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ASTRASIEVERSIANINS IX, XI and XV, CYCLOARTANE DERIVED SAPONINS FROM *ASTRAGALUS SIEVERSIANUS**

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Key Word Index—*Astragalus sieversianus*; Leguminosae; cycloartane triterpene; astrasieversianin; astrasieversiagenin; triterpenoid saponins.

Abstract—Sixteen triterpenoid saponins, astrasieversianins I–XVI, have been isolated from the methanol extract of the roots of *Astragalus sieversianus*. By heterogeneous acidic hydrolysis, all glycosides produced only one common aglycone which was identified as the known natural product astramembrangenin or cycloastragenol. On the basis of spectral analysis and chemical reactions, the structures of two new triterpenoid glycosides, astrasieversianin IX and XI, were assigned as the 3-*O*-[α-L-rhamnopyranosyl(1 → 2)]-(3′-*O*-acetyl)-β-D-xylopyranosyl-6-*O*-β-D-xylopyranoside and the 3-*O*-[α-L-rhamnopyranosyl(1 → 2)]-(4′-*O*-acetyl)-β-D-xylopyranosyl-6-β-D-xylopyranoside of cycloastragenol. Astrasieversianin XV was identified as the 20,24-epimer (20*R*,24*S*) of cyclosieversiside G (20*S*,24*R*).

INTRODUCTION

Astragalus sieversianus Pall is a medicinal plant frequently used in Chinese traditional medicine. In the preceding communication [1] we have briefly reported the chemical investigation of this plant. In this paper we wish to describe the isolation of sixteen cycloartane type triterpenoid glycosides, astrasieversianins I–XVI and the determination of the structures of three of them, astrasieversianins IX (1), XI (2) and XV (3).

RESULTS AND DISCUSSION

The crude saponin fractions (A and B) derived from the methanol extract of *A. sieversianus* were repeatedly chromatographed on alumina and silica gel columns to yield astrasieversianins I–XVI. Astrasieversianin IX (1) and XV (3) were the major components of this plant, and 3 was demonstrated to have significant hypotensive activity [1].

Heterogeneous acidic hydrolysis of the mixture of astrasieversianins I–XVI yielded compound 4 as their common aglycone. The fact that the spectral data and physical properties of 4 and its *O*-acetyl derivatives (5, 6 and 7) were in good agreement with those of astramembrangenin and its corresponding derivatives led us to consider that 4 had to be identical with astramembrangenin which was isolated previously from *A. membranaceus* [2]. It is of interest to note that the absolute configuration at C-20 and C-24 of 4 is contrary to that of cyclosieversigenin (4a) isolated from the same species of the plant grown in Russia [3].

In order to confirm the stereochemistry of the side chain of 4, the triacetate 6 of compound 4 was converted to the γ-lactone 8 by oxidation with CrO_3–acetic acid. The fact that the CD curve of 8 was consistent with that of the authentic sample obtained from astramembrangenin (20*R*,24*S*), the structure of which had been established by X-ray crystallographic analysis [4], revealed that C-20 of 8 should have the 20*R*-configuration.

The ^{1}H NMR spectra of 6 and the authentic sample obtained from astramembrangenin were measured with six different concentrations of Eu(fod)$_3$ by Lavie's method [5, 6]. The similar induced chemical shifts ($\Delta\delta$) of both compounds showed that C-24 of 6 possessed the *S*-configuration. Since 4 has been converted to 6 and 8, so it also has the same 20*R*,24*S*-configuration.

Acidic hydrolysis of 3 yielded 4 as the aglycone and xylose and rhamnose as the sugar components. The ^{13}C NMR spectrum of 3 showed forty-six carbon signals. Thirty signals were accounted for by the aglycone moiety, the remaining sixteen signals were attributed to two xylose and one rhamnose moieties. FDMS of 3 exhibited a quasi-molecular ion peak and a molecular ion peak at *m/z* 924 and 900. Thus, 3 might be considered to be a triglycoside of 4 with the molecular formula of $C_{46}H_{76}O_{17}$. This was further supported by the fact that the ^{1}H NMR spectrum of the permethylate 9 of 3 showed ten *O*-methyl signals at δ3.16–3.60.

