New Triterpenoid Saponins from the Roots of *Sinocrassula asclepiadea*

Jing ZHAO,[a] Norio NAKAMURA,[a] Masao HATTORI,*[,a] Xiu-Wei YANG,[b] Katsuko KOMATSU,[c] and Ming-Hua QIU[d]

[a] *Department of Metabolic Engineering, Institute of Natural Medicine, Toyama Medical and Pharmaceutical University; 2630 Sugitani, Toyama 930–0194, Japan:* [b] *State Key Laboratory of Natural and Biomimetic Drugs, Peking University Health Science Center; Beijing 100083, P. R. China:* [c] *Research Center for Ethnomedicines, Institute of Natural Medicine, Toyama Medical and Pharmaceutical University; 2630 Sugitani, Toyama 930–0194, Japan: and* [d] *Kunming Institute of Botany, Chinese Academy of Sciences; Kunming 650204, P. R. China.*

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Five new triterpenoid monodesmosides (sinocrassulosides I—V, 1—5) and six bisdesmosides (sinocrassulosides VI—XI, 6—11), in which 2—11 possess different acyl groups in the glycosidic moieties, were isolated from the roots of *Sinocrassula asclepiadea* FRANCH. Sinocrassulosides VI (4) and V (5) also contained a novel A-*seco* aglycone in their structures. All of the structures were determined on the basis of spectroscopic and physicochemical evidence.

Key words *Sinocrassula asclepiadea*; Caryophyllaceae; sinocrassuloside; *seco*-A triterpenoid saponin

Sinocrassula asclepiadea FRANCH. (family Caryophyllaceae) is a perennial herb that grows at an altitude of 1800—3600 m in Yunnan Province, China. The roots are used as an analgesic for the treatment of rheumatic arthritis, stomachache, and fracture in traditional Chinese medicins.[1] However, there are no reports to date on its chemical constituents. During our search for new chemical entities from indigenous Yunnan plants, eleven new triterpenoid saponins, sinocrassulosides I—XI (**1**—**11**) (Figs. 1, 2) were isolated from a methanol extract of the roots of *S. asclepiadea* together with one known saponin (**12**) and two phytoecdysteroids (**13**, **14**). Herein, we describe their isolation and structure elucidation.

Results and Discussion

The MeOH extract of the roots of *S. asclepiadea* was suspended in H_2O and successively extracted with $CHCl_3$, EtOAc and BuOH. The BuOH extract was applied to a Diaion HP-20 column eluting in a stepwise manner with increasing concentrations of aq. MeOH to furnish four fractions I—IV. Fractions II—IV were further fractionated by repeated column chromatography on Sephadex LH-20, silica gel and ODS to furnish compounds **1**—**14**. Of these compounds, **12**—**14** were identified as 3-*O*-[β-D-galactopyranosyl(1→2)][β-D-xylopyranosyl(1→3)]-β-D-glucupyranosyl quillaic acid (**12**),[2] 20-hydroxyecdysone (**13**) and its 3-*O*-α-galactoside (**14**),[3] respectively, by spectroscopic analysis and comparison of their NMR data with those reported.

Compound **1**, a white amorphous powder, had the molecular formula $C_{48}H_{76}O_{21}$, as revealed by high resolution (HR)-FAB-MS, *m/z* 989.4922 $[M+H]^+$ (calcd for $C_{48}H_{77}O_{21}$, 989.4957). The proton and carbon chemical shifts were assigned on the basis of 2D NMR spectra [^{1}H–^{1}H correlation spectroscopy (COSY), ^{1}H-detected heteronuclear multiple quantum coherence (HMQC), and heteronuclear multiple bond connectivity (HMBC)]. Six *tert*-methyls [^{1}H-NMR: δ 0.91 (s, H_3-29), 0.98 (s, H_3-30), 1.03 (s, H_3-25), 1.12 (s, H_3-26), 1.63 (s, H_3-24) and 1.74 (s, H_3-27); ^{13}C-NMR: δ 12.2 (C-24), 16.3 (C-25), 17.5 (C-26), 27.2 (C-27), 33.1 (C-24) and 24.6 (C-30)] and a trisubstituted double bond [^{1}H-NMR: δ 5.59 (br s, H-12); ^{13}C-NMR: δ 122.6 (C-12) and 144.4 (C-13)] were attributable to an olean-12-ene skeleton, in which two hydroxy groups were assigned at C-3 and C-16, together with two COOH groups at C-4 and C-17. The relative stereo structure of the aglycon moiety was determined by inspection of the nuclear Overhauser effect spectroscopy (NOESY) spectrum (Fig. 3) and the coupling constants. The appearance of H-16 as a broad singlet at δ 5.20 indicated that a methine proton was equatorially oriented, which was further confirmed by nuclear Overhauser effect (NOE) cross peaks between H-16 and both methylene protons at C-15 (δ 1.65, 2.40). Consequently, axial OH-16 was concluded to be α-oriented. Secondly, since an NOE correlation between signals of an axial methyl at C-10 (H_3-25) and a methyl at C-4 was noted, a COOH group was assigned to be α-oriented at C-4. Finally, observation of an NOE between H-3 and H-5 and the appearance of H-3 as a double doublet (J=10.5, 6.0 Hz) supported β-orientation of OH-3. Therefore, the aglycon was determined to be 3β,16α-dihydroxyolean-12-en-23,28-dioic acid. A trisaccharide moiety was inferred by the presence of three β-anomeric protons at δ 6.18 (d, J=9.0 Hz, H-1′), 5.22 (d, J=7.5 Hz, H-1″) and 4.98 (d, J=7.5 Hz, H-1‴) and corresponding carbons at δ 95.2 (C-1′), 105.6 (C-1″) and 105.3 (C-1‴). The sugar unit was confirmed to be glucose only by thin-layer chromatography after hydrolysis, and the D-configuration was proved by GC-MS after derivatization. The sugar sequence of 28-*O*-{[β-D-glucopyranosyl(1→3)][β-D-glucopyranosyl(1→6)]-β-D-glucopyranosyl} ester was evident from the following HMBC correlations: C-28 (δ 175.8)/H-1′, C-3′ (δ 88.4)/H-1″, C-1″/H-3′ (δ 4.18), C-1‴/H_2-6′ (δ 4.58, 4.24) and C-6′ (δ 68.9)/H-1‴. Based on these findings, the structure of **1** was determined to be 3β,16α-dihydroxyolean-12-en-23,28-dioic acid 28-*O*-[β-D-glucopyranosyl(1→3)][β-D-glucopyranosyl(1→6)]-β-D-glucopyranosyl ester, and named sinocrassuloside I.

Compound **2** was purified as a white amorphous powder. The HR-FAB-MS spectrum showed a quasi-molecular ion peak at *m/z* 1133.5421 $[M+H]^+$ (calcd for $C_{54}H_{85}O_{25}$, 1133.5380), indicating the molecular formula $C_{54}H_{84}O_{25}$. Compound **2** was assumed to have the same aglycon and trisaccharide moiety by direct comparison of the 1D and 2D NMR data with those of **1**. However, additional NMR signals

* To whom correspondence should be addressed. e-mail: saibo421@ms.toyama-mpu.ac.jp

