46 (br t, 8.0)	7.46 (br t, 8.0)	7.50 (br t, 8.0)	7.47 (br t, 8.0)	7.48 (br t, 8.0)	7.47 (br t, 8.0)	7.46 (br t, 8.0)
-5′		7.54 (br t, 8.0)	7.55 (br t, 8.0)	7.57*	7.59 (br t, 8.0)	7.59 (br t, 8.0)	7.54 (br t, 8.0)	7.53 (br t, 8.0)
-6′		7.46 (br t, 8.0)	7.46 (br t, 8.0)	7.50 (br t, 8.0)	7.47 (br t, 8.0)	7.48 (br t, 8.0)	7.47 (br t, 8.0)	7.46 (br t, 8.0)
-7′		8.28 (br d, 8.0)	8.26 (br d, 8.0)	8.32 (br d, 8.0)	8.24 (br d, 8.0)	8.24 (br d, 8.0)	8.24 (br d, 8.0)	8.24 (br d, 8.0)
-8′		—	—	—	—	—	—	
-9′		—	—	—	—	—	—	
Ester moiety linked to the C-19 position								
			Bz		Bz	Sal		
-2″	—	—	—	—	—	—	—	—
-3″	—	—	8.06 (br d, 8.0)	—	8.01 (br d, 8.0)	—	—	—
-4″	—	—	7.04 (br t, 8.0)	—	6.89 (br t, 8.0)	7.69 (br d, 8.0)	—	—
-5″	—	—	7.25 (br t, 8.0)	—	7.23 (br t, 8.0)	6.02 (br t, 8.0)	—	—
-6″	—	—	7.04 (br t, 8.0)	—	6.89 (br t, 8.0)	7.17 (td, 8.0, 1.5)	—	—
-7″	—	—	8.06 (br d, 8.0)	—	8.01 (br d, 8.0)	6.97 (br d, 8.0)	—	—
Ester moiety linked to the C-20 position								
	Bz			Ac	Ac	Ac		
-2‴	—	—	—	1.65 (br s)	1.60*	1.60*	—	—
-3‴	8.19 (br d, 8.0)	—	—	—	—	—	—	—
-4‴	7.29 (br t, 8.0)	—	—	—	—	—	—	—
-5‴	7.49 (br t, 8.0)	—	—	—	—	—	—	—
-6‴	7.29 (br t, 8.0)	—	—	—	—	—	—	—
-7‴	8.19 (br d, 8.0)	—	—	—	—	—	—	—
Anomeric signal of the first cymaropyranose								
	5.15 (dd, 9.5, 2.0)	5.15 (dd, 9.5, 2.0)	5.28 (dd, 9.5, 2.0)	5.27 (dd, 9.5, 2.0)	5.26 (dd, 9.5, 2.0)	5.27 (dd, 9.5, 2.0)	5.28 (dd, 9.5, 2.0)	5.28 (dd, 9.5, 2.0)

Measured in pyridine-d_5 at 35 °C. *: Overlapping with other signals. Bz: benzoyl, Cin: cinnamoyl, Ike: ikemaoyl, Nic: nicotinoyl, Tig: tigloyl, Sal: salicyloyl, Ac: acetyl.

(C-8) and δ 3.38 (H-6) in the HMBC experiment of **22**. Mild acid hydrolysis of **22** yielded **22a**, which was determined to be 12-*O*-benzoyl-5α,6β-glycodeacylmetaplexigenin on the basis of comparing the ^{13}C-NMR spectral data with those of 12-*O*-cinnamoyl-20-*O*-acetyl-5α,6β-glycosarcostin.[23] Yamagishi *et al.* reported that mild acid hydrolysis with 0.05 M H_2SO_4 produced 3,20-di-*O*-acetyl-12-*O*-cinnamoyl-5α,6β-glycosarcostin from 3,20-di-*O*-acetyl-12-*O*-cinnamoyl-5α,6α-epoxysarcostin.[23] Thus, **22a** was a product from 12-*O*-benzoyl-5α,6α-epoxydeacylmetaplexigenin by mild acid hydrolysis, so that the aglycone of **22** was determined to be 12-*O*-benzoyl-5α,6α-epoxydeacylmetaplexigenin. Similarly, the aglycone of **23** was considered to be 12-*O*-benzoyl-5α,6α-epoxylineolon. The structures of **22** and **23** are shown in Chart 1.