A comparison of the ^{13}C NMR spectrum of 3 with that of 4 showed that the chemical shifts at C-3 and C-6 of 3 were displaced downfield, respectively, by 9.3 and 10.1 ppm (Table 1), which may be attributed to the 3-*O*-D- and 6-*O*-D-xylopyranosyl moieties. In addition, methanolysis of 9 afforded methyl 2,3,4-tri-*O*-methyl-D-xylopyranoside, methyl 3,4-di-*O*-methyl-D-xylopyranoside and methyl 2,3,4-tri-*O*-methyl-L-rhamnopyranoside. It was reported [7] that the chemical shifts of the anomeric carbon of the terminal 3-*O*-D- and 6-*O*-D-xylopyranosyl moieties appeared at δ107.3 and 105.3, respectively. The upfield shift (Table 1) of C-1′ of 3 indicated that L-rhamnose unit was attached to the C-2′ of the 3-*O*-D-xylopyranosyl moiety.

On the basis of the chemical shifts (Table 1) of the anomeric carbon and the coupling constants ($J_{1',2'}$

* Part 2 in the series "The Chemical Investigation of *Astragalus sieversianus* Pall". For part 1 see ref. [1].

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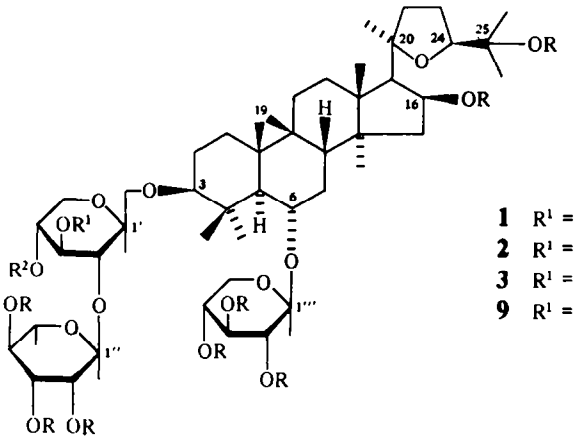
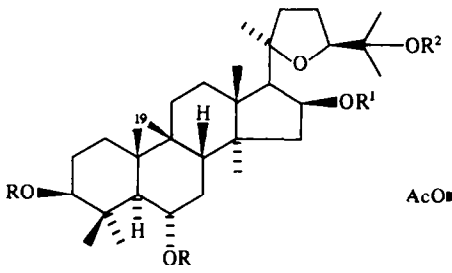
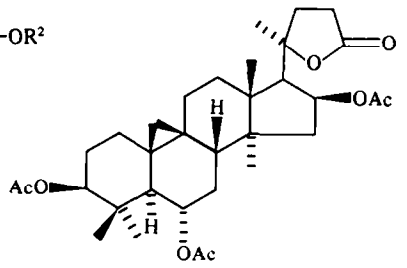


1 R^1 = Ac, R^2 = R = H
2 R^1 = R = H, R^2 = Ac
3 R^1 = R^2 = R = H
9 R^1 = R^2 = R = Me



4 R = R^1 = R^2 = H
5 R = Ac, R^1 = R^2 = H
6 R = R^1 = Ac, R^2 = H
7 R = R^1 = R^2 = Ac



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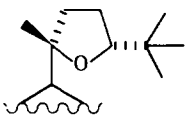

4a

= 7 Hz, $J_{1'',2''}$ = 1.4 Hz, $J_{1''',2'''}$ = 7 Hz) of the anomeric proton of **3**, the two xylopyranosyl moieties were β-orientated [8, 9], and the rhamnopyranosyl moiety was α-orientated [10, 11].

