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THE STRUCTURES OF THIRTEEN ASTRASIEVERSIANINS FROM *ASTRAGALUS SIEVERSIANUS**

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

Abstract—Based on spectroscopic analysis and chemical degradations, the structures of the five new glycosides, astrasieversianins I, III, V, XII and XIII were assigned as the 3-*O*-(2',3',4'-tri-*O*-acetyl)-β-D-xylopyranoside, 3-*O*-(2',4'-di-*O*-acetyl)-β-D-xylopyranoside, 3-*O*-(3'-*O*-acetyl)-β-D-xylopyranosyl-6-*O*-β-D-xylopyranoside, 3-*O*-[α-L-rhamnopyranosyl (1→2)]-(3'-*O*-acetyl)-β-D-xylopyranosyl-6-*O*-β-D-glucopyranoside and 3-*O*-[α-L-rhamnopyranosyl (1→2)]-(4'-*O*-acetyl)-β-D-xylopyranosyl-6-*O*-β-D-glucopyranoside of astramembrangenin, respectively. Astrasieversianins II, VI, X and XVI were established as 20,24-epimers of cyclosieversiosides A, C, E and H respectively. Astrasieversianins IV, VII, VIII and XIV were identified as known naturally occurring triterpenoid glycosides.

INTRODUCTION

In the preceding paper [1], we described the isolation of sixteen triterpenoid glycosides from the root of *A. sieversianus* Pall and the structural elucidation of three of them as well as the common aglycone (**1**) of sixteen glycosides. This paper reports the structural determination of the remaining thirteen glycosides, astrasieversianins I (**2**), II (**3**), III (**4**), V (**5**), VI (**6**), X (**7**), IV (**8**), VII (**9**), VIII (**10**), XIV (**11**), XII (**12**), XIII (**13**) and XVI (**14**), isolated from the same plant. Astrasieversianins IV (**8**), VI (**6**), XIII (**13**) and XVI (**14**) which are the more abundant constituents of this plant, have been demonstrated to possess significant antihypertension activity [2].

RESULTS AND DISCUSSION

Astrasieversianin X (**7**) *and its* O-*acetyl glycosides* (**2–6**)

The IR spectra of **2–6** showed not only a hydroxy absorption band but also an ester carbonyl absorption band. The treatment of **2–6** with 1% KOH–MeOH afforded their parent glycoside **7**. In their FDMS compounds **2**, **3**, **4**, **5** and **6** exhibited molecular ion or quasi-molecular ion peaks at *m/z* 881 $[M+H]^+$, 839 $[M+H]^+$, 838 $[M]^+$ 820 $[M+Na+H]^+$ and 797 $[M+H]^+$, respectively. In their ^{1}H NMR spectra, the methyl signals of acetoxy groups were observed at δ2.04, 2.05 and 2.08 for **2**, at 2.04 and 2.06 for **3**, at 1.97 and 2.00 for **4**, at 1.99 for **5** and at 1.97 for **6**. The above mentioned spectroscopic and chemical data indicated that **2–6** were all *O*-acetyl-derivatives of **7**, therefore we initiated the structural determination of **7**.

The IR spectrum of **7** showed strong hydroxy absorption (3350 cm^{-1}) and the FDMS of **7** exhibited ion peaks corresponding to $[M+Na]^+$, $[M+H]^+$ and $[M]^+$ at *m/z* 777, 755 and 754, respectively. Compound **7** was composed of **1** as aglycone [1] and D-xylose as the only sugar component. On methanolysis of the permethylate (**8**) of **7**, merely methyl 2,3,4,-tri-*O*-methyl-D-xylopyranoside was identified as the methylated monosaccharide. The above mentioned results revealed that **7** was a didesmoside containing two D-xylose moieties. This is also supported by the fact that the ^{1}H NMR spectrum of **8** displayed eight methoxy signals at δ3.13–3.62. The ^{13}C NMR spectrum of **7**, in comparison with that of **1**, exhibited significant glycosidation shifts [3] on the C-3 and C-6 signals of **7** (Table 1, $\Delta\delta_{C\text{-}3} = +10.0$, $\Delta\delta_{C\text{-}6} = +10.4$). Consequently, two xylose residues should be attached to the hydroxy groups at C-3 and C-6 of **7**. Based upon the ^{13}C NMR chemical shifts (Table 1, $\delta_{C\text{-}1'} = 107.4$, $\delta_{C\text{-}1''} = 105.5$) of the anomeric carbons of **7** and the coupling constants ($J_{1',2'} = 7$ Hz, $J_{1'',2''} = 7$ Hz) of the anomeric protons of **8**, the configuration of C-1' and C-1'' of **7** was revealed as β [3, 4]. As described above, astrasieversianin X is represented as **7** which is the 20,24-epimer of cyclosieversioside E [5].