In this phytochemical investigation of the roots of *A. sericifera*, 23 acylated-oxypregane glycosides were obtained. Among these compounds are rare oxypregnane derivatives having a 5α-hydroxy-6-ene structure, which have been afforded from *Gymnema alternifolium* (Asclepiadaceae)[6,7] and *Stephanotis lutchuensis* var. *japonica* (Asclepiadaceae)[29] at present. And as far as we know, this is the first time that salicylated-oxypregnane derivatives have been isolated from Asclepiadaceous plants.

Experimental

General Procedure Instrumental analysis was carried out as described previously.[24]

Extraction and Isolation The dried roots of *Araujia sericifera* (580 g) were extracted three times with MeOH under reflux. The extract was concentrated under reduced pressure and the residue was suspended in H_2O. This suspension was extracted with Et_2O. The Et_2O layer was concentrated, and the residue was then chromatographed on a silica gel column with a $CHCl_3$–MeOH (98 : 2—85 : 15) system and semi-preparative HPLC (Develosil-ODS, -PhA and YMC-ODS: 56—65% MeCN in water and 75—85% MeOH in water) to give compounds **1** (82 mg), **2** (107 mg), **3** (4 mg), **4** (16 mg), **5** (47 mg), **6** (10 mg), **7** (25 mg), **8** (5 mg), **9** (3 mg), **10** (27 mg), **11** (17 mg), **12** (6 mg), **13** (13 mg), **14** (4 mg), **15** (11 mg), **16** (31 mg), **17** (8 mg), **18** (30 mg), **19** (13 mg), **20** (21 mg), **21** (3 mg), **22** (19 mg) and **23** (5 mg).

Table 3. ^{13}C- and ^{1}H-NMR Spectral Data of Compounds **1** and **3**

	1		**3**	
	Cym.		Cym.	
-1′	96.4	5.27 (dd, 9.5, 2.0)	96.4	5.28 (dd, 9.5, 2.0)
-2′	37.4[a)]		37.3[a)]	
-3′	78.2[b)]	4.07*	78.1[b)]	4.09 (q, 3.0)
-4′	83.4	3.50 (dd, 9.5, 3.0)	83.4	3.52 (dd, 9.5, 3.0)
-5′	69.0	4.21 (dq, 9.5, 6.5)	69.1	4.22 (dq, 9.5, 6.5)
-6′	18.6[c)]	1.39 (d, 6.5)	18.6[c)]	1.38 (d, 6.5)
	Cym.		Cym.	
-1″	100.4	5.10 (dd, 9.5, 2.0)	100.5	5.12 (dd, 9.5, 2.0)
-2″	37.1[a)]		37.1[a)]	
-3″	78.0[b)]	4.04 (q, 3.0)	77.8[b)]	4.03 (q, 3.0)
-4″	83.1	3.42 (dd, 9.5, 3.0)	83.0[d)]	3.44 (dd, 9.5, 3.0)
-5″	69.0	4.15 (dq, 9.5, 6.5)	68.9	4.17 (dq, 9.5, 6.5)
-6″	18.6[c)]	1.33 (d, 6.5)	18.5[c)]	1.39 (d, 6.5)
	Cym.		Ole.	
-1‴	100.4	5.09 (dd, 9.5, 2.0)	101.9	4.69 (dd, 9.5, 2.0)
-2‴	37.0[a)]		37.6[a)]	
-3‴	77.9[b)]	4.07*	79.2[b)]	
-4‴	83.1	3.59*	83.2[d)]	3.67 (t, 9.0)
-5‴	69.4	4.22 (dq, 9.5, 6.5)	72.1	
-6‴	18.5[c)]	1.60 (d, 6.5)	18.8[c)]	1.70 (d, 6.5)
-OMe‴			57.2	3.53 (s)
	Thv.		Thv.	
-1⁗	106.2	4.77 (d, 8.0)	104.1	4.95 (d, 8.0)
-2⁗	75.1	3.99*	75.3	3.92 (m)
-3⁗	87.9	3.60*	88.2	3.61*
-4⁗	75.9	3.60*	76.0	3.61*
-5⁗	72.8	3.73 (dq, 9.0, 6.0)	72.9	3.75 (dq, 9.0, 6.0)
-6⁗	18.4[c)]	1.58 (d, 6.0)	18.5[c)]	1.59 (d, 6.0)
-OMe	60.9	3.89 (s)	60.9	3.89 (s)
-OMes	58.9×2	3.61 (s)×2	58.9×2	3.62 (s)
	59.0	3.57 (s)		3.58 (s)

Measured in pyridine-d_5 at 35 °C. *: overlapping with other signals. *a—d*) Interchangeable in each column. Cym.: *β*-D-cymaropyranosyl, Ole.: *β*-D-oleandropyranosyl, Thv.: *β*-D-thevetopyranosyl.

