



## STEROIDAL SAPONINS FROM *SANSEVIERIA TRIFASCIATA*

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**Key Word Index**—*Sansevieria trifasciata*; Agavaceae; steroidal saponins; spirostanol saponins.

**Abstract**—The methanol extract of the whole plant of *Sansevieria trifasciata* has yielded 12 steroidal saponins, 10 of which are new constituents. The respective structures of the new compounds have been shown by the spectroscopic evidence, and alkaline- and acid-catalysed degradation. This is the first report of the isolation of steroidal saponins from *S. trifasciata*. Copyright © 1996 Elsevier Science Ltd

### INTRODUCTION

Plants belonging to the family Agavaceae are well known as rich sources of steroidal saponins [1, 2]. Previously, we have isolated a series of new polyhydroxylated steroidal saponins, one of which is very unique in structure having a fructose as the carbohydrate component [3], and polyhydroxylated cholestane bisdesmosides [4] from the stems of *Nolina recurvata*, an Agavaceae plant indigenous to Mexico.

As part of our program of the chemical investigation of Agavaceae plants, we have now examined the fresh whole plant of *Sansevieria trifasciata* which is native to the subtropical regions of the African Continent. This paper describes the structural assignment of 10 new steroidal saponins from *S. trifasciata* based on spectroscopic analysis, and alkaline- and acid-catalysed hydrolysis.

### RESULTS AND DISCUSSION

The fresh whole plant of *S. trifasciata* was extracted with hot methanol. The crude extract was partitioned between 1-butanol and water. A series of chromatographic separations of the 1-butanol-soluble phase using silica gel, octadecylsilanized (ODS) silica gel, Sephadex LH-20 and Diaion HP-20 furnished compounds **1**–**12**.

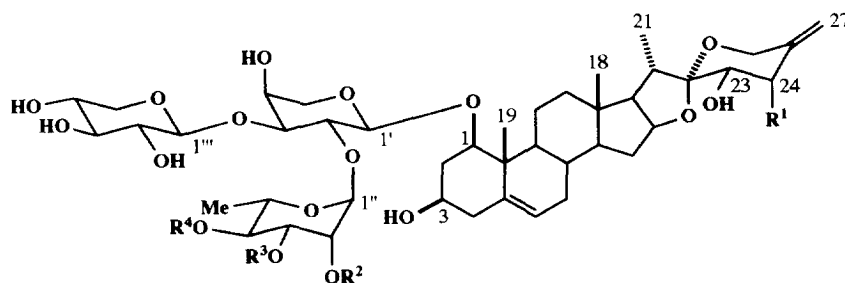
The structures of **1** and **2** were identified by comparison of their spectral data (Table 1 and Experimental) and physical properties with literature values as (23S)-spirosta-5,25(27)-diene- $\beta$ ,3 $\beta$ ,23-triol-1-O- $\{\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-O- $[\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 3)]- $\alpha$ -L-arabinopyranoside} and (23S,24S)-spirosta-5,25(27)-diene-1 $\beta$ ,3 $\beta$ ,23,24-tetrol-1-O- $\{\alpha$ -

-L-rhamno-pyranosyl-(1 $\rightarrow$ 2)-O- $[\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 3)]- $\alpha$ -L-arabinopyranoside}, respectively [3].

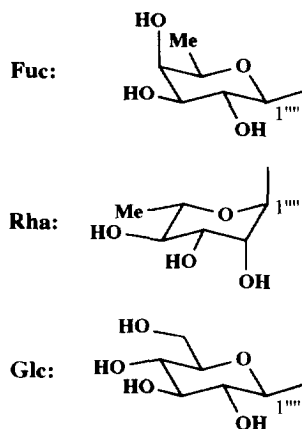
Compound **3**, C<sub>45</sub>H<sub>68</sub>O<sub>18</sub> (negative FAB-mass spectrum  $m/z$  895 [M – H]<sup>–</sup>), [ $\alpha$ ]<sub>D</sub> – 62.5° (methanol), was obtained as an amorphous solid. The <sup>1</sup>H NMR spectrum of **3** contained two tertiary methyl proton signals at  $\delta$  1.35 and 1.06 (each *s*), a secondary methyl proton signal at  $\delta$  1.12 (*d*,  $J$  = 7.0 Hz), an olefinic proton signal at  $\delta$  5.62 (*br d*,  $J$  = 5.5 Hz), exomethylene proton signals at  $\delta$  4.84 and 4.82 coupled to each other with a  $J$  value of less than 0.5 Hz and three anomeric proton signals at  $\delta$  6.47 (*br s*), 4.94 (*d*,  $J$  = 7.5 Hz) and 4.70 (*d*,  $J$  = 7.6 Hz). The above data were indicative of **3** being a steroidal saponin closely related to **1**. In addition, the presence of an acetyl group in **3** was shown by the IR ( $\nu_{\max}$  1730 cm<sup>–1</sup>), <sup>1</sup>H NMR [ $\delta$  2.00 (3H, *s*)] and <sup>13</sup>C NMR [ $\delta$  170.8 (C) and 21.1 (Me)] spectra. In the negative FAB-mass spectrum, the fragment ion peak at  $m/z$  853 was assignable to [M – MeCO]<sup>–</sup>. Alkaline hydrolysis of **3** with 4% potassium hydroxide gave **1**. Therefore, compound **3** was confirmed to be a monoacetate of **1**. On comparison of the <sup>1</sup>H NMR spectrum of **3** with that of **1**, the signal assignable to 4-H of the rhamnose was shifted downfield by 1.51 ppm to appear at  $\delta$  5.78 (*dd*,  $J$  = 9.7, 9.7 Hz), accounting for the ester linkage to the C-4 hydroxyl group of the rhamnose. The structure of **3** was formulated as (23S)-spirosta-5,25(27)-diene-1 $\beta$ ,3 $\beta$ ,23-triol-1-O- $\{\alpha$ -(4-O-acetyl- $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-O- $[\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 3)]- $\alpha$ -L-arabinopyranoside}.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **4** (C<sub>47</sub>H<sub>70</sub>O<sub>19</sub>, negative FAB-mass spectrum  $m/z$  938 [M]<sup>–</sup>) showed the presence of two acetyl groups in the molecule [ $\delta$ <sub>H</sub> 1.96 and 1.94 (each 3H, *s*);  $\delta$ <sub>C</sub> 170.7 (C), 170.4 (C), 21.0 (Me) and 20.9 (Me)]. Alkaline hydrolysis of **4** gave **1**. The ester linkages in the rhamnose C-2 and C-3 hydroxyl groups of **4** were formed from acetic acid, as was evident in the <sup>1</sup>H NMR paramagnetic chemical