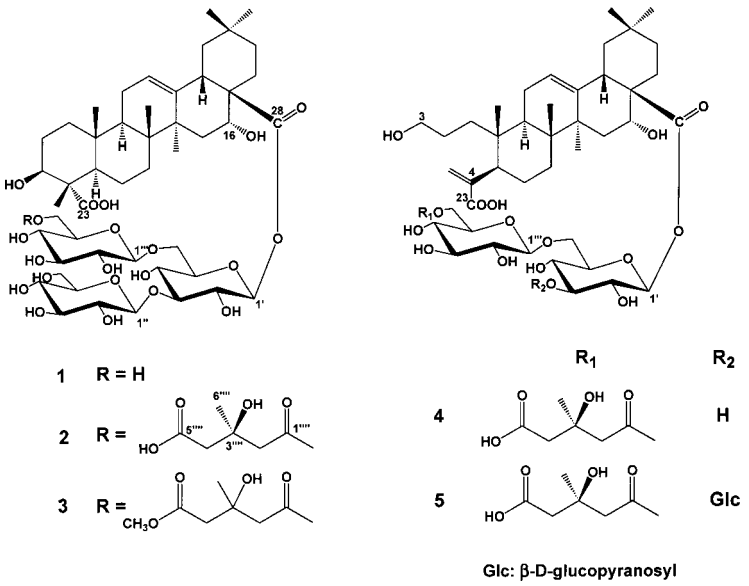

Fig. 1. Structures of Compounds **1**—**5**

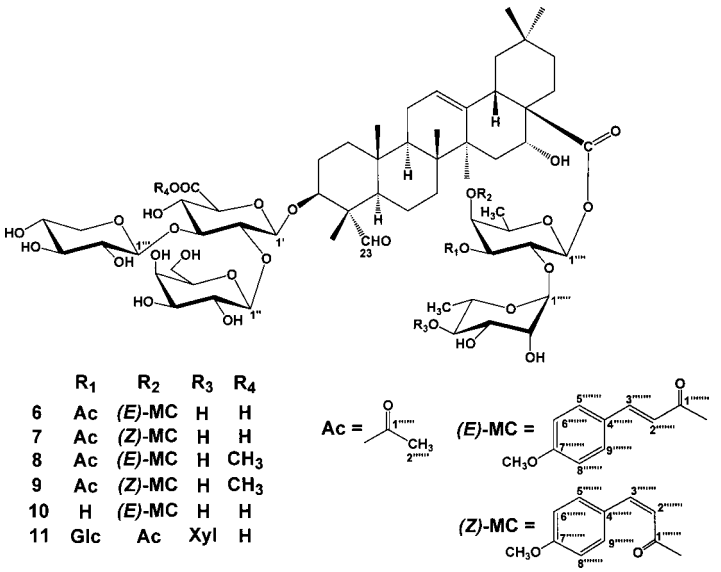

Fig. 2. Structures of Compounds **6**—**11**

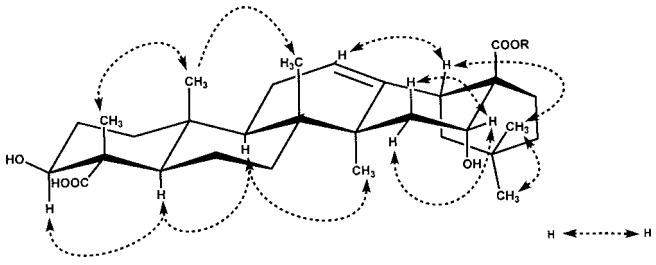

Fig. 3. Selected NOESY Correlations Observed for the Aglycon Moiety of Compound **1**

were observed owing to a *tert*-methyl [$\delta_{H\text{-}6''''}$ 1.70 and $\delta_{C\text{-}6''''}$ 28.2], two methylenes [$\delta_{C\text{-}2''''}$ 46.5, $\delta_{H\text{-}2''''}$ 3.08 and 3.11 (d, J=14.5 Hz); $\delta_{C\text{-}4''''}$ 46.4, $\delta_{H\text{-}4''''}$ 3.10 and 3.15 (d, J=15.0 Hz)] and three quaternary carbons [$\delta_{C\text{-}1''''}$ 171.7, $\delta_{C\text{-}3''''}$ 70.7 and $\delta_{C\text{-}5''''}$ 174.6]. The HMBC experiment allowed construction of a 3-hydroxy 3-methylglutaryl group (HMG), and the location of this group was assigned at C-6‴ by a long range ^{13}C–^{1}H correlation of C-1⁗/H_2-6‴ (δ 4.68, 4.93), which was also implied by the presence of a deshielded signal at C-6 of the terminal glucose unit (by 2.0 ppm). The absolute configuration of HMG was established to be 3*R* by Fujimoto's method.[4] From these findings, the structure of **2** was determined to be 3β,16α-dihydroxyolean-12-en-23,28-dioic acid 28-*O*-[β-D-glucopyranosyl(1→3)][β-D-6-*O*-((3*R*)-3-hydroxy-3-methylglutaryl)glucopyranosyl(1→6)]-β-D-glucopyranosyl ester, and named sinocrassuloside II.

Compound **3**, a white amorphous powder, was assigned the molecular formula $C_{55}H_{86}O_{25}$ by HR-FAB-MS, *m*/*z* 1169.5352 (calcd for $C_{55}H_{86}O_{25}Na$, 1169.5356). The ^{1}H- and ^{13}C-NMR spectra included all of the corresponding signals observed for **2**. An extra methoxy group was also deduced for **3** by observation of a singlet methyl proton signal at δ

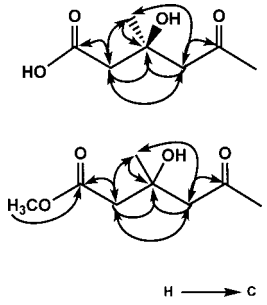

Fig. 4. Significant HMBC Correlations for (3*R*)-HMG (Top) in Compounds **2**, **4** and **5**, and HMG Me (Bottom) in Compound **3**

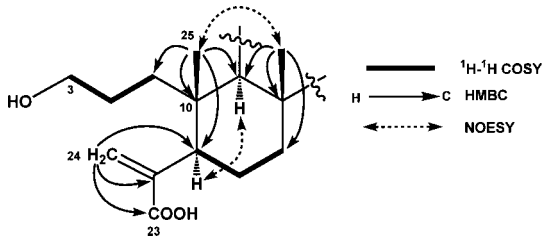

Fig. 5. Partial Structures of Compounds **4** and **5**

3.58 and the corresponding carbon signal at δ 51.3. In the HMBC spectrum, the methoxy signal (δ 3.58) showed a correlation with C-5 of HMG (δ 171.9), indicating the linked site (Fig. 4). Therefore, the structure of **3** was determined to be 3β,16α-dihydroxyolean-12-en-23,28-dioic acid 28-*O*-[β-D-glucopyranosyl(1→3)][β-D-6-*O*-(3-hydroxy-5-methoxy-3-methyl-5-oxopentanoyl)glucopyranosyl(1→6)]-β-D-glucopyranosyl ester, and named sinocrassuloside III.

Compound **4** was obtained as a white amorphous powder, and the molecular formula was determined by HR-FAB-MS, *m/z* 993.4697 $[M+Na]^+$ (calcd for $C_{48}H_{74}O_{20}Na$, 993.4671). In the 1D NMR spectra, the ^{1}H- and ^{13}C signals of rings B, C, D, and E remained almost intact in the comparison with those of **1**—**3**. However, great differences were noticed for those of ring A. Firstly, the DEPT spectrum indicated the replacement of a 3-hydroxymethylene in **1**—**3** with a hydroxymethyl (δ_H 3.74 and 3.89; δ_C 63.3), which implied the cleavage of a bond between C-3 and C-4. Next, inspection of ^{1}H- and ^{13}C-NMR spectra revealed the absence of H_3-24 and quaternary C-4 signals with respect to those of **1**—**3** and the presence of new signals assignable to an olefin [δ_H 6.50 and 5.54 (each s, $H_{a,b}$-24); δ_C 124.3 (C-24) and 146.2 (C-4)] linked both at C-23 (δ 171.5) and C-5 (δ 43.6), as shown by HMBC correlations [C-4/$H_{a,b}$-24, C-23/$H_{a,b}$-24, C-5/$H_{a,b}$-24, and C-4/H-5 (δ 3.22)] (Fig. 5). The NOE correlations of H_3-25 (δ 0.93)/H_3-26 (δ 1.18) and H-5/H-9 (δ 2.33) indicated the orientations of both functional groups at C-5 and C-10 remained the same as the intact counterpart in **1**—**3**. To our knowledge, this aglycon was found for the first time. In addition, characteristic NMR signals assignable to (3*R*)-HMG were also observed. The presence of two glucosyl groups was inferred by observation of anomeric protons at δ 6.19 (d, J=8.0 Hz, H-1′) and 4.95 (d, J=7.5 Hz, H-1‴) as well as carbons at δ 95.7 (C-1′) and 105.1 (C-1‴). Comparison of the ^{1}H- and ^{13}C-NMR data with those of **3** indicated the lack of a 3′-*O*-β-D-glucopyranosyl group in **4** and the structure of the sugar moiety was further confirmed by the HMBC experiment. Hence, **4** was determined to be 3,16α-dihydroxy-3,4-*seco*-olean-4(24),12-dien-23,28-dioic acid 28-*O*-[β-D-6-*O*-(3-hydroxy-3-methylglutaryl)-glucopyranosyl(1→6)]-β-D-glucopyranosyl ester (Fig. 1), and named sinocrassuloside IV.

