Steroidal Glycosides from the Roots of *Asclepias curassavica*

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Twenty-six new acylated-oxypregnane glycosides were obtained along with three known cardenolide glycosides from the roots of *Asclepias curassavica* (Asclepiadaceae). The new compounds were confirmed to contain 12-*O*-benzoylsarcostin, 12-*O*-benzoyldeacylmetaplexigenin, kidjolanin, and 12-*O*-benzoyltayloron, and one new acylated-oxypregnane, 12-*O*-(*E*)-cinnamoyltayloron, as their aglycones, using both spectroscopic and chemical methods.

Key words *Asclepias curassavica*; Asclepiadaceae; curassavioside; acylated-oxypregnane glycoside; 2,6-dideoxyhexopyranose

Asclepias curassavica L. (Asclepiadaceae) is spread widely in Japan, and known to contain many kinds of cardenolides and cardenolide glycosides.[1—3] These cardenolide glycosides were unique doubly linked glycosides as well as the glycosides of Gomphocarpus, Calotropis and Pergularia. In addition, because Asclepiadaceous plants were reported to contain many kinds of pregnane glycosides, *A. currassavica* was also considered to contain them. However, no research has been carried out concerning pregnane glycosides of this plant. Here, we investigated the constituents of its roots in the course of studying on the steroidal glycosides in Asclepiadaceous plants. This paper describes the isolation and structural determination of 26 new pregnane glycosides.

A MeOH extract from the dried roots of *A. curassavica* 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 fractions of cardenolide glycosides and pregnane glycosides from which 26 acylated-oxypregnane glycosides were obtained along with three known cardenolide glycosides, asclepin (**27**),[4] 16α-acetoxyasclepin (**28**),[5] and uscharin (**29**).[4,6,7]

In order to acquire the component aglycones and sugars, the fraction containing pregnane glycosides from the silica gel column chromatography was subjected to acid hydrolysis. The aglycones were identified as 12-*O*-benzoylsarcostin (**1a**),[8] 12-*O*-benzoyldeacylmetaplexigenin (**2a**)[9,10] and kidjolanin (**11a**)[10—12] in view of the ^{1}H- and ^{13}C-NMR spectroscopic data.

The acquired sugar mixtures were fractionated to cymarose, oleandrose, digitoxose, and canarose using silica gel column chromatography. The absolute configurations of these sugars were believed to be D-forms on the basis of the optical rotation values.

The compound **1** was suggested to have the molecular formula $C_{47}H_{70}O_{16}$ based on high resolution (HR)-FAB-MS [*m/z*: 913.4548 $[M+Na]^+$]. In the ^{1}H- and ^{13}C-NMR spectra of **1**, three anomeric proton and carbon signals were observed at δ 4.93, 4.90, 4.55 and δ 95.7, 98.3, 100.4, in addition to signals due to the aglycone, which was identified as **1a** by acid hydrolysis with 0.1 M H_2SO_4. The ^{13}C-NMR spectral comparison of **1** with **1a** showed glycosylation shifts at the C-2, C-3 and C-4 positions [C-2 (−2.0 ppm), C-3 (+6.0 ppm), C-4 (−3.2 ppm)].[13] Thus, **1** was glycosylated at the C-3 position, and was considered to be 12-*O*-benzoylsarcostin 3-*O*-triglycoside. Acid hydrolysis of **1** showed that the sugar moiety consisted of digitoxose and oleandrose, and these sugars were identified as β-D-digitoxopyranose and β-D-oleandropyranose, as judged from the *J* values of each anomeric proton signal (J=9.5, 2.0 Hz). The ^{1}H- and ^{13}C-NMR spectroscopic data for the sugar sequence of **1** were consistent with those of metaplexigenin 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-digitoxopyranoside.[14] Thus, **1** was established to be 12-*O*-benzoylsarcostin 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-digitoxopyranoside and named curassavioside A_1.

The compounds **2**—**25** and **26** were also glycosylated at the C-3 position of each aglycone, based on observations of glycosylation shifts in the ^{13}C-NMR spectra.

The ^{1}H- and ^{13}C-NMR spectroscopic data for the sugar moiety of **2** were consistent with those for **1**. In addition, according to the appearance of signals due to 12-*O*-benzoyldeacylmetaplexigenin in the ^{1}H- and ^{13}C-NMR spectra, **2** was identified as 12-*O*-benzoyldeacylmetaplexigenin 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-digitoxopyranoside, and named curassavioside A_2.

HR-FAB-MS showed the molecular formula of **3** to be $C_{48}H_{72}O_{16}$, suggesting an increase in CH_2 in comparison with **1**. The ^{1}H- and ^{13}C-NMR spectra showed that **3** was also 12-*O*-benzoylsarcostin 3-*O*-triglycoside. On acid hydrolysis, **3** afforded digitoxose and oleandrose together with **1a**. The observation of two methoxyl proton signals at δ 3.40 and 3.41 in the ^{1}H-NMR spectrum suggested that the sugar moiety of **3** consisted of one β-D-digitoxopyranose and two β-D-oleandropyranoses. On the basis of ^{1}H–^{1}H shift correlation spectroscopy (COSY), the signals at δ 4.94 and at δ 4.72 and 4.51 were assigned as the anomeric protons of one β-D-digitoxopyranose and two β-D-oleandropyranoses, respectively. The sequence of the sugar moiety was determined from measurements of the rotating frame nuclear Overhauser effect (ROE) difference spectra irradiating at the anomeric proton signal of each sugar in **3**. ROEs were found between δ 4.94 (H-1′ of β-D-digitoxopyranose) and 3.57 (H-3 of the aglycone), δ 4.51 (H-1″ of β-D-oleandropyranose) and 3.21 (H-4′ of β-D-digitoxopyranose), and δ 4.72 (H-1‴ of β-D-oleandropyranose) and 3.17 (H-4″ of β-D-oleandropyranose). Thus, **3** was established to be 12-*O*-benzoylsarcostin 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-digitoxopyranoside, and named curassavioside B_1.

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Table 1. ^{13}C-NMR Data for the Aglycone and Ester Moieties of Compounds **1**, **2**, **11**, **14** and **16**

	1	**2**	**11**	**14**	**16**
Carbon No.					
1	38.8[a)]	38.8	38.8	37.9	37.9
2	29.0	28.9	28.9	28.7	28.7
3	77.9	77.8	77.9	77.0	77.0
4	38.9[a)]	38.8	38.8	34.0[a)]	34.0[a)]
5	139.8	140.7	140.8	45.2	45.2
6	118.3	117.6	117.6[a)]	24.4	24.4
7	34.5	34.3	34.3	33.9[a)]	33.9[a)]
8	74.0	74.3	74.4	75.8	75.8
9	43.5	43.7	43.7	46.8	46.7
10	37.1[A)]	37.1[A)]	37.2	36.4[B)]	36.5[B)]
11	24.7	24.2	24.2	23.0	23.0
12	74.7	73.2	72.8	74.5	74.0
13	56.3	58.4	58.1	59.3	59.0
14	87.9	88.1	88.0	87.8	87.8
15	33.3	33.3	33.1	33.7[a)]	33.6[a)]
16	31.8	32.1	32.0	31.6	31.6
17	87.9	91.5	91.5	91.1	91.1
18	11.1	9.5	9.4	9.9	9.8
19	18.2[b)]	18.6	18.6	12.6	12.6
20	71.0	209.3	209.1	209.3	209.2
21	18.3[b)]	27.2	27.3	27.4	27.4
Ester moiety					
1e	165.9	165.3	165.7	165.7	166.0
2e	130.2	130.1	117.7[a)]	130.0	117.7
3e	129.6	129.5	145.3	129.5	145.6
4e	128.7	128.4	134.3	128.5	134.2
5e	133.4	133.1	128.1	133.2	128.2
6e	128.7	128.4	128.9	128.5	128.9
7e	129.6	129.5	130.4	129.5	130.5
8e	—	—	128.9	—	128.9
9e	—	—	128.1	—	128.2

Measured in $CDCl_3$ solution at 35 °C. *a*, *b*) Signal assignments may be interchanged in each column. *A*, *B*) Signal assignments may be interchanged between Tables 1 and 2.

HR-FAB-MS showed the molecular formula of **4** to be $C_{54}H_{80}O_{19}$, which suggested that it was larger than **2** by one hexose unit. On acid hydrolysis, **4** afforded digitoxose and oleandrose as the component sugars together with **2a**. The measurements of the two dimensional (2D)-NMR (^{1}H–^{1}H COSY and ^{1}H-detected heteronuclear multiple quantum coherency (HMQC)) of **4** revealed that the signals at δ 4.93, 95.8, and δ 4.89, 98.3 were assignable to the anomeric protons and carbons of two β-D-digitoxopyranoses, and the signals at δ 4.51, 100.3, and δ 4.72, 100.2 were assignable to the anomeric protons and carbons of two β-D-oleandropyranoses, respectively. Comparison of the ^{13}C-NMR spectroscopic data for **4** with those for **1** revealed the presence of a terminal β-D-oleandropyranosyl group and glycosylation shifts around the C-4 position of the first β-D-oleandropyranose [C-3‴ (−1.4 ppm), C-4‴ (+6.9 ppm), C-5‴ (−0.6 ppm)]. Thus, the sugar sequence of **4** was presumed to be 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-digitoxopyranoside. In addition, ROE difference experiments on the anomeric proton signal of the terminal β-D-oleandropyranose (δ 4.72) showed enhancement of the H-4‴ signal of β-D-oleandropyranose [δ 3.17 (1H, t, J=9.0 Hz)]. Hence, the structure of **4** was determined as shown in Chart 1, and the compound was named curassavioside C_2.