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	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
1	H	H	H	H
2	OH	H	H	H
3	H	H	H	Ac
4	H	Ac	Ac	H
5	OH	H	H	Ac
6	OH	Ac	Ac	H
7	OH	Ac	Ac	Ac
8	O-Fuc	H	H	Ac
8a	O-Fuc	H	H	H
9	O-Fuc	Ac	Ac	H
10	O-Fuc	Ac	Ac	Ac
11	O-Rha	Ac	Ac	Ac
12	O-Glc	Ac	Ac	Ac



shifts due to acylation: the 2-H and 3-H protons of the rhamnose were moved to lower fields by 1.36 and 1.30 ppm, respectively, as compared with those of **1**, to be observed at  $\delta$  6.14 (*dd*,  $J = 3.4, 1.4$  Hz) and 5.98 (*dd*,  $J = 9.9, 3.4$  Hz). The structure of **4** was characterized as (23*S*)-spirosta-5,25(27)-diene-1 $\beta$ ,3 $\beta$ ,23-triol 1 - *O* - {*O* - (2,3 - *O* - diacetyl -  $\alpha$  - L - rhamnopyranosyl) - (1  $\rightarrow$  2) - [ $\beta$  - D - xylopyranosyl - (1  $\rightarrow$  3)] -  $\alpha$  - L - arabinopyranoside}.

Alkaline hydrolysis of **5** ( $C_{48}H_{68}O_{14}$ , positive FAB-mass spectrum  $m/z$  951 [ $M + K$ ]<sup>+</sup>, 935 [ $M + Na$ ]<sup>+</sup>, 913 [ $M + H$ ]<sup>+</sup>), **6** ( $C_{47}H_{70}O_{20}$ , negative FAB-mass spectrum  $m/z$  954 [ $M$ ]<sup>-</sup>) and **7** ( $C_{49}H_{72}O_{21}$ , negative FAB-mass spectrum  $m/z$  995 [ $M - H$ ]<sup>-</sup>) yielded a spirostanol triglycoside, identified as **2**. The <sup>1</sup>H and <sup>13</sup>C NMR spectra indicated that **5**–**7** were monoacetyl [ $\delta_H$  2.01 (3H, *s*);  $\delta_C$  170.8 (C) and 21.1 (Me)], diacetyl [ $\delta_H$  1.96 and 1.94 (each 3H, *s*);  $\delta_C$  170.7 (C), 170.4 (C), 21.1 (Me) and 20.9 (Me)] and triacetyl [ $\delta_H$  2.13, 2.03 and 1.88 (each 3H, *s*);  $\delta_C$  170.5 (C), 170.4 (C), 170.2 (C), 20.8 (Me), 20.7 (Me) and 20.6 (Me)] derivatives of **2**, respectively. The following downfield <sup>1</sup>H NMR shifts due to acetylation in comparison with **2** were observed for each of the compounds: 4-H of the rhamnose [ $\delta$  5.78 (*dd*,  $J = 9.7, 9.7$  Hz), + 1.51 ppm] in **5**, 2-H and 3-H of the rhamnose [ $\delta$  6.14 (*dd*,  $J = 3.4, 1.5$  Hz, 2-H), + 1.36 ppm;  $\delta$  5.90 (*dd*,  $J = 9.9, 3.4$  Hz, 3-H), + 1.32 ppm] in **6**, and 2-H, 3-H and 4-H of the rhamnose [ $\delta$  6.10 (*br d*,  $J = 3.4$  Hz, 2-H), + 1.32 ppm;  $\delta$  5.93 (*dd*,  $J = 10.2, 3.4$  Hz, 3-H), + 1.35 ppm;  $\delta$  5.63 (*dd*,  $J = 10.2, 10.2$  Hz, 4-H), + 1.36 ppm] in **7**. The respective structures of **5**–**7** were thus assigned as 1-*O*-

{*O*-(4-*O*-acetyl- $\alpha$ -L-rhamnopyranosyl)-(1  $\rightarrow$  2)-*O*-[ $\beta$ -D-xylopyranosyl-(1  $\rightarrow$  3)]- $\alpha$ -L-arabinopyranoside}, 1-*O*-{*O*-(2,3-*O*-diacetyl- $\alpha$ -L-rhamnopyranosyl)-(1  $\rightarrow$  2)-*O*-[ $\beta$ -D-xylopyranosyl-(1  $\rightarrow$  3)]- $\alpha$ -L-arabinopyranoside} and 1-*O*-{*O*-(2,3,4-*O*-triacetyl- $\alpha$ -L-rhamnopyranosyl)-(1  $\rightarrow$  2)-*O*-[ $\beta$ -D-xylopyranosyl-(1  $\rightarrow$  3)]- $\alpha$ -L-arabinopyranoside} of (23*S*,24*S*)-spirosta-5,25(27)-diene-1 $\beta$ ,3 $\beta$ ,23,24-tetrol.