The locations of the acetoxy groups in the xylopyranosyl moieties of **2**, **3**, **4**, **5** and **6** were ascertained by means of a careful comparison of their ^{13}C NMR data with those of **1**, **7** and the related glycosides [6, 7]. As shown in Table 1, remarkable acetylation shifts [8, 9] appeared at the signals due to C-2', C-3' and C-4' of **2**, C-2' and C-3' of **3**, C-2' and C-4' of **4**, C-3' of **5** and C-2' of **6**. Accordingly, the structure of five *O*-acetylglycosides, astrasieversianins I, II, III, V and VI were established as **2**, **3**, **4**, **5** and **6**, respectively.

Astrasieversianin XIV (**11**) *and its* O-*acetyl glycosides* (**8–10**)

It was known that **11** contained **1** as aglycone [1]. An examination of the physical and chemical data of **11** and its permethylate (**16**) proved that **11** was in agreement in

* Part 3 in the series "The Chemical Investigation of *Astragalus sieversianus* Pall". For part 2 see ref. [1].

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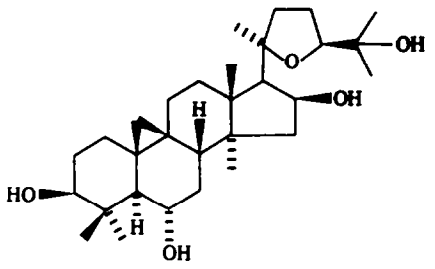
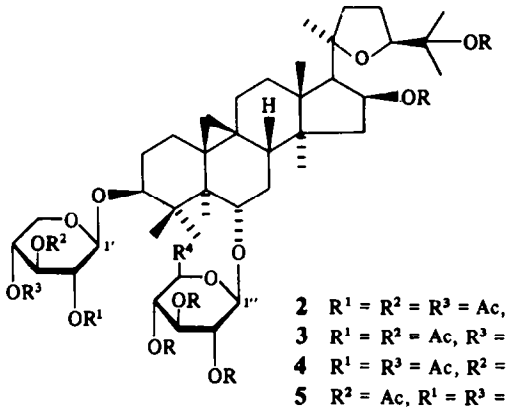
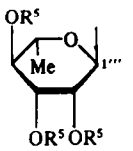


1



2 $R^1 = R^2 = R^3 = Ac$, $R^4 = R = H$
3 $R^1 = R^2 = Ac$, $R^3 = R^4 = R = H$
4 $R^1 = R^3 = Ac$, $R^2 = R^4 = R = H$
5 $R^2 = Ac$, $R^1 = R^3 = R^4 = R = H$
6 $R^1 = Ac$, $R^2 = R^3 = R^4 = R = H$
7 $R^1 = R^2 = R^3 = R^4 = R = H$
8 $R^1 = R^2 = Ac$, $R^3 = R = H$, $R^4 = CH_2OH$
9 $R^1 = Ac$, $R^2 = R^3 = R = H$, $R^4 = CH_2OH$
10 $R^2 = Ac$, $R^1 = R^3 = R = H$, $R^4 = CH_2OH$
11 $R^1 = R^2 = R^3 = R = H$, $R^4 = CH_2OH$
12 R^1 = Rha 1, $R^2 = Ac$, $R^3 = R = H$, $R^4 = CH_2OH$
13 R^1 = Rha 1, $R^3 = Ac$, $R^2 = R = H$, $R^4 = CH_2OH$
14 R^1 = Rha 1, $R^2 = R^3 = R = H$, $R^4 = CH_2OH$
15 $R^1 = R^2 = R^3 = R = Me$, $R^4 = H$
16 $R^1 = R^2 = R^3 = R = Me$, $R^4 = CH_2OMe$
17 R^1 = Rha 2, $R^2 = R^3 = R = Me$, $R^4 = CH_2OMe$



Rha 1: $R^5 = H$
Rha 2: $R^5 = Me$

all respects with naturally occurring astramembrannin I [10] or astragaloside IV [7].

The conclusion that the structures of **8**, **9** and **10** were identical with those of astragaloside I, isoastragaloside and astragaloside II [7], respectively, was drawn from the following facts. (a) Treatment of **8**, **9** and **10** with 1% KOH–MeOH yielded **11** as the common parent glycoside; (b) ^1H NMR spectra and FDMS of **8**, **9** and **10** indicated that **8** had two acetoxyl groups, whereas **9** and **10** had only one acetoxyl group, respectively; (c) the notable acetylation shifts [8, 9] were observed for the signals due to C-2′ and C-3′ of **2**, C-3′ of **3** and C-2′ of **4**.