Compound **5** was assigned the molecular formula $C_{54}H_{84}O_{25}$ by HR-FAB-MS, *m/z* 1133.5380 $[M+H]^+$ (calcd for $C_{54}H_{85}O_{25}$, 1133.5380). The ^{1}H- and ^{13}C-chemical shifts observed for the aglycon were superimposable on those of **4**, suggestive of the same *seco*-A aglycon. In addition, by comparison of 1D NMR data with those of **2** and analysis of the HMBC correlations, a trisaccharide moiety having a (3*R*)-HMG group was shown to be identical with that of **2**. The structure of **5** was consequently concluded to be 3,16α-dihydroxy-3,4-*seco*-olean-4(24),12-dien-23,28-dioic acid 28-*O*-[β-D-glucopyranosyl(1→3)]{β-D-6-*O*-[(3*R*)-3-hydroxy-3-methylglutaryl]-glucopyranosyl(1→6)}-β-D-glucopyranosyl ester (Fig. 1), and named sinocrassuloside V.

Compound **6** was purified as a white amorphous powder. The HR-FAB-MS spectrum showed a quasi-molecular ion peak at *m/z* 1473.6299 $[M+Na]^+$ (calcd for $C_{71}H_{102}O_{31}Na$, 1473.6303), suggesting the molecular formula $C_{71}H_{102}O_{31}$. In contrast to compounds **1**—**5**, the 1D NMR spectra showed different signal patterns due to both the aglycon and the sugar unit. First, a proton singlet signal at δ 9.85 (H-23) and the corresponding carbon signal at δ_C 209.8 (C-23) suggested the presence of an aldehyde group, and a different aglycon from those of **1**—**5**. After analysis of 2D NMR data and by comparison with the literature data, the aglycon was concluded to be quillaic acid (3β,16α-dihydroxy-23-oxo-12-oleanen-28-oic acid).[5] Second, the presence of five monosaccharide residues was deduced from observation of anomeric signals at δ 4.88 (d, J=7.2 Hz, Fuc-H-1), 5.55 (d, J=7.2 Hz, Gal-H-1), 5.32 (d, J=7.7 Hz, Xyl-H-1), 6.18 (d, J=9.0 Hz, Fuc-H-1) and 5.76 (s, Rha-H-1) in the ^{1}H-NMR spectrum and δ 103.9 (Fuc-C-1), 104.3 (Gal-C-1), 105.0 (Xyl-C-1), 94.3 (Fuc-C-1) and 102.3 (Rha-C-1) in the ^{13}C-NMR spectrum. They were identified to be galactose (Gal), xylose (Xyl), fucose (Fuc), rhamnose (Rha) and glucuronic acid (Glc A) by co-TLC with authentic samples after hydrolysis. Except Rha, all the other monosaccharide units were concluded to be of D-configuration by GC-MS analysis after derivatization. The total correlation spectroscopy (TOCSY) and COSY spectra discerned ^{1}H–^{1}H couplings from anomeric to terminal protons within a monosaccharide unit. Next, the HMBC spectrum provided the exclusive evidence of their connectivities, which secured two sugar chains as 3-*O*-[β-D-galactopyranosyl(1→2)][β-D-xylopyranosyl(1→3)]-β-D-glucuronopyranosyl and 28-*O*-[α-L-rhamnopyranosyl(1→2)]-β-D-fucopyranosyl ester. In addition, the ^{1}H- and ^{13}C-NMR data suggested the presence of an acetyl group (δ_H 2.01, s, 3H) and an (*E*)-*para*-methoxycinnamoyl [(*E*)-MC] group [δ_H 6.60 and 7.95, 1H each, d, J=15.5 Hz, (*E*)-MC-H-2 and H-3; δ 7.53 and 7.01, 2H each, d, J=9.0 Hz, (*E*)-MC-H-5, 9 and H-6, 8] (Fig. 6). The carboxyl carbons of the acetyl and the (*E*)-MC groups displayed HMBC correlations with H-3 (δ 5.68) and H-4 (δ 5.76) of Fuc, respectively, which confirmed their attachments at C-3 and C-4 of Fuc. From the above evidence, the structure of **6** was determined to be 3-*O*-[β-D-galactopyranosyl(1→2)][β-D-xylopyranosyl(1→3)]-β-D-glucuronopyranosylquillaic acid 28-*O*-[α-L-rhamnopyranosyl(1→2)]-3-*O*-acetyl-4-*O*-(*E*)-*para*-methoxycinnamoyl-β-D-fu-

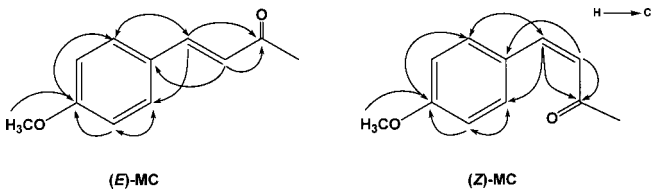

Fig. 6. Significant HMBC Correlations Observed for (*E*)- and (*Z*)-*para*-methoxycinnamoyl Groups in **6**—**10**

copyranosyl ester, and named sinocrassuloside VI.

Compound **7** had the molecular formula $C_{71}H_{102}O_{31}$, as revealed by HR-FAB-MS (*m/z* 1451.6462 $[M+H]^+$, calcd for $C_{71}H_{103}O_{31}$, 1451.6483). In comparison with those of **6**, the 1D NMR spectra showed highly analogous signals ascribable to an aglycon quillaic acid, an acetyl group, and two oligosaccharide units. Furthermore, the remaining ten carbon signals resembled those of (*E*)-MC. However, notable differences were observed for proton signals. Particularly, the coupling constant of 12.9 Hz between H-2 (δ 5.93) and H-3 (δ 6.97) of the MC group confirmed (*Z*)-geometry of this functionality. As well, an HMBC experiment showed the location of the (*Z*)-MC group to be at C-4 of Fuc. Thus, the structure of **7** was determined to be 3-*O*-[β-D-galactopyranosyl(1→2)][β-D-xylopyranosyl(1→3)]-β-D-glucuronopyranosyl quillaic acid 28-*O*-[α-L-rhamnopyranosyl(1→2)]-3-*O*-acetyl-4-*O*-(*Z*)-*para*-methoxycinnamoyl-β-D-fucopyranosyl ester, and named sinocrassuloside VII.

Compound **8** was obtained as a white amorphous powder. HR-FAB-MS established the molecular formula $C_{72}H_{104}O_{31}$. The 1D NMR data exhibited close similarity to those of **6** except for the presence of a methoxy group [δ_H 3.72 (3H, s); δ_C 52.2] in **8**. The HMBC cross peak of C-6′ (δ 169.9)/H_3-OMe concluded its attachment. Therefore, **8** was determined to be 3-*O*-[β-D-galactopyranosyl(1→2)][β-D-xylopyranosyl(1→3)]-[6-*O*-methyl-β-D-glucuronopyranosyl] quillaic acid 28-*O*-[α-L-rhamnopyranosyl(1→2)]-[3-*O*-acetyl-4-*O*-(*E*)-*para*-methoxycinnamoyl-β-D-fucopyranosyl] ester, and named sinocrassuloside VIII.

Compound **9**, a white amorphous powder, possessed the molecular formula $C_{72}H_{104}O_{31}$, the same as that of **8**. Comparison of the NMR data with those of **8** revealed the replacement of an (*E*)-MC group by a (*Z*)-MC group. The HMBC correlations observed for **9** were consistent with those for **8**. Compound **9** was consequently determined to be 3-*O*-[β-D-galactopyranosyl(1→2)][β-D-xylopyranosyl(1→3)]-[6-*O*-methyl-β-D-glucuronopyranosyl] quillaic acid 28-*O*-[α-L-rhamnopyranosyl(1→2)]-3-*O*-acetyl-4-*O*-(*Z*)-*para*-methoxyciunamoyl-β-D-fucopyranosyl ester, and named sinocrassuloside IX.