The <sup>1</sup>H NMR spectrum of **8** ( $C_{51}H_{78}O_{23}$ , positive FAB-mass spectrum  $m/z$  1081 [ $M + Na$ ]<sup>+</sup>) displayed four anomeric proton signals at  $\delta$  6.45 (*br s*), 5.16 (*d*,  $J = 7.8$  Hz), 4.93 (*d*,  $J = 7.5$  Hz) and 4.68 (*d*,  $J = 7.4$  Hz) in addition to signals arising from the aglycone for two tertiary methyl groups at  $\delta$  1.37 and 0.95 (each *s*), a secondary methyl group at  $\delta$  1.07 (*d*,  $J = 7.0$  Hz), an olefinic proton at  $\delta$  5.63 (*br d*,  $J = 5.5$  Hz) and exomethylene protons at  $\delta$  5.23 and 5.09 coupled to each other with a  $J$  value of 1.1 Hz. The presence of an acetyl group in **8** was shown by the IR ( $\nu_{max}$  1730  $cm^{-1}$ ), <sup>1</sup>H NMR [ $\delta$  2.01 (3H, *s*)] and <sup>13</sup>C NMR [ $\delta$  170.8 (C) and 21.1 (Me)] spectra. Alkaline hydrolysis of **8** gave a bisdesmosidic steroidal saponin (**8a**), identified as 24-*O*- $\beta$ -D-fucopyranoside of **2**, which was previously isolated by us from the stems of *Nolina recurvata* [3]. In the <sup>1</sup>H NMR spectrum of **8**, the downfield-shifted <sup>1</sup>H NMR signal at  $\delta$  5.77 (*dd*,  $J = 9.7, 9.7$  Hz) was assigned to 4-H of the rhamnose, which was moved to lower field by 1.52 ppm as compared with that of **8a**. The structure of **8** was thus shown to be (23*S*,24*S*)-spirosta-5,25(27)-diene-1 $\beta$ ,3 $\beta$ ,23,24-tetrol 1 - *O* - {*O*-(4-*O*-acetyl- $\alpha$ -L-rhamno-

Table 1.  $^{13}\text{C}$  NMR spectral data for compounds 1–8, 8a and 9–12\*

C	1	2	3	4	5	6	7	8	8a	9	10	11	12
1	83.7	83.7	84.0	84.1	84.0	84.0	84.0	83.9	83.7	84.0	84.0	84.0	84.0
2	37.4	37.5	37.7	37.7	37.6	37.6	37.7	37.6	37.5	37.6	37.7	37.8	37.8
3	68.3	68.2	68.0	68.2	68.0	68.2	67.9	68.0	68.2	68.2	68.0	68.0	68.0
4	43.9	43.8	44.0	43.8	44.0	43.8	43.8	44.0	43.9	43.8	43.9	43.9	43.9
5	139.6	139.5	139.4	139.5	139.4	139.5	139.2	139.5	139.7	139.6	139.4	139.3	139.3
6	124.7	124.7	125.0	124.7	124.9	124.7	125.0	124.9	124.6	124.7	125.0	125.0	125.0
7	32.1	32.0	32.1	32.0	32.0	32.0	32.0	32.0	31.9	32.0	32.0	32.0	32.0
8	33.1	33.0	33.0	33.0	33.0	33.0	33.0	33.0	33.0	33.0	33.0	33.0	33.0
9	50.4	50.4	50.4	50.3	50.4	50.3	50.3	50.3	50.4	50.2	50.3	50.3	50.3
10	42.9	42.9	42.9	42.9	42.9	42.9	42.8	42.9	42.9	42.9	42.9	42.9	42.9
11	24.1	24.1	24.0	24.0	24.0	24.1	24.0	23.9	24.0	24.0	24.0	24.0	24.0
12	40.6	40.6	40.6	40.6	40.5	40.5	40.5	40.4	40.5	40.4	40.4	40.5	40.4
13	40.8	40.7	40.8	40.8	40.7	40.7	40.6	40.7	40.8	40.7	40.8	40.7	40.8
14	56.9	56.9	56.8	56.9	56.9	56.9	56.8	56.7	56.8	56.7	56.7	56.8	56.7
15	32.4	32.3	32.4	32.4	32.3	32.3	32.3	32.4	32.3	32.4	32.4	32.5	32.5
16	82.0	83.3	82.0	82.0	83.2	83.3	83.2	82.1	82.2	82.2	82.1	82.5	82.5
17	62.5	61.4	62.5	62.5	61.4	61.4	61.3	61.5	61.5	61.5	61.5	61.5	61.5
18	16.9	16.8	16.9	16.9	16.9	16.9	16.9	16.8	16.8	16.8	16.8	16.8	16.9
19	15.0	15.0	14.9	15.0	14.9	15.0	14.8	15.0	15.1	15.1	14.9	14.9	15.0
20	35.8	37.1	35.8	35.8	37.1	37.1	37.1	37.4	37.5	37.4	37.5	37.5	37.5
21	14.6	14.6	14.6	14.6	14.6	14.6	14.6	14.8	14.7	14.8	14.8	14.8	14.8
22	111.8	112.7	111.9	111.8	112.7	112.7	112.6	111.8	111.8	111.7	111.8	111.8	111.8
23	68.6	69.6	68.6	68.6	69.6	69.7	69.6	70.3	70.4	70.3	70.4	70.2	70.4
24	38.9	74.2	38.9	38.9	74.1	74.2	74.1	83.0	83.0	83.0	83.0	83.0	83.0
25	144.4	146.4	144.4	144.4	146.4	146.4	146.4	143.9	144.0	143.9	144.0	144.0	143.7
26	64.3	60.8	64.3	64.3	60.8	60.8	60.8	61.5	61.5	61.5	61.5	61.5	61.5
27	109.3	112.3	109.4	109.3	112.4	112.4	112.4	113.7	113.7	113.8	113.8	113.7	114.1
1'	100.5	100.5	100.7	100.4	100.7	100.4	100.3	100.7	100.5	100.4	100.3	100.3	100.3
2'	74.3	74.2	72.9	73.7	72.9	73.7	72.7	72.9	74.3	73.7	72.7	72.8	72.8
3'	84.4	84.5	85.2	84.7	85.2	84.7	85.1	85.2	84.4	84.7	85.1	85.1	85.1
4'	69.6	69.6	70.0	69.9	70.0	69.9	69.9	69.9	69.5	69.9	69.9	69.9	69.9
5'	67.1	67.1	67.2	67.1	67.2	67.1	67.1	67.1	67.1	67.1	67.1	67.2	67.2
1''	101.9	101.8	100.9	98.3	100.9	98.3	97.7	100.9	101.8	98.2	97.7	97.7	97.7
2''	72.5	72.5	72.3	70.8	72.3	70.8	70.6	72.2	72.5	70.8	70.6	70.6	70.6
3''	72.6	72.6	69.9	73.2	69.9	73.2	70.1	70.0	72.6	73.2	70.1	70.1	70.1
4''	74.3	74.2	76.5	69.3	76.5	69.3	71.9	76.5	74.2	69.3	72.0	72.0	72.0
5''	69.6	69.6	66.6	70.8	66.6	70.8	66.3	66.6	69.5	70.8	66.4	66.4	66.4
6''	19.1	19.1	18.5	18.9	18.5	18.9	18.2	18.5	19.1	18.9	18.2	18.3	18.2
1'''	106.5	106.5	106.8	106.5	106.8	106.5	106.7	106.7	106.4	106.5	106.7	106.7	106.7
2'''	74.7	74.6	74.6	74.6	74.6	74.6	74.6	74.5	74.6	74.6	74.6	74.6	74.6
3'''	78.5	78.3	78.5	78.3	78.5	78.3	78.4	78.5	78.2	78.2	78.4	78.4	78.4
4'''	71.0	71.0	71.0	71.1	71.0	71.1	70.9	70.9	71.0	71.0	71.0	71.0	71.0
5'''	66.9	67.0	67.4	67.4	67.4	67.4	67.5	67.3	66.9	67.3	67.5	67.5	67.5
1''''								106.3	106.3	106.3	106.3	106.3	106.1
2''''								73.1	73.1	73.1	73.1	72.6	75.9
3''''								75.4	75.4	75.4	75.4	73.3	78.6
4''''								72.8	72.8	72.8	72.9	74.3	71.6
5''''								71.6	71.6	71.6	71.6	70.7	78.6
6''''								17.3	17.2	17.3	17.3	18.7	62.7
Ac			170.8	170.7	170.8	170.7	170.5	170.8		170.7	170.5	170.5	170.5
			21.1	170.4	21.1	170.4	170.4	21.1		170.4	170.4	170.4	170.4
				21.0		21.1	170.2			21.0	170.3	170.3	170.3
				20.9		20.9	20.8			20.9	20.9	20.9	20.9
							20.7				20.8	20.8	20.8
							20.6				20.7	20.7	20.7