HR-FAB-MS showed the molecular formula of **5** to be $C_{53}H_{80}O_{19}$. Acid hydrolysis of **5** yielded digitoxose, oleandrose, canarose, and **1a**. The sugar moiety of **5** was found to contain two β-D-digitoxopyranoses, one β-D-canaropyranose, and one β-D-oleandropyranose which was the terminal sugar unit, on comparing the ^{1}H- and ^{13}C-NMR spectroscopic data of **5** with those of **4**. Based on 2D-NMR measurements, the anomeric proton and carbon signals in **5** were assigned as shown in Table 2 and the Experimental. The sugar sequence of **5** was determined based on the ROE difference spectra for the anomeric proton signals. ROEs were observed between δ 4.93 (H-1′ of β-D-digitoxopyranose) and 3.57 (H-3 of the aglycone), δ 4.89 (H-1″ of β-D-digitoxopyranose) and 3.22 (H-4′ of β-D-digitoxopyranose), δ 4.57 (H-1‴ of β-D-canaropyranose) and 3.20 (H-4″ of β-D-digitoxopyranose), and δ 4.49 (H-1⁗ of β-D-oleandropyranose) and 2.96 (H-4‴ of β-D-canaropyranose). Thus, **5** was identified to be 12-*O*-benzoylsarcostin 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-canaropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-digitoxopyranoside. This sugar sequence was also supported by the ^{1}H-detected heteronuclear multiple-bond connectivity (HMBC) experiment. The compound was named curassavioside D_1.

HR-FAB-MS showed the molecular formulae of **6** and **7** to be $C_{53}H_{80}O_{19}$ and $C_{53}H_{78}O_{19}$, respectively. Based on the ^{1}H- and ^{13}C-NMR spectroscopic data, the aglycone moieties of **6** and **7** were identified as **1a** and **2a**, and the sugar moieties of **6** and **7** were considered to have the same structure, owing to the similarity of their NMR spectroscopic data. **6** was identified as be 12-*O*-benzoylsarcostin 3-*O*-tetraglycoside based on four anomeric proton and carbon signals in the ^{1}H- and ^{13}C-NMR spectra (δ 4.94, 4.56, 4.50, 4.49: δ 101.1×2, 100.4, 95.7). Acid hydrolysis of **6** afforded digitoxose, oleandrose, and canarose as the component sugars. In addition, the ^{1}H-NMR spectrum showed one methoxyl proton signal for β-D-oleandropyranose at δ 3.41 (3H, s) and one characteristic H-3 signal for β-D-digitoxopyranose at δ 4.22 (1H, br q, J=3.0 Hz). The above evidence suggested that the sugar moiety of **6** consisted of one β-D-digitoxopyranose, one β-D-oleandropyranose, and two β-D-canaropyranoses. The signal assignments of the sugar moiety of **6** are shown in Table 2 and Experimental, on the basis of the 2D-NMR measurements and homonuclear Hartmann–Hahn (HOHAHA) experiments for the anomeric proton and/or H-4 signals of β-D-oleandropyranose and β-D-canaropyranose. Moreover, the sugar sequence of **6** was determined as 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-canaropyranosyl-(1→4)-β-D-canaropyranosyl-(1→4)-β-D-digitoxopyranoside based on the ROE difference spectra for each anomeric proton signal and the HMBC measurements. The compounds **6** and **7** are shown in Chart 1, and were named curassavioside E_1 and E_2.

The NMR spectra and HR-FAB-MS revealed **8** to be 12-*O*-benzoyldeacylmetaplexigenin 3-*O*-tetraglycoside with the molecular formula $C_{54}H_{80}O_{19}$. On acid hydrolysis, **8** afforded digitoxose, oleandrose, and canarose the same as **6**. However, two sets of methoxyl proton and carbon signals derived from β-D-oleandropyranoses were observed at δ 3.42, 3.40 and δ 57.0, 56.4. Thus, the sugar moiety of **8** was composed of one β-D-digitoxopyranose, one β-D-canaropyranose, and two β-D-oleandropyranoses. Comparison of the NMR spectroscopic data on **8** with those on **6** and **4** suggested the sugar sequence to be 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-canaropyranosyl-(1→4)-β-D-digitoxopy-

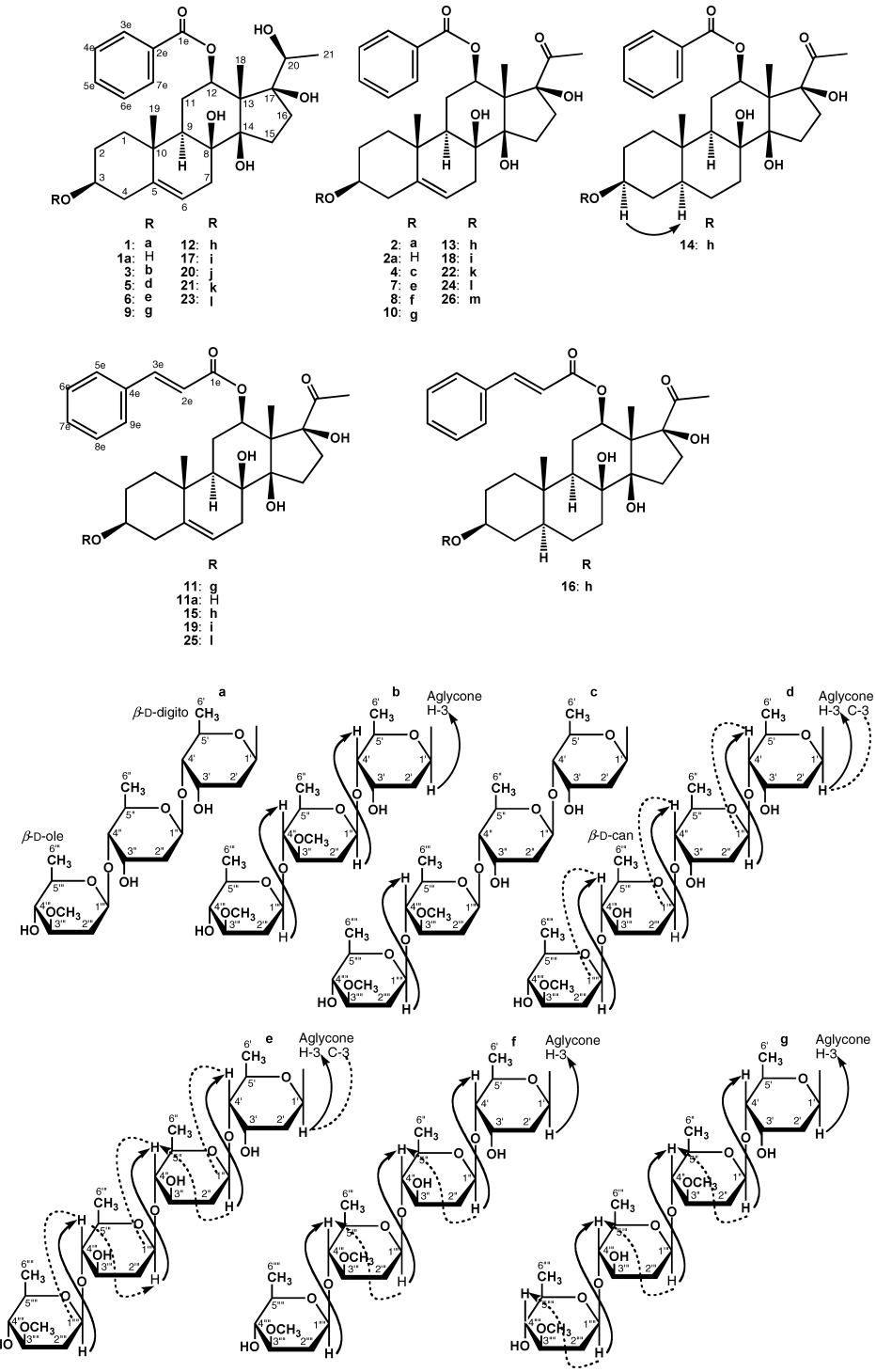
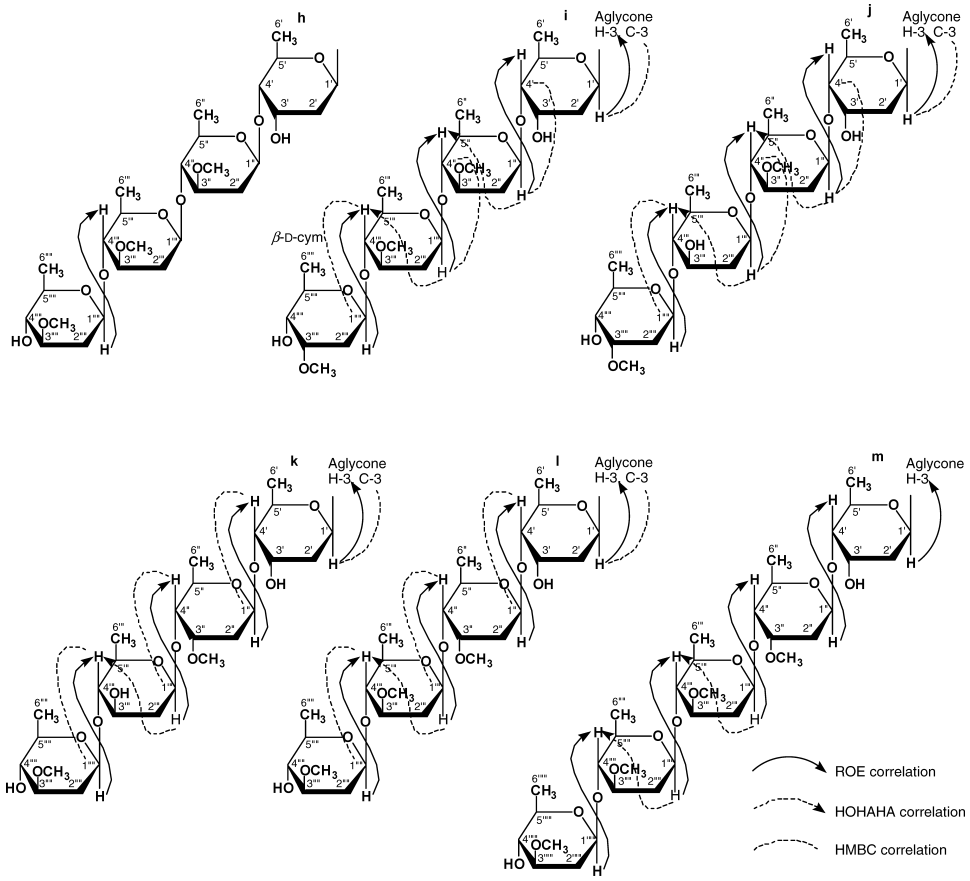