Compound **10** was obtained as a white amorphous powder. The molecular formula $C_{69}H_{101}O_{30}$ was assigned by HR-FAB-MS, *m/z* 1409.6387 $[M+H]^+$ (calcd for $C_{69}H_{100}O_{30}$, 1409.6378), which suggested the absence of an acetyl group in comparison with the MS spectra of **6** and **7**. The absence of the acetyl group was further supported by lack of the corresponding signal in the NMR spectrum. In addition to the diagnostic proton and carbon signals due to quillaic acid, and two oligosaccharide moieties at C-3 and C-28, an (*E*)-MC group was implied by observation of a $J_{2,3}$ of 16.1 Hz and likewise, its location at C-4 of Fuc was confirmed by an HMBC correlation of MC-C-1 (δ 167.6)/Fuc-H-4 (δ 4.28). The structure was concluded to be 3-*O*-[β-D-galactopyranosyl(1→2)][β-D-xylopyranosyl(1→3)]-β-D-glucuronopyranosyl quillaic acid 28-*O*-[α-L-rhamnopyranosyl(1→2)]-4-*O*-(*E*)-*para*-methoxyciunamoyl-β-D-fucopyranosyl ester, and named sinocrassuloside X.

Compound **11** was isolated as a white amorphous powder. The HR-FAB-MS spectrum established the molecular formula $C_{72}H_{112}O_{38}$, *m/z* 1585.6886, $[M+H]^+$ (calcd for $C_{72}H_{113}O_{38}$, 1585.6910). The ^{1}H- and ^{13}C-NMR spectra also showed typical signals due to quillaic acid and an acetyl group. However, different from all the above compounds, there were seven monosaccharide units in **11**, as deduced by the presence of anomeric proton signals at δ 6.55 (s, Rha-H-1), 6.00 (d, J=8.2 Hz, Fuc-H-1), 5.54 (d, J=6.4 Hz, Gal-H-1), 5.31 (d, J=7.6 Hz, Glc A-H-1), 5.24 (d, J=7.8 Hz, Rha-3-Xyl-H-1), 5.04 (d, J=7.6 Hz, Glu-H-1), and 4.87 (d, J=7.6 Hz, Glc A-3-Xyl-H-1) and carbon signals at δ 94.5 (Fuc-C-1), 100.9 (Rha-C-1), 103.9 (Glc A-C-1), 104.3 (Gal-C-1), 105.0 (Glc A-3-Xyl-C-1), 105.6 (Glc A-3-Xyl-C-1), and 106.3 (Rha-3-Xyl-C-1). Aside from the same sugars as those in **6**—**10**, glucose (Glc) and additional xylose were inferred by observation of the chemical shifts and TLC after hydrolysis. As well, the absolute configurations of all the sugars were established by GC-MS analysis. Next, the connectivities of the sugar residues were investigated by HMBC. The trisaccharide moiety at C-3 remained unchanged, in agreement with those of **6**—**10** and **12**. Meanwhile, the following HMBC correlations were observed: C-28 (δ 175.9)/Fuc-H-1, Fuc-C-2 (δ 72.3)/Rha-H-1, Rha-C-1/Fuc-H-2 (δ 4.65), Rha-C-4 (δ 82.4)/Xyl-H-1, Xyl-C-1/Rha-H-4, Fuc-C-3 (δ 83.1)/Glc-H-1 and Glc-C-1/Fuc-H-3 (δ 4.40). From these findings, we concluded that the remaining four monosaccharide residues constituted a sugar chain as 28-*O*-{[β-D-xylopyranosyl(1→4)]-α-L-rhamnopyranosyl(1→2)}[β-D-glucopyranosyl(1→4)]-β-D-fucopyranosyl ester. The acetyl group was subsequently assigned at C-4 of Fuc on the basis of the observed HMBC cross peak between signals of a carboxyl carbon of the acetyl group (δ 171.3) and a portion of Fuc-H-4 (δ 5.86). From these findings, the structure of **11** was determined to be 3-*O*-[β-D-galactopyranosyl(1→2)][β-D-xylopyranosyl(1→3)]-β-D-glucuronopyranosyl quillaic acid 28-*O*-{[β-D-xylopyranosyl(1→4)]-α-L-rhamnopyranosyl(1→2)}[β-D-glucopyranosyl(1→3)]-4-*O*-acetyl-β-D-fucopyranosyl ester (Fig. 2), and named sinocrassuloside XI.

It is worth noting that saponins with various acylated sugar moieties were isolated from the roots of *S. asclepiadea*. According to some reports in the literature, (*E*)- and (*Z*)-MC groups underwent isomerization under light, and they were obtained as inseparable mixtures in general. In our experiment, compounds having two isomeric groups were separable as two peaks by HPLC and could be purified to elucidate their chemical properties. Furthermore, since saponins with acyl groups on the oligosaccharide moiety were reported to have diverse bioactivities,[6,7] it is of interest to examine the role of acyl groups in an appropriate bio-assay system.

Experimental

General Optical rotations were measured with a JASCO DIP-360 automatic polarimeter. IR spectra were measured using a Jasco FT/IR-230 Fourier Transform Infrared Spectrometer. 1D and 2D NMR spectra were recorded on Varian UNITY PLUS 500 and Jeol JNM-LA 400 WB Lambda

Table 1. ^{1}H- and ^{13}C-NMR Data for Compounds **1**—**5** Isolated from the Roots of *Sinocrassula asclepiadea*