\*Spectra were measured in pyridine- $d_5$ .

pyranosyl)-(1  $\rightarrow$  2)-*O*-[ $\beta$ -D-xylopyranosyl-(1  $\rightarrow$  3)]- $\alpha$ -L-arabinopyranoside} 24-*O*- $\beta$ -D-fucopyranoside.

Alkaline hydrolysis of **9** ( $\text{C}_{53}\text{H}_{80}\text{O}_{24}$ , negative FAB-mass spectrum  $m/z$  1099  $[\text{M} - \text{H}]^-$ ) and **10**

( $\text{C}_{55}\text{H}_{82}\text{O}_{25}$ , negative FAB-mass spectrum  $m/z$  1141  $[\text{M} - \text{H}]^-$ ) gave **8a**. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra indicated that **9** and **10** were diacetyl [ $\delta_{\text{H}}$  1.96 and 1.94 (each 3H, s);  $\delta_{\text{C}}$  170.7 (C), 170.4 (C), 21.0 (Me) and

20.9 (Me)] and triacetyl [ $\delta_{\text{H}}$  2.13, 2.03 and 1.88 (each 3H, s);  $\delta_{\text{C}}$  170.5 (C), 170.4 (C), 170.3 (C), 20.9 (Me), 20.8 (Me) and 20.7 (Me)] derivatives of **8a**, respectively. The following downfield  $^1\text{H}$  NMR shifts due to acetylation in comparison with **8a** were observed for each of the compounds: 2-H and 3-H of the rhamnose [ $\delta$  6.13 (*dd*,  $J = 3.5, 1.5$  Hz, 2-H), + 1.37 ppm;  $\delta$  5.89 (*dd*,  $J = 9.9, 3.5$  Hz, 3-H), + 1.32 ppm] in **9**, and 2-H, 3-H and 4-H of the rhamnose [ $\delta$  6.09 (*dd*,  $J = 3.4, 1.5$  Hz, 2-H), + 1.33 ppm;  $\delta$  5.93 (*dd*,  $J = 10.2, 3.4$  Hz, 3-H), + 1.36 ppm;  $\delta$  5.63 (*dd*,  $J = 10.2, 10.2$  Hz, 4-H), + 1.38 ppm] in **10**. The respective structures of **9** and **10** were thus assigned as 1-*O*-{*O*-(2,3-*O*-diacetyl- $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-*O*-[ $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 3)]- $\alpha$ -L-arabinopyranoside} and 1-*O*-{*O*-(2,3,4-*O*-triacetyl- $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-*O*-[ $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 3)]- $\alpha$ -L-arabinopyranoside} of (23S,24S)-spirosta-5,25(27)-diene-1 $\beta$ ,3 $\beta$ ,23,24-tetrol 24-*O*- $\beta$ -D-fucopyranoside.

The NMR data of **11** ( $\text{C}_{55}\text{H}_{82}\text{O}_{25}$ , negative FAB-mass spectrum  $m/z$  1141 [ $\text{M} - \text{H}$ ] $^-$ ) showed that it was identical to **10** in terms of the structures of the aglycone and the triacetyltriglycoside attached to C-1 of the aglycone, but differed from it in the monosaccharide structure attached to C-24. In the  $^1\text{H}$  NMR spectrum of **11**, the signal due to the anomeric proton of the monosaccharide attached to C-24, which was observed at  $\delta$  5.16 (*d*,  $J = 7.9$  Hz) in **10**, was displaced by the signal at  $\delta$  4.97 (*br s*). Furthermore, in the  $^{13}\text{C}$  NMR spectrum, the six signals appearing at  $\delta$  106.3 (CH), 72.6 (CH), 73.3 (CH), 74.3 (CH), 70.7 (CH) and 18.7 (Me) were assigned to C-1-C-6 of an  $\alpha$ -L-rhamnopyranoside by comparing them with those of an authentic methyl  $\alpha$ -L-rhamnopyranoside [5, 6]. Total acid hydrolysis of **11** with 1M hydrochloric acid in dioxane-H<sub>2</sub>O (1:1) at 100° for 2 hr yielded D-xylose, L-arabinose and L-rhamnose, and partial hydrolysis with 0.2M hydrochloric acid at 95° for 30 min gave **7** and L-rhamnose. Accordingly, the structure of **11** was determined to be (23S,24S)-spirosta-5,25(27)-diene-1 $\beta$ ,3 $\beta$ ,23,24-tetrol 1-*O*-{*O*-(2,3,4-*O*-triacetyl- $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-*O*-[ $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 3)]- $\alpha$ -L-arabinopyranoside} 24-*O*- $\alpha$ -L-rhamnopyranoside.