Based on the above results, compound **3** was established as the 20,24-epimer (20*R*,24*S*) of cyclosieversioside G (20*S*,24*R*) [12]. Alkaline hydrolysis of **1** and **2** yielded **3** as a common deacetylation product. In the ^{1}H NMR spectra of **1** and **2**, the signals of acetoxy groups appeared at δ1.98 and 1.90, respectively. The FDMS of **1** and **2** exhibited a quasi-molecular ion peak at 965 $[M+Na]^+$ and 966 $[M+Na+H]^+$, respectively. These data indicated that **1** and **2** were mono-*O*-acetyl derivatives of **3**. A careful comparison of the ^{13}C NMR data of **1**, **2**, **3** (Table 1) and the related *O*-acetyl-glycosides [7, 13] revealed that the signals of C-3′ of **1** and C-4′ of **2** exhibited significant acetylation shifts [14, 15], therefore the acetoxyl groups of **1** and **2** were attached to C-3′ and C-4′ of the 3-*O*-xylopyranosyl moiety, respectively. The structures of astrasieversianins IX and XI were elucidated therefore as **1** and **2**, respectively.

EXPERIMENTAL

All mps were determined on a MEL-TEMP apparatus and are uncorr. Both ^{1}H and ^{13}C NMR spectra [δ(ppm), *J* (Hz)] were obtained on a Varian XL 200 spectrometer. TMS was used as an internal standard for ^{1}H NMR (200 MHz), C_5D_5N was used as secondary reference standard for ^{13}C NMR (50.3 MHz), and then ^{13}C NMR data were converted to the TMS scale. FDMS and EIMS were determined on Hitachi M-80 and Finnigan 4021 instruments, respectively. IR spectra were recorded on a Shimadzu IR-440 spectrophotometer. GLC was performed on a GC-100 chromatograph with FID and a stainless steel column packed with 102 white support material impregnated with 10% PEG. The column temp. was 126° and the N_2 carrier gas was at 26 ml/min. The CD spectra were measured on a JASCO-500 C spectropolarimeter. The spots for TLC or PC were detected by spraying with the following reagents; a soln of vanillin (3 g) and conc. H_2SO_4 (3 ml) in 95% EtOH (100 ml); 1% $Ce(SO_4)_2$ soln in 10% H_2SO_4; 1% aniline hydrogen phthalate soln in 70% EtOH; H_2O (for prep. TLC of glycoside).

Plant material. The roots of *Astragalus sieversianus* were

Table 1. ^{13}C NMR chemical shift values (δ, C_5D_5N) for astrasieversianins IX (1), XI (2), XV (3) and the aglycone (4)*

Carbon	4†	3	2	1
3	78.2	87.5	87.6	87.8
6	68.3	78.4	78.4	78.2
16	73.4	73.4	73.4	73.3
20	87.2	87.3	87.3	87.2
24	81.6	81.5	81.6	81.5
25	71.2	71.3	71.3	71.2
xyl-1′		105.7	105.1	105.1
2′		78.0	77.4	76.4
3′		77.8	73.1	78.2
4′		71.4	74.7	70.4
5′		66.8	62.5	66.4
rha-1″		101.8	101.9	102.2
2″		71.0	71.1	70.9
3″		72.4	72.5	71.9
4″		74.2	74.1	73.6
5″		69.6	69.6	68.9
6″		18.7	18.7	18.5
xyl-1‴		105.7	105.8	105.6
2‴		75.4	75.5	75.3
3‴		77.1	77.0	77.1
4‴		72.4	72.4	72.2
5‴		66.8	66.9	66.7
MeCO			170.6	170.7
MeCO			20.8	21.0

*The signal for the carbons bearing an acetoxy group are underlined.

†For the chemical shifts of the other carbons of 4 see Experimental.

collected from the Tacheng area, west of Tian-Shan Mountain, in the Xinjian Uygur Autonomous Region of China in August 1982.

