Acylated-Oxypregnane Glycosides from the Roots of *Asclepias syriaca*

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Twenty new pregnane glycosides were obtained from the roots of *Asclepias syriaca* L. (Asclepiadaceae). These glycosides were confirmed to contain ikemagenin, 12-*O*-nicotinoyllineolon, 5α,6-dihydroikemagenin, and 12-*O*-tigloylisolineolon, as their aglycones, using both spectroscopic and chemical methods.

Key words *Asclepias syriaca* L.; Asclepiadaceae; syriacoside; acylated-oxypregnane glycoside; 2,6-dideoxyhexopyranose

Asclepias syriaca L. is a plant indigenous to North America and distributed widely. The monarch butterfly (*Danaus plexippus* L.) feeds on the *Asclepias* genus for protection from vertebrate predators.[1] *Asclepias* species are known to contain many kinds of cardenolides and their glycosides.[2—9] *A. syriaca* has also been reported to contain these compounds.[10—12] We have previously studied cardenolides and their glycosides.[13] But, until now, there have been no reports about pregnane glycosides from *A. syriaca*. Pregnane glycosides are considered characteristic of *Asclepias* species.[14—18] Accordingly, we started an investigation of pregnane glycosides and found twenty new 12-*O*-acylated-oxypregnane glycosides in the roots of *A. syriaca*. The present paper describes the isolation and structural determination of these new pregnane glycosides.

A MeOH extract from the dried roots of *A. syriaca* was suspended in water. The suspension was extracted with diethyl ether and partitioned into an ether-soluble fraction, a water-soluble fraction and an ether–water emulsified fraction. The residues of these fractions were chromatographed on a silica gel column to give fractions of acylated-oxypregnane glycosides from which twenty new compounds were obtained along with seven known compounds. The structural determination of the known compounds **7**, **10**, **12**, **13**, **18**, **23**, and **27** was made based on comparisons of NMR spectral data with data in the literature.[16,17,19]

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 afforded aglycones were identified as ikemagenin (**1a**),[19,20] 5α,6-dihydroikemagenin (**20a**),[17] and 12-*O*-tigloylisolineolon (**21a**),[17] in view of the ^{1}H- and ^{13}C-NMR spectral 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.

Compound **1** was suggested to have the molecular formula $C_{47}H_{70}O_{16}$ based on high resolution (HR)-FAB-MS [*m/z*: 791.3992 $[M+Na]^+$]. In the ^{1}H- and ^{13}C-NMR spectra of **1**, two anomeric proton and carbon signals were observed at δ 5.50, 4.81 and δ 96.4, 101.6, 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 (−2.2 ppm), C-3 (+6.1 ppm), C-4 (−4.1 ppm)].[21] Thus, **1** was glycosylated at the C-3 position, and was considered to be ikemagenin 3-*O*-diglycoside. Moreover, 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, 2.5 Hz). 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 of each sugar in **1**. ROEs were found between δ 5.50 (H-1′ of β-D-digitoxopyranose) and 3.89 (H-3 of the aglycone), and δ 4.81 (H-1″ of β-D-oleandropyranose) and 3.56 (H-4′ of β-D-digitoxopyranose). Thus, **1** was established to be ikemagenin 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-digitoxopyranoside, and named syriacoside A.

The compounds **2**—**6**, **8**, **9**, **11**, **14**—**17**, **19**—**22**, **24**, **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.

HR-FAB-MS showed the molecular formula of **2** to be $C_{50}H_{72}O_{15}$, suggesting that it was larger by one hexose unit than **1**. Because the ^{1}H- and ^{13}C-NMR spectra of **2** showed three anomeric proton and carbon signals at δ 5.47, 5.18, and 4.76 and δ 96.4, 99.7, and 102.2, respectively, along with signals due to **1a**, **2** was indicated to be ikemagenin 3-*O*-triglycoside. Acid hydrolysis of **2** afforded digitoxose, cymarose, and oleandrose with **1a**. Thus, the sugar moiety of **2** consisted of one β-D-digitoxopyranose, one β-D-cymaropyranose, and one β-D-oleandropyranose. In the ^{1}H-NMR spectrum, the characteristic H-3 signals of β-D-digitoxopyranose and β-D-cymaropyranose were observed at δ 4.64 (1H, br s) and 4.06 (1H, q, J=3.0 Hz), respectively. In consideration of the result of ^{1}H–^{1}H shift correlation spectroscopy (COSY) experiment, the signals at δ 5.47 and 5.18 were assigned to the anomeric protons of β-D-digitoxopyranose and β-D-cymaropyranose, and the remaining signal at δ 4.76 was assigned to the anomeric proton of β-D-oleandropyranose. The ROE difference spectra irradiating at the anomeric protons exhibited ROEs between δ 5.47 (H-1′ of β-D-digitoxopyranose) and 3.87 (H-3 of the aglycone), δ 5.18 (H-1″ of β-D-cymaropyranose) and 3.51 (H-4′ of β-D-digitoxopyranose), and δ 4.76 (H-1‴ of β-D-oleandropyranose) and 3.45 (H-4″ of β-D-cymaropyranose). On comparison of the ^{13}C-NMR spectral data of the sugar moiety of **2** with those of **1**, the signals due to the terminal β-D-oleandropyranosyl group were observed. Therefore, **2** was determined as ikemagenin 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-

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β-D-digitoxopyranoside, and named syriacoside B.

The molecular formula of both **3** and **4** was $C_{50}H_{72}O_{15}$ from measurements of HR-FAB-MS, the same as **2**. The ^{1}H- and ^{13}C-NMR data suggested these compounds to be ikemagenin 3-*O*-triglycosides. Acid hydrolysis yielded digitoxose, oleandrose, and cymarose from **3**, and digitoxose and cymarose from **4** together with **1a**. Comparison of the ^{13}C-NMR spectral data for **3** with those for curassavioside I_1[18] and **1** revealed the presence of a terminal β-D-cymaropyranose and glycosylation shifts around the C-4″ position of the β-D-oleandropyranosyl group [C-3″ (−2.4 ppm), C-4″ (+6.5 ppm), C-5″ (−1.2 ppm)]. Thus, the sugar sequence of **3** was indicated to be 3-*O*-β-D-cymaropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-digitoxopyranoside, which was confirmed in the ROE difference experiment irradiating each anomeric proton. Namely, ROEs were observed between δ 4.93 (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), and δ 4.87 (H-1‴ of β-D-cymaropyranose) and 3.16 (H-4″ of β-D-oleandropyranose). From the observation of two signals due to the methoxyl group (δ 3.62, 3.46) in the ^{1}H-NMR spectrum of **4** and the result of acid hydrolysis, the sugar moiety of **4** was composed of one β-D-digitoxopyranose and two β-D-cymaropyranoses. ROEs were observed between δ 5.27 (H-1′ of β-D-cymaropyranose) and 3.85 (H-3 of the aglycone), δ 5.32 (H-1″ of β-D-digitoxopyranose) and 3.53 (H-4′ of β-D-cymaropyranose), and δ 5.12 (H-1‴ of β-D-cymaropyranose) and 3.46 (H-4″ of β-D-digitoxopyranose). Thus, the sugar sequence of **4** was established to be 3-*O*-β-D-cymaropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-cymaropyranoside. **3** and **4** are shown in Chart 1, and were named syriacoside C and D, respectively.

HR-FAB-MS showed the molecular formula of compounds **5** and **6** to be $C_{50}H_{72}O_{15}$ and $C_{51}H_{74}O_{15}$, respectively. The ^{1}H- and ^{13}C-NMR data suggested these compounds were also ikemagenin 3-*O*-triglycosides. Acid hydrolysis yielded canarose and oleandrose from **5**, and oleandrose from **6**, together with **1a**. The sugar moieties consisted of one β-D-canaropyranose and two β-D-oleandropyranoses in **5**, and three β-D-oleandropyranoses in **6**. The assignment of the signals due to the sugar moieties was carried out based on the results of COSY and homonuclear Hartmann-Hahn (HOHAHA) experiments irradiating each anomeric proton, and sugar sequences were determined based on the observations of ROEs. ROEs were observed between δ 4.59 (H-1′ of β-D-canaropyranose) and 3.57 (H-3 of the aglycone), δ 4.45 (H-1″ of β-D-oleandropyranose) and 2.96 (H-4′ of β-D-canaropyranose), and δ 4.70 (H-1‴ of β-D-oleandropyranose) and 3.22 (H-4″ of β-D-oleandropyranose) in **5**, and δ 4.53 (H-1′ of β-D-oleandropyranose) and 3.56 (H-3 of the aglycone), δ 4.67 (H-1″ of β-D-oleandropyranose) and 3.17 (H-4′ of β-D-oleandropyranose), and δ 4.72 (H-1‴ of β-D-oleandropyranose) and 3.18 (H-4″ of β-D-oleandropyranose) in **6**. Thus, compounds **5** and **6** were identified as shown in Chart 1, and named syriacoside E and F, respectively.

The molecular formula of compound **8** was suggested to be $C_{57}H_{84}O_{20}$ based on HR-FAB-MS. On the basis of observation of four anomeric proton and carbon signals at δ 5.28, 5.12×2, and 4.69 and at δ 96.5, 100.5, 101.9, and 104.5 with the signals due to **1a**, in the ^{1}H- and ^{13}C-NMR spectra of **8**, **8** was considered to be ikemagenin 3-*O*-tetraglycoside. The NMR spectral data of the sugar moiety in **8** were consistent with those of cynanchoside D_2,[22] so **8** was proposed to possess the same sugar sequence as cynanchoside D_2. Hence, **8** was elucidated to be ikemagenin 3-*O*-β-D-glucopyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside, and named syriacoside G.