	1		**2**		**3**		**4**		**5**	
	δ_H mult (J in Hz)[a]	δ_C[b]	δ_H mult (J in Hz)[a]	δ_C[b]	δ_H mult (J in Hz)[a]	δ_C[b]	δ_H mult (J in Hz)[a]	δ_C[b]	δ_H mult (J in Hz)[a]	δ_C[b]
The aglycone moiety										
1	1.21, 1.63	39.2	1.19, 1.63	39.1	1.21, 1.64	39.2	1.10 td (12.5, 4.5) 1.55 t (12.5)	37.2	1.58, 1.14	37.2
2	1.93, 1.96	27.9	1.92, 1.94	27.8	1.93, 1.96	27.9	1.72, 2.38	27.6	2.40, 1.77	27.6
3	4.68 dd (10.5, 6.0)	75.5	4.64 dd (10.0, 6.5)	75.3	4.68 dd (11.0, 6.0)	75.5	3.74, 3.89	63.3	3.91, 3.78	63.3
4		54.5		54.4		54.5		146.2		146.3
5	2.02	52.1	1.99	52.0	2.03	52.1	3.22 d (12.5)	43.6	3.26 d (13.0)	43.6
6	1.50, 1.69	21.8	1.46, 1.67	21.7	1.50, 1.70	21.8	1.35 d (10.5) 1.84 d (13.0)	26.0	1.83, 1.34	26.0
7	1.00, 1.29	33.3	0.96, 1.27	33.2	1.00, 1.30	33.2	1.28, 1.60	32.4	1.61, 1.27	32.4
8		40.5		40.4		40.4		39.8		39.8
9	1.94	47.5	1.93	47.5	1.97	47.5	2.33	37.5	2.36	37.5
10		36.9		36.8		36.9		39.8		39.8
11	2.04, 1.96	23.9	2.01, 2.04	23.8	1.98, 2.04	23.9	2.04, 2.04	24.4	2.11, 2.06	24.4
12	5.59 br s	122.6	5.55 br s	122.6	5.58 br s	122.7	5.56 t (4.0)	122.8	5.58 br s	122.9
13		144.4		144.3		144.3		144.4		144.3
14		42.1		42.0		42.0		42.7		42.6
15	1.65, 2.40	36.1	1.63, 2.36	36.0	1.64, 2.41	36.1	1.70, 2.45 d (12.0)	36.1	2.39, 1.70	36.1
16	5.20 br s	74.2	5.17 br s	74.1	5.19 br s	74.1	5.25 br s	74.3	5.22 br s	74.2
17		49.0		49.0		49.1		49.2		49.2
18	3.47 dd (14.0, 4.0)	41.3	3.44 dd (14.0, 4.0)	41.2	3.47 dd (13.5, 3.0)	41.2	3.47 dd (14.0, 4.0)	41.4	3.48 dd (14.0, 4.0)	41.4
19	2.74 t (14.0), 1.32	47.1	2.70 t (14.0), 1.29	47.1	2.74 t (13.5), 1.28	47.1	2.73 t (14.0), 1.30	47.3	2.76 t (14.0), 1.32	47.3
20		30.8		30.7		30.8		30.8		30.9
21	1.22, 2.34	35.9	1.21, 2.34	35.8	1.22, 2.37	35.9	1.25, 2.33	35.9	2.38, 1.22	35.9
22	2.08, 2.32	32.3	2.04, 2.29	32.1	2.10, 2.34	32.2	2.12 td (15.0, 5.0) 2.36	32.2	2.39, 2.09	32.2
23		180.6		180.5		180.6		171.5		171.7
24	1.63 s	12.2	1.60 s	12.2	1.64 s	12.3	6.50 s, 5.54 s	124.3	6.54 s, 5.57 s	124.0
25	1.03 s	16.3	1.02 s	16.2	1.05 s	16.3	0.93 s	19.1	0.98 s	19.1
26	1.12 s	17.5	1.08 s	17.4	1.12 s	17.5	1.18 s	17.7	1.19 s	17.7
27	1.74 s	27.2	1.70 s	27.1	1.74 s	27.2	1.73 s	27.2	1.76 s	27.2
28		175.8		175.7		175.7		176.0		175.8
29	0.91 s	33.1	0.89 s	33.1	0.92 s	33.1	0.94 s	33.2	0.97 s	33.2
30	0.98 s	24.6	0.98 s	24.6	1.01 s	24.6	1.00 s	24.7	1.02 s	24.7
28-*O*-*β*-D-Glucopyranosyl										
1′	6.18 d (9.0)	95.2	6.14 d (9.0)	95.1	6.18 d (9.0)	95.1	6.19 d (9.0)	95.7	6.18 d (9.0)	95.2
2′	4.04 t (9.0)	72.7	3.99 t (9.0)	72.5	4.01 t (9.0)	72.6	4.01 t (9.0)	73.9	4.04 t (9.0)	72.7
3′	4.18	88.4	4.13 t (9.0)	88.5	4.17 t (9.0)	88.5	4.16 t (9.0)	78.7	4.18 t (9.0)	88.6
4′	4.24	69.0	4.23	68.9	4.25 t (9.0)	68.8	4.27 t (9.0)	71.0	4.27 t (9.0)	68.9
5′	4.00	77.6	3.98	77.5	4.00	77.6	4.03	78.0	4.00	77.6
6′	4.58 d (11.0), 4.24	68.9	4.59 d (10.5), 4.21	68.7	4.61 d (10.5), 4.26	68.9	4.71 d (11.0) 4.31 dd (11.0, 5.0)	69.5	4.64 d (10.5) 4.29	68.8
3′-*O*-*β*-D-Glucopyranosyl										
1″	5.22 d (7.5)	105.6	5.18 d (8.0)	105.6	5.20 d (8.0)	105.7			5.23 d (8.0)	105.7
2″	3.95	75.1	3.92	75.1	3.96	75.4			3.96	75.4
3″	4.13	78.4	4.09	78.2	4.12	78.3			4.14	78.3
4″	4.14	71.6	4.08	71.5	4.12	71.6			4.14	71.6
5″	3.94	78.6	3.91	78.5	3.92	78.6			3.95	78.6
6″	4.48 dd (11.5, 2.0), 4.25	62.4	4.44 dd (11.5, 2.5), 4.20	62.3	4.47 d (10.0), 4.23	62.4			4.48 dd (11.5, 2.0), 4.25	62.3
6′-*O*-*β*-D-Glucopyranosyl										
1‴	4.98 d (7.5)	105.3	4.92 d (7.5)	105.1	4.94 d (8.0)	105.2	4.95 d (8.5)	105.1	4.96 d (7.5)	105.2
2‴	3.95	75.4	3.92	74.9	3.94	75.0	3.95 t (8.5)	75.0	3.96	75.0
3‴	4.19	78.3	4.11	78.0	4.14	78.1	4.12 t (8.5)	78.1	4.15	78.1
4‴	4.20	71.6	3.95	71.5	3.98	71.5	3.99 t (8.5)	71.5	4.00	71.6
5‴	3.85	78.4	3.92	75.1	3.95	75.1	3.96	75.2	3.96	75.2
6‴	4.45 dd (12.0, 2.0), 4.33 dd (12.0, 5.0)	62.6	4.68 dd (11.5, 6.0), 4.93 d (10.5)	64.6	4.71 dd (11.5, 6.0) 4.94 d (9.0)	64.7	4.69 dd (11.0, 6.0) 4.93 d (11.0)	64.7	4.73 dd (11.0, 6.0) 4.97 d (11.0)	64.7
3-Hydroxy-3-methyl-glutaryl group (HMG)										
1⁗				171.7		171.9		171.7		171.8
2⁗			3.08 d (14.5) 3.11 d (14.5)	46.5	3.02 br s	46.3	3.08 d (14.5) 3.12 d (14.5)	46.6	3.11 d (14.0) 3.15 d (14.0)	46.6
3⁗				70.0		69.9		70.0		70.0
4⁗			3.10 d (15.0) 3.15 d (15.0)	46.4	3.06 d (14.5) 3.00 d (14.5)	46.6	3.14 br s	46.4	3.18 br s	46.3
5⁗				174.6		171.6		174.6		174.6
6⁗			1.70 s	28.2	1.65 s	28.2	1.71 s	28.2	1.74 s	28.2
OMe					3.58 s	51.3				

a) 500 MHz for ^{1}H, *b*) 100 MHz for ^{13}C, in C_5D_5N. The ^{1}H and ^{13}C chemical shifts were assigned by a combination of ^{1}H–^{1}H COSY, HMQC and HMBC experiments.

Table 2. ^{1}H- and ^{13}C-NMR Data for Compounds **6**—**10** Isolated from the Roots of *Sinocrassula asclepiadea*