Astrasieversianin XVI (**14**) *and its* O-*acetyl glycosides* (**12** *and* **13**).

The IR spectrum of **14** showed the presence of hydroxyl absorption (3460, 3280 cm^{-1}) and its FDMS exhibited the quasi-molecular ion and molecular ion peaks at *m/z* 954 $[M+Na+H]^+$ and 930 $[M]^+$. Compound **14** contained **1** as aglycone [1], and D-xylose, D-glucose and L-rhamnose as sugar residues. The above experimental results indicated the **14** was a triglycoside with molecular formula $C_{47}H_{78}O_{18}$. The ^{13}C NMR spectrum of **14** showed the presence of three anomeric carbon signals at δ105.7, 105.4 and 101.9. The latter corresponded with the α-anomeric carbon of an L-rhamnose moiety [11], the rest were in good agreement with the β-anomeric carbons of D-xylose and D-glucose moieties [3].

A comparison of the ^{13}C NMR spectrum of **14** with those of **1** and **11** revealed that C-3 and C-6 of **14** exhibited remarkable glycosidation shifts (Table 1) [3]. The permethylate (**17**) of **14** was subjected to methanolysis to afford methyl 2,3,4-tri-*O*-methyl-L-rhamnopyranoside, methyl 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside and methyl 3,4-di-*O*-methyl-D-xylopyranoside. The above mentioned data suggested that **14** was a didesmosidic triglycoside, in which three sugar residues, D-xylose, D-glucose and L-rhamnose, were attached to the hydroxyl groups at C-3, C-6 and C-2′, respectively. In the ^1H NMR spectrum of **17**, three anomeric proton signals appeared at δ4.28 (*d*, $J = 7.5$ Hz), 4.37 (*d*, $J = 7$ Hz) and 5.36 (*d*, $J = 1.4$ Hz). This further confirmed β-, β- and α-configurations of the glycosidic linkages for D-xylose,

Table 1. ^{13}C NMR chemical shifts* (δ, C_5D_5N) of aglycone (1) and astrasieversianins (2–14)

Carbon	1	7	6	5†	4	3	2	11	8	9†	10	14	12	13†
3	78.2	88.2	88.6	88.6	88.8	88.9	89.0	88.5	89.1	89.1	88.9	87.7	88.1	87.9
6	68.3	78.7	78.5	78.6	78.6	78.6	78.7	79.3	79.3	79.6	79.3	78.8	78.9	78.4
16	73.4	73.3	73.4	73.4	73.4	73.4	73.4	73.4	73.4	73.6	73.4	73.4	73.3	73.3
20	87.2	87.2	87.3	87.2	87.3	87.3	87.3	87.2	87.2	87.2	87.2	87.3	87.2	87.2
24	81.6	81.6	81.6	81.6	81.6	81.6	81.6	81.6	81.6	81.7	81.7	81.6	81.6	81.5
25	71.2	71.2	71.3	71.3	71.3	71.3	71.2	71.3	71.3	71.6	71.4	71.3	71.2	71.2
xyl-1′		107.4	104.7	107.3	104.3	103.9	103.4	107.6	104.0	107.2	104.7	105.7	105.1	105.0
2′		75.2	76.1‡	73.2	75.3‡	73.0‡	72.2‡	75.5	73.0‡	73.6	76.1‡	79.4	76.0	77.5
3′		78.6	75.5	79.4‡	72.5	76.7‡	72.6‡	78.4	76.7‡	79.6‡	75.5	78.3	78.5‡	74.0
4′		71.1	71.0	69.3	72.2‡	68.7	69.8‡	71.2	68.7	69.5	71.2	71.5	70.5	73.0‡
5′		66.8	66.7	66.7	63.0	66.7	62.5	67.0	66.6	67.0	67.0	66.9	66.2	63.1
xyl- or Glc-														
1″		105.5	105.7	105.8	105.6	105.7	105.7	105.5	105.2	105.3	105.2	105.4	105.3	105.3
2″		75.4	75.4	75.4	75.3	75.4	75.4	75.5	75.5	75.6	75.5	75.7	75.7	75.6
3″		77.8	77.8	77.7	77.9	77.8	77.9	79.1	79.1	79.6	79.1	78.0	78.0	78.0
4″		71.0	71.3	71.0	71.0	71.0	71.1	71.7	71.7	72.4	71.8	72.5	71.9	71.9
5″		67.0	67.0	67.0	67.0	67.0	67.0	78.1	78.1	78.4	78.0	78.0	78.0	78.0
6″								63.0	63.0	63.4	63.0	63.2	63.1	62.2
Rha-1‴												101.9	102.3	101.9
2‴												72.0	72.0	71.2
3‴												72.5	72.4	72.3
4‴												74.2	73.8	74.3
5‴												69.6	68.9	69.8
6‴												18.8	18.7	18.7
Me CO			170.1	170.8	170.5	170.5	170.2		169.8	170.8	170.1		170.6	170.4
					169.9	169.8	170.0		170.5					
							169.6							
MeCO			20.9	21.2	20.8	20.8	20.6		20.8	21.1	21.2		20.8	20.8
					20.6	20.8	20.6		21.2					
							20.6							