Compound **12** ( $\text{C}_{55}\text{H}_{82}\text{O}_{26}$ , negative FAB-mass spectrum  $m/z$  1157 [ $\text{M} - \text{H}$ ] $^-$ ) was also different from **10** in terms of the structure of the monosaccharide linked to C-24 of the aglycone. The  $^1\text{H}$  NMR spectrum of **12** contained signals for four anomeric protons at  $\delta$  6.55 (*br s*), 5.40 (*d*,  $J = 7.9$  Hz), 4.80 (*d*,  $J = 7.6$  Hz) and 4.65 (*d*,  $J = 7.6$  Hz). Total acid hydrolysis of **12** yielded D-glucose, D-xylose, L-arabinose and L-rhamnose, and partial acid hydrolysis gave **7** and D-glucose. The structure of **12** was revealed to be (23S,24S)-spirosta-5,25(27)-diene-1 $\beta$ ,3 $\beta$ ,23,24-tetrol 1-*O*-{*O*-(2,3,4-*O*-triacetyl- $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-*O*-[ $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 3)]- $\alpha$ -L-arabinopyranoside} 24-*O*- $\beta$ -D-glucopyranoside.

Compounds **3**–**12** are new steroidal saponins. The

occurrence of steroidal saponins in certain Agavaceae plants, especially those belonging to the representative genera *Agave* and *Yucca*, is well documented [1, 2]. However, a survey of literature showed that no steroidal saponins have been detected previously in *S. trifasciata*, one of the most common Agavaceae plants.

## EXPERIMENTAL

**General.** NMR (ppm,  $J$  Hz): Bruker AM-400 (400 MHz for  $^1\text{H}$  NMR). CC: silica gel (Fuji-Silysia Chemical), ODS silica gel (Nacalai Tesque), Diaion HP-20 (Mitsubishi-Kasei) and Sephadex LH-20 (Pharmacia). TLC: precoated Kieselgel 60 F<sub>254</sub> (0.25 mm thick, Merck) and RP-18 F<sub>254</sub>S (0.25 mm thick, Merck). HPLC: a Tosoh HPLC system (pump, CCPM; controller, CCP controller PX-8010; detector, UV-8000) equipped with a TSK-gel ODS-Prep column (Tosoh, 4.6 mm i.d.  $\times$  250 mm, ODS, 5  $\mu\text{m}$ ).

**Plant material.** *Sansevieria trifasciata* was purchased from Exotic Plants, Japan, and the plant specimen is on file in our laboratory.

**Extraction and isolation.** The plant material (fresh weight 5.4 kg) was extracted with hot MeOH. The MeOH extract was concd under red. pres., and the viscous concentrate was partitioned between H<sub>2</sub>O and *n*-BuOH. CC of the *n*-BuOH-soluble phase on silica gel and elution with a gradient mixt. of CHCl<sub>3</sub>-MeOH, and finally with MeOH, gave six frs (I–VI). Fr. II was further sepd by a silica gel column eluting with CHCl<sub>3</sub>-MeOH into three frs (IIa–IIc). Fr. IIa was subjected to ODS silica gel CC eluting with MeOH-H<sub>2</sub>O (4:1) to give compound **7** (48.4 mg). Fr. IIb was subjected to CC on ODS silica gel eluting with MeOH-H<sub>2</sub>O (4:1, 2:1) and MeCN-H<sub>2</sub>O (5:6), and silica gel with CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (180:20:1) to furnish **4** (33.3 mg), **6** (24.4 mg), **10** (498 mg) and **11** (7.7 mg). Fr. IIc was chromatographed on Sephadex LH-20 eluting with MeOH, ODS silica gel with MeOH-H<sub>2</sub>O (2:1) and MeCN-H<sub>2</sub>O (5:6), and on silica gel with CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (60:10:1) to yield **9** (62.9 mg). Fr. III was chromatographed on Sephadex LH-20 eluting with MeOH, ODS silica gel with MeOH-H<sub>2</sub>O (2:1) and MeCN-H<sub>2</sub>O (2:5), and on silica gel with CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (60:10:1) to give **3** (14.2 mg) and **12** (4.5 mg). Fr. IV was purified by CC on Sephadex LH-20 eluting with MeOH, ODS silica gel with MeOH-H<sub>2</sub>O (2:1), and on silica gel with CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (40:10:1) to give **1** (26.5 mg) and **5** (19.5 mg). Fr. V furnished **2** (20.2 mg) and **8** (42.2 mg) on purification by CC on Sephadex LH-20 eluting with MeOH, ODS silica gel with MeOH-H<sub>2</sub>O (2:1), and on silica gel with CHCl<sub>3</sub>-Et<sub>2</sub>O-MeOH-H<sub>2</sub>O (5:5:4:1, 14:8:7:1).

**Compound 1.** Amorphous solid,  $[\alpha]_{\text{D}}^{26} -62.9^\circ$  (MeOH;  $c$  0.25). Negative FAB-MS  $m/z$  853 [ $\text{M} - \text{H}$ ] $^-$ ; IR  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 3420 (OH), 2900 (CH), 1035;  $^1\text{H}$  NMR (pyridine- $d_5$ ):  $\delta$  6.32 (1H, *br s*, 1''-H), 5.56 (1H,

*br d*,  $J=5.4$  Hz, 6-H), 4.98 (1H, *d*,  $J=7.5$  Hz, 1''-H), 4.83 and 4.82 (each 1H, *br s*, 27-H<sub>2</sub>), 4.78 (1H, *br d*,  $J=3.5$  Hz, 2''-H), 4.77 (overlapping, 5''-H), 4.73 (1H, *d*,  $J=7.3$  Hz, 1'-H), 4.59 (1H, *dd*,  $J=9.6$ , 3.5 Hz, 3''-H), 4.41 and 3.99 (each 1H, *d*,  $J=12.1$  Hz, 26-H<sub>2</sub>), 4.27 (1H, *dd*,  $J=9.6$ , 9.6 Hz, 4''-H), 1.71 (3H, *d*,  $J=6.1$  Hz, 6''-Me), 1.38 (3H, *s*, 19-Me), 1.12 (3H, *d*,  $J=7.0$  Hz, 21-Me), 1.03 (3H, *s*, 18-Me).