Compound **1**: Amorphous powder. $[\alpha]_D^{21}$ −3.08° (*c*=2.26, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 229 (4.08). FAB-MS *m/z*: 1083 $[M+Na]^+$, HR-FAB-MS *m/z*: 1083.5515 (Calcd for $C_{56}H_{84}O_{19}Na$: 1083.5505).

Compound **2**: Amorphous powder. $[\alpha]_D^{21}$ +11.9° (*c*=2.20, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 229 (4.12). FAB-MS *m/z*: 1099 $[M+Na]^+$, HR-FAB-MS *m/z*: 1099.5470 (Calcd for $C_{56}H_{84}O_{20}Na$: 1099.5454).

Compound **3**: Amorphous powder. $[\alpha]_D^{24}$ −0.66° (*c*=0.38, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 201 (4.32), 229 (4.08). FAB-MS *m/z*: 1099 $[M+Na]^+$, HR-FAB-MS *m/z*: 1099.5448 (Calcd for $C_{56}H_{84}O_{20}Na$: 1099.5454).

Compound **4**: Amorphous powder. $[\alpha]_D^{23}$ +22.9° (*c*=1.52, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 201 (4.50), 216 (4.25), 222 (4.19), 277 (4.35). FAB-MS *m/z*: 1109 $[M+Na]^+$, HR-FAB-MS *m/z*: 1109.5668 (Calcd for $C_{58}H_{86}O_{19}Na$: 1109.5661).

Compound **5**: Amorphous powder. $[\alpha]_D^{22}$ +38° (*c*=0.78, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 201 (4.37), 216 (4.14), 222 (4.08), 278 (4.28). FAB-MS *m/z*: 1125 $[M+Na]^+$, HR-FAB-MS *m/z*: 1125.5610 (Calcd for $C_{58}H_{86}O_{20}Na$: 1125.5610).

Compound **6**: Amorphous powder. $[\alpha]_D^{23}$ +2.8° (*c*=0.98, MeOH). FAB-MS *m/z*: 1089 $[M+Na]^+$, HR-FAB-MS *m/z*: 1089.5968 (Calcd for $C_{56}H_{90}O_{19}Na$: 1089.5974).

Compound **7**: Amorphous powder. $[\alpha]_D^{23}$ +19° (*c*=0.81, MeOH). FAB-MS *m/z*: 1105 $[M+Na]^+$, HR-FAB-MS *m/z*: 1105.5898 (Calcd for $C_{56}H_{90}O_{20}Na$: 1105.5923).

Compound **8**: Amorphous powder. $[\alpha]_D^{23}$ +10° (*c*=0.36, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 202 (4.25), 217 (4.18), 250 (3.71), 255 (3.74), 260 (3.70). FAB-MS *m/z*: 1100 $[M+Na]^+$, HR-FAB-MS *m/z*: 1100.5377 (Calcd for $C_{55}H_{83}NO_{20}Na$: 1100.5406).

Compound **9**: Amorphous powder. $[\alpha]_D^{24}$ +34° (*c*=0.27, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 203 (4.23), 216 (4.11), 222 (4.05), 278 (4.24). FAB-MS *m/z*: 1127 $[M+Na]^+$, HR-FAB-MS *m/z*: 1127.5771 (Calcd for $C_{58}H_{88}O_{20}Na$: 1127.5767).

Compound **10**: Amorphous powder. $[\alpha]_D^{24}$ +37.6° (*c*=1.58, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 228 (4.11). FAB-MS *m/z*: 1083 $[M+Na]^+$, HR-FAB-MS *m/z*: 1083.5525 (Calcd for $C_{56}H_{84}O_{19}Na$: 1083.5505).

Compound **11**: Amorphous powder. $[\alpha]_D^{22}$ +28.1° (*c*=1.67, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 229 (4.13). FAB-MS *m/z*: 1085 $[M+Na]^+$, HR-FAB-MS *m/z*: 1085.5673 (Calcd for $C_{56}H_{86}O_{19}Na$: 1085.5661).

Compound **12**: Amorphous powder. $[\alpha]_D^{22}$ +2.1° (*c*=0.66, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 201 (4.24), 216 (4.08). FAB-MS *m/z*: 1061 $[M+Na]^+$, HR-FAB-MS *m/z*: 1061.5680 (Calcd for $C_{54}H_{86}O_{19}Na$: 1061.5661).