Chart 1. The Structures of Compounds **1**—**26**

ranoside, which was confirmed by the ROE measurements of irradiation at the anomeric proton signals. Thus, the structure of **8** was determined, as shown in Chart 1, and the compound was named curassavioside F_2.

HR-FAB-MS revealed the molecular formulae of **9**—**11** to be $C_{54}H_{82}O_{19}$, $C_{54}H_{80}O_{19}$, and $C_{56}H_{82}O_{19}$, respectively. Because of the consistency of the ^{1}H- and ^{13}C-NMR spectroscopic data on the sugar moieties of **9**—**11**, these compounds were considered to have the same sugar sequences. The aglycone moieties of **9**—**11** were suggested to be **1a**, **2a**, and kidjolanin (**11a**) according to their ^{13}C-NMR spectroscopic data. The results of acid hydrolysis and the ^{1}H-NMR spectroscopic data suggested that the sugar moieties of **9**—**11** consisted of one β-D-digitoxopyranose, one β-D-canaropyranose, and two β-D-oleandropyranoses the same as **8**, but the sequence was different from that of **8**. ROEs in **9** were observed between δ 4.94 (H-1′ of β-D-digitoxopyranose) and 3.57 (H-3 of the aglycone), δ 4.50 (H-1″ of β-D-oleandropyranose) and 3.20 (H-4′ of β-D-digitoxopyranose), δ 4.71 (H-1‴ of β-D-canaropyranose) and 3.16 (H-4″ of β-D-oleandropyranose), and



Important ROE, HOHAHA, and HMBC correlations were observed in compounds **3**—**6**, **8**, **9**, **12**, **14**, **17**, **20**, **21**, **23** and **26**

Chart 1. (Continued)

δ 4.49 (H-1‴ of β-D-oleandropyranose) and 2.98 (H-4‴ of β-D-canaropyranose). Thus, the structure of **9** was established to be 12-*O*-benzoylsarcostin 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-canaropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-digitoxopyranoside. The compounds **10** and **11** are also described in Chart 1. Compounds **9**—**11** were named curassavioside G_1, G_2 and G_3, respectively.

HR-FAB-MS indicated **12**—**16** to have the molecular formulae $C_{55}H_{84}O_{19}$, $C_{55}H_{82}O_{19}$, $C_{55}H_{84}O_{19}$, $C_{57}H_{84}O_{19}$, and $C_{57}H_{86}O_{19}$, respectively. The NMR data for the sugar moieties suggested that **12**—**16** possessed the same sugar sequence. On comparison of the ^{13}C-NMR spectroscopic data for **12** with those for **3**, shifts in glycosylation were found around the C-4 position of the second β-D-oleandropyranosyl group [C-3‴ (−1.7 ppm), C-4‴ (+7.0 ppm), C-5‴ (−0.6 ppm)], and the ^{13}C-NMR spectrum of **12** suggested the presence of a terminal β-D-oleandropyranosyl unit. Moreover, an ROE was observed between δ 4.71 (H-1‴ of the terminal β-D-oleandropyranose) and 3.18 (H-4‴ of β-D-oleandropyranose). Thus, the sugar sequence of **12** was established to be 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-digitoxopyranoside. On acid hydrolysis, **12**, **13** and **15** afforded **1a**, **2a**, and **11a** with digitoxose and oleandrose. With regard to the aglycone moieties of **14** and **16**, the ^{13}C-NMR spectroscopic data were similar to those for **2a** and **11a**, but sp^3 carbon signals were exhibited at δ 45.2 and 24.4 instead of the sp^2 carbon signals due to C-5 and -6. In addition, in the ^{1}H-NMR spectrum of **14**, an H-5 signal was found at δ 1.08 (1H, br t, J=13.0 Hz), which revealed an ROE to the H-3α signal (δ 3.65). These findings proved that the aglycone of **14** was 12-*O*-benzoyltayloron.[15] The aglycone of **16** was identified to be 12-*O*-(*E*)-cinnamoyltayloron based on the similarity of the ^{1}H- and ^{13}C-NMR data except for the ester moiety. The compounds **12**—**16** are shown in Chart 1, and were named curassavioside H_1, H_2, H_4, H_3 and H_5, respectively.

HR-FAB-MS showed the molecular formulae of **17**—**19** to be $C_{55}H_{84}O_{19}$, $C_{55}H_{82}O_{19}$, and $C_{57}H_{84}O_{19}$, respectively. Acid hydrolysis of **17**—**19** produced digitoxose, oleandrose, and cymarose as the component sugars along with each aglycone. The similarity of the ^{1}H- and ^{13}C-NMR spectroscopic data for the sugar moieties of **17**—**19** with those for lineolon 3-*O*-β-D-cymaropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-digitoxopyranoside[16] suggested that these compounds had the same sugar sequence, which was confirmed on the basis of the ROE difference spectra irradiating at each anomeric proton and HMBC measurements for **17**. Thus, the structures of **17**—**19** were established, as shown in Chart 1, and the compounds were named curassavioside I_1, I_2, and I_3.

HR-FAB-MS showed that **20** had the molecular formula $C_{54}H_{82}O_{19}$, the same as **9**. Comparison of the ^{1}H- and ^{13}C-NMR spectroscopic data for **20** with those for **9** and **17** suggested the presence of a terminal β-D-cymaropyranosyl group, which was attached at the C-4 position of β-D-canaropyranose. Thus, the structure of **20** was determined, as

Table 2. ^{13}C-NMR Data for the Sugar Moiety of Compounds **1**, **3**—**6**, **8**, **9**, **12**, **17**, **20**, **21**, **23** and **26**