Isolation of astrasieversianins. Dried powder (12 kg) of the roots of *A. sieversianus* were extracted with MeOH until the MeOH extract became colourless. The MeOH soln was evaporated to dryness, dissolved in H_2O and extracted with *n*-BuOH satd with H_2O. The *n*-BuOH extract was evaporated under red. pres. to give a dark brown tarry mass (790 g). It was dissolved in 1.6 l. MeOH and the soln was poured into 15 vols of Me_2CO with stirring. The resulting ppt was collected as fraction A (340 g) and a syrupy residue on concn of the Me_2CO soln was obtained as fraction B (440 g).

Fraction A (total 300 g, 150 g for each run) was chromatographed on a silica gel column (4.5 kg for each run) and eluted successively with $CHCl_3$–MeOH (95:5; 90:10; 85:15) to afford eight crude saponin subfractions: A_1 (10 g), A_2 (12 g), A_3 (6 g), A_4 (13 g), A_5 (13 g), A_6 (7 g), A_7 (20 g) and A_8 (70 g). A_1 was rechromatographed on a silica gel column ($CHCl_3$–MeOH, 95:5) to give astrasieversianin I (650 mg). By repeated CC or prep. TLC or a combination of both on silica gel ($CHCl_3$–MeOH, 90:10; 85:15; 80:20), astrasieversianins II (2.1 g) and III (1.1 g) were obtained from A_2, IV (2.4 g) from A_3, V (10 mg) from A_4, VI (4 g) from A_5, VII (28 mg) and VIII (900 mg) from A_6, IX (6.4 g) from A_7. All chromatographic fractions containing astrasieversianin X from A_6 and A_7 were combined and purified by repeated prep. TLC ($CHCl_3$–MeOH, 80:20) to yield astrasieversianin X (14 mg). A_8 was not investigated because its saponin constituent corresponded with that of subfractions B_1 and B_2.

The fraction B was subjected to CC on silica gel (5 kg) eluted successively with ($CHCl_3$–MeOH, 80:20), ($CHCl_3$–MeOH–H_2O, 70:23:4) to afford five subfractions: B_1 (60 g), B_2 (60 g), B_3 (57 g), B_4 (30 g) and B_5 (18 g). B_1 contained astrasieversianin IX as the major saponin constituent. B_2 was successively chromatographed on a silica gel column ($CHCl_3$–MeOH–H_2O, 80:20:2) and an Al_2O_3 column ($CHCl_3$–MeOH–H_2O, 70:30:5) to give, besides astrasieversianin XIII (2.15 g), a mixture of astrasieversianins XI and XII which was repeatedly purified by CC on silica gel ($CHCl_3$–MeOH–H_2O, 80:20:3.4) to afford astrasieversianins XI (81 mg) and XII (182 mg). B_3 (30 g) was purified by recrystallization from MeOH–H_2O to produce astrasieversianin XV (10 g). The mother liquor from the above-mentioned crystals was evaporated and was repeatedly subjected to CC on silica gel ($CHCl_3$–MeOH, 8:2) to give a mixture (0.5 g) of astrasieversianins XII, XIII and XIV, which after treating with 1% KOH–MeOH was further purified by CC on silica gel ($CHCl_3$–MeOH–H_2O, 80:20:2) to obtain astrasieversianin XIV (35 mg). Astrasieversianin XVI (2.7 g) was isolated from B_4 (10 g) by CC on silica gel with ($CHCl_3$–MeOH–H_2O, 70:23:4). R_f value of astrasieversianins I–XVI on TLC (silica gel): for I–IX ($CHCl_3$–MeOH, 80:20), 0.83, 0.73, 0.68, 0.47, 0.37, 0.35, 0.27; for IX–XVI ($CHCl_3$–MeOH–H_2O, 70:26:4), 0.45, 0.42, 0.415, 0.31, 0.30, 0.295, 0.23, 0.17.