*For the remaining signals of 1 see ref. [1]. The other signals of 2–14 are omitted.

†^{13}C NMR spectra of 5, 9 and 13 were recorded on a JEOL JNM-FX 90 Q FT-NMR spectrometer.

‡Signals of carbons bearing an acetoxyl group.

D-glucose and L-rhamnose moieties [4, 12]. As described above, the structure of astrasieversianin XVI was assigned as **14** which was the 20,24-epimer of cyclosieversioside H [13].

The IR spectra of **12** and **13** showed the presence of hydroxy and acetoxyl absorptions. In the ^{1}H NMR spectra of **12** and **13**, the acetoxyl group signals appeared at δ2.00 and 1.92, respectively. The FDMS of **12** and **13** exhibited a molecular ion peak at m/z 972 $[M]^+$, and quasi-molecular ion peaks at m/z 995 $[M+Na]^+$ and m/z 973 $[M+H]^+$, respectively. Alkaline hydrolysis of **12** and **13** produced **14** as the common deacetylation glycoside. The above physical and chemical data showed that **12** and **13** were mono-*O*-acetyl derivatives of **14**.

On the basis of the acetylation shift effect [8, 9] of the acetoxy group, a comparison of the ^{13}C NMR spectra of **1** and **8–14** (Table 1) revealed that the acetoxyl group of **12** was located at C-3′ and in **13** at C-4′.

EXPERIMENTAL

The instruments used to obtain physical data and the experimental conditions for chromatography were the same as described in our previous paper [1].

Isolation of the astrasieversianins. The isolation of thirteen astrasieversianins (**2–14**) from *A. sieversianus* Pall has been reported in the previous paper [1].

Astrasieversianin I (**2**). Colourless needles (from MeOH), mp 236–237°, $[\alpha]_D^{12}$ +5.3° (*c* 0.30; MeOH). (Found: C, 62.0; H, 8.2. $C_{46}H_{72}O_{16}\cdot 1/2H_2O$ requires: C, 62.1; H, 8.2%.) IR ν_{max}^{nujol} cm^{-1}: 3450 (OH), 1750, 1730, 1720 (OAc). FDMS *m/z* (rel. int.): 881 $[M+H]^+$ (8.4), 800 $[M]^+$ (8.1). ^{1}H NMR (200 MHz, $CDCl_3$): δ0.28, 0.50 (1H each, *d*, *J* = 4 Hz, H-19), 0.90, 0.95, 1.06, 1.18, 1.32 (3H each, *s*, 5 × Me), 1.23 (6H, *s*, 2 × Me), 2.04, 2.05, 2.08 (3H each, *s*, 3 × OAc).

Astrasieversianin II (**3**). Colourless crystals (from MeOH–EtOAc), mp 239–241°, $[\alpha]_D^{25}$ +10.9° (*c* 0.39; MeOH). (Found: C, 63.0; H, 8.4. $C_{44}H_{70}O_{15}$ requires: C, 63.0; H, 8.4%.) IR ν_{max}^{nujol} cm^{-1}: 3420 (OH), 1730, 1740 (OAc). FDMS *m/z* (rel. int.): 839 $[M+H]^+$ (10.3), 838 $[M]^+$ (20.5). ^{1}H NMR (200 MHz, $CDCl_3$): δ0.26, 050 (1H each, *d*, *J* = 4 Hz, H-19) 0.90, 0.96, 1.06, 1.16, 1.32 (3H each, *s*, 5 × Me), 1.24 (6H, *s*, 2 × Me), 2.04, 2.06 (3H each, *s*, 2 × OAc).