	1	**3**	**4**	**5**	**6**	**8**	**9**	**12**	**17**	**20**	**21**	**23**	**26**
Carbon No.													
	Dig	Dig	Dig	Dig	Dig	Dig	Dig	Dig	Dig	Dig	Dig	Dig	Dig
1′	95.7	95.8	95.8	95.7	95.7	95.8	95.8	95.7	95.8	95.8	95.8	95.8	95.8
2′	37.2[A)]	37.2[A)]	37.2[A)]	37.1	37.1	37.2[A)]	37.2[A)]	37.2[A)]	37.2[A)]	37.2[A)]	37.1	37.1	37.2[A)]
3′	66.6[a)]	66.7	66.6[a)]	66.6[a)]	66.7	66.7	66.6	66.6	66.6	66.6	66.4	66.4	66.4
4′	82.6[b)]	82.9	82.6	82.6	82.8	82.8	82.8	82.8	82.8	82.8	82.5[a)]	82.5[a)]	82.5[a)]
5′	68.2[c)]	67.9	68.2[b)]	68.2[b)]	67.9	68.0	67.9	67.9	67.9	67.9	68.1	68.1	68.1
6′	18.2	18.4[a)]	18.4[c)]	18.2[c)]	18.2[a)]	18.2[a)]	18.3[a)]	18.4[a)]	18.4[a)]	18.3[a)]	18.3[b)]	18.4[b)]	18.4[b)]
	Dig	Ole	Dig	Dig	Can	Can	Ole	Ole	Ole	Ole	Cym	Cym	Cym
1″	98.3	100.3[b)]	98.3	98.3	100.4	100.4	100.3	100.3[b)]	100.3	100.4[b)]	98.4	98.4	98.4
2″	36.8	36.3	36.8	36.8	38.4	38.4	36.4	36.5[B,c)]	36.5[b)]	36.4	35.9	35.8	35.7
3″	66.5[a)]	79.1	66.5[a)]	66.5[a)]	69.3[b)]	69.4	79.1	79.3[d)]	79.0	79.2	77.0	77.0	77.0
4″	82.5[b)]	82.2	82.4[d)]	82.4	88.1	88.0	82.3	82.2	82.2	82.3	82.4[a)]	82.4[a)]	82.5[a)]
5″	68.1[c)]	71.2	68.1[b)]	68.1[b)]	70.8	70.5	71.2	71.2	71.3[c)]	71.3	68.7	68.7	68.7
6″	18.2	18.2[a)]	18.2[c)]	18.1[c)]	17.6[a)]	18.1[a)]	18.2[a)]	18.4[a)]	18.4[a)]	18.2[a)]	18.1[b)]	18.2[b)]	18.4[b)]
	Ole	Ole	Ole	Can	Can	Ole	Can	Ole	Ole	Can	Can	Ole	Ole
1‴	100.4	100.2[b)]	100.3[e)]	100.4	101.1	100.9	100.3	100.2[b)]	100.1	100.3[b)]	101.5	101.4	101.4
2‴	35.3	35.5	36.3[B)]	38.4	38.1	36.2	38.6	36.3[B,c)]	36.4[b)]	38.6	38.5	36.4	36.5[c)]
3‴	80.5	80.7	79.1	69.3	69.2[b)]	78.9	69.5	79.0[d)]	79.0	69.5	69.5	79.1	79.3[d)]
4‴	75.3	75.5	82.2[d)]	88.1	87.8	81.9	88.4	82.5	82.4	88.3	88.3	82.3[a)]	82.4[a)]
5‴	71.9	71.8	71.3	70.6	70.6	71.5	70.5	71.2	71.2[c)]	70.6	70.4	71.1	71.2[e)]
6‴	17.9	18.0	18.2[c)]	17.9[c)]	17.8[a)]	18.0[a)]	17.9	18.2[a)]	18.3[a)]	17.9[a)]	17.9	18.2[b)]	18.2[b)]
			Ole	Ole	Ole	Ole	Ole	Ole	Cym	Cym	Ole	Ole	Ole
1⁗	—	—	100.2[e)]	101.0	101.1	100.2	101.0	100.1[b)]	98.2	99.1	101.0	100.2	100.2[f)]
2⁗	—	—	35.5	35.2	35.2	35.5	35.2	35.5	33.9	33.7	35.2	35.5	36.4[c)]
3⁗	—	—	80.7	80.3	80.3	80.7	80.4	80.8	77.6	77.2	80.4	80.8	79.1[d)]
4⁗	—	—	75.5	75.1	75.1	75.5	75.1	75.5	72.5	72.2	75.1	75.5	82.3[a)]
5⁗	—	—	71.8	72.1	72.2	71.8	72.1	71.7	71.1[c)]	71.3	72.1	71.7	71.1[e)]
6⁗	—	—	18.0	17.6	17.6	17.9[a)]	17.6	18.0[a)]	18.2[a)]	17.9[a)]	17.6	18.0	18.2[b)]
													Ole
1⁗′	—	—	—	—	—	—	—	—	—	—	—	—	100.1[f)]
2⁗′	—	—	—	—	—	—	—	—	—	—	—	—	35.5
3⁗′	—	—	—	—	—	—	—	—	—	—	—	—	80.8
4⁗′	—	—	—	—	—	—	—	—	—	—	—	—	75.5
5⁗′	—	—	—	—	—	—	—	—	—	—	—	—	71.7
6⁗′	—	—	—	—	—	—	—	—	—	—	—	—	18.0
OMes	56.4	56.9	56.9	56.5	56.5	57.0	57.0	56.9	57.1	57.4	58.5	58.4	58.4
		56.3	56.4			56.4	56.5	56.8	56.9	57.1	56.5	56.7	56.8
								56.3	56.6			56.3	56.7
													56.3

Measured in $CDCl_3$ solution at 35 °C. *a*—*f*) Signal assignments may be interchanged in each column. *A*, *B*) Signal assignments may be interchanged between Tables 1 and 2. Dig=*β*-D-digitoxopyranose, Ole=*β*-D-oleandropyranose, Can=*β*-D-canaropyranose, Cym=*β*-D-cymaropyranose.

shown in Chart 1, and this sugar sequence was confirmed by measurements of ROE difference spectra and the HMBC experiment. The compound was named curassavioside J_1.

HR-FAB-MS indicated the molecular formulae of **21** and **22** to be $C_{54}H_{82}O_{19}$ and $C_{54}H_{80}O_{19}$, respectively. These compounds had the same sugar sequence, because the ^{1}H- and ^{13}C-NMR spectroscopic data for the sugar moieties were similar. Acid hydrolysis of **21** and **22** afforded digitoxose, oleandrose, cymarose, and canarose as the component sugars with each aglycone. The overall structural assignment of **21** was accomplished using a combination of 1D- and 2D-NMR spectra. Comparison of the ^{1}H- and ^{13}C-NMR spectroscopic data for the sugar moiety of **21** and **9** and the result of acid hydrolysis suggested its sequence to be 3-*O*-*β*-D-oleandropyranosyl-(1→4)-*β*-D-canaropyranosyl-(1→4)-*β*-D-cymaropyranosyl-(1→4)-*β*-D-digitoxopyranoside, which was confirmed from the ROE difference spectra and HMBC experiment. Thus, **21** and **22** were established as shown in Chart 1, and were named curassavioside K_1 and K_2, respectively.

The molecular formulae of the compounds **23**—**25** were determined to be $C_{55}H_{84}O_{19}$, $C_{55}H_{82}O_{19}$, and $C_{57}H_{84}O_{19}$ based on HR-FAB-MS. The NMR spectroscopic data for the sugar moieties in these compounds were consistent. Acid hydrolysis of **23**—**25** gave digitoxose, oleandrose, and cymarose in addition to **1a**, **2a**, and **11a**, respectively. The NMR signals of the sugar moiety in **23** were assigned in Table 2 and Experimental, owing to the 1D- and 2D-NMR experiments. Comparing the ^{1}H- and ^{13}C-NMR data for **23** and **21**, the sugar sequence of **23** was suggested to have a *β*-D-canaropyranosyl group for the *β*-D-oleandropyranosyl group with the anomeric proton signal resonating at δ 4.45 (1H, dd, J=9.5, 2.0 Hz). Thus, **23** was elucidated to be 12-*O*-benzoylsarcostin 3-*O*-*β*-D-oleandropyranosyl-(1→4)-*β*-D-oleandropyranosyl-(1→4)-*β*-D-cymaropyranosyl-(1→4)-*β*-D-digitoxopyranoside, and **24** and **25** are also shown in Chart 1. **23**—**25** were named curassavioside L_1, L_2 and L_3, respectively.

The compound **26** was considered to be 12-*O*-benzoyldeacymetaplexigenin 3-*O*-pentaglycoside whose molecular formula was $C_{62}H_{94}O_{22}$ on the basis of the NMR data and HR-FAB-MS. Comparing the NMR spectral data for **26** with those for **23**, **26** had one more *β*-D-oleandropyranosyl group in its sugar moiety. Moreover, the position of this

oleandropyranosyl group was presumed to be C-4‴ of β-D-oleandropyranose, because of the observation of glycosylation shifts [C-3‴ (−1.7 ppm), C-4‴ (+6.8 ppm), C-5‴ (−0.6 ppm)]. The ROEs observed at the anomeric proton signals supported this sugar sequence. **26** was established to be 12-*O*-benzoyldeacymetaplexigenin 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-digitoxopyranoside, and was named curassavioside M_2.

A. curassavica has been found to contain many kinds of acylated-oxypregnane glycosides along with cardenolide glycosides.[1—3] This plant is considered toxic. Recently, it was reported that an acylated-oxypregnane glycoside in Asclepiadaceous plants acts as an appetite suppressant.[17] We are interested in the biological activities including the appetite-suppressing properties of oxypregnane glycosides.

Experimental

General Procedures The instrumental analysis was carried out as described previously.[18] UV spectra were measured with a Jasco V-630 spectrophotometer.

Plant Material The roots of *Asclepias curassavica* L. (No. 2379M) were collected from the botanical garden of the University of Shizuoka in Japan in September, 2001 and identified by Dr. T. Warashina. These dried materials were stored in herbarium.

Extraction and Isolation The dried roots of *Asclepias curassavica* L. (840 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 extract was evaporated dry, and the residue (10.8 g) was subjected to silica gel CC with a $CHCl_3$–MeOH (98 : 2) system to get three fractions (A (1.50 g), B (1.77 g) and C (0.66 g)). Using semi-preparative HPLC (Develosil-ODS-15/30 50 mm i.d.×100 cm, Develosil-C8 20 mm i.d.×25 cm and YMC-ODS 20 mm i.d.×25 cm: 46—55% MeCN in water and 75—80% MeOH in water), the fraction B (1.56 g) afforded compounds **1** (20 mg), **2** (10 mg), **3** (4 mg), **4** (3 mg), **5** (12 mg), **6** (16 mg), **7** (4 mg), **8** (4 mg), **9** (47 mg), **10** (22 mg), **11** (8 mg), **12** (34 mg), **13** (39 mg), **14** (3 mg), **15** (40 mg), **16** (6 mg), **17** (11 mg), **18** (11 mg), **19** (4 mg), **20** (6 mg), **21** (6 mg), **22** (11 mg), **23** (4 mg), **24** (17 mg), **25** (4 mg), **26** (18 mg), **27** (32 mg), **28** (25 mg) and **29** (9 mg).