Astrasieversianin IX (1). Mp 208–209° (colourless crystals from MeOH), $[\alpha]_D^{12}$ −6.5° (*c* 0.17; MeOH). (Found: C, 60.0; H, 8.4. $C_{48}H_{78}O_{18}\cdot H_2O$ requires: C 60.0; H, 8.3%.) IR ν_{max}^{KCl} cm^{-1}: 3350 (OH), 1730 (OAc). FDMS *m/z* (rel. int.): 965 $[M+Na]^+$ (6.0), 943 $[M+1]^+$ (1.8), 942 $[M]^+$ (1.9). ^1H NMR (200 MHz, $CDCl_3+C_5D_5N$): δ0.21, 0.55 (1H each, *d*, *J* = 4 Hz, H-19), 1.00, 1.07, 1.19, 1.22, 1.27, 1.32, 1.38 (3H each, *s*, 7 × Me), 1.20 (3H, *d*, *J* = 6 Hz, H-6″), 1.98 (3H, *s*, OAc).

Astrasieversianin XI (2). Mp 192–193° (colourless needles from MeOH), $[\alpha]_D^{12}$ −9.0° (*c* 0.20; MeOH). (Found: C, 59.7 H, 8.3. $C_{48}H_{78}O_{18}\cdot H_2O$ requires: C, 60.0; H, 8.4%.) IR ν_{max}^{nujol} cm^{-1}: 3350 (OH), 1720 (OAc). FDMS *m/z* (rel. int.): 966 $[M+Na+H]^+$ (2.8), 943 $[M+H]^+$ (3.2). ^1H NMR (200 MHz, C_5D_5N): δ0.23, 0.56 (1H each, *br s*, H-19), 1.10, 1.31, 1.50, 1.58 (3H each, *s*, 4 × Me), 1.24 (9H, *s*, 3 × Me), 1.56 (3H, *d*, *J* = 6 Hz, H-6″), 1.90 (3H, *s*, OAc).

Astrasieversianin XV (3). Mp 255–256° (colourless needles from MeOH), $[\alpha]_D^{10}$ −6.7° (*c* 0.14; MeOH). (Found: C, 60.6; H, 8.7. $C_{46}H_{76}O_{17}\cdot\frac{1}{2}H_2O$ requires: C, 60.7; H, 8.5%.) IR ν_{max}^{nujol} cm^{-1}: 3320 (OH). FDMS *m/z* (rel. int.): 924 $[M+Na+H]^+$ (6.0), 901 $[M+H]^+$ (0.5), 900 $[M]^+$ (0.6). ^1H NMR (200 MHz, $CDCl_3+C_5D_5N$): δ0.13, 0.57 (1H each, *br s*, H-19), 1.06, 1.22, 1.24, 1.29, 1.44, 1.47, 1.50 (3H each, *s*, 7 × Me), 1.21 (3H, *d*, *J* = 6 Hz, H-6″).

Heterogeneous acidic hydrolysis of 3. A soln of 3 (100 mg) in EtOH (5 ml) was mixed with 10% aq. HCl (2 ml) and C_6H_6 (10 ml) and the whole mixture was refluxed for 5 hr. The reaction mixture was poured into ice-water and the whole was extracted with EtOAc. The EtOAc extract was washed successively with 4% $NaHCO_3$ soln and H_2O and dried over Na_2SO_4. The crude product (74 mg) was separated by CC on silica gel with $CHCl_3$–EtOAc–MeOH (25:25:1) to give 4 (42 mg), mp 241–243° (colourless needles from EtOH), $[\alpha]_D^{23}$ +53.0 (*c* 0.39; MeOH). (Found: C, 72.1; H, 10.3. Calc. for $C_{30}H_{50}O_5\cdot\frac{1}{2}H_2O$; C, 72.1; H, 10.2%.) IR ν_{max}^{nujol} cm^{-1}: 3450, 3260 (OH), 3020 (CH_2 of cyclopropane). EIMS *m/z* (rel. int.): 490 $[M]^+$ (0.5), 472 $[M-H_2O]^+$ (2.0), 437 $[M+H-3H_2O]^+$ (3.1), 419 $[M+H-4H_2O]^+$ (1.0), 143 $[C_8H_{15}O_2]^+$ (100). ^1H NMR (200 MHz, $CDCl_3$): δ0.37, 0.53 (1H each, *d*, *J* = 4 Hz, H-19), 0.97, 0.98, 1.18, 1.26, 1.33 (3H each, *s*, 5 × Me), 1.28 (3H, *s*, 2 × Me), 22.34 (1H, *d*, *J* = 8 Hz, H-17), 3.32 (1H, *dd*, *J* = 4.5, 11 Hz, H-3), 3.56 (1H, *td*, *J* = 4.5, 9.5, 9.5 Hz, H-6), 3.78 (1H, *dd*, *J* = 7.9 Hz, H-24), 4.70 (1H, *td*, *J* = 5, 8, 8 Hz, H-