HR-FAB-MS showed the molecular formula of compound **9** to be $C_{56}H_{82}O_{18}$, which was smaller by CH_2 than **10**. The ^{1}H- and ^{13}C-NMR spectra revealed that **9** was also ikemagenin 3-*O*-tetraglycoside. On acid hydrolysis, **9** afforded digitoxose, cymarose and oleandrose together with **1a**, and two methoxyl proton signals were observed at δ 3.58 and 3.47 in the ^{1}H-NMR spectrum. Thus, the sugar moiety of **9** consisted of two β-D-digitoxopyranoses, one β-D-cymaropyranose, and one β-D-oleandropyranose. Comparison of the ^{1}H- and ^{13}C-NMR spectral data of **9** with those of **10** and **2** suggested the sugar sequence to be 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-digitoxopyranoside, which was confirmed by the ROE difference experiment. ROEs were observed between δ 5.46 (H-1′ of β-D-digitoxopyranose) and 3.87 (H-3 of the aglycone), δ 5.37 (H-1″ of β-D-digitoxopyranose) and 3.57 (H-4′ of β-D-digitoxopyranose), δ 5.15 (H-1‴ of β-D-cymaropyranose) and 3.44 (H-4″ of β-D-digitoxopyranose) and δ 4.76 (H-1⁗ of β-D-oleandropyranose) and 3.46 (H-4‴ of β-D-cymaropyranose). Thus, **9** was identified as shown in Chart 1, and named syriacoside H.

The molecular formula of compound **11** was suggested to be $C_{57}H_{84}O_{18}$ based on HR-FAB-MS. The ^{1}H- and ^{13}C-NMR spectra of **11** were similar to those of **10**, but with a terminal β-D-cymaropyranosyl group instead of the β-D-oleandropyranosyl group. Thus, the sugar sequence of **11** was presumed to be 3-*O*-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-cymaropyranoside. ROEs were revealed between δ 5.27 (H-1′ of β-D-cymaropyranose) and 3.84 (H-3 of the aglycone), δ 5.31 (H-1″ of β-D-digitoxopyranose) and 3.52 (H-4′ of β-D-cymaropyranose), δ 5.15 (H-1‴ of β-D-cymaropyranose) and 3.45 (H-4″ of β-D-digitoxopyranose) and δ 5.07 (H-1⁗ of β-D-cymaropyranose) and 3.43 (H-4‴ of β-D-cymaropyranose). These results supported the above sugar sequence. This compound was named syriacoside I.

HR-FAB-MS revealed the molecular formula of compound **14** to be $C_{55}H_{83}NO_{18}$. Based on acid hydrolysis, and the ^{1}H- and ^{13}C-NMR spectral data, this compound was identified as 12-*O*-nicitinoyllineolon 3-*O*-β-D-cymaropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside, a sugar sequence reported previously.[16,19] This compound was named syriacoside J.

The molecular formula of both **15** and **16** was shown to be $C_{58}H_{86}O_{18}$ based on HR-FAB-MS. Acid hydrolysis, and the ^{1}H- and ^{13}C-NMR spectra revealed these compounds to also be ikemagenin 3-*O*-tetraglycosides, their sugar sequences composed of two β-D-cymaropyranoses and two β-D-oleandropyranoses. In the ROE difference experiment, ROEs were observed between δ 4.85 (H-1′ of β-D-cymaropyranose) and 3.56 (H-3 of the aglycone), δ 4.44 (H-1″ of β-D-oleandropyranose) and 3.22 (H-4′ of β-D-cymaropyranose), δ 4.95 (H-1‴ of β-D-cymaropyranose) and 3.18 (H-4″ of β-D-oleandropyranose), and δ 4.50 (H-1⁗ of β-D-oleandropyranose)

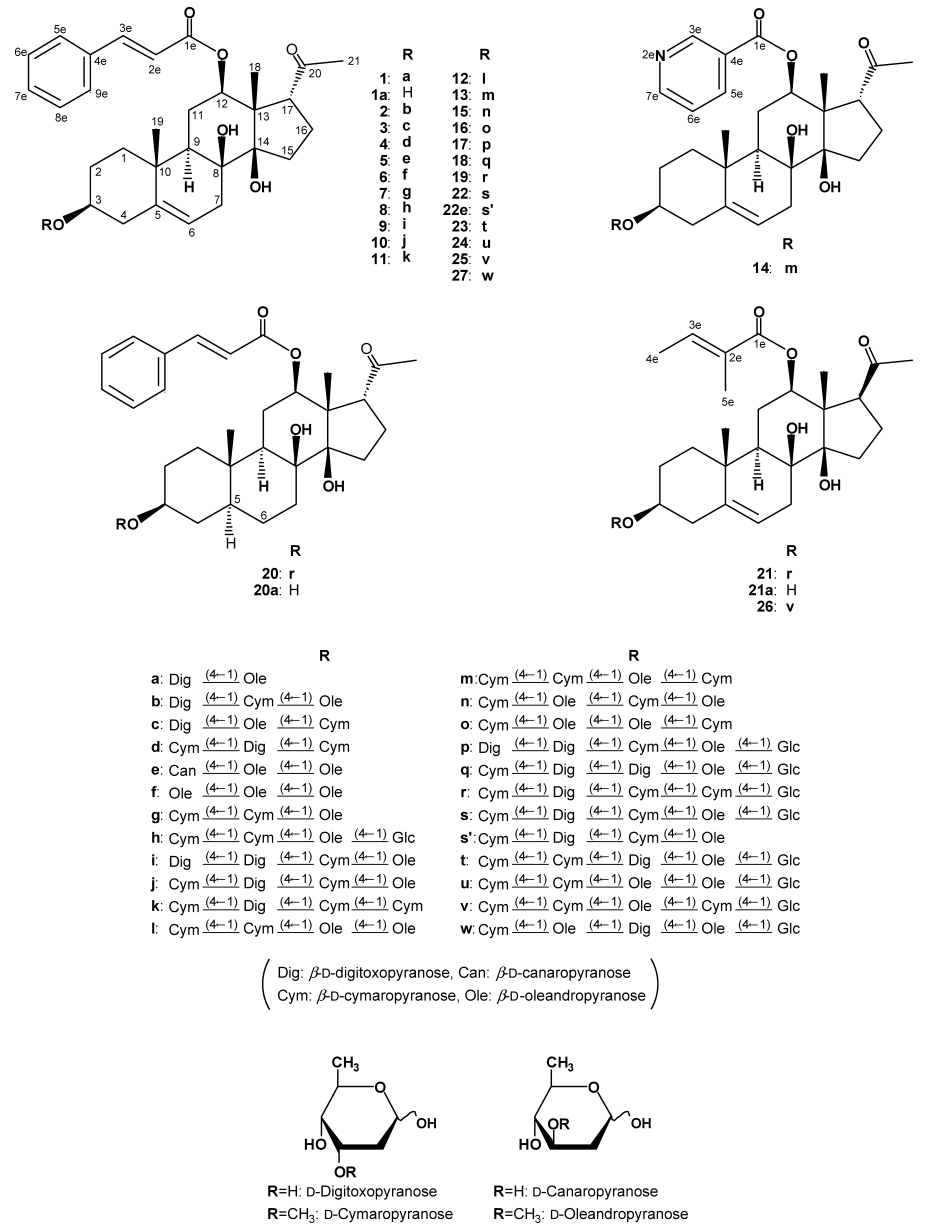

Chart 1. Structures of Compounds **1**—**27**

and 3.24 (H-4‴ of β-D-cymaropyranose). Thus, **15** was identified as ikemagenin 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranoside. The ^{1}H- and ^{13}C-NMR spectra of **16** showed the presence of a terminal β-D-cymaropyranosyl group in its sugar sequence, and glycosylation shifts around the C-4‴ position of β-D-oleandropyranose [C-3‴ (−1.7 ppm), C-4‴ (+6.9 ppm), C-5‴ (−0.7 ppm)] in comparison with cynanchogenin 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranoside.[19] Thus, the structure of **16** was elucidated to be ikemagenin 3-*O*-β-D-cymaropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranoside, which was confirmed by the ROE difference experiment irradiating each anomeric proton signal. These compounds were named syriacoside K and L, respectively.

The ^{1}H- and ^{13}C-NMR spectra of **17** showed the presence of a terminal β-D-glucopyranosyl group. Enzymatic hydrolysis of **17** afforded **9**, and a glycosylation shift was observed around the C-4⁗ position of β-D-oleandropyranose on comparison of the ^{13}C-NMR spectral data of **17** with those of **9** [C-3⁗ (−2.1 ppm), C-4⁗ (+6.8 ppm), C-5⁗ (−0.9 ppm)]. Therefore, this terminal β-D-glucopyranosyl group was attached at the C-4⁗ position of β-D-oleandropyranose, and the ROE difference experiment irradiating the anomeric proton of this β-D-glucopyranosyl group supported this linkage. From the above results, **17** was determined as shown in Chart 1, and named syriacoside M.