Curassavioside A_1 (**1**): Amorphous powder. $[\alpha]_D^{23}$ +7.48° (c=1.31, MeOH). UV λ_{max}^{MeOH} nm (log ε): 229 (4.05). FAB-MS m/z: 913 $[M+Na]^+$. HR-FAB-MS m/z: 913.4548 (Calcd for $C_{47}H_{70}O_{16}Na$: 913.4562). ^{13}C-NMR: shown in Tables 1 and 2. ^{1}H-NMR ($CDCl_3$ at 35 °C) δ: 8.09 (2H, br d, 7.0, H-3e and -7e), 7.59 (1H, br t, 7.0, H-5e), 7.47 (2H, br t, 7.0, H-4e and -6e), 5.38 (1H, br s, H-6), 4.93 (1H, dd, 9.5, 2.0, H-1′), 4.90 (1H, dd, 9.5, 2.0, H-1″), 4.55 (1H, dd, 9.5, 2.0, H-1‴), 4.24 (2H, br s, H-3′ and -3″), 3.84 (1H, dq, 9.5, 6.5, H-5″), 3.78 (1H, dq, 9.5, 6.5, H-5′), 3.77 (1H, m, H-20), 3.58 (1H, m, H-3), 3.40 (3H, s, C-3‴-OMe), 3.33 (1H, dq, 9.0, 6.0, H-5‴), 3.22 (1H, dd, 9.5, 3.0, H-4′), 3.20 (1H, dd, 9.5, 3.0, H-4″), 3.12 (1H, t, 9.0, H-4‴), 2.97 (1H, br s, C-3′-OH), 2.86 (1H, br s, C-3″-OH), 1.64 (3H, s, H-18), 1.32 (3H, d, 6.0, H-6‴), 1.24 (3H, d, 6.5, H-6″), 1.23 (3H, d, 6.5, H-6′), 1.16 (3H, s, H-19), 1.06 (3H, d, 6.5, H-21). ^{13}C-NMR (pyridine-d_5 at 35 °C) δ: 166.7 (C-1e), 139.2 (C-5), 133.2 (C-5e), 131.8 (C-2e), 130.5×2 (C-3e and -7e), 128.8×2 (C-4e and -6e), 119.5 (C-6), 101.6 (C-1‴), 99.8 (C-1″), 96.4 (C-1′), 88.8 (C-14), 88.6 (C-17), 83.5, 83.3 (C-4′ and -4″), 81.4 (C-3‴), 77.7 (C-3), 76.2 (C-4‴), 75.4 (C-12), 74.3 (C-8), 73.0 (C-5‴), 70.9 (C-20), 68.7, 68.6 (C-5′ and -5″), 67.6, 67.5 (C-3′ and -3″), 57.2 (C-13), 57.0 (C-3‴-OMe), 44.2 (C-9), 39.4 (C-4), 39.1 (C-2′ or -2″), 38.9 (C-1), 38.7 (C-2″ or -2′), 37.3 (C-10), 37.0 (C-2‴), 35.1 (C-7), 34.2 (C-15), 32.9 (C-16), 30.0 (C-2), 25.6 (C-11), 19.4 (C-21), 18.7, 18.6×2 (C-6′, -6″ and -6‴), 18.2 (C-19), 11.7 (C-18). ^{1}H-NMR (pyridine-d_5 at 35 °C) δ: 8.55 (2H, br d, 7.0, H-3e and -7e), 7.48 (1H, br t, 7.0, H-5e), 7.39 (2H, br t, 7.0, H-4e and -6e), 5.55 (1H, br s, C-3″-OH), 5.48 (1H, dd, 9.5, 2.0, H-1′), 5.39 (1H, dd, 9.5, 2.0, H-1″), 5.37 (overlapping, H-6 and -12), 5.15 (1H, br s, C-3′-OH), 4.79 (1H, dd, 9.5, 2.0, H-1‴), 4.66 (1H, br q, 3.0, H-3′), 4.63 (1H, br q, 3.0, H-3″), 4.30 (2H, dq, 9.5, 6.5, H-5′ and -5″), 4.10 (1H, m, H-20), 3.88 (1H, m, H-3), 3.57 (1H, dq, 9.0, 6.0, H-5‴), 3.53 (1H, dd, 9.5, 3.0, H-4′), 3.48 (1H, dd, 9.5, 3.0, H-4″), 3.46 (3H, s, C-3‴-OMe), 2.19 (3H, s, H-18), 1.50 (3H, d, 6.0, H-6‴), 1.44 (3H, d, 6.5, H-6″), 1.40 (3H, d, 6.5, H-6′), 1.35 (3H, s, H-19), 1.26 (3H, d, 6.0, H-21).

Curassavioside A_2 (**2**): Amorphous powder. $[\alpha]_D^{21}$ −9.39° (c=1.07, MeOH). UV λ_{max}^{MeOH} nm (log ε): 229 (4.09). FAB-MS m/z: 911 $[M+Na]^+$. HR-FAB-MS m/z: 911.4402 (Calcd for $C_{47}H_{68}O_{16}Na$: 911.4405). ^{13}C-NMR: shown in Table 1. ^{1}H-NMR data of the aglycone moiety ($CDCl_3$ at 35 °C) δ: 7.94 (2H, br d, 7.0, H-3e and-7e), 7.55 (1H, br t, 7.0, H-5e), 7.43 (2H, br t, 7.0, H-4e and -6e), 5.37 (1H, t-like, H-5), 4.86 (1H, dd, 11.5, 4.5, H-12), 3.59 (1H, m, H-3), 2.87 (1H, m, H-16), 2.07 (3H, s, H-21), 1.55 (3H, s, H-18), 1.13 (3H, s, H-19). The ^{13}C- and ^{1}H-NMR spectroscopic data of the sugar moiety were in good agreement with those of **1**.

Curassavioside B_1 (**3**): Amorphous powder. $[\alpha]_D^{21}$ −3.8° (c=0.43, MeOH). UV λ_{max}^{MeOH} nm (log ε): 229 (4.07). FAB-MS m/z: 927 $[M+Na]^+$. HR-FAB-MS m/z: 927.4717 (Calcd for $C_{48}H_{72}O_{16}Na$: 927.4718). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.94 (1H, dd, 9.5, 2.0, H-1′), 4.72 (1H, dd, 9.5, 2.0, H-1‴), 4.51 (1H, dd, 9.5, 2.0, H-1″), 4.22 (1H, br q, 3.0, H-3′), 3.80 (1H, dq, 9.5, 6.5, H-5′), 3.41 (3H, s, C-3″-OMe), 3.40 (3H, s, C-3‴-OMe), 3.34 (1H, dq, 9.0, 6.0, H-5″), 3.31 (1H, dq, 9.0, 6.0, H-5‴), 3.21 (1H, dd, 9.5, 3.0, H-4′), 3.17 (1H, t, 9.0, H-4″), 3.13 (1H, t, 9.0, H-4‴), 2.85 (1H, br s, C-3′-OH), 1.35 (3H, d, 6.0, H-6‴), 1.30 (3H, d, 6.0, H-6″), 1.24 (3H, d, 6.5, H-6′). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement of those of **1**.

Curassavioside C_2 (**4**): Amorphous powder. $[\alpha]_D^{25}$ −11° (c=0.37, MeOH). UV λ_{max}^{MeOH} nm (log ε): 230 (4.04). FAB-MS m/z: 1055 $[M+Na]^+$. HR-FAB-MS m/z: 1055.5183 (Calcd for $C_{54}H_{80}O_{19}Na$: 1055.5192). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.93 (1H, dd, 9.5, 2.0, H-1′), 4.89 (1H, dd, 9.5, 2.0, H-1″), 4.72 (1H, dd, 9.5, 2.0, H-1⁗), 4.51 (1H, dd, 9.5, 2.0, H-1‴), 4.24 (1H, br q, 3.0, H-3′), 4.22 (1H, br q, 3.0 H-3″), 3.83 (1H, dq, 9.5, 6.0, H-5″), 3.79 (1H, dq, 9.5, 6.0, H-5′), 3.41 (3H, s, C-3‴-OMe), 3.40 (3H, s, C-3⁗-OMe), 3.35 (1H, dq, 9.0, 6.0, H-5‴), 3.31 (1H, dq, 9.0, 6.0, H-5⁗), 3.22 (1H, dd, 9.5, 3.0, H-4′), 3.19 (1H, dd, 9.5, 3.0, H-4″), 3.17 (1H, t, 9.0, H-4‴), 3.13 (1H, t, 9.0, H-4⁗), 2.96 (1H, br s, C-3′-OH), 2.81 (1H, br s, C-3″-OH), 1.35 (3H, d, 6.0, H-6⁗), 1.30 (3H, d, 6.0, H-6‴), 1.23 (6H, d, 6.0, H-6″ and -6′). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement of those of **2**.

Curassavioside D_1 (**5**): Amorphous powder. $[\alpha]_D^{21}$ +2.66° (c=1.28, MeOH). UV λ_{max}^{MeOH} nm (log ε): 229 (4.09). FAB-MS m/z: 1043 $[M+Na]^+$. HR-FAB-MS m/z: 1043.5208 (Calcd for $C_{53}H_{80}O_{19}Na$: 1043.5192). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.93 (1H, dd, 9.5, 2.0, H-1′), 4.89 (1H, dd, 9.5, 2.0, H-1″), 4.59 (1H, br s, C -3‴-OH), 4.57 (1H, dd, 9.5, 2.0, H-1‴), 4.49 (1H, dd, 9.5, 2.0, H-1⁗), 4.23 (2H, br s, H-3′ and -3″), 3.84 (1H, dq, 9.5, 6.5, H-5″), 3.78 (1H, dq, 9.5, 6.5, H-5′), 3.59 (overlapping, H-3‴), 3.42 (1H, dq, 9.0, 6.0, H-5⁗), 3.41 (3H, s, C-3⁗-OMe), 3.35 (1H, dq, 9.0, 6.0, H-5‴), 3.22 (1H, dd, 9.5, 3.0, H-4′), 3.20 (1H, dd, 9.5, 3.0, H-4″), 3.17 (1H, t, 9.0, H-4⁗), 2.96 (1H, t, 9.0, H-4‴), 1.36 (3H, d, 6.0, H-6⁗), 1.28 (3H, d, 6.0, H-6‴), 1.23 (6H, d, 6.5, H-6′ and -6″). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement of those of **1**.