Compound **13**: Amorphous powder. $[\alpha]_D^{22}$ +15.8° (*c*=1.27, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 201 (4.25), 217 (4.05). FAB-MS *m/z*: 1077 $[M+Na]^+$, HR-FAB-MS *m/z*: 1077.5602 (Calcd for $C_{54}H_{86}O_{20}Na$: 1077.5610).

Compound **14**: Amorphous powder. $[\alpha]_D^{24}$ −6.0° (*c*=0.39, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 202 (4.55), 205 (4.55), 239 (4.01), 303 (3.65). FAB-MS *m/z*: 1099 $[M+Na]^+$, HR-FAB-MS *m/z*: 1099.5448 (Calcd for $C_{56}H_{84}O_{20}Na$: 1099.5454).

Compound **15**: Amorphous powder. $[\alpha]_D^{22}$ +6.48° (*c*=1.05, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 202 (4.49), 205 (4.48), 238 (3.95), 306 (3.57). FAB-MS *m/z*: 1115 $[M+Na]^+$, HR-FAB-MS *m/z*: 1115.5397 (Calcd for $C_{56}H_{84}O_{21}Na$: 1115.5403).

Compound **16**: Amorphous powder. $[\alpha]_D^{22}$ +141° (*c*=1.67, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 201 (4.84), 220 (4.69), 223 (4.71), 231 (sh), 279 (4.65). FAB-MS *m/z*: 1247 $[M+Na]^+$, HR-FAB-MS *m/z*: 1247.5989 (Calcd for $C_{65}H_{92}O_{22}Na$: 1247.5978).

Compound **17**: Amorphous powder. $[\alpha]_D^{22}$ +19° (*c*=0.72, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 201 (4.43), 228 (4.18). FAB-MS *m/z*: 1115 $[M+Na]^+$, HR-FAB-MS *m/z*: 1115.5393 (Calcd for $C_{56}H_{84}O_{21}Na$: 1115.5403).

Compound **18**: Amorphous powder. $[\alpha]_D^{22}$ +15.7° (*c*=1.44, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 201 (4.59), 228 (4.38). FAB-MS *m/z*: 1219 $[M+Na]^+$, HR-FAB-MS *m/z*: 1219.5654 (Calcd for $C_{63}H_{88}O_{22}Na$: 1219.5665).

Compound **19**: Amorphous powder. $[\alpha]_D^{24}$ +28.6° (*c*=1.28, $CHCl_3$). UV λ_{max}^{MeOH} nm (log *ε*): 229 (4.11). FAB-MS *m/z*: 1121 $[M+H]^+$, 1143 $[M+Na]^+$, HR-FAB-MS *m/z*: 1121.5887, 1143.5679 (Calcd for $C_{58}H_{89}O_{21}$: 1121.5896, $C_{58}H_{88}O_{21}Na$: 1143.5716).

Compound **20**: Amorphous powder. $[\alpha]_D^{23}$ +59.5° (*c*=1.36, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 225 (4.46). FAB-MS *m/z*: 1263 $[M+Na]^+$, HR-FAB-MS *m/z*: 1263.5922 (Calcd for $C_{65}H_{92}O_{23}Na$: 1263.5927).

Compound **21**: Amorphous powder. $[\alpha]_D^{24}$ +62° (*c*=0.32, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 201 (4.66), 231 (4.25), 305 (3.59). FAB-MS *m/z*: 1279 $[M+Na]^+$, HR-FAB-MS *m/z*: 1279.5864 (Calcd for $C_{65}H_{92}O_{24}Na$: 1279.5876).

Compound **22**: Amorphous powder. $[\alpha]_D^{24}$ +1.8° (*c*=0.56, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 229 (4.13). FAB-MS *m/z*: 1115 $[M+Na]^+$, HR-FAB-MS *m/z*: 1115.5421 (Calcd for $C_{56}H_{84}O_{21}Na$: 1115.5403).

Compound **23**: Amorphous powder. $[\alpha]_D^{24}$ −13° (*c*=0.51, $CHCl_3$). UV λ_{max}^{MeOH} nm (log *ε*): 229 (4.14). FAB-MS *m/z*: 1099 $[M+Na]^+$, HR-FAB-MS *m/z*: 1099.5435 (Calcd for $C_{56}H_{84}O_{20}Na$: 1099.5453).