16); ^{13}C NMR (50.3 MHz, C_5D_5N): δ58.4 (C-17), 53.9 (C-5), 47.2 (C-8), 46.7 (C-15), 46.1 (C-14), 45.0 (C-13), 42.4 (C-4), 38.8 (C-7), 34.9 (C-22), 33.4 (C-12), 32.7 (C-1), 31.5 (C-19), 31.0 (C-2), 29.8 (C-10), 29.5 (C-29), 28.6 (C-26), 28.2 (C-27), 27.1 (C-21), 26.5 (C-11), 26.2 (C-23), 21.6 (C-28), 20.9 (C-9), 20.2 (C-18), 16.1 (C-30). For the other signals see Table 1.

Heterogeneous acidic hydrolysis of the mixture of astrasieversianins I–XVI. To a soln of the mixture (1.23 g) of astrasieversianins I–XVI in EtOH (65 ml), C_6H_6 (130 ml) and 10% aq. HCl (26 ml) were added. The reaction mixture was stirred at boiling temp. for 30 hr and worked up in the same manner as above. The product (560 mg) was obtained as colourless needles (from EtOH) and was shown to be identical in every aspect with **4** obtained directly from **3**.

Diacetate (**5**) *of* **4**. Compound **4** (100 mg) was acetylated with Ac_2O–pyridine at room temp. Usual work-up gave 80 mg **5**, mp 225–227° (colourless needles from MeOH), $[\alpha]_D^{22}$ +70° (*c* 0.28; MeOH). (Found: C, 69.9; H, 9.5. calc. for $C_{34}H_{54}O_7 \cdot \frac{1}{2}H_2O$: C, 70.0; H, 9.4%.) IR ν_{max}^{nujol} cm^{-1}: 3420 (OH), 1730, 1715 (OAc). EIMS *m/z* (rel. int.): 575 $[M+H]^+$ (0.4), 515 $[M+H-60]^+$ (1.2), 454 $[M-2\times60]^+$ (2.5), 143 $[C_8H_{15}O_2]^+$ (100). ^{1}H NMR (200 MHz, $CDCl_3$): δ0.36, 0.61 (1H each, *d*, *J* = 4 Hz, H-19), 0.85, 0.95, 1.00, 1.17, 1.24, 1.25, 1.32 (3H each, *s*, 7 × Me), 2.00, 2.06 (3H each, *s*, 2 × OAc), 2.20 (2H, *s*, 2 × OH), 2.34 (1H, *d*, *J* = 8 Hz, H-17), 3.78 (1H, *dd*, *J* = 7, 9 Hz, H-24), 4.61 (1H, *dd*, *J* = 4.5, 11 Hz, H-3), 4.70 (1H, *td*, *J* = 5, 8, 8 Hz, H-16), 4.77 (1H, *td*, *J* = 4.5, 9.5, 9.5 Hz, H-6).