Curassavioside E_1 (**6**): Amorphous powder. $[\alpha]_D^{21}$ −5.97° (c=1.34, MeOH). UV λ_{max}^{MeOH} nm (log ε): 229 (4.09). FAB-MS m/z: 1043 $[M+Na]^+$. HR-FAB-MS m/z: 1043.5178 (Calcd for $C_{53}H_{80}O_{19}Na$: 1043.5192). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.94 (1H, dd, 9.5, 2.0, H-1′), 4.60 (1H, s, C-3‴-OH), 4.56 (1H, dd, 9.5, 2.0, H-1″), 4.50 (1H, dd, 9.5, 2.0, H-1‴), 4.50 (1H, s, C-3″-OH), 4.49 (1H, dd, 9.5, 2.0, H-1⁗), 4.22 (1H, br q, 3.0, H-3′), 3.81 (1H, dq, 9.5, 6.0, H-5′), 3.62 (overlapping, H-3‴), 3.60 (overlapping, H-3″), 3.43 (1H, dq, 9.0, 6.0, H-5‴), 3.41 (overlapping, H-5⁗), 3.41 (3H, s, C-3⁗-OMe), 3.35 (1H, dq, 9.0, 6.0, H-5″), 3.21 (1H, dd, 9.5, 3.0, H-4′), 3.16 (1H, t, 9.0, H-4⁗), 3.01 (1H, t, 9.0, H-4‴), 2.96 (1H, t, 9.0, H-4″), 2.84 (1H, br s, C-3′-OH), 1.36 (3H, d, 6.0, H-5⁗), 1.33 (3H, d, 6.0, H-6‴), 1.27 (3H, d, 6.0, H-6″), 1.24 (3H, d, 6.0, H-6′). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement of those of **1**.

Curassavioside E_2 (**7**): Amorphous powder. $[\alpha]_D^{21}$ −18° (c=0.40, MeOH). UV λ_{max}^{MeOH} nm (log ε): 228 (4.07). FAB-MS m/z: 1041 $[M+Na]^+$. HR-FAB-MS m/z: 1041.5031 (Calcd for $C_{53}H_{78}O_{19}Na$: 1041.5035). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement of those of **2**. The ^{13}C- and ^{1}H-NMR data of the sugar moiety were similar to those of **6**.

Curassavioside F_2 (**8**): Amorphous powder. $[\alpha]_D^{25}$ −18° (c=0.39, MeOH). UV λ_{max}^{MeOH} nm (log ε): 230 (4.08). FAB-MS m/z: 1055 $[M+Na]^+$. HR-FAB-MS m/z: 1055.5190 (Calcd for $C_{54}H_{80}O_{19}Na$: 1055.5192). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.94 (1H, dd, 9.5, 2.0, H-1′), 4.71 (1H, dd, 9.5, 2.0, H-1⁗), 4.56 (1H, dd, 9.5, 2.0, H-1″), 4.53 (1H, s, C-3″-OH), 4.44 (1H, dd, 9.5, 2.0, H-1‴), 4.22 (1H, br q, 3.0, H-3′), 3.81 (1H, dq, 9.5, 6.0, H-5′), 3.61 (1H, m, H-3″), 3.43 (overlapping, H-5‴), 3.42 (3H, s, C-3‴-OMe), 3.40 (3H, s, C-3⁗-OMe), 3.34 (1H, dq, 9.0,

6.0, H-5″), 3.31 (1H, dq, 9.0, 6.0, H-5‴), 3.22 (1H, t, 9.0, H-4‴), 3.21 (1H, dd, 9.5, 3.0, H-4′), 3.13 (1H, t, 9.0, H-4‴), 2.96 (1H, t, 9.0, H-4″), 2.83 (1H, br s, C-3′-OH), 1.35 (3H, d, 6.0, H-6‴), 1.34 (3H, d, 6.0, H-6″), 1.27 (3H, d, 6.0, H-6″), 1.25 (3H, d, 6.0, H-6′). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement of those of **2**.

Curassavioside G_1 (**9**): Amorphous powder. $[\alpha]_D^{21}$ −7.21° (c=1.56, MeOH). UV λ_{max}^{MeOH} nm (log ε): 229 (4.09). FAB-MS m/z: 1057 $[M+Na]^+$. HR-FAB-MS m/z: 1057.5327 (Calcd for $C_{54}H_{82}O_{19}Na$: 1057.5348). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.94 (1H, dd, 9.5, 2.0, H-1′), 4.71 (1H, dd, 9.5, 2.0, H-1‴), 4.58 (1H, s, C-3‴-OH), 4.50 (1H, dd, 9.5, 2.0, H-1″), 4.49 (1H, dd, 9.5, 2.0, H-1‴), 4.22 (1H, br q, 3.0, H-3′), 3.80 (1H, dq, 9.5, 6.5, H-5′), 3.61 (overlapping, H-3‴), 3.41 (6H, s, C-3″-OMe and -3‴-OMe), 3.41 (overlapping, H-5‴), 3.34 (1H, dq, 9.0, 6.0, H-5‴), 3.33 (1H, dq, 9.0, 6.0, H-5″), 3.20 (1H, dd, 9.5, 3.0, H-4′), 3.16 (2H, t, 9.0, H-4″ and -4‴), 2.98 (1H, t, 9.0, H-4‴), 2.86 (1H, br s, C-3′-OH), 1.36 (3H, d, 6.0, H-6‴), 1.31 (3H, d, 6.0, H-6″), 1.28 (3H, d, 6.0, H-6″), 1.24 (3H, d, 6.5, H-6′). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement of those of **1**.

Curassavioside G_2 (**10**): Amorphous powder. $[\alpha]_D^{21}$ −23.0° (c=1.46, MeOH). UV λ_{max}^{MeOH} nm (log ε): 228 (4.15). FAB-MS m/z: 1055 $[M+Na]^+$. HR-FAB-MS m/z: 1055.5199 (Calcd for $C_{54}H_{80}O_{19}Na$: 1055.5192). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement of those of **2**. The ^{13}C- and ^{1}H-NMR data of the sugar moiety were similar to those of **9**.

Curassavioside G_3 (**11**): Amorphous powder. $[\alpha]_D^{25}$ +2.1° (c=0.83, MeOH). UV λ_{max}^{MeOH} nm (log ε): 218 (4.20), 223 (4.15), 279 (4.38). FAB-MS m/z: 1081 $[M+Na]^+$. HR-FAB-MS m/z: 1081.5343 (Calcd for $C_{56}H_{82}O_{19}Na$: 1081.5348). ^{13}C-NMR: shown in Table 1. ^{1}H-NMR data of the aglycone moiety ($CDCl_3$ at 35 °C) δ: 7.62 (1H, d, 16.0, H-3e), 7.51 and 7.38 (overlapping, H-5e—-9e), 6.30 (1H, d, 16.0, H-2e), 5.36 (1H, t-like, H-6), 4.70 (overlapping, H-12), 3.58 (1H, m, H-3), 2.20 (3H, s, H-21), 1.52 (3H, s, H-18), 1.14 (3H, s, H-19). The ^{13}C- and ^{1}H-NMR data of the sugar moiety were similar to those of **9**.

Curassavioside H_1 (**12**): Amorphous powder. $[\alpha]_D^{21}$ −7.97° (c=1.06, MeOH). UV λ_{max}^{MeOH} nm (log ε): 229 (4.08). FAB-MS m/z: 1071 $[M+Na]^+$. HR-FAB-MS m/z: 1071.5529 (Calcd for $C_{55}H_{84}O_{19}Na$: 1071.5505). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.94 (1H, dd, 9.5, 2.0, H-1′), 4.71 (1H, dd, 9.5, 2.0, H-1‴), 4.66 (1H, dd, 9.5, 2.0, H-1‴), 4.50 (1H, dd, 9.5, 2.0, H-1″), 4.21 (1H, br q, 3.0, H-3′), 3.80 (1H, dq, 9.5, 6.0, H-5′), 3.41 (3H, s, C-3″-OMe or -3‴-OMe), 3.40 (3H, s, C-3‴-OMe or -3″-OMe), 3.40 (3H, s, C-3‴-OMe), 3.33 (2H, dq, 9.0, 6.0, H-5″ and -5‴), 3.31 (1H, dq, 9.0, 6.0, H-5‴), 3.20 (1H, dd, 9.5, 3.0, H-4′), 3.18 (1H, t, 9.0, H-4‴), 3.16 (1H, t, 9.0, H-4″), 3.13 (1H, t, 9.0, H-4‴), 2.86 (1H, br s, C-3′-OH), 1.34 (3H, d, 6.0, H-6‴), 1.32 (3H, d, 6.0, H-6″), 1.28 (3H, d, 6.0, H-6″), 1.24 (1H, d, 6.5, H-6′). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement of those of **1**.