Astrasieversianin III (**4**). Colourless needles (from MeOH), mp 250–254°, $[\alpha]_D^{24}$ +15.7° (*c* 0.49; MeOH). (Found: C, 61.7; H, 8.4. $C_{44}H_{70}O_{15}\cdot H_2O$ requires: C, 61.7; H, 8.4%.) IR ν_{max}^{nujol} cm^{-1}: 3340, 3450 (OH), 1740, 1750 (OAc). FDMS *m/z* (rel. int.): 838 $[M]^+$ (15.3). ^{1}H NMR (200 MHz, $CDCl_3$–C_5D_5N): δ0.22, 0.49 (1H each, *d*, *J* = 4 Hz, H-19), 0.95, 0.99, 1.19, 1.25, 1.37 (3H each, *s*, 5 × Me), 1.22 (6H, *s*, 2 × Me), 1.97, 2.00 (3H each, *s*, 2 × OAc).

Astrasieversianin V (**5**). Colourless crystals (from MeOH), mp 233–234°, $[\alpha]_D^{31}$ +12.6° (*c* 0.10; MeOH). IR ν_{max}^{KCl} cm^{-1}: 3350 (OH), 1720 (OAc). FDMS *m/z* (rel. int.): 820 $[M+Na+H]^+$ (10.3). ^{1}H NMR (200 MHz, $CDCl_3$–C_5D_5N): δ0.18, 0.48 (1H each, *d*, *J* = 4 Hz, H-19), 0.99, 1.05, 1.24, 1.35, 1.49 (3H each, *s*, 5 × Me), 1.21 (6H, *s*, 2 × Me), 1.99 (3H, *s*, OAc).

Astrasieverianin VI (**6**). Colourless needles (from MeOH), mp 245–258°, $[\alpha]_D^{31}$ +30.4° (*c* 0.5; MeOH). (Found: C, 60.6; H, 8.4. $C_{42}H_{64}O_{14}\cdot 2H_2O$ requires: C, 60.6; H, 8.7%.) IR ν_{max}^{nujol} cm^{-1}: 3350 (OH), 1730 (OAc) FDMS *m/z* (rel. int.): 797 $[M+H]^+$ (4.0). ^{1}H NMR (200 MHz), $CDCl_3$–C_5D_5N): δ0.23, 0.48 (1H each, *d*, *J* = 4 Hz, H-19), 0.93, 0.98, 1.23, 1.25, 1.36 (3H each, *s*, 5 × Me), 1.18 (6H, *s*, 2 × Me), 1.97 (3H, *s*, OAc).

Astrasieversianin X (**7**). Colourless needles (from MeOH), mp 238–241°, $[\alpha]_D^{12}$ +26.7° (*c* 0.12; MeOH). (Found: C, 62.2; H, 8.8. $C_{40}H_{66}O_{13}\cdot H_2O$ requires: C, 62.2; H, 8.8%.) IR ν_{max}^{nujol} cm^{-1}: 3350 (OH). FDMS *m/z* (rel. int.): 778 $[M+Na+H]^+$ (5.4), 755 $[M+H]^+$ (6.1), 754 $[M]^+$ (4.9). ^{1}H NMR (200 MHz, $CDCl_3$–C_5D_5N): δ0.16, 0.54 (1H each, *d*, *J* = 4 Hz, H-19), 1.03, 1.09, 1.22, 1.24, 1.30, 1.44, 1.59 (3H each, *s*, 7 × Me), 4.54 (1H, *d*, *J* = 7 Hz, H-1″), 4.58 (1H, *d*, *J* = 7 Hz, H-1′).

Astrasieversianin IV (**8**). Mp 183–187° (colourless crystals from MeOH–Me_2CO), $[\alpha]_D^{25}$ +16.3° (*c* 0.38; MeOH). (Found: C, 59.5; H, 8.1. Calc. for $C_{45}H_{72}O_{16}\cdot 2H_2O$: C, 59.7; H, 8.4%.) IR ν_{max}^{nujol} cm^{-1}: 3400 (OH), 1735, 1730 (OAc). FDMS *m/z* (rel. int.): 892 $[M+Na+H]^+$ (100), 869 $[M+H]^+$ (1.2). ^{1}H NMR (200 MHz, $CDCl_3$–C_5D_5N): δ0.28, 0.56 (1H each, *d*, *J* = 4 Hz, H-19), 0.99, 1.03, 1.24, 1.27, 1.31, 1.35, 1.43 (3H each, *s*, 7 × Me), 1.97, 1.99 (3H each, *s*, 2 × OAc).