Acid Hydrolysis of a Mixture of Pregnane Glycosides The fraction of pregnane glycosides eluted with the $CHCl_3$–MeOH (95 : 5) system on a silica gel column (370 mg) was heated at 60 °C for 4 h with dioxane (6 ml) and 0.1 M H_2SO_4 (1.5 ml) to obtain the aglycones and sugars. After hydrolysis, this reaction mixture was diluted with H_2O and extracted with EtOAc. The EtOAc layer was concentrated to dryness. Purification of the residue by HPLC (YMC-ODS, 72.5% MeOH in water) afforded two new acylated-pregnanes (**11a** (5 mg) and **18a** (3 mg)), along with 12-*O*-benzoyllineolon (**1a**, 2 mg), 12-*O*-benzoyldeacylmetaplexigenin (**2a**, 10 mg), kidjolanin (**5a**, 3 mg), gagaminin (**24a**, 4 mg) and 20-*O*-benzoyl-12-*O*-(*E*)-cinnamoyl-3*β*,5*α*,8*β*,12*β*,14*β*,17*β*,20-heptahydroxy-(20*S*)-pregn-6-ene (**16a**, 2 mg).

11a: Amorphous powder. $[\alpha]_D^{24}$ +9.8° (*c*=0.49, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 229 (4.13). FAB-MS *m/z*: 471 $[M+H]^+$, 493 $[M+Na]^+$, HR-FAB-MS *m/z*: 471.2747, 493.2545 (Calcd for $C_{28}H_{39}O_6$: 471.2746, $C_{28}H_{38}O_6Na$: 493.2566). ^{13}C-NMR (pyridine-d_5 at 35 °C): *δ*: 166.7 (C-1′), 140.1 (C-5), 133.4 (C-5′), 131.5 (C-2′), 130.0×2 (C-3′, 7′), 129.1×2 (C-4′, 6′), 119.1 (C-6), 85.7 (C-14), 78.8 (C-12), 74.2 (C-8), 71.7 (C-3), 65.5 (C-20), 54.0 (C-13), 52.3 (C-17), 45.2 (C-9), 43.5 (C-4), 39.4 (C-1), 37.6 (C-10), 36.3, 36.1 (C-7, 15), 32.2 (C-2), 24.9 (C-11), 22.5 (C-21), 19.0 (C-16), 18.5 (C-19), 12.1 (C-18). ^{1}H-NMR (MeOH-d_4 at 35 °C): *δ*: 8.02 (2H, dd, 8.0, 1.5, H-3′, 7′), 7.62 (td, 8.0, 1.5, H-5′), 7.49 (2H, br t, 8.0, H-4′, 6′), 5.34 (br s, H-6), 4.89 (dd, 12.0, 4.0, H-12), 3.96 (br q, 6.0, H-20), 3.45 (m, H-3), 1.84 (overlapping, H-17), 1.63 (dd, 12.0, 3.5, H-9), 1.44 (3H, s, H-18), 1.21 (3H, s, H-19), 1.03 (3H, d, 6.0, H-21).

18a: Amorphous powder. $[\alpha]_D^{24}$ −15° (*c*=0.26, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 228 (4.38). FAB-MS *m/z*: 627 $[M+Na]^+$, HR-FAB-MS *m/z*: 627.2552 (Calcd for $C_{35}H_{40}O_9Na$: 627.2570). ^{13}C-NMR (pyridine-d_5 at 35 °C): *δ*: 210.1 (C-20), 166.4 (C-1″), 165.4 (C-1′), 136.1 (C-5), 133.3 (C-5′), 133.0 (C-5″), 129.8×2 (C-3′, 7′), 129.6×2 (C-3″, 7″), 128.9×2 (C-4′,

6′), 128.6×2 (C-4″, 6″), 123.0 (C-6), 92.5 (C-17), 89.5 (C-14), 74.3 (C-8), 74.1 (C-12), 71.0 (C-3), 64.4 (C-19), 58.2 (C-13), 44.2 (C-9), 43.7 (C-4), 41.6 (C-10), 35.1 (C-7), 34.1 (C-15), 33.6 (C-1), 33.2 (C-16), 32.1 (C-2), 27.7 (C-21), 26.6 (C-11), 10.9 (C-18). ^{1}H-NMR (pyridine-d_5 at 35 °C): δ: 8.28 (2H, dd, 8.0, 1.5, H-3′, 7′), 8.10 (2H, dd, 8.0, 1.5, H-3″, 7″), 7.56 (overlapping, H-5′), 7.47 (2H, br t, 8.0, H-4′, 6′), 7.27 (br t, 8.0, H-5″), 7.05 (2H, br t, 8.0, H-4″, 6″), 5.58 (br s, H-6), 5.50 (d, 12.0, H-19), 5.41 (dd, 11.5, 4.5, H-12), 5.21 (d, 12.0, H-19), 3.94 (m, H-3), 2.36 (3H, s, H-21), 2.07 (3H, s, H-18).