	6		**7**		**8**		**9**		**10**	
	δ_H mult (J in Hz)[a]	δ_C[b]	δ_H mult (J in Hz)[a]	δ_C[b]	δ_H mult (J in Hz)[a]	δ_C[b]	δ_H mult (J in Hz)[a]	δ_C[b]	δ_H mult (J in Hz)[a]	δ_C[b]
The aglycone moiety										
1	0.83, 1.36	38.2	0.84, 1.36	38.2	0.85, 1.36	38.1	0.85, 1.37	38.2	0.85, 1.38	38.1
2	1.80, 2.08 d (9.0)	25.2	1.80, 2.08	25.2	1.79, 2.02	25.1	1.80, 2.02	25.2	1.80, 2.10	25.2
3	3.95 t (9.0)	84.4	3.95	84.4	4.09	84.4	4.09	84.4	3.93	84.3
4		55.1		55.1		55.0		55.1		55.1
5	1.35	48.6	1.35	48.5	1.35	48.6	1.36	48.7	1.31	48.5
6	0.89, 1.36	20.5	0.89, 1.36	20.5	0.89, 1.36	20.5	0.90, 1.37	20.5	0.87, 1.32	20.5
7	1.50	32.8	1.51	32.7	1.51	32.7	1.51	32.8	1.53	32.7
8		40.4		40.3		40.3		40.4		40.3
9	1.77	47.0	1.77	47.0	1.78	46.9	1.77	47.0	1.80	47.0
10		36.2		36.3		36.2		36.3		36.2
11	1.90	23.8	1.90	23.8	1.90	23.7	1.91	23.8	1.91	23.7
12	5.58 br s	122.2	5.57 br s	122.2	5.60 br s	122.2	5.58 br s	122.2	5.56 br s	122.0
13		144.4		144.3		144.4		144.5		145.1
14		42.2		42.2		42.1		42.2		42.2
15	1.90, 2.18	36.3	1.89, 2.17	36.3	1.94, 2.19	36.2	1.92, 2.19	36.3	1.92, 2.20	36.2
16	5.21 br s	73.9	5.19 br s	73.9	5.22 br s	73.8	5.19 br s	73.9	5.28 br s	73.9
17		48.8		48.5		48.6		48.7		48.5
18	3.39 d (14.0)	41.6	3.38	41.5	3.40 d (14.0)	41.5	3.40	41.6	3.39	41.6
19	1.34, 2.74 t (14.0)	47.4	1.34, 2.75 t (13.2)	47.5	1.36, 2.75 t (14.0)	47.4	1.37, 2.75 t (13.7)	47.5	1.33, 2.74 t (12.4)	47.5
20		30.8		30.7		30.7		30.8		30.7
21	1.30, 2.40	36.0	1.32, 2.41	36.0	1.31, 2.41	35.9	1.32, 2.41	36.0	1.28, 2.41	36.0
22	2.21, 2.39	32.8	2.20, 2.38	32.7	2.22, 2.40	32.7	2.20, 2.38	32.8	2.20, 2.40	32.7
23	9.85 s	209.8	9.86 s	209.7	9.85 s	209.8	9.85 s	209.8	9.82 s	209.7
24	1.40 s	11.0	1.41 s	11.0	1.39 s	11.0	1.40 s	11.0	1.37 s	10.9
25	0.81 s	15.8	0.85 s	15.8	0.84 s	15.8	0.87 s	15.8	0.80 s	15.8
26	1.05 s	17.4	1.06 s	17.4	1.07 s	17.3	1.07 s	17.4	1.06 s	17.3
27	1.75 s	27.0	1.77 s	27.0	1.79 s	27.0	1.76 s	27.0	1.75 s	26.9
28		175.8		175.7		175.8		175.8		176.0
29	0.95 s	33.1	0.97 s	33.2	0.97 s	33.1	0.98 s	33.2	0.95 s	33.1
30	1.00 s	24.5	1.02 s	24.5	1.02 s	24.5	1.03 s	24.5	0.99 s	24.5
3-*O*-*β*-D-Glucuronopyranosyl										
1′	4.88 d (9.0)	103.9	4.88 d (7.1)	103.9	4.86 d (7.1)	103.9	4.86 d (7.3)	103.8	4.86 d (7.3)	103.7
2′	4.36 t (9.0)	78.6	4.35	78.6	4.36	78.5	4.35	78.5	4.32	78.6
3′	4.28 t (9.0)	86.1	4.27	86.0	4.29	85.6	4.27	85.7	4.23	86.0
4′	4.44	71.3	4.44	71.1	4.24	71.1	4.24	71.1	4.41	71.3
5′	4.51	77.3	4.50	77.3	4.39	76.4	4.39	76.4	4.48	77.3
6′		ND		ND		169.9		169.9		ND
2′-*O*-*β*-D-Galactopyranosyl										
1″	5.55 d (7.6)	104.3	5.55 d (7.8)	104.3	5.54 d (7.8)	104.3	5.52 d (7.8)	104.3	5.52 d (7.3)	104.2
2″	4.46	73.8	4.45	73.7	4.47	73.7	4.46	73.7	4.46	73.6
3″	4.14 dd (9.8, 3.4)	75.6	4.14 dd (9.8, 3.4)	75.6	4.14 dd (9.8, 3.2)	75.5	4.14 dd (10.0, 3.2)	75.5	4.14	75.3
4″	4.57	70.4	4.57	70.4	4.56	70.2	4.56	70.2	4.57	70.2
5″	4.02	76.8	4.02	76.8	4.02	76.8	4.02	76.8	4.01	76.6
6″	4.42, 4.51	61.7	4.40, 4.50	61.7	4.41, 4.51	61.7	4.41, 4.50	61.8	4.40, 4.50	61.7
3′-*O*-*β*-D-Xylopyranosyl										
1‴	5.32 d (8.0)	105.0	5.31 d (7.8)	105.0	5.28 d (7.8)	104.9	5.28 d (8.0)	105.0	5.28 d (7.5)	104.9
2‴	3.95 t (8.0)	75.3	3.93 t (7.8)	75.3	3.93 t (7.8)	75.2	3.93 t (8.0)	75.3	3.93	75.2
3‴	4.08	78.6	4.08	78.6	4.08	78.5	4.07	78.6	4.08	78.5
4‴	4.10	70.8	4.10	70.8	4.10	70.8	4.09	70.8	4.10	70.7
5‴	3.63, 4.22	67.4	3.63, 4.21	67.3	3.64, 4.21	67.3	3.63, 4.21	67.3	3.63, 4.21	67.3
28-*O*-*β*-D-Fucopyranosyl										
1⁗	6.18 d (9.0)	94.3	6.14 d (9.0)	94.3	6.18 d (9.0)	94.3	6.14 d (9.0)	94.3	6.09 d (8.8)	94.8
2⁗	4.71 t (9.0)	72.5	4.62 t (9.0)	72.4	4.71 t (9.0)	72.4	4.62 t (9.0)	72.4	4.75 t (8.8)	73.6
3⁗	5.68 dd (9.0, 4.0)	75.0	5.66 dd (9.0, 4.0)	74.9	5.68 dd (9.0, 2.7)	74.9	5.66 dd (9.0, 3.2)	74.9	4.45	74.5
4⁗	5.76	71.2	5.76	71.2	5.75	71.1	5.76	71.1	5.71	74.7
5⁗	4.20	70.6	4.21	70.2	4.20	70.2	4.21	70.2	4.11	70.9
6⁗	1.24 d (6.0)	16.2	1.21 d (6.3)	16.1	1.24 d (5.8)	16.1	1.21 d (6.4)	16.1	1.26 d (5.8)	16.6
2⁗-*O*-*α*-L-Rhamnopyranosyl										
1⁗′	5.76 s	102.3	5.74 s	102.3	5.77 s	102.2	5.74 s	102.3	5.71 s	101.9
2⁗′	4.52	72.0	4.53	71.9	4.54	71.9	4.53	71.9	4.52	72.2
3⁗′	4.36	72.3	4.36	72.2	4.36	72.2	4.35	72.2	4.78	72.3
4⁗′	4.23	73.6	4.23	73.6	4.24	73.6	4.23	73.6	4.28	73.8
5⁗′	4.40	70.8	4.40	70.8	4.41	70.8	4.41	70.8	4.56	70.0
6⁗′	1.64 d (6.5)	18.8	1.64 d (5.8)	18.8	1.64 d (6.1)	18.8	1.64 d (6.1)	18.8	1.68 d (5.8)	18.8
The acetyl group										
1⁗′		170.1		170.1		170.1		170.1		
2⁗′	2.01 s	20.7	2.00 s	20.7	2.02 s	20.6	2.00 s	20.7		

Table 2. continued

	6		**7**		**8**		**9**		**10**	
	δ_H mult (*J* in Hz)[a]	δ_C[b]	δ_H mult (*J* in Hz)[a]	δ_C[b]	δ_H mult (*J* in Hz)[a]	δ_C[b]	δ_H mult (*J* in Hz)[a]	δ_C[b]	δ_H mult (*J* in Hz)[a]	δ_C[b]
The *para*-methoxycinnamoyl group (MC)										
1‴″		167.2		166.3		167.2		166.3		167.6
2‴″	6.60 d (15.5)	115.2	5.93 d (12.9)	116.0	6.60 d (16.1)	115.2	5.94 d (12.9)	116.0	6.45 d (16.1)	116.1
3‴″	7.95 d (15.5)	146.1	6.97 d (12.9)	145.0	7.96 d (16.1)	146.0	6.96 d (12.9)	145.2	7.86 d (16.1)	145.1
4‴″		127.3		127.7		127.3		127.7		127.4
5‴″ & 9‴″	7.53 d (9.0)	130.6	7.98 d (8.3)	133.2	7.54 d (7.8)	130.6	7.97 d (8.3)	133.2	7.35 d (8.5)	130.3
6‴″ & 8‴″	7.01 d (9.0)	114.8	6.97 d (8.3)	114.1	7.02 d (7.8)	114.8	6.97 d (8.3)	114.1	6.96 d (8.5)	114.7
7‴″		162.2		161.3		162.2		161.3		161.9
p-OCH_3	3.67 s	55.3	3.66 s	55.3	3.69 s	55.4	3.66 s	55.3	3.66 s	55.3
6′-OCH_3					3.72 s	52.2	3.72 s	52.2		

a) 500 MHz for ^{1}H, *b*) 400 MHz for ^{1}H and 100 MHz for ^{13}C, in C_5D_5N. The ^{1}H and ^{13}C chemical shifts were assigned by a combination of ^{1}H–^{1}H COSY, HMQC and HMBC experiments. ND, not detected.