Astrasieversianin VII (**9**). Mp 222–225° (amorphous solid from MeOH) $[\alpha]_D^{12}$ +11.3° (*c* 0.08; MeOH). (Found: C, 60.2; H, 8.3. Calc. for $C_{43}H_{70}O_{15}\cdot 2H_2O$: C, 59.9; H, 8.6%.) IR ν_{max}^{nujol} cm^{-1}: 3380, 3480 (OH), 1720 (OAc). FDMS *m/z* (rel. int.): 850 $[M+Na+H]^+$ (2.3), 826 $[M]^+$ (13.9). ^{1}H NMR (200 MHz, C_5D_5N): δ0.10, 0.46 (1H each, *d*, *J* = 4 Hz, H-19), 0.92, 1.13, 1.40 (3H each, *s*, 3 × Me), 1.28 (6H, *s*, 2 × Me), 1.57 (6H, *s*, 2 × Me), 1.97 (3H, *s*, OAc).

Astrasieversianin VIII (**10**). Mp 249–250° (colourless crystals from MeOH), $[\alpha]_D^{31}$ +30.4° (*c* 0.46; MeOH). (Found: C, 58.5; H, 8.4. Calc. for $C_{43}H_{70}O_{15}\cdot 3H_2O$: C, 58.6; H, 8.6%.) IR ν_{max}^{nujol} cm^{-1}: 3260, 3380 (OH), 1740 (OAc). FDMS *m/z* (rel. int.): 850 $[M+Na+H]^+$ (17.4), 826 $[M]^+$ (2.8). ^{1}H NMR (200 MHz, $CDCl_3$–C_5D_5N): δ0.28, 0.62 (1H each, *d*, *J* = 4 Hz, H-19), 1.02, 1.11, 1.28, 1.30, 1.36, 1.48, 1.50 (3H each, *s*, 7 × Me), 2.00 (3H, *s*, OAc).

Astrasieversianin XII (**12**). Mp 235–237° (colourless crystals from MeOH–Me_2CO–$CHCl_3$), $[\alpha]_D^{12}$ −4.0° (*c* 0.20, MeOH). (Found: C, 59.3; H, 8.3. $C_{49}H_{80}O_{19}\cdot H_2O$ requires: C, 59.4; H, 8.3%.) IR ν_{max}^{nujol} cm^{-1}: 3350 (OH), 1735 (OAc). FDMS *m/z* (rel. int.): 995 $[M+Na]^+$ (0.6), 972 $[M]^+$ (1.6). ^{1}H NMR (200 MHz, C_5D_5N): δ0.14, 0.57 (1H each, *d*, *J* = 4 Hz, H-19), 0.97, 1.30, 1.34, 1.52, 1.69 (3H each, *s*, 5 × Me), 1.26 (6H, *s*, 2 × Me), 1.58 (3H, *d*, *J* = 6 Hz, H-6‴), 2.00 (3H, *s*, OAc).

Astrasieversianin XIII (**13**). Mp 223–225° (colourless crystals from MeOH–H_2O), $[\alpha]_D^{12}$ −6.3° (*c* 0.18; MeOH–H_2O). (Found: C, 58.9; H, 8.2. $C_{49}H_{80}O_{19}\cdot 1\frac{1}{2}H_2O$ requires: C, 58.9; H, 8.3%.) IR ν_{max}^{nujol} cm^{-1}: 3320 (OH), 1735 (OAc). FDMS *m/z* (rel. int.): 973 $[M+H]^+$ (3.8), 972 $[M]^+$ (3.2). ^{1}H NMR (200 MHz, $CDCl_3$–C_5D_5N): δ0.15, 0.54 (1H each, *d*, *J* = 4 Hz, H-19), 0.94, 1.18, 1.22, 1.29, 1.44, 1.48, 1.59 (3H each, *s*, 7 × Me), 1.20 (3H, *d*, *J* = 6 Hz, H-6‴), 1.92 (3H, *s*, OAc).

Astrasieversianin XIV (**11**). Mp 285–286° (colourless needles from EtOH), $[\alpha]_D^{12}$ +21.4° (*c* 0.14; MeOH). (Found: C, 60.3; H, 8.7. Calc. for $C_{41}H_{68}O_{14}\cdot 2H_2O$: C, 60.0; H, 8.8%.) IR ν_{max}^{nujol} cm^{-1}: 3380 (OH). FDMS *m/z* (rel. int.): 808 $[M+Na+H]^+$ (0.3), 785 $[M+H]^+$ (1.5), 784 $[M]^+$ (1.3). ^{1}H NMR (200 MHz, $CDCl_3$–C_5D_5N): δ0.21, 0.56 (1H each, *d*, *J* = 4 Hz, H-19), 0.93, 1.10, 1.32, 1.46, 1.72 (3H each, *s*, 5 × Me), 1.23 (6H, *s*, 2 × Me), 4.60 (1H, *d*, *J* = 7 Hz, H-1′), 4.67 (1H, *d*, *J* = 7.5 Hz, H-1″).