Curassavioside H_2 (**13**): Amorphous powder. $[\alpha]_D^{23}$ −22° (c=0.78, MeOH). UV λ_{max}^{MeOH} nm (log ε): 230 (4.09). FAB-MS m/z: 1069 $[M+Na]^+$. HR-FAB-MS m/z: 1069.5353 (Calcd for $C_{55}H_{82}O_{19}Na$: 1069.5348). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement of those of **2**. The ^{13}C- and ^{1}H-NMR spectral data of the sugar moiety were similar to those of **12**.

Curassavioside H_4 (**14**): Amorphous powder. $[\alpha]_D^{25}$ −19° (c=0.30, MeOH). UV λ_{max}^{MeOH} nm (log ε): 230 (4.14). FAB-MS m/z: 1071 $[M+Na]^+$. HR-FAB-MS m/z: 1071.5514 (Calcd for $C_{55}H_{84}O_{19}Na$: 1071.5505). ^{13}C-NMR: shown in Table 1. ^{1}H-NMR data of the aglycone moiety ($CDCl_3$ at 35 °C) δ: 7.90 (2H, br d, 7.5, H-3e and -7e), 7.55 (1H, br t, 7.5, H-5e), 7.43 (2H, br t, 7.5, H-4e and -6e), 4.80 (1H, dd, 11.5, 4.5, H-12), 3.65 (1H, m, H-3), 2.75 (1H, m, H-16), 2.03 (3H, s, H-21), 1.44 (3H, s, H-18), 1.08 (1H, br t, 13.0, H-5), 0.94 (3H, s, H-19). The ^{13}C- and ^{1}H-NMR spectroscopic data of the sugar moiety were similar to those of **12**, but the C-1′ signal was shown at δ 95.4.

Curassavioside H_3 (**15**): Amorphous powder. $[\alpha]_D^{23}$ +4.1° (c=0.69, MeOH). UV λ_{max}^{MeOH} nm (log ε): 218 (4.09), 223 (4.04), 279 (4.28). FAB-MS m/z: 1095 $[M+Na]^+$. HR-FAB-MS m/z: 1095.5546 (Calcd for $C_{57}H_{84}O_{19}Na$: 1095.5505). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement with those of **11**. The ^{13}C- and ^{1}H-NMR data of the sugar moiety were similar to those of **12**.

Curassavioside H_5 (**16**): Amorphous powder. $[\alpha]_D^{25}$ +9.0° (c=0.55, MeOH). UV λ_{max}^{MeOH} nm (log ε): 218 (4.13), 223 (4.09), 279 (4.30). FAB-MS m/z: 1097 $[M+Na]^+$. HR-FAB-MS m/z: 1097.5647 (Calcd for $C_{57}H_{86}O_{19}Na$: 1097.5661). ^{13}C-NMR: shown in Table 1. ^{1}H-NMR data of the aglycone moiety ($CDCl_3$ at 35 °C) δ: 7.59 (1H, d, 16.0, H-3e), 7.51 and 7.38 (overlapping, H-5e—-9e), 6.29 (1H, d, 16.0, H-2e), 4.66 (1H, dd, 11.5, 4.5, H-12), 3.65 (1H, m, H-3), 2.15 (3H, s, H-21), 1.37 (3H, s, H-18), 0.94 (3H, s, H-19). The ^{13}C- and ^{1}H-NMR spectroscopic data of the sugar moiety were similar to those of **12**, but the C-1′ signal was shown at δ 95.4.

Curassavioside I_1 (**17**): Amorphous powder. $[\alpha]_D^{21}$ +9.37° (c=1.06, MeOH). UV λ_{max}^{MeOH} nm (log ε): 226 (4.19). FAB-MS m/z: 1071 $[M+Na]^+$. HR-FAB-MS m/z: 1071.5505 (Calcd for $C_{55}H_{84}O_{19}Na$: 1071.5505). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.94 (1H, dd, 9.5, 2.0, H-1′), 4.87 (1H, dd, 9.5, 2.0, H-1‴), 4.66 (1H, dd, 9.5, 2.0, H-1‴), 4.50 (1H, dd, 9.5, 2.0, H-1″), 4.21 (1H, br q, 3.0, H-3′), 3.80 (1H, dq, 9.5, 6.0, H-5′), 3.61 (1H, q, 3.0, H-3‴), 3.60 (1H, dq, 9.5, 6.5, H-5‴), 3.42 (3H, s, C-3‴-OMe), 3.42 (3H, s, C-3″-OMe or 3‴-OMe), 3.40 (3H, s, C-3‴-OMe or 3″-OMe), 3.33 (1H, dq, 9.0, 6.0, H-5″), 3.32 (1H, dq, 9.0, 6.0, H-5‴), 3.20 (1H, dd, 9.5, 3.0, H-4′), 3.17 (1H, t, 9.0, H-4‴), 3.16 (1H, t, 9.0, H-4″), 2.85 (1H, br s, C-3′-OH), 1.31 (3H, d, 6.0, H-6‴), 1.30 (3H, d, 6.5, H-6‴), 1.28 (3H, d, 6.0, H-6″), 1.24 (3H, d, 6.0, H-6′). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement with those of **1**.

Curassavioside I_2 (**18**): Amorphous powder. $[\alpha]_D^{25}$ −8.99° (c=1.14, MeOH). UV λ_{max}^{MeOH} nm (log ε): 230 (4.10). FAB-MS m/z: 1069 $[M+Na]^+$. HR-FAB-MS m/z: 1069.5365 (Calcd for $C_{55}H_{82}O_{19}Na$: 1069.5348). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement with those of **2**. The ^{13}C- and ^{1}H-NMR data of the sugar moiety were similar to those of **17**.

Curassavioside I_3 (**19**): Amorphous powder. $[\alpha]_D^{25}$ +18° (c=0.46, MeOH). UV λ_{max}^{MeOH} nm (log ε): 218 (4.10), 223 (4.05), 279 (4.30). FAB-MS m/z: 1095 $[M+Na]^+$. HR-FAB-MS m/z: 1095.5504 (Calcd for $C_{57}H_{84}O_{19}Na$: 1095.5505). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement with those of **11**. The ^{13}C- and ^{1}H-NMR data of the sugar moiety were similar to those of **17**.

Curassavioside J_1 (**20**): Amorphous powder. $[\alpha]_D^{21}$ +3.8° (c=0.60, MeOH). UV λ_{max}^{MeOH} nm (log ε): 229 (4.09). FAB-MS m/z: 1057 $[M+Na]^+$. HR-FAB-MS m/z: 1057.5350 (Calcd for $C_{54}H_{82}O_{19}Na$: 1057.5348). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.94 (1H, dd, 9.5, 2.0, H-1′), 4.70 (1H, dd, 9.5, 2.0, H-1‴), 4.68 (1H, s, C-3‴-OH), 4.66 (1H, dd, 9.5, 2.0, H-1‴), 4.50 (1H, dd, 9.5, 2.0, H-1″), 4.21 (1H, br q, 3.0, H-3′), 3.80 (1H, dq, 9.5, 6.0, H-5′), 3.70 (1H, dq, 9.5, 6.0, H-5‴), 3.64 (1H, q, 3.0, H-3‴), 3.57 (overlapping, H-3‴), 3.44 (3H, s, C-3‴-OMe), 3.41 (3H, s, C-3″-OMe), 3.33 (1H, dq, 9.0, 6.0, H-5″), 3.32 (1H, dq, 9.0, 6.0, H-5‴), 3.20 (1H, dd, 9.5, 3.0, H-4′), 3.16 (1H, t, 9.0, H-4″), 2.95 (1H, t, 9.0, H-4‴), 2.83 (1H, br s, C-3′-OH), 1.31 (3H, d, 6.0, H-6‴), 1.30 (3H, d, 6.0, H-6‴), 1.28 (3H, d, 6.0, H-6″), 1.24 (3H, d, 6.0, H-6′). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement with those of **1**.

Curassavioside K_1 (**21**): Amorphous powder. $[\alpha]_D^{25}$ +5.2° (c=0.61, MeOH). UV λ_{max}^{MeOH} nm (log ε): 231 (4.13). FAB-MS m/z: 1057 $[M+Na]^+$. HR-FAB-MS m/z: 1057.5353 (Calcd for $C_{54}H_{82}O_{19}Na$: 1057.5348). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.93 (1H, dd, 9.5, 2.0, H-1′), 4.81 (1H, dd, 9.5, 2.0, H-1″), 4.55 (1H, s, C-3‴-OH), 4.51 (1H, dd, 9.5, 2.0, H-1‴), 4.49 (1H, dd, 9.5, 2.0, H-1‴), 4.23 (1H, br q, 3.0, H-3′), 3.91 (1H, dq, 9.5, 6.5, H-5″), 3.79 (1H, q, 3.0, H-3″), 3.78 (1H, dq, 9.5, 6.5, H-5′), 3.60 (overlapping, H-3‴), 3.46 (3H, s, C-3″-OMe), 3.41 (3H, s, C-3‴-OMe), 3.40 (overlapping, H-5‴), 3.32 (1H, dq, 9.0, 6.0, H-5″), 3.21 (1H, dd, 9.5, 3.0, H-4″), 3.20 (1H, dd, 9.5, 3.0, H-4′), 3.16 (1H, t, 9.0, H-4‴), 2.98 (1H, t, 9.0, H-4‴), 1.36 (3H, d, 6.0, H-6‴),1.29 (3H, d, 6.0, H-6‴), 1.23 (3H, d, 6.5, H-6′), 1.21 (3H, d, 6.5, H-6″). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement with those of **1**.