HR-FAB-MS revealed the molecular formula of compounds **19**—**21** to be $C_{63}H_{94}O_{23}$, $C_{63}H_{96}O_{23}$, and $C_{59}H_{94}O_{23}$, respectively. Based on the ^{1}H- and ^{13}C-NMR spectral data for the sugar moieties of **19**—**21**, these compounds were considered to have the same sugar sequences, which included a terminal β-D-glucopyranosyl group. The aglycone moieties of **19**—**21** were suggested to be **1a**, **20a**, and **21a**, according to their ^{13}C-NMR spectral data and acid hydrolysis. On the

basis of the production of **11** from **19** by enzymatic hydrolysis, observation of the glycosylation shifts around the C-4‴ position of β-D-cymaropyranose on comparison of the ^{13}C-NMR spectral data of **19** with those of **11** [C-3‴ (−0.8 ppm), C-4‴ (+8.9 ppm), C-5‴ (−1.6 ppm)], and observation of an ROE between the anomeric proton of the terminal β-D-glucopyranosyl group [δ 4.93 (1H, d, J=8.0 Hz)] and H-4‴ of β-D-cymaropyranosyl group [δ 3.65 (1H, dd, J=9.5, 3.0 Hz)], the structure of **19** was determined as shown in Chart 1. Compounds **20** and **21** are also described in Chart 1. Compounds **19**—**21** were named syriacoside N, O, and P, respectively.

The molecular formula of compound **22** was considered to be $C_{63}H_{94}O_{23}$ based on HR-FAB-MS. Compound **22e** obtained from **22** by enzymatic hydrolysis was found to be identical to ikemagenin 3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-cymaropyranoside[17] by HPLC with an authentic sample. The observation of an ROE between δ 5.11 (H-1‴ of the terminal β-D-glucopyranose) and δ 3.71 (H-4‴ of β-D-oleandropyranose), and glycosylation shifts around the C-4‴ position of β-D-oleandropyranosyl group [C-3‴ (−2.0 ppm), C-4‴ (+6.8 ppm), C-5‴ (−0.9 ppm)] revealed the terminal β-D-glucopyranosyl group to be linked at C-4‴ of β-D-oleandropyranose, the same as **17**. Thus, **22** was identified as shown in Chart 1, and named syriacoside Q.

Compounds **24**—**26** were elucidated to have the molecular formula $C_{64}H_{96}O_{23}$, $C_{64}H_{96}O_{23}$, and $C_{60}H_{96}O_{23}$, respectively, based on HR-FAB-MS. The ^{1}H- and ^{13}C-NMR spectra showed the aglycone moieties to be **1a** on **24** and **25**, and **21a** on **26**. The sugar moieties of **24**—**26** were identified as shown in Chart 1, according to the consistency of the ^{1}H- and ^{13}C-NMR spectral data of these compounds with those of previously reported ones.[14,23] Thus, **24**—**26** were identified as described in Chart 1, and named syriacoside R, S, and T, respectively.

A. syriaca has been found to contain many kinds of acylated-oxypregnane glycosides along with cardenolide glycosides. Recently, it was reported that a 12-tigloyl pregnane glycoside named P57AS3 from *Hoodia gordonii* in Asclepiadaceous plants acts as an appetite suppressant.[24] Because similar oxypregnane glycosides have been discovered in this plant, we are interested in not only the toxicity of cardenolide glycosides, but also the biological activities including the appetite-suppressing effects of these 12-tigloyl oxypregnane glycosides.

Experimental

General Procedures The instrumental analysis was carried out as described previously.[25]

Plant Material The roots of *Asclepias syriaca* L. (No. 2380M) were collected from the botanical garden of the University of Shizuoka in Japan in September, 1998 and identified by Prof. T. Noro. These dried materials were stored in a herbarium.

Extraction and Isolation The dried roots of *Asclepias syriaca* L. (1.15 kg) 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 diethyl ether, which was partitioned into three fractions: an ether-soluble fraction, a water-soluble fraction, and an ether–water emulsified fraction. The ether and ether–water emulsified fractions were evaporated dry, and the total residue (33.3 g) was subjected to silica gel CC with a $CHCl_3$–MeOH (98 : 2—8 : 2) system to obtain five fractions (A (7.71 g), B (2.70 g), C (3.23 g), D (2.81 g) and E (3.17 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: 51—67.5% MeCN in water and 75—82.5% MeOH in water), fractions B (2.15 g) and D (2.21 g) afforded compounds **1** (6 mg), **2** (13 mg), **3** (4 mg), **4** (11 mg), **5** (6 mg), **6** (6 mg), **7** (11 mg), **9** (10 mg), **10** (8 mg), **11** (8 mg), **12** (36 mg), **13** (15 mg), **14** (6 mg), **15** (6 mg), **16** (6 mg), **17** (7 mg), **18** (8 mg), **19** (21 mg), **20** (6 mg), **21** (11 mg), **22** (6 mg), **23** (6 mg), **24** (3 mg), **25** (18 mg), **26** (6 mg), and **27** (6 mg). The water-soluble fraction of the MeOH extract was passed through a porous polymer gel (Mitsubishi Diaion HP-20) column and the absorbed material was eluted with MeOH–H_2O (1 : 1), MeOH–H_2O (7 : 3) and MeOH, respectively. The MeOH fraction from the column was then evaporated dry, and the residue (13.9 g) was subjected to silica gel CC with a $CHCl_3$–MeOH (98 : 2—8 : 2) system to obtain five fractions (A′ (2.45 g), B′ (3.05 g), C′ (2.32 g), D′ (3.57 g) and E′ (1.24 g)). Using semi-preparative HPLC (Develosil-ODS-15/30 50 mm i.d.×100 cm, Develosil-PhA 20 mm i.d.×25 cm, and YMC-ODS 20 mm i.d.×25 cm: 45—55% MeCN in water and 80% MeOH in water), fraction B′ (2.15 g) afforded compounds **8** (4 mg), **17** (21 mg), **18** (9 mg), **19** (12 mg), **22** (7 mg), and **26** (8 mg).

Syriacoside A (**1**): Amorphous powder. $[\alpha]_D^{22}$ −5.0° (c=0.62, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.18), 222 (4.12), 278 (4.35). FAB-MS m/z: 791 $[M+Na]^+$. HR-FAB-MS m/z: 791.3992 (Calcd for $C_{43}H_{60}O_{12}Na$: 791.3982). ^{13}C-NMR: shown in Tables 1 and 2. ^{1}H-NMR data of the aglycone and ester moieties (pyridine-d_5 at 35 °C) δ: 7.98 (1H, d, 16.0, H-3e), 7.62 and 7.34 (5H, m, H-5e—9e), 6.78 (1H, d, 16.0, H-2e), 5.30 (1H, br s, H-6), 5.26 (1H, dd, 11.5, 4.0, H-12), 3.89 (1H, m, H-3), 2.28 (3H, s, H-21), 2.01 (3H, s, H-18), 1.35 (3H, s, H-19). ^{1}H-NMR data of the sugar moiety (pyridine-d_5 at 35 °C) δ: 5.50 (1H, dd, 9.5, 2.5, H-1′), 4.81 (1H, dd, 9.5, 2.5, H-1″), 4.67 (1H, br s, H-3′), 4.34 (1H, dq, 9.5, 6.0, H-5′), 3.59 (1H, dq, 9.0, 6.0, H-5″), 3.56 (1H, dd, 9.5, 3.0, H-4′), 3.46 (3H, s, C-3-OMe), 1.51 (6H, d, 6.0, H-6′, H-6″).

Syriacoside B (**2**): Amorphous powder. $[\alpha]_D^{22}$ +6.1° (c=1.09, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.16), 222 (4.09), 278 (4.33). FAB-MS m/z: 935

Table 1. ^{13}C-NMR Data for the Aglycone and Ester Moieties of Compounds **1**, **14**, **20**, and **21**

Carbon No.	**1**	**14**	**20**	**21**
Aglycone moieties				
1	39.0	39.0	38.1	39.0
2	29.9	29.9	29.6	29.9
3	77.7	77.7	76.7	77.7[a]
4	39.3	39.3	35.0	39.3
5	139.5	139.5	45.4	139.2
6	119.2[a]	119.2	25.2	119.4
7	35.2	35.2	34.6	35.9
8	74.6	74.5	76.5	74.3
9	44.8	44.7	47.5	45.1
10	37.6	37.6	36.6	37.6
11	25.0	25.0	24.0	24.7[b]
12	73.4	74.3	73.9	77.6[a]
13	55.9	56.1	56.3	55.0
14	87.5	87.5	87.5	86.6
15	34.2	34.2	33.9	36.7
16	22.6	22.2	22.4	24.6[b]
17	60.6	60.2	60.4	59.2
18	15.8	15.8	16.2	12.6
19	18.2	18.2	13.1	18.4
20	209.3	209.8	209.4	214.3
21	32.2	32.4	32.3	31.6
Ester moieties				
1e	165.9	164.5	165.9	167.8
2e	119.4[a]	—	119.4	129.4
3e	144.8	153.8	144.8	137.7
4e	135.1	127.0	135.1	12.3
5e	128.6	137.1	128.5	14.3
6e	129.3	[c]	129.3	—
7e	130.6	151.1	130.5	—
8e	129.3	—	129.3	—
9e	128.6	—	128.5	—

Measured in pyridine-d_5 at 35 °C. *a*, *b*) Signal assignments may be interchanged in each column. *c*) Overlapping with the pyridine-d_5 signals.