Table 3. ^{1}H- and ^{13}C-NMR Data of **11**[a] Isolated from the Roots of *S. asclepiadea*

	δ_H	δ_C		δ_H	δ_C
The aglycone			3″	4.15	75.4
1	0.80, 1.40	38.1	4″	4.57	70.2
2	1.80, 2.10	25.2	5″	4.02	76.7
3	4.02	84.2	6″	4.42, 4.52	61.7
4		55.1	3′-*O*-*β*-D-Xylopyranosyl		
5	1.28	48.6	1‴	5.31 d (8.0)	105.0
6	0.90, 1.37	20.6	2‴	3.94 t (8.0)	75.3
7	1.48	32.8	3‴	4.06	78.5
8		40.2	4‴	4.07	70.8
9	1.78	46.9	5‴	3.64 t (12.0), 4.25	67.3
10		36.2	28-*O*-*β*-D-Fucopyranosyl		
11	1.91	23.7	1⁗	6.00 d (8.3)	94.5
12	5.55	122.0	2⁗	4.65	72.3
13		144.6	3⁗	4.40	83.1
14		42.1	4⁗	5.86 d (3.7)	74.3
15	1.99, 2.18	36.2	5⁗	4.50	70.6
16	5.21	73.9	6⁗	1.15 d (6.4)	16.5
17		49.3	2‴-*O*-*α*-L-Rhamnopyranosyl		
18	3.32 dd (13.9, 3.9)	41.6	1⁗	6.55 s	100.9
19	1.30, 2.70	47.5	2⁗	4.73 s	72.0
20		30.7	3⁗	4.65	72.3
21	1.25, 2.40	36.0	4⁗	4.41	82.4
22	2.12, 2.38	31.9	5⁗	4.52	68.5
23	9.85 s	209.8	6⁗	1.70 d like	18.6
24	1.41 s	11.1	3‴-*O*-*β*-D-Glucopyranosyl		
25	0.78 s	15.8	1⁗′	5.04 d (7.6)	105.6
26	1.03 s	17.4	2⁗′	3.94	75.0
27	1.71 s	27.0	3⁗′	4.14	78.5
28		175.9	4⁗′	4.04	70.6
29	0.92 s	33.1	5⁗′	3.86	78.3
30	0.94 s	24.4	6⁗′	4.25, 4.43	62.7
3-*O*-*β*-D-Glucuronopyranosyl			2⁗′-*O*-*β*-D-Xylopyranosyl		
1′	4.87 d (8.0)	103.9	1⁗″	5.24 d (7.8)	106.3
2′	4.35 t (8.0)	78.7	2⁗″	3.99	76.1
3′	4.26	86.0	3⁗″	4.07	78.5
4′	4.43	71.4	4⁗″	4.13	71.0
5′	4.47	77.3	5⁗″	3.41 t (9.0), 4.23	67.3
6′		ND	The acetyl group		
2′-*O*-*β*-D-Galactopyranosyl			CH_3	1.90 s	20.8
1″	5.54 d (6.4)	104.3	CO		171.3
2″	4.47	73.8			

a) Measured in pyridine-d_5, 400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR. The chemical shifts were assigned on the basis of ^{1}H–^{1}H COSY, HMQC, HMBC and TOCSY experiments. ND, not detected.

NMR spectrometers. HR-FAB-MS spectra were obtained with a Jeol JMS-700 mass spectrometer with a resolution of 5000, and glycerol as a matrix. Reversed-phase HPLC separations were carried out on a TSK-gel ODS-80T_S column (21.5×300 mm; eluent, CH_3OH/H_2O–0.1% trifluoroacetic acid (TFA); flow rate, 5.0 ml/min; UV detection, 210 nm).

Material The roots of *S. asclepiadea* were purchased from Juhua County of Kuuming, Yunnan Province, P. R. China, in February 2001, and the botanical source was identified by K. K. The voucher specimen (TMPW No. 20579) is deposited at the Museum of Toyama Medical and Pharmaceutical University.

Extraction and Isolation The roots (4.5 kg) of *S. asclepiadea* were ground and extracted with MeOH at room temperature. After removal of the solvent *in vacuo*, the MeOH extract (192.8 g) was dissolved in H_2O and extracted with $CHCl_3$, EtOAc, and BuOH successively to obtain $CHCl_3$ (2.1 g), EtOAc (14.3 g), and BuOH extracts (60.4 g). The BuOH extract was subjected to Diaion HP-20 column chromatography eluting with H_2O, MeOH–H_2O (3 : 7 and 3 : 2), and MeOH to yield fractions I (14.1 g), II (10.1 g), III (19.6 g), and IV (15.7 g). Fractions II, III, and IV underwent continued repeated column chromatography on Sephadex LH-20, silica gel, and ODS. Finally, compounds **12** (1.6 mg) and **13** (2.5 mg) were obtained from fraction II. Compounds **1** (11.2 mg), **2** (48.6 mg), **3** (5.9 mg), **4** (6.6 mg), and **5** (7.8 mg) were obtained from fraction III by preparative HPLC using MeOH–H_2O/0.1% TFA of different ratios as the eluting solvents, while **6** (8.2 mg), **7** (4.3 mg), **8** (4.5 mg), **9** (4.2 mg), **10** (3.9 mg), **11** (6.7 mg), and **12** (10.5 mg) were obtained from fraction IV.

Determination of Absolute Configurations of Sugars A solution of saponin (1 mg) in H_2O (0.1 ml) was treated with 5% aq. NaOH (0.1 ml) and the mixture was heated at 80 °C for 2 h. The reaction mixture was then neutralized with Dowex resin (H^+ form) and extracted with EtOAc (2 ml×5). The remaining H_2O layer was evaporated to dryness *in vacuo*. The resulting residue was refluxed with 5% aq. H_2SO_4–dioxane (1 : 1, 1 ml) for 3 h, neutralized with saturated $NaHCO_3$ and extracted with $CHCl_3$. The water layers were evaporated *in vacuo* to give a residue. The residue was dissolved in pyridine (0.1 ml), then a pyridine solution (0.2 ml) of L-cysteine methyl ester hydrochloride (0.1 M) was added to the solution. The mixture was kept at 60 °C for 1.5 h, dried *in vacuo*, and trimethylsilylated with hexamethyldisilazane-trimethylchlorosilane (HMDS-TMCS) (0.1 ml) at 60 °C for 1 h. After partition between hexane (0.3 ml) and H_2O (0.3 ml), the hexane extract was analyzed by GC-MS (column, DB-1, J & W Scientific, 0.25 mm i.d.×30 m; temperature, 50—230 °C, 15 °C/min then 230 °C, 18 min; carrier gas, He). The D- and L-Fuc, D- and L-Glc, D-Gal, D-Xyl, L-Rha, and D-Glc A derivatives had retention times of 20.48, 21.54, 25.46, 26.33, 26.54, 18.58, 19.53, and 20.41 min, respectively. Under the same conditions, the sugar derivatives after hydrolysis showed retention times identical to those observed for D-Glc, Gal, Fuc, Glc A, and L-Rha.