Triacetate (**6**) *and tetracetate* (**7**) *of* **4**. A mixture of 60 mg **4**, 1 ml pyridine and 0.75 ml Ac_2O was heated at 70° for 30 hr. The crude product (66 mg) was subjected to CC on silica gel with petrol–EtOAc (85:15) to give **6** (32 mg) and **7** (18 mg). Compound **6**: mp 200–201° (colourless crystals from MeOH), $[\alpha]_D^{21}$ +108° (*c* 0.30; MeOH). (Found: C, 70.0; H, 9.0 calc. for $C_{36}H_{56}O_8$: C, 70.1; H, 9.1%.) IR ν_{max}^{nujol} cm^{-1}: 3520 (OH), 1730 (OAc). EIMS *m/z* (rel. int.): 617 $[M+H]^+$ (0.8), 556 $[M-60]^+$ (4.6), 496 $[M-2\times60]^+$ (16.5), 437 $[M+H-3\times60]^+$ (14.4), 143 $[C_8H_{15}O_2]^+$ (100). ^{1}H NMR (200 MHz, $CDCl_3$): δ0.39, 0.62 (1H each, *d*, *J* = 4 Hz, H-19), 0.88, 1.11, 1.23, 1.30, 1.32 (3H each, *s*, 5 × Me), 1.01 (6H, *s*, 2 × Me), 1.60 (1H, *s*, OH), 2.01, 2.04, 2.07 (3H each, *s*, 3 × OAc), 2.51 (1H, *d*, *J* = 8 Hz, H-17), 3.72 (1H, *dd*, *J* = 7, 9 Hz, H-24), 4.60 (1H, *dd*, *J* = 4.5, 11 Hz, H-3), 4.37 (1H, *td*, *J* = 4.5, 9.5, 9.5 Hz, H-6), 5.43 (1H, *td*, *J* = 5, 8, 8 Hz, H-16).

Compound **7**: mp 95–96° (amorphous solid from MeOH–H_2O), $[\alpha]_D^{21}$ +98.9 (*c* 0.44; MeOH). (Found: C, 69.3; H, 9.8. calc. for $C_{38}H_{58}O_9$: C, 69.3; H, 8.8%.) IR ν_{max}^{nujol} cm^{-1}: 1730 (OAc). EIMS *m/z* (rel. int.): 658 $[M]^+$ (0), 643 $[M-Me]^+$ (2.0), 598 $[M-60]^+$ (7.8), 538 $[M-2\times60]^+$ (35.9), 478 $[M-3\times60]^+$ (22.5), 418 $[M-4\times60]^+$ (12.8), 185 $(C_8H_{15}O_2+MeCO)^+$ (90.1), 143 $[C_8H_{15}O_2]^+$ (24.2), 125 $[185-60]^+$ (100). ^{1}H NMR (200 MHz, $CDCl_3$): δ0.39, 0.60 (1H each, *d*, *J* = 4 Hz, H-19), 0.86, 0.98, 1.00, 1.42, 1.44 (3H each, *s*, 5 × Me), 1.34 (6H, *s*, 2 × Me), 1.98, 2.00, 2.03, 2.07 (3H each, *s*, 4 × OAc), 2.43 (1H, *d*, *J* = 8 Hz, H-17), 4.02 (1H, *dd*, *J* = 7, 9 Hz, H-24), 4.59 (1H, *d*, *J* = 4.5, 11 Hz, H-3), 4.73 (1H, *td*, *J* = 4.5, 9.5, 9.5 Hz, H-6), 5.34 (1H, *td*, *J* = 5, 8, 8 Hz, H-16).