Table 2. ^{13}C-NMR Data for the Sugar Moieties of Compounds **1**—**6**, **8**, **9**, **11**, **13**, **15**—**17**, **19**, **22**, **24**, and **26**

Carbon No.	**1**	**2**	**3**	**4**	**5**	**6**	**8**	**9**	**11**	**14**	**15**	**16**	**17**	**19**	**22**	**24**	**25**
	Dig	Dig	Dig	Cym	Can	Ole	Cym	Dig	Cym	Cym	Cym	Cym	Dig	Cym	Cym	Cym	Cym
1′	96.4	96.4	96.4	96.4	98.2	98.1	96.5	96.4	96.4	96.5	96.4	96.4	96.4	96.4	96.4	96.5	96.5
2′	39.2	39.0	39.2	37.3	40.2	37.9[a]	37.5[a]	39.1[a]	37.3	37.3[a]	37.3[a]	37.2	39.1[a]	37.3	37.4[a]	37.3[a]	37.2[a]
3′	67.6	67.5	67.6	78.1	70.1	79.4[b]	78.0[b]	67.5[b]	78.1	78.0[b]	78.0[b]	77.9	67.5[b]	78.0	78.1	78.0[b]	78.0[b]
4′	83.7	83.4	83.7	83.1	88.5	83.2[c]	83.4[c]	83.5	83.4	83.4	83.5[c]	83.5	83.5[c]	83.4	83.4[b]	83.4[c]	83.4[c]
5′	68.6	68.6	68.5	69.1	70.9	71.8[d]	69.1[d]	68.7[c]	69.2[a]	69.1[c]	69.3[d]	69.0	68.7[d]	69.1	69.1	69.1[d]	68.9[d]
6′	18.7[a]	18.7[a]	18.7[a]	18.5[a]	18.2	18.7[e]	18.6[e]	18.7[d]	18.6[b]	18.6[d]	18.7[e]	18.7[a]	18.7[e]	18.6[a]	18.6[c]	18.7[e]	18.6[e]
	Ole	Cym	Ole	Dig	Ole	Ole	Cym	Dig	Dig	Cym	Ole	Ole	Dig	Dig	Dig	Cym	Cym
1″	101.6	99.7	101.1	100.5	101.2	100.2[f]	100.5	99.8	100.5	100.5	102.0[f]	102.0	99.8[f]	100.5[b]	100.5	100.5	100.5
2″	37.0	37.2	37.4	38.9	37.3	37.8[a]	37.3[a]	38.6[a]	38.9	37.1[a]	37.8	37.8[b]	38.5[a]	38.8	38.8	37.0[a]	37.0[a]
3″	81.4	77.8	79.0[b]	67.4	78.9	79.3[b]	77.7[b]	67.4[b]	67.4	77.8[b]	78.9	79.2[c]	67.4[b]	67.5	67.5	77.8[b]	77.8[b]
4″	76.2	83.1	82.7	83.4	82.3	83.0[c]	83.3[c]	83.1[e]	83.1	83.2	82.7	83.0	83.3[c]	83.1[c]	83.3[b]	83.4[c]	83.2[c]
5″	73.0	69.1	71.8	68.6	71.9	71.6[d]	68.9[d]	68.6[c]	68.5	68.9[c]	71.8	71.7[d]	68.6[d]	68.5	68.5	68.9[d]	69.1[d]
6″	18.6[a]	18.7[a]	18.7[a]	18.8[a]	18.6[a]	18.8[e]	18.5[e]	18.7[d]	18.5[b]	18.7[d]	18.6[e]	18.8[a]	18.5[e]	18.4[a]	18.4[c]	18.9[e]	18.7[e]
		Ole	Cym	Cym	Ole	Ole	Ole	Cym	Cym	Ole	Cym	Ole	Cym	Cym	Cym	Ole	Ole
1‴	—	102.2	98.5	99.8	100.2	100.3[f]	101.9	99.8	99.8	102.0	98.5	100.1	99.7[f]	99.8	99.8	101.9	101.9
2‴	—	36.7	35.9	35.7	37.3	37.4	37.1[a]	37.2	36.7	37.7	37.2[a]	37.7[b]	36.8	36.8	37.3[a]	37.7	37.7
3‴	—	81.4	78.9[b]	78.8	81.6	81.7	79.3	77.8	77.9	78.9[d]	77.9[b]	79.1[c]	77.7	77.9	77.7	79.0	78.8
4‴	—	76.2	74.2	74.1	76.3	76.4	83.2[c]	83.0[e]	83.1	82.7	83.3[c]	82.8	83.1[c]	83.0[c]	83.1[b]	82.7	82.6
5‴	—	73.0	71.3	71.0	73.0	73.0	72.1	69.1	69.1[a]	71.8	69.0[d]	71.6[d]	69.1	69.1	69.1	72.2[f]	71.8[f]
6‴	—	18.5[a]	19.0[a]	18.6[a]	18.4[a]	18.8[e]	18.9[e]	18.5[d]	18.4[b]	18.5[d]	18.6[e]	18.7[a]	18.9[e]	18.6[a]	18.9[c]	18.6[e]	18.5[e]
							Glc	Ole	Cym	Cym	Ole	Cym	Ole	Cym	Ole	Ole	Cym
1⁗	—	—	—	—	—	—	104.5	102.2	100.5	98.5	102.2[f]	98.6	101.9	100.4[b]	101.9	100.0	98.3
2⁗	—	—	—	—	—	—	75.7	36.8	35.9	35.9	37.0[a]	35.9	37.4	36.8	36.8	37.5[a]	36.8
3⁗	—	—	—	—	—	—	78.7	81.4	78.8	79.0[d]	81.4	79.0[c]	79.3	78.0	79.4	79.6	78.2[b]
4⁗	—	—	—	—	—	—	72.1	76.2	74.1	74.2	76.3	74.2	83.0[c]	83.0[c]	83.0[b]	83.2[c]	83.2[c]
5⁗	—	—	—	—	—	—	78.1	73.0	71.0	71.3	73.0	71.2	72.1	69.4	72.1	71.6[f]	69.7
6⁗	—	—	—	—	—	—	63.2	18.5[d]	19.0[b]	19.0[d]	18.6[e]	19.0[a]	18.4[e]	18.5[a]	18.5[c]	18.5[e]	18.7[e]
													Glc	Glc	Glc	Glc	Glc
1⁗′	—	—	—	—	—	—	—	—	—	—	—	—	104.5	106.6	104.5	104.5	106.6
2⁗′	—	—	—	—	—	—	—	—	—	—	—	—	75.7	75.4	75.7	75.7	75.4
3⁗′	—	—	—	—	—	—	—	—	—	—	—	—	78.7	78.4	78.7	78.7	78.4
4⁗′	—	—	—	—	—	—	—	—	—	—	—	—	72.1	71.9	72.1	72.1[f]	71.9[f]
5⁗′	—	—	—	—	—	—	—	—	—	—	—	—	78.1	78.4	78.1	78.0	78.4
6⁗′	—	—	—	—	—	—	—	—	—	—	—	—	63.2	63.1	63.2	63.2	63.2
OMes	57.0	58.9	58.0	58.9	57.4	57.3×2	59.0	58.9	58.9	58.9×2	58.9	58.8	59.0	59.0	59.0	58.9×2	58.9×2
	—	57.0	57.3	58.1	57.0	57.0	58.9	57.0	58.8	58.0	58.8	58.0	57.2	58.9	58.9	57.3	58.6
	—	—	—	—	—	—	57.2	—	58.2	57.3	57.4	57.4×2	—	58.8	57.2	57.1	57.4
	—	—	—	—	—	—	—	—	—	—	57.0	—	—	—	—	—	—

Measured in pyridine-d_5 at 35 °C. *a*—*f*) Signal assignments may be interchanged in each column. Dig: β-D-digitoxopyranose, Ole: β-D-oleandropyranose, Cym: β-D-cymaropyranose, Can: β-D-canaropyranose, Glc: β-D-glucopyranose.

$[M+Na]^+$. HR-FAB-MS *m/z*: 935.4774 (Calcd for $C_{50}H_{72}O_{15}Na$: 935.4769). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety (pyridine-d_5 at 35 °C) δ: 5.47 (1H, dd, 9.5, 2.0, H-1′), 5.18 (1H, dd, 9.5, 2.0, H-1″), 4.76 (1H, dd, 9.5, 2.0, H-1‴), 4.64 (1H, br s, H-3′), 4.29 (1H, dq, 9.5, 6.5, H-5′), 4.20 (1H, dq, 9.5, 6.5, H-5″), 4.06 (1H, q, 3.0, H-3″), 3.58 (3H, s, C-3″-OMe), 3.51 (1H, dd, 9.5, 3.0, H-4′), 3.47 (3H, s, C-3‴-OMe), 3.45 (overlapping, H-4″), 1.57 (3H, d, 6.0, H-6‴), 1.44 (3H, d, 6.5, H-6′), 1.36 (3H, d, 6.5, H-6″). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were consistent with those of **1**.