**Compound 2.** Amorphous solid,  $[\alpha]_D^{26} -60.0^\circ$  (MeOH;  $c$  0.36). Negative FAB-MS  $m/z$  869 [M-H]<sup>-</sup>; IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup>: 3420 (OH), 2905 (CH), 1040; <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>):  $\delta$  6.32 (1H, *br s*, 1''-H), 5.55 (1H, *br d*,  $J=5.6$  Hz, 6-H), 5.09 and 4.99 (each 1H, *d*,  $J=1.3$  Hz, 27-H<sub>2</sub>), 4.98 (1H, *d*,  $J=7.7$  Hz, 1''-H), 4.82 and 4.01 (each 1H, *d*,  $J=12.3$  Hz, 26-H<sub>2</sub>), 4.78 (1H, *br d*,  $J=3.4$  Hz, 2''-H), 4.77 (overlapping, 5''-H), 4.73 (1H, *d*,  $J=7.3$  Hz, 1'-H), 4.58 (1H, *dd*,  $J=9.4$ , 3.4 Hz, 3''-H), 4.27 (1H, *dd*,  $J=9.4$ , 9.4 Hz, 4''-H), 1.72 (3H, *d*,  $J=6.2$  Hz, 6''-Me), 1.38 (3H, *s*, 19-Me), 1.11 (3H, *d*,  $J=7.0$  Hz, 21-Me), 1.01 (3H, *s*, 18-Me).

**Compound 3.** Amorphous solid,  $[\alpha]_D^{26} -62.5^\circ$  (MeOH;  $c$  0.25). Negative FAB-MS  $m/z$  895 [M-H]<sup>-</sup>, 853 [M-Ac]<sup>-</sup>; IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup>: 3430 (OH), 2925 (CH), 1730 (C=O), 1450, 1375, 1250, 1135, 1035, 980; <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>):  $\delta$  6.47 (1H, *br s*, 1''-H), 5.78 (1H, *dd*,  $J=9.7$ , 9.7 Hz, 4''-H), 5.62 (1H, *br d*,  $J=5.5$  Hz, 6-H), 4.94 (1H, *d*,  $J=7.5$  Hz, 1''-H), 4.90 (1H, *dq*,  $J=9.7$ , 6.2 Hz, 5''-H), 4.84 and 4.82 (each 1H, *br s*, 27-H<sub>2</sub>), 4.73 (1H, *br d*,  $J=3.4$  Hz, 2''-H), 4.70 (1H, *d*,  $J=7.6$  Hz, 1'-H), 4.67 (1H, *dd*,  $J=9.7$ , 3.4 Hz, 3''-H), 4.42 and 4.00 (each 1H, *d*,  $J=12.2$  Hz, 26-H<sub>2</sub>), 2.00 (3H, *s*, Ac), 1.43 (3H, *d*,  $J=6.2$  Hz, 6''-Me), 1.35 (3H, *s*, 19-Me), 1.12 (3H, *d*,  $J=7.0$  Hz, 21-Me), 1.06 (3H, *s*, 18-Me).

**Compound 4.** Amorphous solid,  $[\alpha]_D^{26} -62.4^\circ$  (MeOH;  $c$  0.25). Negative FAB-MS  $m/z$  938 [M]<sup>-</sup>, 707 [M-rhamnosyl-Ac $\times$ 2]<sup>-</sup>; IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup>: 3435 (OH), 2920 (CH), 1730 (C=O), 1445, 1375, 1265, 1135, 1045, 980; <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>):  $\delta$  6.46 (1H, *d*,  $J=1.4$  Hz, 1''-H), 6.14 (1H, *dd*,  $J=3.4$ , 1.4 Hz, 2''-H), 5.89 (1H, *dd*,  $J=9.9$ , 3.4 Hz, 3''-H), 5.56 (1H, *br d*,  $J=5.4$  Hz, 6-H), 4.98 (1H, *dq*,  $J=9.9$ , 6.1 Hz, 5''-H), 4.84 (1H, *d*,  $J=7.5$  Hz, 1''-H), 4.83 and 4.82 (each 1H, *br s*, 27-H<sub>2</sub>), 4.62 (overlapping, 1'-H), 4.42 and 3.99 (each 1H, *d*,  $J=12.4$  Hz, 26-H<sub>2</sub>), 4.23 (1H, *dd*,  $J=9.9$ , 9.9 Hz, 4''-H), 1.96 and 1.94 (each 3H, *s*, Ac), 1.73 (3H, *d*,  $J=6.1$  Hz, 6''-Me), 1.38 (3H, *s*, 19-Me), 1.12 (3H, *d*,  $J=7.0$  Hz, 21-Me), 1.04 (3H, *s*, 18-Me).

**Compound 5.** Amorphous solid,  $[\alpha]_D^{26} -66.4^\circ$  (MeOH;  $c$  0.25). Positive FAB-MS  $m/z$  951 [M+K]<sup>+</sup>, 935 [M+Na]<sup>+</sup>, 913 [M+H]<sup>+</sup>; IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup>: 3430 (OH), 2925 (CH), 1730 (C=O), 1455, 1375, 1250, 1135, 1040, 980; <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>):  $\delta$  6.47 (1H, *br s*, 1''-H), 5.78 (1H, *dd*,  $J=9.7$ , 9.7 Hz, 4''-H), 5.61 (1H, *br d*,  $J=5.6$  Hz, 6-H), 5.09 and 4.99 (each 1H, *br s*, 27-H<sub>2</sub>), 4.94 (1H, *d*,  $J=7.5$  Hz, 1''-H), 4.90 (1H, *dq*,  $J=9.7$ , 6.2 Hz, 5''-H), 4.83 and 4.01 (each 1H, *d*,  $J=12.3$  Hz, 26-H<sub>2</sub>), 4.73 (1H, *br d*,  $J=3.2$  Hz, 2''-H),

4.70 (1H, *d*,  $J=7.1$  Hz, 1'-H), 4.67 (1H, *dd*,  $J=9.7$ , 3.2 Hz, 3''-H), 2.01 (3H, *s*, Ac), 1.43 (3H, *d*,  $J=6.2$  Hz, 6''-Me), 1.36 (3H, *s*, 19-Me), 1.11 (3H, *d*,  $J=7.0$  Hz, 21-Me), 1.03 (3H, *s*, 18-Me).