Curassavioside K_2 (**22**): Amorphous powder. $[\alpha]_D^{23}$ −6.9° (c=0.27, MeOH). UV λ_{max}^{MeOH} nm (log ε): 231 (4.12). FAB-MS m/z: 1055 $[M+Na]^+$. HR-FAB-MS m/z: 1055.5214 (Calcd for $C_{54}H_{80}O_{19}Na$: 1055.5192). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement with those of **2**. The ^{13}C- and ^{1}H-NMR data of the sugar moiety were similar to those of **21**.

Curassavioside L_1 (**23**): Amorphous powder. $[\alpha]_D^{23}$ +19° (c=0.05, MeOH). UV λ_{max}^{MeOH} nm (log ε): 230 (4.39). FAB-MS m/z: 1071 $[M+Na]^+$. HR-FAB-MS m/z: 1071.5516 (Calcd for $C_{55}H_{84}O_{19}Na$: 1071.5505). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.93 (1H, dd, 9.5, 2.0, H-1′), 4.81 (1H, dd, 9.5, 2.0, H-1″), 4.72 (1H, dd, 9.5, 2.0, H-1‴), 4.45 (1H, dd, 9.5, 2.0, H-1‴), 4.23 (1H, br q, 3.0, H-3′), 3.91 (1H, dq, 9.5, 6.0, H-5″), 3.79 (1H, q, 3.0, H-3″), 3.78 (1H, dq, 9.5, 6.0, H-5′), 3.45 (3H, s, C-3″-OMe), 3.40 (6H, s, C-3‴-OMe and -3‴-OMe), 3.37 (1H, m, H-3‴), 3.31 (2H, dq, 9.0, 6.0, H-5‴ and -5‴), 3.21 (1H, dd, 9.5, 3.0, H-4′ or -4″), 3.20 (1H, dd, 9.5, 3.0, H-4″ or -4′), 3.17 (1H, t, 9.0, H-4‴), 3.13 (1H, t, 9.0, H-4‴), 3.01 (1H, br s, C-3′-OH), 1.35 (3H, d, 6.0, H-6‴), 1.30

(3H, d, 6.0, H-6‴), 1.23 (3H, d, 6.0, H-6′), 1.21 (3H, d, 6.0, H-6″). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement with those of **1**.

Curassavioside L_2 (**24**): Amorphous powder. $[\alpha]_D^{25}$ −10.6° (c=1.31, MeOH). UV λ_{max}^{MeOH} nm (log ε): 231 (4.07). FAB-MS m/z: 1069 $[M+Na]^+$. HR-FAB-MS m/z: 1069.5361 (Calcd for $C_{55}H_{82}O_{19}Na$: 1069.5348). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement with those of **2**. The ^{13}C- and ^{1}H-NMR data of the sugar moiety were similar to those of **23**.

Curassavioside L_3 (**25**): Amorphous powder. $[\alpha]_D^{25}$ +20° (c=0.38, MeOH). UV λ_{max}^{MeOH} nm (log ε): 218 (4.14), 223 (4.09), 279 (4.31). FAB-MS m/z: 1095 $[M+Na]^+$. HR-FAB-MS m/z: 1095.5533 (Calcd for $C_{57}H_{84}O_{19}Na$: 1095.5505). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement with those of **11**. The ^{13}C- and ^{1}H-NMR data of the sugar moiety were similar to those of **23**.

Curassavioside M_2 (**26**): Amorphous powder. $[\alpha]_D^{25}$ +14.1° (c=1.12, MeOH). UV λ_{max}^{MeOH} nm (log ε): 231 (4.08). FAB-MS m/z: 1213 $[M+Na]^+$. HR-FAB-MS m/z: 1213.6140 (Calcd for $C_{62}H_{94}O_{22}Na$: 1213.6134). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.93 (1H, dd, 9.5, 2.0, H-1′), 4.81 (1H, dd, 9.5, 2.0, H-1″), 4.72 (1H, dd, 9.5, 2.0, H-1⁗), 4.67 (1H, dd, 9.5, 2.0, H-1⁗), 4.45 (1H, dd, 9.5, 2.0, H-1‴), 4.23 (1H, br q, 3.0, H-3′), 3.90 (1H, dq, 9.5, 6.0, H-5″), 3.79 (1H, q, 3.0, H-3″), 3.78 (1H, dq, 9.5, 6.0, H-5′), 3.45 (3H, s, C-3″-OMe), 3.40 (3H, s, C-3‴-OMe, -3⁗-OMe or -3⁗-OMe), 3.39 (6H, s, C-3‴-OMe, -3⁗-OMe or -3⁗-OMe), 3.33 (1H, dq, 9.0, 6.0, H-5⁗), 3.31 (1H, dq, 9.0, 6.0, H-5⁗), 3.30 (1H, dq, 9.0, 6.0, H-5‴), 3.21 (2H, dd, 9.5, 3.0, H-4′ and -4″), 3.18 (1H, t, 9.0, H-4⁗), 3.16 (1H, t, 9.0, H-4‴), 3.13 (1H, t, 9.0, H-4⁗), 3.02 (1H, br s, C-3′-OH), 1.34 (3H, d, 6.0, H-6⁗), 1.32 (3H, d, 6.0, H-6⁗), 1.29 (3H, d, 6.0, H-6‴), 1.23 (3H, d, 6.0, H-6′), 1.21 (1H, d, 6.0, H-6″). The ^{13}C- and ^{1}H-NMR spectroscopic data of the aglycone moiety were in good agreement with those of **2**.

Acid Hydrolysis of a Mixture of Pregnane Glycosides The fraction of pregnane glycosides eluted with the $CHCl_3$–MeOH (98 : 2) system on a silica gel column (fraction B, 207 mg) was heated at 60 °C for 2.5 h with dioxane (4 ml) and 0.1 M H_2SO_4 (1 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, 45% MeCN in water and 60, 65% MeOH in water) afforded 12-*O*-benzoylsarcositn (**1a** (3 mg)), 12-*O*-benzoyldeacylmetaplexigenin (**2a** (10 mg)) and kidjolanin (**11a** (8 mg)).

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 and 7 : 1.5 : 1.2 bottom layer) system to obtain cymarose, oleandrose, digitoxose, and canarose. As to the absolute configuration, these monosaccharides were believed to have D-forms based on their optical rotation values.

D-Cymarose: $[\alpha]_D^{24}$ +39° (c=0.59, 24 h after dissolution in H_2O). (lit: $[\alpha]_D^{21}$ +51.6° (c=1.02, H_2O)[19]).

D-Oleandrose: $[\alpha]_D^{21}$ −8.81° (c=1.47, 24 h after dissolution in H_2O). (lit: $[\alpha]_D$ −11° (c=1.1, H_2O)[20]).

D-Digitoxose: $[\alpha]_D^{24}$ +29° (c=0.37, 24 h after dissolution in H_2O). (lit: $[\alpha]_D^{26}$ +43.8° (c=0.71, H_2O)[21]).

D-Canarose: $[\alpha]_D^{24}$ +19° (c=0.18, 24 h after dissolution in H_2O). (lit: $[\alpha]_D^{21}$ +25° (c=1.4, H_2O)[22]).

Acid Hydrolysis of Compounds 1—26 Compounds **1**—**25** and **26** (*ca.* 0.5 mg) were dissolved in dioxane (80 μl) and 0.1 M H_2SO_4 (20 μl), respectively. The solution was heated at 60 °C for 1 h. After hydrolysis, this solution was neutralized with an Amberlite IRA-60E column, and the eluate was concentrated to dryness. The residues from **1**—**26** were partitioned between H_2O and EtOAc, and the EtOAc extract was analyzed using HPLC to identify the aglycone through a comparison with authentic samples. HPLC conditions: column, YMC-ODS 4.6 mm i.d.×25 cm; flow rate, 1.0 ml/min; 45% MeCN in water; t_R, 9.0 min (12-*O*-benzoylsarcostin (**1a**)), 10.8 min (12-*O*-benzoyldeacymetaplexigenin (**2a**)), 16.0 min (kidjolanin (**11a**)). 12-*O*-Benzoylsarcostin was detected from **1**, **3**, **5**, **6**, **9**, **12**, **17**, **20**, **21**, and **23**. Similarly, 12-*O*-benzoyldeacylmetaplexigenin and kidjolanin were identified from **2**, **4**, **7**, **8**, **10**, **13**, **18**, **22**, **24**, **26** and **11**, **15**, **19**, **25**, respectively. Detection of the aglycones of compounds **14** and **16** could not be performed without authentic samples.

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, digitoxitol acetate, and canaritol acetate were detected by GC. GC conditions: column, Supelco SP-2380™ capillary column 0.25 mm×30 m; carrier gas, N_2; column temperature 200 °C; t_R, 6.8 min (cymaritol acetate), 7.6 min (oleandritol acetate), 9.6 min (digitoxitol acetate), 10.7 min (canaritol acetate). Cymaritol acetate was detected from **17**—**25** and **26**. Canaritol acetate was found in **5**—**11**, **20**, **21** and **22**. Oleandritol acetate and digitoxitol acetate were observed in all compounds.

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