The H_2O layer was passed though an Amberlite IRA-60E column and the eluate was concentrated to dryness. The residue was chromatographed on silica gel with a $CHCl_3$–MeOH–H_2O (7 : 1 : 1.2 bottom layer) system to obtain cymarose. As to the absolute configuration, cymarose was believed to have a D-form based on its optical rotation value.

D-Cymarose: $[\alpha]_D^{20}$ +51.8° (c=2.45, 24 h after dissolution in H_2O). (lit: $[\alpha]_D^{21}$ +51.6° (c=1.02, H_2O)[25]).

This H_2O layer also produced a disaccharide, thevetopyranosyl-(1→4)-cymaropyranoside (22 mg). A part of this disaccharide (*ca.* 1 mg) was hydrolyzed with 0.05 M HCl–dioxane (1 : 1) at 95 °C for 1 h. After hydrolysis, the reaction mixture was passed through an Amberlite IRA-60E column, and the eluate was evaporated under reduced pressure. The residue was stirred with D-cysteine methyl ester hydrochloride (3 mg) in pyridine (25 μl) using the same procedures as in previous reports.[26,27] After the reaction, the supernatant was subjected to GC analysis. GC conditions: column, GL capillary column TC-1 (GL Sciences, Inc., Tokyo, Japan) 0.25 mm×30 m, carrier gas N_2, column temperature 220 °C; t_R D-thevetose 15.5 min, L-thevetose 14.6 min. The t_R for L-thevetose was obtained from its enantiomer (D-thevetose+L-cysteine). D-Thevetose was detected from this disaccharide.

Acid Hydrolysis of Compounds 1—22 and 23 Solutions of compounds **1**—**23** (*ca.* 0.5 mg) in dioxane and 0.05 M HCl (50 μl each) were heated at 95 °C for 1 h. After hydrolysis, this solution was passed through an Amberlite IRA-60E column and concentrated to dryness. The residues from **1**—**23** were partitioned between H_2O and EtOAc, and the EtOAc extract was analyzed by HPLC to identify the aglycone *via* comparison with authentic samples. HPLC conditions: column, YMC-ODS 4.6 mm i.d.×25 cm; flow rate, 1.0 ml/min; 32.5% MeCN in water; t_R, rostratamine (**8a**) 10.4 min; 42.5% MeCN in water; t_R, 12-*O*-benzoyllineolon (**1a**) 12.4 min; 45% MeCN in water; t_R, 12-*O*-benzoyldeacylmetaplexigenin (**2a**) 10.8 min, penupogenin (**9a**) 12.4 min, 50% MeCN in water; t_R, ikemagenin (**4a**) 10.4 min, kidjolanin (**5a**) 11.0 min, cynanchogenin (**6a**) 13.6 min, caudatin (**7a**) 14.0 min, 12-*O*-benzoylisolineolon (**10a**) 15.6 min, 52.5% MeCN in water; t_R, 12-*O*-benzoyl-19-benzoyloxydeacylmetaplexigenin (**18a**) 10.4 min, 55% MeCN in water; t_R, 12-*O*-benzoyl-20*S*-hydroxyisolineolon (**11a**) 8.8 min.

The acquired aglycones from **12**—**15** were hydrolyzed with 2 M NaOH aq. and dioxane (80 μl each) at 60 °C for 5 h in a N_2 atmosphere. After hydrolysis, the reaction mixture was diluted with H_2O and divided into two parts. Then, 1 M HCl (*ca.* 200 μl) was added to one part, and the ester moiety was extracted with Et_2O. HPLC analysis suggested that tiglic acid and salicylic acid were yielded from the aglycones of **12**, **13** and **14**, **15**, respectively. HPLC conditions: column, YMC-ODS 4.6 mm i.d.×25 cm; flow rate, 1.0 ml/min; 37.5% MeOH in water +0.05% trifluoroacetic acid (TFA); t_R, tiglic acid 13.8 min, 55% MeOH in water +0.05% TFA; t_R, salicylic acid 10.0 min. The reaction mixture in another part was neutralized with an Amberlite IR-120B column, and the eluate was concentrated to dryness. The residue was also analyzed with HPLC. Linelon and deacylmetaplexigenin were detected from the aglycones of **12**, **14**, and **13**, **15**, respectively. HPLC conditions: column, YMC-ODS 4.6 mm i.d.×25 cm; flow rate, 1.0 ml/min; 17.5% MeCN in water; t_R, deacylmetaplexigenin 8.4 min, lineolon 9.8 min.