**Compound 6.** Amorphous solid,  $[\alpha]_D^{26} -70.2^\circ$  (MeOH;  $c$  0.25). Negative FAB-MS  $m/z$  954 [M]<sup>-</sup>, 912 [M-Ac]<sup>-</sup>, 723 [M-rhamnosyl-Ac $\times$ 2]<sup>-</sup>; IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup>: 3450 (OH), 2920 (CH), 1740 (C=O), 1445, 1375, 1260, 1140, 1045, 980; <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>):  $\delta$  6.46 (1H, *d*,  $J=1.5$  Hz, 1''-H), 6.14 (1H, *dd*,  $J=3.4$ , 1.5 Hz, 2''-H), 5.90 (1H, *dd*,  $J=9.9$ , 3.4 Hz, 3''-H), 5.55 (1H, *br d*,  $J=5.5$  Hz, 6-H), 5.09 and 4.99 (each 1H, *d*,  $J=1.2$  Hz, 27-H<sub>2</sub>), 4.98 (1H, *dq*,  $J=9.9$ , 6.1 Hz, 5''-H), 4.84 (1H, *d*,  $J=7.6$  Hz, 1''-H), 4.82 and 4.01 (each 1H, *d*,  $J=12.2$  Hz, 26-H<sub>2</sub>), 4.62 (overlapping, 1'-H), 4.23 (1H, *dd*,  $J=9.9$ , 9.9 Hz, 4''-H), 1.96 and 1.94 (each 3H, *s*, Ac), 1.74 (3H, *d*,  $J=6.1$  Hz, 6''-Me), 1.39 (3H, *s*, 19-Me), 1.10 (3H, *d*,  $J=7.0$  Hz, 21-Me), 1.02 (3H, *s*, 18-Me).

**Compound 7.** Amorphous solid,  $[\alpha]_D^{26} -72.0^\circ$  (MeOH;  $c$  0.25). Negative FAB-MS  $m/z$  995 [M-H]<sup>-</sup>, 954 [M-Ac]<sup>-</sup>, 724 [M-rhamnosyl-Ac $\times$ 3]<sup>-</sup>; IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup>: 3450 (OH), 2900 (CH), 1745 (C=O), 1370, 1255, 1225, 1135, 1075, 1040, 980; <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>):  $\delta$  6.54 (1H, *br s*, 1''-H), 6.10 (1H, *br d*,  $J=3.4$ , 2''-H), 5.93 (1H, *dd*,  $J=10.2$ , 3.4 Hz, 3''-H), 5.63 (1H, *dd*,  $J=10.2$ , 10.2 Hz, 4''-H), 5.62 (overlapping, 6-H), 5.10 and 5.00 (each 1H, *br s*, 27-H<sub>2</sub>), 5.03 (1H, *dq*,  $J=10.2$ , 6.1 Hz, 5''-H), 4.83 and 4.02 (each 1H, *d*,  $J=12.4$  Hz, 26-H<sub>2</sub>), 4.80 (1H, *d*,  $J=7.8$  Hz, 1''-H), 4.65 (1H, *d*,  $J=7.7$  Hz, 1'-H), 2.13, 2.03 and 1.88 (each 3H, *s*, Ac), 1.46 (3H, *d*,  $J=6.1$  Hz, 6''-Me), 1.34 (3H, *s*, 19-Me), 1.11 (3H, *d*,  $J=6.9$  Hz, 21-Me), 1.05 (3H, *s*, 18-Me).

**Compound 8.** Amorphous solid,  $[\alpha]_D^{26} -57.2^\circ$  (MeOH;  $c$  0.25). Positive FAB-MS  $m/z$  1081 [M+Na]<sup>+</sup>; IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup>: 3425 (OH), 2930 (CH), 1730 (C=O), 1450, 1375, 1255, 1130, 1040; <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>):  $\delta$  6.45 (1H, *br s*, 1''-H), 5.77 (1H, *dd*,  $J=9.7$ , 9.7 Hz, 4''-H), 5.63 (1H, *br d*,  $J=5.5$  Hz, 6-H), 5.23 and 5.09 (each 1H, *d*,  $J=1.1$  Hz, 27-H<sub>2</sub>), 5.16 (1H, *d*,  $J=7.8$  Hz, 1''-H), 4.93 (1H, *d*,  $J=7.5$  Hz, 1''-H), 4.89 (1H, *dq*,  $J=9.7$ , 6.1 Hz, 5''-H), 4.83 and 3.99 (each 1H, *d*,  $J=11.9$  Hz, 26-H<sub>2</sub>), 4.73 (1H, *br d*,  $J=3.5$  Hz, 2''-H), 4.68 (1H, *d*,  $J=7.4$  Hz, 1'-H), 4.67 (1H, *dd*,  $J=9.7$ , 3.5 Hz, 3''-H), 2.01 (3H, *s*, Ac), 1.48 (3H, *d*,  $J=6.4$  Hz, 6'''-Me), 1.42 (3H, *d*,  $J=6.1$  Hz, 6''-Me), 1.37 (3H, *s*, 19-Me), 1.07 (3H, *d*,  $J=7.0$  Hz, 21-Me), 0.95 (3H, *s*, 18-Me).