Syriacoside C (**3**): Amorphous powder. $[\alpha]_D^{22}$ +13.5° (*c*=0.34, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.22), 222 (4.15), 277 (4.37). FAB-MS *m/z*: 935 $[M+Na]^+$. HR-FAB-MS *m/z*: 935.4794 (Calcd for $C_{50}H_{72}O_{15}Na$: 935.4769). ^{13}C-NMR: shown in Table 2. ^{13}C-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 100.3 (C-1″), 98.2 (C-1‴), 95.9 (C-1′), 82.8 (C-4′), 82.1 (C-4″), 78.8 (C-3″), 77.6 (C-3‴), 72.5 (C-4‴), 71.4 (C-5″), 71.1 (C-5‴), 68.0 (C-5′), 66.6 (C-3′), 57.1 (C-3‴-OMe), 56.8 (C-3″-OMe), 37.1 (C-2′), 36.3 (C-2″), 33.9 (C-2‴), 18.4, 18.3, 18.2 (C-6′, C-6″, C-6‴). ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.93 (1H, dd, 9.5, 2.0, H-1′), 4.87 (1H, dd, 9.5, 2.0, H-1‴), 4.50 (1H, dd, 9.5, 2.0, H-1″), 4.22 (1H, br s, H-3′), 3.80 (1H, dq, 9.5, 6.5, H-5′), 3.61 (1H, dq, 9.5, 6.5, H-5‴), 3.43, 3.42 (each 3H, s, C-3″-OMe, C-3‴-OMe), 3.33 (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″), 1.30 (3H, d, 6.5, 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 spectral data of the aglycone and ester moieties were consistent with those of **1**.

Syriacoside D (**4**): Amorphous powder. $[\alpha]_D^{22}$ +27.9° (*c*=1.05, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.15), 222 (4.08), 279 (4.32). FAB-MS *m/z*: 935 $[M+Na]^+$. HR-FAB-MS *m/z*: 935.4795 (Calcd for $C_{50}H_{72}O_{15}Na$: 935.4769). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety (pyridine-d_5 at 35 °C) δ: 5.32 (1H, dd, 9.5, 2.0, H-1″), 5.27 (1H, dd, 9.5, 2.0, H-1′), 5.12 (1H, dd, 9.5, 2.0, H-1‴), 4.61 (1H, br s, H-3″), 4.26 (1H, dq, 9.5, 6.5, H-5″), 4.22 (1H, dq, 9.5, 6.5, H-5′), 4.10 (overlapping, H-3′, H-5‴), 3.73 (1H, q, 3.0, H-3‴), 3.62 (3H, s, C-3′-OMe), 3.53 (1H, dd, 9.5, 3.0, H-4′), 3.46 (1H, dd, 9.5, 3.0, H-4″), 3.46 (3H, s, C-3‴-OMe), 1.46 (3H, d, 6.0, H-6‴) 1.40 (3H, d, 6.5, H-6″), 1.38 (3H, d, 6.5, H-6′). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were consistent with those of **1**.

Syriacoside E (**5**): Amorphous powder. $[\alpha]_D^{22}$ −18.3° (*c*=0.47, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.18), 222 (4.11), 278 (4.35). FAB-MS *m/z*: 935 $[M+Na]^+$. HR-FAB-MS *m/z*: 935.4791 (Calcd for $C_{50}H_{72}O_{15}Na$: 935.4769). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.70 (1H, dd, 9.5, 2.0, H-1‴), 4.59 (1H, dd, 9.5, 2.0, H-1′), 4.45 (1H, dd, 9.5, 2.0, H-1″), 3.60 (1H, m, H-3′), 3.43 (3H, s, C-3″-OMe), 3.43 (overlapping, H-5″), 3.40 (3H, s, C-3‴-OMe), 3.40 (overlapping, H-3″), 3.32 (1H, dq, 9.0, 6.0, H-5′), 3.31 (1H, dq, 9.5, 6.0, H-5‴), 3.22 (1H, t, 9.5, H-4″), 2.96 (1H, t, 9.0, H-4′), 1.35 (3H, d, 6.0, H-6‴), 1.34 (3H, d, 6.0, H-6″), 1.29 (3H, d, 6.0, H-6′). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were consistent with those of **1**.

Syriacoside F (**6**): Amorphous powder. $[\alpha]_D^{22}$ −16.9° (*c*=0.59, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.18), 223 (4.11), 279 (4.35). FAB-MS *m/z*: 949 $[M+Na]^+$. HR-FAB-MS *m/z*: 949.4967 (Calcd for $C_{51}H_{74}O_{15}Na$: 949.4925). ^{13}C-NMR: shown in Table 2. ^{13}C-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 100.2×2 (C-1″, C-1‴), 97.9 (C-1′), 82.6, 82.5 (C-4′, C-4″), 80.8 (C-3‴), 79.3, 79.4 (C-3′, C-3″), 75.5 (C-4‴), 71.7 (C-5‴), 71.1, 71.0 (C-5′, C-5″), 56.8, 56.6 (C-3′-OMe, C-3″-OMe), 56.3 (C-3‴-OMe), 36.6, 36.5 (C-2′, C-2″), 35.5 (C-2‴), 18.5, 18.4, 18.0 (C-6′, C-6″, C-6‴). ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.72 (1H, dd, 9.5, 2.0, H-1‴), 4.67 (1H, dd, 9.5, 2.0, H-1″), 4.53 (1H, dd, 9.5, 2.0, H-1′), 3.41, 3.40, 3.39 (each 3H, s, C-3′-OMe, C-3″-OMe, C-3‴-OMe), 3.33 (1H, dq, 9.0, 6.0, H-5″), 3.31 (2H, dq, 9.0, 6.0, H-5′, H-5‴), 3.18 (1H, t, 9.0, H-4″), 3.17 (1H, t, 9.0, H-4′), 3.15 (overlapping, H-4‴), 1.35, 1.30 (each 3H, d, 6.0, H-6′, H-6‴), 1.32 (3H, d, 6.0, H-6″). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were in good agreement with those of **1**.

Syriacoside G (**8**): Amorphous powder. $[\alpha]_D^{22}$ +12.0° (*c*=0.71, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.20), 222 (4.13), 277 (4.36). FAB-MS *m/z*: 1111 $[M+Na]^+$. HR-FAB-MS *m/z*: 1111.5477 (Calcd for $C_{57}H_{84}O_{20}Na$: 1111.5454). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety (pyridine-d_5 at 35 °C) δ: 5.28 (1H, dd, 9.5, 2.0, H-1′), 5.12 (1H, dd, 9.5, 2.0, H-1″), 5.12 (1H, d, 8.0, H-1⁗), 4.69 (1H, dd, 9.5, 2.0, H-1‴), 4.52 (1H, dd, 11.5, 2.5, H-6⁗), 4.34 (1H, dd, 11.5, 5.5, H-6⁗), 4.22 (overlapping, H-5′), 4.16 (1H, dq, 9.5, 6.5, H-5″), 4.09 (1H, q, 3.0, H-3′), 4.02 (1H, q, 3.0, H-3″), 3.95 (1H, m, H-5⁗), 3.72 (1H, t, 9.0, H-4⁗), 3.66 (overlapping, H-5‴), 3.62, 3.58 (each 3H, s, C-3′-OMe, C-3″-OMe), 3.53 (3H, s, C-3‴-OMe), 3.51 (overlapping, H-4′), 3.43 (1H, dd, 9.5, 3.0, H-4″), 1.71 (3H, d, 6.0, H-6‴), 1.40 (3H, d, 6.5, H-6′), 1.38 (3H, d, 6.5, H-6″). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were consistent with those of **1**.

Syriacoside H (**9**): Amorphous powder. $[\alpha]_D^{22}$ +11.4° (*c*=0.87, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.12), 222 (4.05), 278 (4.28). FAB-MS *m/z*: 1065 $[M+Na]^+$. HR-FAB-MS *m/z*: 1065.5361 (Calcd for $C_{56}H_{82}O_{18}Na$: 1065.5399). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety (pyridine-d_5 at 35 °C) δ: 5.46 (1H, dd, 9.5, 2.0, H-1′), 5.37 (1H, dd, 9.5, 2.0, H-1″), 5.15 (1H, dd, 9.5, 2.0, H-1‴), 4.76 (1H, dd, 9.5, 2.0, H-1⁗), 4.64 (1H, br s, H-3′), 4.60 (1H, br s, H-3″), 4.29 (1H, dq, 9.5, 6.5, H-5′), 4.26 (1H, dq, 9.5, 6.5, H-5″), 4.19 (1H, dq, 9.5, 6.5, H-5‴), 4.06 (1H, q, 3.0, H-3‴), 3.58 (3H, s, C-3⁗-OMe), 3.57 (1H, dd, 9.5, 3.0, H-4′), 3.47 (3H, s, C-3⁗-OMe), 3.46 (overlapping, H-4‴), 3.44 (1H, dd, 9.5, 3.0, H-4″), 1.56 (3H, d, 6.0, H-6⁗), 1.43 (3H, d, 6.5, H-6′), 1.35 (3H, d, 6.5, H-6″), 1.34 (overlapping, H-6‴). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were consistent with those of **1**.