Subsequently, the H_2O layer was reduced with $NaBH_4$ (*ca.* 1 mg) for 1 h at room temperature. The reaction mixture was passed through an Amberlite IR-120B column and the eluate was concentrated to dryness. Boric acid was removed by co-distillation with MeOH, and the residue was acetylated overnight with acetic anhydride and pyridine (5 drops each) at room temperature. After evaporation of the reagents under a stream of air, cymaritol acetate, oleandritol acetate and thevetitol acetate were detected by GC analysis. GC condition: column, Supelco SP-2380™ capillary column 0.25 mm×30 m, carrier gas N_2, column temperature 215 °C; t_R cymaritol acetate 5.7 min, oleandoritol acetate 6.2 min, thevetitol acetate 10.5 min.

Mild Acid Hydrolysis of Compounds 16, 19, 20 and 22 Solutions of compounds **16**, **19**, **20** and **22** (**16**: *ca.* 0.5 mg, **19**: 11 mg, **20**: 7 mg, **22**: 12 mg) in dioxane and 0.1 M H_2SO_4 (4 : 1) were heated at 60 °C for 1 h to 2 h. The following procedures for the detection and acquisition of the aglycone in each compound were described above. HPLC analysis suggested that 20-*O*-benzoyl-12-*O*-(*E*)-cinnamoyl-3β,5α,8β,12β,14β,17β,20-heptahydroxy-(20*S*)-pregn-6-ene (**16a**) was yielded from **16**. HPLC conditions: column, YMC-ODS 4.6 mm i.d.×25 cm; flow rate, 1.0 ml/min; 62.5% MeCN in water; t_R, 20-*O*-benzoyl-12-*O*-(*E*)-cinnamoyl-3β,5α,8β,12β,14β,17β,20-heptahydroxy-(20*S*)-pregn-6-ene (**16a**) 8.6 min. The residues of the EtOAc layers from **19**, **20** and **22** were chromatographed on semi-preparative HPLC to give compound **19a** (2 mg), **20a** (2 mg) and **22a** (3 mg). HPLC conditions: column, YMC-ODS 10 mm i.d.×25 cm; flow rate, 3.0 ml/min; 40% MeCN in water, **19a**, 45% MeCN in water, **20a**, 57.5% MeOH in water, **22a**.

19a: Amorphous powder. $[\alpha]_D^{24}$ +12° (c=0.24, $CHCl_3$) (lit: $[\alpha]_D^{25}$ +9.0°±3.0° (c=0.8, $CHCl_3$)).[21] UV λ_{max}^{MeOH} nm (log ε): 201 (4.41), 230 (4.13). FAB-MS *m/z*: 551 $[M+Na]^+$, HR-FAB-MS *m/z*: 551.2646 (Calcd for $C_{30}H_{40}O_8Na$: 551.2621). ^{13}C-NMR (MeOH-d_4 at 35 °C): δ: 171.4 (C-1‴), 167.8 (C-1′), 140.7 (C-5), 134.2 (C-5′), 132.6 (C-2′), 130.6×2 (C-3′, 7′), 129.4×2 (C-4′, 6′), 119.4 (C-6), 89.6 (C-14), 88.2 (C-17), 75.7 (C-12), 75.6 (C-20), 75.0 (C-8), 72.6 (C-3), 57.8 (C-13), 44.7 (C-9), 42.9 (C-4), 39.8 (C-1), 37.9 (C-10), 35.2 (C-7), 34.2, 34.0 (C-15, 16), 31.7 (C-2), 26.3 (C-11), 21.4 (C-2‴), 18.5 (C-19), 11.2 (C-18). ^{1}H-NMR (MeOH-d_4 at 35 °C): δ: 7.95 (2H, br d, 8.0, H-3′, 7′), 7.60 (br t, 8.0, H-5′), 7.47 (2H, br t, 8.0, H-4′, 6′), 5.33 (br s, H-6), 4.99 (dd, 11.5, 4.5, H-12), 4.56 (br q, 6.0, H-20), 3.44 (m, H-3), 1.67 (3H, br s, H-2‴), 1.64 (3H, s, H-18), 1.46 (3H, s, H-19), 1.16 (br d, 6.0, H-21).