Determination of the Absolute Configuration of HMG in 2, 3 and 5 Reductive hydrolysis of **2**, **3** and **5** was worked up as reported by Fujimoto *et al.*[4] with moderate modifications. A solution of $LiEt_3$-BH (1.0 M) in dry THF (20 μl) (Aldrich) was added to a solution of **2**, **3** and **5** (2.0 mg) in dry THF (500 μl) under ice bath in an Ar stream. The reaction mixture was stirred under ice-cooling in Ar gas for 30 min. After addition of H_2O (100 μl) to the reaction mixture, 0.1 N HCl was added drop wise to adjust the pH to 3—4. The reaction mixture was stirred under Ar gas for 48 h. However, TLC check with authentic (3*RS*)- and (3*R*)-mevalonolactones showed no trace of mevalonolactone production. Therefore, the reaction mixture was dried *in vacuo* and 5% NaOH (1 ml) was added and refluxed for 2 h. After the reaction, it was neutralized with Dowex resin (H^+ form) and evaporated to dryness *in vacuo*. Likewise, (3*RS*)- and (3*R*)-mevalonolactones were also treated with 5% NaOH, neutralized with Dowex resin (H^+ form) and evaporated to dryness *in vacuo* to yield (3*RS*)- and (3*R*)-3,5-dihydroxy-3-methyl-1-pentanoic acids. The prepared authentic samples together with saponin derivatives were dissolved in MeOH and subjected to chiral HPLC analysis [column: CD-Ph column (4.6×250 mm, Shiseido); solvent: hexane–EtOH (3 : 2); wavelength: 210 nm; flow rate: 0.5 ml/min]. The reduced saponin hydrolysate gave a retention time identical to that of (3*R*)-3,5-dihydroxy-3-methyl-1-pentanoic acid (8.7 min), while (3*S*)-3,5-dihydroxy-3-methyl-1-pentanoic acid and (3*R*)- and (3*S*)-mevalonolactones had retention times of 8.0, 12.0 and 12.7 min, respectively.

Sinocrassuloside I (**1**): A white amorphous powder, $[\alpha]_D^{26}$ +17.6° (c=0.051, MeOH). IR ν_{max} (KBr) cm^{-1} 3410, 2936, 1752, 1654, 1459, 1381, 1265, 1064, 699, 511, 419. FAB-MS *m/z* 989 $[M+H]^+$ and 1011 $[M+Na]^+$; HR-FAB-MS *m/z* 989.4922 $[M+H]^+$ (calcd for $C_{48}H_{77}O_{21}$, 989.4957). ^{1}H- and ^{13}C-NMR data are presented in Table 1.

Sinocrassuloside II (**2**): A white amorphous powder, $[\alpha]_D^{26}$ +13.9° (c=0.074, MeOH). IR ν_{max} (KBr) cm^{-1} 3422, 2935, 1736, 1718, 1702, 1214, 1164, 1074, 912, 512, 419. FAB-MS *m/z* 1133 $[M+H]^+$ and 1155 $[M+Na]^{+1}$; HR-FAB-MS *m/z* 1133.5421 $[M+H]^+$ (calcd for $C_{54}H_{85}O_{25}$, 1133.5380). ^{1}H- and ^{13}C-NMR data are presented in Table 1.

Sinocrassuloside III (**3**): A white amorphous powder, $[\alpha]_D^{26}$ +30.4° (c=0.023, MeOH). IR ν_{max} (KBr) cm^{-1} 3421, 2939, 1720, 1651, 1539, 1458, 1399, 1072, 520. FAB-MS *m/z* 1147 $[M+H]^+$ and 1169 $[M+Na]^+$. HR-FAB-MS *m/z* 1169.5352 $[M+Na]^+$ (calcd for $C_{55}H_{86}O_{25}Na$, 1169.5356). ^{1}H- and ^{13}C-NMR data are presented in Table 1.

Sinocrassuloside IV (**4**): A white amorphous powder, $[\alpha]_D^{26}$ +22.6° (c=0.031, MeOH). IR ν_{max} (KBr) cm^{-1} 3421, 2924, 1720, 1462, 1061, 710, 517, 424. FAB-MS *m/z* 971 $[M+H]^+$ and 993 $[M+Na]^+$. HR-FAB-MS *m/z*, 993.4697 $[M+Na]^+$ (calcd for $C_{48}H_{74}O_{20}Na$ 9934671). ^{1}H- and ^{13}C-NMR data are presented in Table 1.

Sinocrassuloside V (**5**): A white amorphous powder, $[\alpha]_D^{26}$ +39.7° (c=0.026, MeOH). IR ν_{max} (KBr) cm^{-1} 3429, 2924, 1720, 1381, 1068, 717, 517, 447. FAB-MS *m/z* 1133 $[M+H]^+$ and 1155 $[M+Na]^+$. HR-FAB-MS *m/z* 1133.5380 $[M+H]^+$ (calcd for $C_{54}H_{85}O_{25}$, 1133.5380). ^{1}H- and ^{13}C-NMR data are presented in Table 1.

Sinocrassuloside VI (**6**): A white amorphous powder, $[\alpha]_D^{26}$ +18.4° (c=0.076, MeOH). IR ν_{max} (KBr) cm^{-1} 3448, 2964, 1685, 1512, 1434, 1207, 1076, 802, 725, 521, 451, 420. FAB-MS *m/z* 1451 $[M+H]^+$. HR-FAB-MS *m/z* 1473.6299 $[M+Na]^+$ (calcd for $C_{71}H_{102}O_{31}Na$, 1473.6303). ^{1}H- and ^{13}C-NMR data are presented in Table 2.

Sinocrassuloside VII (**7**): A white amorphous powder, $[\alpha]_D^{26}$ +8.3° (c=0.004, MeOH). IR ν_{max} (KBr) cm^{-1} 3448, 2924, 1720, 1512, 1149, 1041, 706, 521, 420. FAB-MS *m/z* 1451 $[M+H]^+$. HR-FAB-MS *m/z* 1451.6462 $[M+H]^+$ (calcd for $C_{71}H_{103}O_{31}$, 1451.6483). ^{1}H- and ^{13}C-NMR data are presented in Table 2.

Sinocrassuloside VIII (**8**): A white amorphous powder, $[\alpha]_D^{26}$ +12.1° (c=0.022, MeOH). IR ν_{max} (KBr) cm^{-1} 3448, 2935, 1736, 1627, 1512, 1462, 1396, 1265, 1153, 1080, 517. FAB-MS *m/z* 1487 $[M+Na]^+$. HR-FAB-MS *m/z* 1487.6488 $[M+Na]^+$ (calcd for $C_{72}H_{104}O_{31}Na$, 1487.6459). ^{1}H- and ^{13}C-NMR data are presented in Table 2.

Sinocrassuloside IX (**9**): A white amorphous powder, $[\alpha]_D^{26}$ +37.5° (c=0.016, MeOH). IR ν_{max} (KBr) cm^{-1} 3448, 2935, 1735, 1627, 1511, 1461, 1396, 1265, 1153, 1079, 516. FAB-MS *m/z* 1487 $[M+Na]^+$; HR-FAB-MS *m/z* 1487.6462 $[M+Na]^+$ (calcd for $C_{72}H_{104}O_{31}Na$, 1487.6459). ^{1}H- and ^{13}C-NMR data are presented in Table 2.

Sinocrassuloside X (**10**): A white amorphous powder, $[\alpha]_D^{26}$ +38.5° (c=0.026, MeOH). IR ν_{max} (KBr) cm^{-1} 3421, 2935, 1735, 1635, 1511, 1253, I157, 1041, 516. FAB-MS *m/z* 1409 $[M+H]^+$. HR-FAB-MS *m/z* 1409.6387 $[M+H]^+$ (calcd for $C_{69}H_{101}O_{30}$, 1409.6378). ^{1}H- and ^{13}C-NMR data are presented in Table 2.

Sinocrassuloside XI (**11**): A white amorphous powder, $[\alpha]_D^{26}$ +3.5° (c=0.019, MeOH). IR ν_{max} (KBr) cm^{-1} 3425, 2927, 1735, 1377, 1045, 710, 521, 444. FAB-MS *m/z* 1607 $[M+Na]^+$. HR-FAB-MS *m/z* 1585.6886 $[M+H]^+$ (calcd for $C_{72}H_{113}O_{38}$, 1585.6910). ^{1}H- and ^{13}C-NMR data are presented in Table 3.

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