Syriacoside I (**11**): Amorphous powder. $[\alpha]_D^{22}$ +33.1° (*c*=0.80, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.18), 222 (4.11), 278 (4.33). FAB-MS *m/z*: 1079 $[M+Na]^+$. HR-FAB-MS *m/z*: 1079.5565 (Calcd for $C_{57}H_{84}O_{18}Na$: 1079.5555). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety (pyridine-d_5 at 35 °C) δ: 5.31 (1H, dd, 9.5, 2.0, H-1″), 5.27 (1H, dd, 9.5, 2.0, H-1′), 5.15 (1H, dd, 9.5, 2.0, H-1‴), 5.07 (1H, dd, 9.5, 2.0, H-1⁗), 4.59 (1H, br s, H-3″), 4.24 (1H, dq, 9.5, 6.5, H-5″), 4.22 (1H, dq, 9.5, 6.5, H-5′), 4.19 (1H, dq, 9.5, 6.5, H-5‴), 4.09 (1H, q, 3.0, H-3′), 4.09 (overlapping, H-5⁗), 3.75 (1H, q, 3.0, H-3⁗), 3.62 (3H, s, C-3′-OMe), 3.59 (3H, s, C-3‴-OMe), 3.52 (1H, dd, 9.5, 3.0, H-4′), 3.47 (3H, s, C-3⁗-OMe), 3.45 (1H, dd, 9.5, 3.0, H-4″), 3.43 (1H, dd, 9.5, 3.0, H-4‴), 1.51 (3H, d, 6.5, H-6⁗), 1.39 (3H, d, 6.5, H-6″), 1.38 (3H, d, 6.5, H-6′), 1.32 (3H, d, 6.5, H-6‴). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were consistent with those of **1**.

Syriacoside J (**14**): Amorphous powder. $[\alpha]_D^{22}$ −4.9° (*c*=0.60, MeOH). UV λ_{max}^{MeOH} nm (log ε): 219 (3.94), 258 (sh), 263 (3.39), 269 (sh). FAB-MS *m/z*: 1046 $[M+H]^+$, 1068 $[M+Na]^+$. HR-FAB-MS *m/z*: 1046.5658, 1068.5508 (Calcd for $C_{55}H_{84}NO_{18}$: 1046.5688, $C_{55}H_{83}NO_{18}Na$: 1068.5508). ^{13}C-NMR: shown in Tables 1 and 2. ^{1}H-NMR data of the aglycone and ester moieties (pyridine-d_5 at 35 °C) δ: 9.56 (1H, d, 2.0, H-3e), 8.86 (1H, dd, 4.5, 2.0, H-7e), 8.43 (1H, dt, 8.0, 2.0, H-5e), 7.35 (1H, dd, 8.0, 4.5, H-6e), 5.43 (1H, dd, 12.0, 4.5, H-12), 5.31 (1H, br s, H-6), 3.84 (1H, m, H-3), 2.10 (3H, s, H-21), 2.00 (3H, s, H-18), 1.36 (3H, s, H-19). ^{13}C-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 101.4 (C-1‴), 99.7 (C-1″), 98.2 (C-1⁗), 96.2 (C-1′), 82.6, 82.5 (C-4′, C-4″), 82.2 (C-4‴), 78.9 (C-3‴), 77.6 (C-3⁗), 77.1×2 (C-3′, C-3″), 72.5 (C-4⁗), 71.1×2 (C-5‴, C-5⁗), 68.6, 68.3 (C-5′, C-5″), 58.3, 58.1 (C-3′-OMe, C-3″-OMe), 57.1 (C-3⁗-OMe), 56.5 (C-3‴-OMe), 36.4 (C-2‴), 35.7×2 (C-2′, C-2″), 33.9 (C-2⁗), 18.4, 18.3, 18.2×2 (C-6′, C-6″, C-6‴, C-6⁗). ^{1}H-NMR data of the sugar moiety ($CDCl_3$at 35 °C) δ: 4.88 (1H, dd, 9.5, 2.0, H-1⁗), 4.85 (1H, dd, 9.5, 2.0, H-1′), 4.75 (1H, dd, 9.5, 2.0, H-1″), 4.45 (1H, dd, 9.5, 2.0, H-1‴), 3.86 (1H, dq, 9.5, 6.5, H-5″), 3.84 (1H, dq, 9.5, 6.5, H-5′), 3.81 (1H, q, 3.0, H-3′), 3.78 (1H, q, 3.0, H-3″), 3.62 (1H, q, 3.0, H-3⁗), 3.60 (1H, dq, 9.5, 6.5, H-5⁗), 3.45, 3.44 (each 3H, s, C-3′-OMe, C-3″-OMe), 3.42 (3H, s, C-3‴-OMe), 3.40 (3H, s, C-3⁗-OMe), 3.29 (1H, dq, 9.0, 6.0, H-5‴), 3.21 (2H, dd, 9.5, 3.0, H-4′, H-4″), 3.21 (overlapping, H-4⁗), 3.16 (1H, t, 9.0, H-4‴), 1.30 (3H, d, 6.5, H-6⁗), 1.29 (3H, d, 6.0, H-6‴), 1.21 (6H, d, 6.5, H-6′, H-6″).

Syriacoside K (**15**): Amorphous powder. $[\alpha]_D^{22}$ +3.5° (*c*=0.59, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.18), 223 (4.11), 279 (4.37). FAB-MS *m/z*: 1093 $[M+Na]^+$. HR-FAB-MS *m/z*: 1093.5735 (Calcd for $C_{58}H_{86}O_{18}Na$: 1093.5712). ^{13}C-NMR: shown in Table 2. ^{13}C-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 101.5, 101.4 (C-1″, C-1⁗), 98.5 (C-1‴), 96.1 (C-1′), 82.7×2 (C-4′, C-4‴), 82.2 (C-4″), 80.7 (C-3⁗), 78.9 (C-3″), 77.1×2 (C-3′, C-3‴), 75.5 (C-4⁗), 71.6 (C-5⁗), 71.2 (C-5″), 68.7, 68.5 (C-5′, C-5‴), 58.3, 58.0 (C-3′-OMe, C-3‴-OMe), 56.6 (C-3-OMe), 56.3 (C-3⁗-OMe), 36.4 (C-2″), 36.0 (C-2′), 35.6, 35.4 (C-2‴, C-2⁗), 18.4, 18.2×2, 18.0 (C-6′, C-6″, C-6‴, C-6⁗). ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.95 (1H, dd, 9.5, 2.0, H-1‴), 4.85 (1H, dd, 9.5, 2.0, H-1′), 4.50 (1H, dd, 9.5, 2.0, H-1⁗), 4.44 (1H, dd, 9.5, 2.0, H-1″), 3.90 (1H, dq, 9.5, 6.5, H-5‴), 3.86 (1H, dq, 9.5, 6.5, H-5′), 3.80 (1H, q, 3.0, H-3‴), 3.79 (1H, q, 3.0, H-3′), 3.45, 3.44 (each 3H, s, C-3′-OMe, C-3‴-OMe), 3.40, 3.39 (each 3H, s, C-3″-OMe, C-3⁗-OMe), 3.35 (1H, m, H-3″), 3.28 (2H, dq, 9.5, 6.0, H-5″, H-5⁗), 3.24 (1H, dd, 9.5, 3.0, H-4‴), 3.22 (1H, dd, 9.5, 3.0, H-4′), 3.18 (1H, t, 9.0, H-4″), 1.32 (3H, d, 6.0, H-6⁗), 1.28 (3H, d, 6.0, H-6″), 1.24 (3H, d, 6.5, H-6‴), 1.22 (3H, d, 6.5, H-6′). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were in good agreement with those of **1**.

Syriacoside L (**16**): Amorphous powder. $[\alpha]_D^{22}$ +6.5° (*c*=0.59, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.19), 222 (4.12), 278 (4.37). FAB-MS *m/z*: 1093 $[M+Na]^+$. HR-FAB-MS *m/z*: 1093.5730 (Calcd for $C_{58}H_{86}O_{18}Na$: 1093.5712). ^{13}C-NMR: shown in Table 2. ^{13}C-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 101.4 (C-1″), 100.1 (C-1‴), 98.2 (C-1⁗), 96.1 (C-1′),

82.7 (C-4′), 82.5, 82.4 (C-4″, C-4‴), 79.2, 79.1 (C-3″, C-3‴), 77.6 (C-3⁗), 77.1 (C-3′), 72.5 (C-4⁗), 71.3 (C-5⁗), 71.1, 71.0 (C-5″, C-5‴), 68.5 (C-5′), 58.3 (C-3′-OMe), 57.7 (C-3⁗-OMe), 56.7×2 (C-3″-OMe, C-3‴-OMe), 36.5, 36.4 (C-2″, C-2‴), 35.9 (C-2′), 33.9 (C-2⁗), 18.4×2, 18.3, 18.2 (C-6′, C-6″, C-6‴, C-6⁗). ^{1}H-NMR data of the sugar moiety ($CDCl_3$ at 35 °C) δ: 4.87 (1H, dd, 9.5, 2.0, H-1⁗), 4.85 (1H, dd, 9.5, 2.0, H-1′), 4.66 (1H, dd, 9.5, 2.0, H-1‴), 4.44 (1H, dd, 9.5, 2.0, H-1″), 3.86 (1H, dq, 9.5, 6.5, H-5′), 3.79 (1H, q, 3.0, H-3′), 3.62 (1H, q, 3.0, H-3⁗), 3.60 (1H, dq, 9.5, 6.5, H-5⁗), 3.45 (3H, s, C-3′-OMe), 3.42 (3H, s, C-3⁗-OMe), 3.42, 3.39 (each 3H, s, C-3″-OMe, C-3‴-OMe), 3.31 (1H, dq, 9.0, 6.0, H-5‴), 3.30 (1H, dq, 9.0, 6.0, H-5″), 3.22 (1H, dd, 9.5, 3.0, H-4′), 3.17 (1H, t, 9.0, H-4‴), 3.15 (1H, t, 9.0, H-4″), 1.31 (3H, d, 6.5, H-6⁗), 1.30 (3H, d, 6.0, H-6‴), 1.29 (3H, d, 6.0, H-6″), 1.22 (3H, d, 6.5, H-6′). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were in good agreement with those of **1**.