20a: Amorphous powder. $[\alpha]_D^{24}$ +68° (c=0.23, MeOH). UV λ_{max}^{MeOH} nm (log ε): 228 (4.31). FAB-MS *m/z*: 649 $[M+H]^+$, 671 $[M+Na]^+$, HR-FAB-MS *m/z*: 649.3000, 671.2841 (Calcd for $C_{37}H_{45}O_{10}$: 649.3013, $C_{37}H_{44}O_{10}Na$: 671.2832). ^{13}C-NMR (pyridine-d_5 at 70 °C): δ: 166.6, 166.4 (C-1′, 1″), 136.0 (C-5), 133.0 (C-5′), 132.8 (C-5″), 130.1×2 (C-3′, 7′), 129.5×2 (C-3″, 7″), 128.7×2, 128.6×2 (C-4′, 4″, 6′, 6″), 123.3 (C-6), 88.8 (C-14), 87.7 (C-17), 75.1 (C-12), 74.7 (C-20), 74.4 (C-8), 71.1 (C-3), 64.3 (C-19), 57.2 (C-13), 44.0 (C-4), 43.7 (C-9), 35.4 (C-7), 34.0 (C-15), 33.6 (C-16), 33.4 (C-1), 32.1 (C-2), 27.5 (C-11), 21.1 (C-2‴), 15.2 (C-21), 11.5 (C-18). The C-1‴ signal of the acetyl group was not detected. ^{1}H-NMR (pyridine-d_5 at 70 °C): δ: 8.19 (2H, dd, 8.0, 1.5, H-3′, 7′), 8.02 (2H, dd, 8.0, 1.5, H-3″, 7″), 7.55 (tt, 8.0, 1.5, H-5′), 7.44 (2H, br t, 8.0, H-4′, 6′), 7.23 (tt, 8.0, 1.5, H-5″), 6.92 (2H, br t, 8.0, H-4″, 6″), 5.59 (br s, H-5), 5.48 (d, 12.0, H-19), 5.38 (dd, 11.5, 4.5, H-12), 5.12 (d, 12.0, H-19), 5.03 (q, 6.0, H-20), 3.85 (m, H-3), 1.99 (3H, s, H-18), 1.63 (3H, br s, H-2‴), 1.34 (3H, d, 6.0, H-21).

22a: Amorphous powder. $[\alpha]_D^{24}$ −35° (c=0.28, MeOH). UV λ_{max}^{MeOH} nm (log ε): 229 (4.10). FAB-MS *m/z*: 541 $[M+Na]^+$, HR-FAB-MS *m/z*: 541.2414 (Calcd for $C_{28}H_{38}O_9Na$: 541.2414). ^{13}C-NMR (pyridine-d_5 at 35 °C): δ: 210.0 (C-20), 165.3 (C-1′), 133.2 (C-5′), 131.4 (C-2′) 129.9×2 (C-3′, 7′), 128.9×2 (C-4′, 6′), 92.5 (C-17), 89.4 (C-14), 78.6 (C-8), 77.6 (C-6), 75.4 (C-5), 74.7 (C-12), 67.0 (C-3), 58.8 (C-13), 42.1 (C-4), 40.0 (C-9), 39.3 (C-10), 34.5 (C-7), 34.0 (C-1), 33.6 (C-16), 32.6 (C-15), 31.5 (C-2), 27.8 (C-21), 24.3 (C-11), 18.2 (C-19), 11.0 (C-18). ^{1}H-NMR (pyridine-d_5 at 35 °C): δ: 8.30 (2H, br d, 8.0, H-3′, 7′), 7.54 (br t, 8.0, H-5′), 7.47 (2H, br t, 8.0, H-4′, 6′), 5.39 (dd, 11.5, 4.5, H-12), 4.84 (m, H-3), 4.26 (m, $J_{1/2HW}$=9.5 Hz,[28] H-6), 2.35 (3H, s, H-21), 2.04 (3H, s, H-18), 1.73 (3H, s, H-19).

Compound **19a** was hydrolyzed with 2 M NaOH aq. and dioxane (80 μl each) at 60 °C for 5 h in N_2 atmosphere. The following procedures were described above. HPLC analysis suggested that sarcostin and benzoic acid were yielded from **19a**. HPLC conditions: column, YMC-ODS 4.6 mm i.d.×25 cm; flow rate, 1.0 ml/min; 45% MeOH in water; t_R, sarcostin 12.1 min, 55% MeOH in water +0.05% TFA; t_R, benzoic acid 7.8 min.

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