Astrasieversianin XVI (**14**). Mp 257–260° (colourless needles from MeOH–H_2O), $[\alpha]_D^{20}$ −1.7° (*c* 0.24, MeOH). (Found: C, 58.1; H, 8.3. $C_{47}H_{78}O_{18}\cdot 2H_2O$ requires: C, 58.4; H, 8.5%.) IR ν_{max}^{nujol} cm^{-1}: 3350 (OH). FDMS *m/z* (rel. int.): 954 $[M+Na+H]^+$ (16.5), 930 $[M]^+$ (2.3). ^{1}H NMR (200 MHz, C_5D_5N): δ −0.007, 0.49 (1H each, *d*, *J* = 4 Hz, H-19), 0.92, 1.16, 1.17, 1.25, 1.33, 1.46, 1.76 (3H each, *s*, 7 × Me), 1.62 (3H, *d*, *J* = 6 Hz, H-6‴).

Deacetylation of astrasieversianins I (**2**), *II* (**3**), *III* (**4**), *V* (**5**) *and VI* (**6**). A soln of **2**, **3**, **4**, **5** and **6** (8 mg each) in MeOH (8 ml) was refluxed with 1% KOH–MeOH (8 ml) for 30 min. The solvent

was evaporated, and the crude product (35 mg) was filtered, washed with ice H_2O and recrystallized from MeOH. The pure product (30 mg) was obtained as colourless needles, mp 238–241°, $[\alpha]_D^{12}$ + 27.4° (*c* 0.14; MeOH), and was found to be identical with the naturally occurring **7** by mmp determination, element analysis, and TLC, IR and FDMS comparisons.

Deacetylation of astrasieversianins XII (**12**) *and XIII* (**13**). A soln of **12** (22 mg) and **13** (22 mg) in 4 ml MeOH was refluxed with 1% KOH–MeOH (4 ml) on a steam bath for 30 min. The ppt left after removal of solvent was chromatographed on silica gel ($CHCl_3$–MeOH, 3:2). The compound **14** (35 mg) was obtained as colourless needles (from MeOH–H_2O) and was shown to be identical with the naturally occurring **14** by mmp determination, elemental analysis, and TLC and IR comparisons.

Deacetylation of astrasieversianin IV (**8**), *VII* (**9**) *and VIII* (**10**). A soln of **8**, **9** and **10** (5 mg each) in 2 ml MeOH was refluxed with 1% KOH–MeOH (2 ml) for 30 min. The residue left after removal of solvent was filtered and washed with ice H_2O to yield **11** (11 mg) as colourless needles (from EtOH), mp 285–286°, $[\alpha]_D^{10}$ + 21.8° (*c* 0.11; MeOH), which was found to be identical with naturally occurring **11** by mmp determination, elemental analysis, and TLC and IR comparisons.

Acidic hydrolysis of **7**. Compound **7** (1 mg) was refluxed with 4 N aq. HCl–MeOH (1:1, 1 ml) for 2 hr. The reaction was worked up as described in our previous paper [1] and subjected to PC (EtOAc–C_5H_5N–H_2O, 36:10:11.5) to identify the sugar component as xylose by comparison with authentic samples.

Acidic hydrolysis of **14**. A soln of 15 mg **14** in 4 ml MeOH was refluxed with 4 N aq. HCl (4 ml) for 2 hr. The reaction mixture was worked up as described above to identify the sugar components as xylose, glucose and rhamnose.

Acidic hydrolysis of **11**. A soln of 5 mg **11** in 2 ml MeOH was refluxed with 4 N aq. HCl (4 ml) for 2 hr. Work-up of the reaction mixture as described above gave xylose and glucose as the sugar components.