Syriacoside M (**17**): Amorphous powder. $[\alpha]_D^{22}$ +12.0° (c=0.74, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.16), 222 (4.10), 279 (4.32). FAB-MS m/z: 1227 $[M+Na]^+$. HR-FAB-MS m/z: 1227.5897 (Calcd for $C_{62}H_{92}O_{23}Na$: 1227.5927). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety (pyridine-d_5 at 35 °C) δ: 5.46 (1H, dd, 9.5, 2.0, H-1′), 5.36 (1H, dd, 9.5, 2.0, H-1″), 5.14 (1H, dd, 9.5, 2.0, H-1‴), 5.11 (1H, d, 8.0, H-1⁗), 4.67 (1H, dd, 9.5, 2.0, H-1⁗), 4.63 (1H, br s, H-3′), 4.59 (1H, br s, H-3″), 4.51 (1H, br d, 11.5, H-6⁗), 4.33 (1H, dd, 11.5, 5.5, H-6⁗), 4.29 (1H, dq, 9.5, 6.5, H-5′), 4.24 (1H, dq, 9.5, 6.5, H-5″), 4.16 (1H, dq, 9.5, 6.5, H-5‴), 3.94 (1H, m, H-5⁗), 3.71 (1H, t, 9.0, H-4⁗), 3.57 (3H, s, C-3‴-OMe), 3.53 (3H, s, C-3⁗-OMe), 3.51 (overlapping, H-4′), 3.42 (1H, dd, 9.5, 3.0, H-4″), 3.38 (1H, dd, 9.5, 3.0, H-4‴), 1.71 (3H, d, 6.0, H-6⁗), 1.42 (3H, d, 6.5, H-6′), 1.34 (3H, d, 6.5, H-6″), 1.30 (3H, d, 6.5, H-6‴). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were in good agreement with those of **1**.

Syriacoside N (**19**): Amorphous powder. $[\alpha]_D^{22}$ +30.1° (c=0.90, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.18), 222 (4.11), 278 (4.35). FAB-MS m/z: 1241 $[M+Na]^+$. HR-FAB-MS m/z: 1241.6078 (Calcd for $C_{63}H_{94}O_{23}Na$: 1241.6084). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety (pyridine-d_5 at 35 °C) δ: 5.30 (overlapping, H-1″), 5.27 (1H, dd, 9.5, 2.0, H-1′), 5.13 (1H, dd, 9.5, 2.0, H-1‴), 5.07 (1H, dd, 9.5, 2.0, H-1⁗), 4.93 (1H, d, 8.0, H-1⁗), 4.57 (1H, br s, H-3″), 4.56 (1H, br d, 11.5, H-6⁗), 4.38 (1H, br d, 11.5, H-6⁗), 4.23 (overlapping, H-5″, H-5⁗), 4.22 (overlapping, H-5′), 4.15 (1H, dq, 9.5, 6.5, H-5‴), 4.11 (1H, q, 3.0, H-3⁗), 4.08 (1H, q, 3.0, H-3′), 4.02 (1H, q, 3.0, H-3‴), 3.97 (1H, m, H-5⁗), 3.65 (1H, dd, 9.5, 3.0, H-4⁗), 3.61, 3.60, 3.53 (each 3H, s, C-3′-OMe, C-3‴-OMe, C-3⁗-OMe), 3.52 (overlapping, H-4′), 3.43 (1H, dd, 9.5, 3.0, H-4″), 3.37 (1H, dd, 9.5, 3.0, H-4‴), 1.60 (3H, d, 6.5, H-6⁗), 1.37 (6H, d, 6.5, H-6′, H-6″), 1.27 (3H, d, 6.5, H-6‴). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were in good agreement with those of **1**.

Syriacoside O (**20**): Amorphous powder. $[\alpha]_D^{22}$ +28.9° (c=0.52, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.23), 222 (4.16), 279 (4.38). FAB-MS m/z: 1243 $[M+Na]^+$. HR-FAB-MS m/z: 1243.6233 (Calcd for $C_{63}H_{96}O_{23}Na$: 1243.6240). ^{13}C-NMR: shown in Table 1. ^{1}H-NMR data of the aglycone and ester moieties (pyridine-d_5 at 35 °C) δ: 7.96 (1H, d, 16.0, H-3e), 7.61 and 7.34 (5H, m, H-5e—9e), 6.76 (1H, d, 16.0, H-2e), 5.19 (1H, dd, 11.5, 4.0, H-12), 3.89 (1H, m, H-3), 2.27 (3H, s, H-21), 1.98 (3H, s, H-18), 1.19 (3H, s, H-19) The ^{13}C- and ^{1}H-NMR spectral data of the sugar moiety were consistent with those of **19**, but the C-1′ and H-1′ signals were observed at δ 96.0 and δ 5.30 (1H, dd, 9.5, 2.0), respectively.

Syriacoside P (**21**): Amorphous powder. $[\alpha]_D^{23}$ +40.3° (c=1.04, MeOH). FAB-MS m/z: 1193 $[M+Na]^+$. HR-FAB-MS m/z: 1193.6095 (Calcd for $C_{59}H_{94}O_{23}Na$: 1193.6084). ^{13}C-NMR: shown in Table 1. ^{1}H-NMR data of the aglycone and ester moieties (pyridine-d_5 at 35 °C) δ: 7.14 (1H, qq, 7.0, 2.0, H-3e), 5.33 (1H, br s, H-6), 5.06 (1H, dd, 12.0, 4.0, H-12), 3.84 (1H, m, H-3), 3.21 (1H, dd, 9.5, 5.5, H-17), 2.24 (3H, s, H-21), 1.98 (3H, br s, H-5e), 1.72 (3H, br d, 7.0, H-4e), 1.54 (3H, s, H-18), 1.35 (3H, s, H-19). The ^{13}C- and ^{1}H-NMR spectral data of the sugar moiety were consistent with those of **19**.

Syriacoside Q (**22**): Amorphous powder. $[\alpha]_D^{22}$ +14.8° (c=0.63, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.18), 222 (4.11), 279 (4.34). FAB-MS m/z: 1241 $[M+Na]^+$. HR-FAB-MS m/z: 1241.6090 (Calcd for $C_{63}H_{94}O_{23}Na$: 1241.6084). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety (pyridine-δ_5 at 35 °C) δ: 5.31 (1H, dd, 9.5, 2.0, H-1″), 5.28 (1H, dd, 9.5, 2.0, H-1′), 5.15 (1H, dd, 9.5, 2.0, H-1‴), 5.11 (1H, d, 8.0, H-1⁗), 4.68 (1H, dd, 9.5, 2.0, H-1⁗), 4.60 (1H, br s, H-3″), 4.51 (1H, br d, 11.5, H-6⁗), 4.34 (1H, dd, 11.5, 5.5, H-6⁗), 4.23 (1H, dq, 9.5, 6.5, H-5″), 4.22 (overlapping, H-5′), 4.17 (overlapping, H-5‴), 4.10 (1H, q, 3.0, H-3′), 4.01 (1H, q, 3.0, H-3‴), 3.94 (1H, m, H-5⁗), 3.71 (1H, t, 9.0, H-4⁗), 3.62, 3.58, 3.54 (each 3H, s, C-3′-OMe, C-3‴-OMe, C-3⁗-OMe), 3.52 (overlapping, H-4′), 3.45 (1H, dd, 9.5, 3.0, H-4″), 3.39 (1H, dd, 9.5, 3.0, H-4‴), 1.71 (3H, d, 6.0, H-6⁗), 1.38 (6H, d, 6.5, H-6′, H-6″), 1.31 (3H, d, 6.5, H-6‴). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were in good agreement with those of **1**.

Syriacoside R (**24**): Amorphous powder. $[\alpha]_D^{22}$ +7.8° (c=0.71, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.16), 277 (4.31). FAB-MS m/z: 1255 $[M+Na]^+$. HR-FAB-MS m/z: 1255.6240 (Calcd for $C_{64}H_{96}O_{23}Na$: 1255.6240). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety (pyridine-d_5 at 35 °C) δ: 5.28 (1H, dd, 9.5, 2.0, H-1′), 5.13 (overlapping, H-1″), 5.12 (1H, d, 8.0, H-1⁗), 4.89 (1H, dd, 9.5, 2.0, H-1⁗), 4.69 (1H, dd, 9.5, 2.0, H-1‴), 4.51 (1H, br d, 11.5, H-6⁗), 4.34 (1H, m, H-6⁗), 4.22 (1H, dq, 9.5, 6.5, H-5′), 4.17 (overlapping, H-5″), 4.09 (1H, q, 3.0, H-3′), 4.03 (1H, q, 3.0, H-3″), 3.93 (1H, m, H-5⁗), 3.73 (1H, t, 9.0, H-4⁗), 3.66 (1H, dd, 9.5, 3.0, H-4″), 3.63, 3.58, 3.55, 3.49 (each 3H, s, C-3′-OMe, C-3″-OMe, C-3‴-OMe, C-3⁗-OMe), 3.52 (overlapping, H-4′), 1.74 (3H, d, 6.0, H-6⁗), 1.43 (3H, d, 6.0, H-6‴), 1.41 (3H, d, 6.5, H-6′), 1.39 (3H, d, 6.5, H-6″). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were in good agreement with those of **1**.