Oxidation of **6**. Oxidation of **6** (8 mg) with CrO_3–AcOH gave **8** which was purified by CC on silica gel with $CHCl_3$–EtOAc (7:3) to give colourless needles (from MeOH), mp 179–180°, $[\alpha]_D^{22}$ +112.9° (*c* 0.30; MeOH). (Found: C, 68.2; H, 8.3. calc for $C_{33}H_{48}O_8 \cdot \frac{1}{2}H_2O$: C, 68.2; H, 8.4%.) IR ν_{max}^{nujol} cm^{-1}: 1770, 1245 (γ-lactone), 1730 (OAc). EIMS *m/z* (rel. int.): 573 $[M+1]^+$ (4.1), 512 $[M-60]^+$ (5.8), 453 $[M+H-2\times60]^+$ (40.1), 393 $[M+H-3\times60]^+$ (37.7), 99 $[C_5H_7O_3]^+$ (22.7). ^{1}H NMR (200 MHz, $CHCl_3$): 0.40, 0.62 (1H each, *d*, *J* = 4 Hz, H-19), 0.87, 1.30, 1.52 (3H each, *s*, 3 × Me), 1.00 (6H, *s*, 2 × Me), 2.01, 2.03, 2.07 (3H each, *s*, 3 × OAc), 4.66 (1H, *dd*, *J* = 4.5, 11 Hz, H-3), 4.73 (1H, *td*, *J* = 4.5, 9.5, 9.5 Hz, H-6), 5.39 (1H, *td*, *J* = 5, 8, 8 Hz, H-16). CD: $\Delta\varepsilon_{212}$ +2.41 (MeOH; *c* 0.11). CD of the authentic sample which was obtained from astramembrangenin through the same chemical reactions as above: $\Delta\varepsilon_{212}$ +2.49 (MeOH; *c* 0.084).

Deacetylation of astrasieversianins IX (**1**) *and XI* (**2**). A soln of **1** and **2** (20 mg each) in MeOH (5 ml) and 1% KOH–MeOH (5 ml) was refluxed for 30 min. After evaporation of the solvent, the crude product (35 mg) was collected, washed with ice H_2O and recrystallized from MeOH. The pure product was obtained as colourless needles, mp 255–259°, $[\alpha]_D^{10}$ −7.7° (*c* 0.20; MeOH), and was found to be identical with the natural compound **3** by mmp determination, element analysis, TLC, IR and ^{1}H NMR comparisons.

Acidic hydrolysis of **3**. Compound **3** (9 mg) was refluxed with 4 N aq. HCl–MeOH (1:1, 4 ml) for 2 hr. The reaction mixture left after removal of solvent was diluted with H_2O (2 ml) and neutralized with Ag_2CO_3 powder. The filtrate was further concd under red. pres. and subjected to PC(EtOAc–C_5H_5N–H_2O, 36:10:1.15) to identify the sugar components as xylose and rhamnose by comparison with authentic samples.

Per-O-methylation of **3**. Compound **3** (9 mg) was methylated by the Hakomori method [16] and the crude product was purified by CC on silica gel with petrol–EtOAc–Me_2CO (80:20:5) to afford deca-*O*-methyl ether (**9**) of **3**. Mp 175–178° (amorphous powder from MeOH), $[\alpha]_D^{19}$ −2.2° (*c* 0.50; $CHCl_3$). (Found: C, 64.5; H, 9.4. $C_{56}H_{96}O_{17}$ requires: C, 64.6; H, 9.2%.) IR ν_{max}^{nujol} cm^{-1}: no OH, 3030 (CH_2 of cyclopropane ring). ^{1}H NMR (200 MHz, $CDCl_3$): δ0.18, 0.51 (1H each, *d*, *J* = 4 Hz, H-19), 0.95, 0.99, 1.09, 1.17, 1.20 (3H each, *s*, 5 × Me), 1.18 (3H, *d*, *J* = 6 Hz, H-6″), 1.26 (6H, *s*, 2 × Me), 3.15, 3.27, 3.45, 3.41, 3.48, 3.49, 3.55, 3.59, 3.60 (3H each, *s*, 10 × OMe), 4.29 (1H, *d*, *J* = 7 Hz, 1‴-H), 4.35 (1H, *d*, *J* = 7 Hz, H-1′), 5.34 (1H, *d*, *J* = 1.4 Hz, H-1″).

Methanolysis of **9**. A soln of **9** (10 mg) in dry 2 N HCl–MeOH (4 ml) was heated under reflux for 1 hr. Work-up as usual gave a mixture, from which methyl 2,3,4-tri-*O*-Me-L-rhamnopyranoside (*RR*$_t$: 2′42″ and 3′42″) and methyl 3,4-di-*O*-Me-D-xylopyranoside (*RR*$_t$: 10′30″ and 13′36″) were identified by GC comparison with authentic samples.

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