Methylation of **7**. Compound **7** (100 mg) was methylated by the Hakomori method and the reaction mixture was worked up as usual. The crude product (100 mg) was chromatographed on silica gel (petrol–EtOAc–Me_2CO, 85:15:4) to give **15** (74 mg) as colourless needles (from MeOH), mp 170–172°, $[\alpha]_D^{12}$ + 22.7° (*c* 0.27; $CHCl_3$). (Found: C, 66.5; H, 9.6. $C_{48}H_{82}O_{13}$ requires: C, 66.5; H, 9.5%.) IR ν_{max}^{nujol} cm^{-1}: no OH; ^1H NMR (200 MHz, $CDCl_3$): δ0.21, 0.51 (1H each, *d*, *J* = 4 Hz, H-19), 0.94, 0.98, 1.01, 1.17, 1.21, 1.24, 1.27 (3H each, *s*, 7 × Me), 3.13, 3.27, 3.54, 3.60 (3H each, *s*, 4 × OMe), 3.46, 3.62 (6H each, *s*, 4 × OMe), 4.26 (1H, *d*, *J* = 7 Hz, H-1″), 4, 30 (1H, *d*, *J* = 7 Hz, H-1′).

Methylation of **14**. Compound **14** (100 mg) was methylated by the Hakomori method and the crude product (120 mg) was purified by CC on silica gel (petrol–EtOAc–Me_2CO, 25:5:1) to give **17** (70 mg) as amorphous powder (from MeOH), mp 164–165°, $[\alpha]_D^{20}$ + 2.7° (*c* 0.42; $CHCl_3$). (Found: C, 64.5; H, 9.5. $C_{58}H_{100}O_{18}$ requires: C, 64.2; H, 9.2%.) IR ν_{max}^{nujol} cm^{-1}: no OH. ^1H NMR (200 MHz, $CDCl_3$): δ0.23, 0.74 (1H each, *d*, *J* = 4 Hz, H-19), 0.97, 0.99, 1.11, 1.19, 1.23, 1.24, 1.29, (3H each, *s*, 7 × Me), 1.27 (3H, *d*, *J* = 6 Hz, H-6‴), 3.13, 3.29, 3.41, 3.47, 3.51, 3.52, 3.54, 3.55, 3.57, 3.61, 3.64 (3H each, *s*, 11 × OMe), 4.28 (1H, *d*, *J* = 7.5 Hz, H-1″), 4.37 (1H, *d*, *J* = 7 Hz, H-1′), 5.36 (1H, *d*, *J* = 1.4 Hz, H-1‴).

Methylation of **11**. Compound **11** (100 mg) was methylated by Hakomori method, and the crude product (110 mg) was chromatographed on silica gel (petrol–EtOAc–Me_2CO, 85:15:4) to give **16** (76 mg) as colourless crystals (from MeOH), mp 184–185°, $[\alpha]_D^{18}$ + 31.3° (*c* 0.36; $CHCl_3$). (Found: C, 65.9; H, 9.6. Calc. for $C_{50}H_{86}O_{14}$: C, 65.9; H, 9.5%.) IR ν_{max}^{nujol} cm^{-1}: no OH. ^1H NMR (200 MHz, $CDCl_3$): δ0.28, 0.54 (1H each, *d*, *J* = 4 Hz, H-19), 0.96, 1.00, 1.11, 1.19, 1.23 (3H each, *s*, 5 × Me), 1.28 (6H, *s*, 2 × Me), 3.14, 3.24, 3.42, 3.49, 3.54, 3.56, 3.65 (3H each, *s*, 7 × Me), 3.64 (6H, *s*, 2 × OMe), 4.28 (1H, *d*, *J* = 7.5 Hz, H-1″), 4.31 (1H, *d*, *J* = 7 Hz, H-1′).

Methanolysis of **15**. A soln of 7.5 mg **15** in 2 N dry HCl–MeOH (3 ml) was refluxed for 1 hr, and the reaction mixture was neutralized with Ag_2CO_3 powder. The filtrate was evapd and the residue was examined by GC, and the methylated sugars were identified as methyl 2,3,4-tri-*O*-methyl-D-xylopyranoside (*RR*, 2′42″ and 3′42″) by comparison with the authentic samples.

Methanolysis of **17**. Compound **17** (8 mg) was methanolysed by the same method as described in **15**, the methylated sugars were identified as methyl 2,3,4-tri-*O*-methyl-L-rhamnopyranoside (*RR*, 2′54″ and 4′54″), methyl 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside (*RR*, 7′42″ and 12′6″) and methyl 3,4-di-*O*-methyl-D-xylopyranoside (*RR*, 10′30″ and 13′36″).

Methanolysis of **16**. Compound **16** (10 mg) was methanolysed and worked up in the same manner described in **15**. The methylated sugars were identified as methyl 2,3,4-tri-*O*-methyl-D-xylopyranoside (*RR*, 2′42″ and 3′42″) and methyl 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside (*RR*, 7′42′ and 12′6″).

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