Syriacoside S (**25**): Amorphous powder. $[\alpha]_D^{22}$ +17.0° (c=0.42, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.16), 222 (4.09), 279 (4.33). FAB-MS m/z: 1255 $[M+Na]^+$. HR-FAB-MS m/z: 1255.6245 (Calcd for $C_{64}H_{96}O_{23}Na$: 1255.6240). ^{13}C-NMR: shown in Table 2. ^{1}H-NMR data of the sugar moiety (pyridine-d_5 at 35 °C) δ: 5.27 (2H, dd, 9.5, 2.0, H-1′, H-1⁗), 5.11 (1H, dd, 9.5, 2.0, H-1″), 4.93 (1H, d, 8.0, H-1⁗), 4.68 (1H, dd, 9.5, 2.0, H-1‴), 4.57 (1H, br d, 11.5, H-6⁗), 4.39 (1H, dd, 11.5, 5.5, H-6⁗), 4.28 (1H, dq, 9.5, 6.5, H-5⁗), 4.22 (overlapping, H-5′), 4.22 (1H, t, 8.0, H-3⁗), 4.20 (1H, t, 8.0, H-4⁗), 4.17 (overlapping, H-5″), 4.14 (overlapping, H-3⁗), 4.09 (1H, q, 3.0, H-3′), 4.01 (1H, q, 3.0, H-3″), 3.99 (1H, t, 8.0, H-2⁗), 3.97 (1H, m, H-5⁗), 3.67 (1H, dd, 9.5, 3.0, H-4⁗), 3.62, 3.57, 3.54, 3.51 (each 3H, s, C-3′-OMe, C-3″-OMe, C-3‴-OMe, C-3⁗-OMe), 3.52 (overlapping, H-4⁗), 3.50 (overlapping, H-4′), 3.44 (1H, dd, 9.5, 3.0, H-4″), 1.63 (3H, d, 6.5, H-6⁗), 1.42 (3H, d, 6.0, H-6‴), 1.39 (3H, d, 6.5, H-6′), 1.38 (3H, d, 6.5, H-6″). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were in good agreement with those of **1**.

Syriacoside T (**26**): Amorphous powder. $[\alpha]_D^{23}$ +31.4° (c=0.54, MeOH). FAB-MS m/z: 1207 $[M+Na]^+$. HR-FAB-MS m/z: 1207.6277 (Calcd for $C_{60}H_{96}O_{23}Na$: 1207.6240). The ^{13}C- and ^{1}H-NMR spectral data of the aglycone and ester moieties were in good agreement with those of **21**. The ^{13}C- and ^{1}H-NMR data of the sugar moiety were consistent with those of **25**.

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, 550 mg) was heated at 60 °C for 2.5 h with dioxane (8 ml) and 0.1 M H_2SO_4 (2 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 dry. Purification of the residue by HPLC (YMC-ODS 10 mm i.d.×25 cm and 20 mm i.d.×25 cm, 67.5% MeOH in water and 42.5, 45% MeCN in water) afforded ikemagenin (**1a** (25 mg)), 5α,6-dihydroikemagenin (**20a** (4 mg)) and 12-*O*-tigloylisolineolon (**21a** (11 mg)).

The H_2O layer was passed through an Amberlite IRA-60E column and the eluate was concentrated dry. 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: $[\alpha]_D^{22}$ +50.1° (c=1.76, 24 h after dissolution in H_2O).
(lit: $[\alpha]_D^{21}$ +51.6° (c=1.02, H_2O)[26]).

D-Oleandrose: $[\alpha]_D^{22}$ −10.3° (c=1.52, 24 h after dissolution in H_2O).
(lit: $[\alpha]_D$ −11° (c=1.1, H_2O)[27]).

D-Digitoxose: $[\alpha]_D^{22}$ +44.0° (c=0.96, 24 h after dissolution in H_2O).
(lit: $[\alpha]_D^{26}$ +48.4° (c=0.90, H_2O)[14]).

D-Canarose: $[\alpha]_D^{22}$ +17.8° (c=0.30, 24 h after dissolution in H_2O).
(lit: $[\alpha]_D^{21}$ +25° (c=1.4, H_2O)[28]).

Acid Hydrolysis of Compounds 1—3, 5, 9, 11, 14, 15, and 16 Compounds **1**—**3**, **5**, **9**, **11**, **14**, **15**, and **16** (*ca.* 0.5 mg) were each dissolved in dioxane (80 μl) and 0.1 M H_2SO_4 (20 μl). The solutions were heated at 60 °C for 45 min. After hydrolysis, each solution was neutralized on an Amberlite IRA-60E column, and the eluate was concentrated dry. Each residue was 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; 70% MeOH in water; t_R, 12.0 min (ikemagenin (**1a**)), 50% MeOH in water; t_R, 13.4 min (12-*O*-nicotinoyllineolon (**14a**)). Ikemagenin

was detected in **1**—**3**, **5**, **9**, **11**, **15**, and **16**. Similarly, 12-*O*-nicotinoyllineolon was identified in **14**.

Subsequently, the H_2O layer was reduced with $NaBH_4$ (*ca.* 1 mg) for 1 h at room temperature. The following procedures were described in a previous report.[18] 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, 7.2 min (cymaritol acetate), 8.1 min (oleandritol acetate), 10.4 min (digitoxitol acetate), 11.6 min (canaritol acetate). Cymaritol acetate was detected in **2**, **3**, **9**, **11**, **14**, **15**, and **16**. Oleandritol acetate was identified in **1**—**3**, **5**, **9**, **14**, **15**, and **16**. Digitoxitol acetate was found in **1**—**3**, **9**, and **11**. Canaritol acetate was observed in **5**.

Acid Hydrolysis of a Mixture of Pregnane Glycosides to Determine the Configuration of Glucose The fraction of pregnane glycosides eluted with the $CHCl_3$–MeOH (98 : 2) system on a silica gel column (fraction D, 10 mg) was heated at 98 °C for 1 h with 0.05 M HCl and dioxane (0.2 ml each). After hydrolysis, this reaction mixture was diluted with H_2O and extracted with EtOAc. The H_2O layer was neutralized on Amberlite IRA-60E column, and the eluate was concentrated dry. The residue was stirred with D-cysteine methyl ester hydrochloride hexamethyldisilazane and trimethylsilylchloride in pyridine, as described.[29,30] After reactions, the supernatant was subjected to GC. GC conditions: column, GL capillary column TC-1 0.32 mm×30 m (GL Science Co.), carrier gas, N_2; column temperature 210 °C; t_R 16.5 min (D-glucose), 15.6 min (L-glucose). D-Glucose was detected in the mixture of pregnane glycosides.

Acid Hydrolysis of Compounds 4, 6, 8, 17, 19—22, 24, 25, and 26 Solutions of compounds **4**, **6**, **8**, **17**, **19**—**22**, **24**, **25**, and **26** (*ca.* 0.5 mg) in dioxane and 0.05 M HCl (50 μl each) were heated at 98 °C for 1 h. The subsequent procedures, and HPLC and GC conditions for the detection of the component aglycones and sugars were described above and as follows: HPLC conditions: column, YMC-ODS-AM 4.6 mm×25 cm; flow rate, 1.0 ml/min; 70% MeOH in water; t_R, 10.4 min (ikemagenin (**1a**)), 11.2 min (12-*O*-tigloylisolineolon (**21a**)), 12.0 min (5*a*,6-dihydroikemagenin (**20a**)). Ikemagenin was detected in **4**, **6**, **8**, **17**, **19**, **22**, **24**, and **25**. 5α,6-Dihydroikemagenin and 12-*O*-tigloylisolineolon were found in **20** and in **21** and **26**, respectively. GC conditions: column, Supelco SP-2380™ capillary column 0.25 mm×30 m, carrier gas, N_2; column temperature 250 °C; t_R 11.8 min (glucitol acetate). Cymaritol acetate was detected in **4**, **8**, **17**, **19**—**22**, **24**, **25**, and **26**. Oleandritol acetate was found in **6**, **8**, **17**, **22**, **24**, **25**, and **26**. Digitoxitol acetate and glucitol acetate were observed in **4**, **17**, and **19**—**22**, and in **8**, **17**, **19**—**22**, and **24**—**26**, respectively.

Enzymatic Hydrolysis of Compounds 8, 17, 19, 22, 24, and 25 Compounds **8**, **17**, **19**, **22**, **24**, and **25** (*ca.* 1 mg) were dissolved in EtOH (30 μl) and H_2O (0.3 ml), respectively, then cellulase (Sigma Chem. Co.) (*ca.* 10 mg) was added to each solution. The mixtures were stirred at 40 °C for 7 d. After hydrolysis, the reaction mixtures were diluted with H_2O and extracted with EtOAc, and each EtOAc extract was analyzed by HPLC for identification *via* comparison with authentic samples. HPLC conditions: column, YMC-ODS-AM 4.6 mm×25 cm; flow rate, 1.0 ml/min; 80% MeOH in water; t_R, 14.2 min (**7**), 12.0 min (**9**), 19.0 min (**11**), 17.6 min (**22e**), 19.4 min (**12**), 20.6 min (**13**). Compounds **7**, **9**, **11**, **22e**, **12**, and **13** were detected in the EtOAc extracts of **8**, **17**, **19**, **22**, **24**, and **25**, respectively.

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