**Compound 9.** Amorphous solid,  $[\alpha]_D^{26} -57.2^\circ$  (MeOH;  $c$  0.25). Negative FAB-MS  $m/z$  1099 [M-H]<sup>-</sup>, 1057 [M-Ac]<sup>-</sup>, 869 [M-rhamnosyl-Ac $\times$ 2]<sup>-</sup>, 737 [M-rhamnosyl-Ac $\times$ 2-xylosyl]<sup>-</sup>, 605 [M-rhamnosyl-Ac $\times$ 2-xylosyl-arabinosyl]<sup>-</sup>; IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup>: 3425 (OH), 2920 (CH), 1730 (C=O), 1450, 1375, 1255, 1135, 1045; <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>):  $\delta$  6.46 (1H, *d*,  $J=1.5$  Hz, 1''-H), 6.13 (1H, *dd*,  $J=3.5$ , 1.5 Hz, 2''-H), 5.89 (1H, *dd*,  $J=9.9$ , 3.5 Hz, 3''-H), 5.57 (1H, *br d*,  $J=5.7$  Hz, 6-H), 5.28 and 5.09 (each 1H, *br s*,

27-H<sub>2</sub>), 5.15 (1H, *d*, *J* = 7.9 Hz, 1'''-H), 4.97 (1H, *dq*, *J* = 9.9, 6.1 Hz, 5''-H), 4.84 (1H, *d*, *J* = 7.6 Hz, 1'''-H), 4.83 and 3.99 (each 1H, *d*, *J* = 12.3 Hz, 26-H<sub>2</sub>), 4.61 (overlapping, 1'-H), 4.22 (1H, *dd*, *J* = 9.9, 9.9 Hz, 4''-H), 1.96 and 1.94 (each 3H, *s*, Ac), 1.72 (3H, *d*, *J* = 6.1 Hz, 6''-Me), 1.48 (3H, *d*, *J* = 6.4 Hz, 6'''-Me), 1.41 (3H, *s*, 19-Me), 1.07 (3H, *d*, *J* = 7.0 Hz, 21-Me), 0.94 (3H, *s*, 18-Me).

**Compound 10.** Amorphous solid,  $[\alpha]_D^{26} - 71.2^\circ$  (MeOH; *c* 0.25). Negative FAB-MS *m/z* 1141 [M-H]<sup>-</sup>, 1099 [M-Ac]<sup>-</sup>, 869 [M-rhamnosyl-Ac×3]<sup>-</sup>, 737 [M-rhamnosyl-Ac×3-xylosyl]<sup>-</sup>, 605 [M-rhamnosyl-Ac×3-xylosyl-arabinosyl]<sup>-</sup>; IR  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>: 3440 (OH), 2970 and 2900 (CH), 1740 (C=O), 1445, 1370, 1230, 1135, 1040; <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>):  $\delta$  6.54 (1H, *d*, *J* = 1.5 Hz, 1''-H), 6.09 (1H, *dd*, *J* = 3.4, 1.5 Hz, 2''-H), 5.93 (1H, *dd*, *J* = 10.2, 3.4 Hz, 3''-H), 5.64 (overlapping, 6-H), 5.63 (1H, *dd*, *J* = 10.2, 10.2 Hz, 4''-H), 5.24 and 5.10 (each 1H, *d*, *J* = 1.2 Hz, 27-H<sub>2</sub>), 5.16 (1H, *d*, *J* = 7.9 Hz, 1'''-H), 5.02 (1H, *dq*, *J* = 10.2, 6.2 Hz, 5''-H), 4.84 and 4.00 (each 1H, *d*, *J* = 12.2 Hz, 26-H<sub>2</sub>), 4.79 (1H, *d*, *J* = 7.7 Hz, 1'''-H), 4.64 (1H, *d*, *J* = 7.7 Hz, 1'-H), 2.13, 2.03 and 1.88 (each 3H, *s*, Ac), 1.48 (3H, *d*, *J* = 6.4 Hz, 6'''-Me), 1.44 (3H, *d*, *J* = 6.2 Hz, 6''-Me), 1.36 (3H, *s*, 19-Me), 1.08 (3H, *d*, *J* = 7.0 Hz, 21-Me), 0.98 (3H, *s*, 18-Me).

**Compound 11.** Amorphous solid,  $[\alpha]_D^{26} - 69.5^\circ$  (MeOH; *c* 0.10). Negative FAB-MS *m/z* 1141 [M-H]<sup>-</sup>, 1099 [M-Ac]<sup>-</sup>, 869 [M-rhamnosyl-Ac×3]<sup>-</sup>, 737 [M-rhamnosyl-Ac×3-xylosyl]<sup>-</sup>, 605 [M-rhamnosyl-Ac×3-xylosyl-arabinosyl]<sup>-</sup>; IR  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>: 3440 (OH), 2905 (CH), 1740 (C=O), 1450, 1370, 1255, 1230, 1160, 1135, 1075, 1040, 975; <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>):  $\delta$  6.55 (1H, *br s*, 1''-H), 6.11 (1H, *br d*, *J* = 3.4, 2''-H), 5.93 (1H, *dd*, *J* = 10.2, 3.4 Hz, 3''-H), 5.63 (1H, *dd*, *J* = 10.2, 10.2 Hz, 4''-H), 5.63 (overlapping, 6-H), 5.19 and 5.06 (each 1H, *br s*, 27-H<sub>2</sub>), 5.02 (1H, *dq*, *J* = 10.2, 6.1 Hz, 5''-H), 4.97 (1H, *br s*, 1'''-H), 4.90 and 4.00 (each 1H, *d*, *J* = 12.0 Hz, 26-H<sub>2</sub>), 4.80 (1H, *d*, *J* = 7.7 Hz, 1'''-H), 4.64 (1H, *d*, *J* = 7.9 Hz, 1'-H), 2.14, 2.04 and 1.88 (each 3H, *s*, Ac), 1.52 (3H, *d*, *J* = 6.1 Hz, 6'''-Me), 1.44 (3H, *d*, *J* = 6.1 Hz, 6''-Me), 1.36 (3H, *s*, 19-Me), 1.07 (3H, *d*, *J* = 7.0 Hz, 21-Me), 0.99 (3H, *s*, 18-Me).

**Compound 12.** Amorphous solid,  $[\alpha]_D^{26} - 65.0^\circ$  (MeOH; *c* 0.10). Negative FAB-MS *m/z* 1157 [M-H]<sup>-</sup>, 1115 [M-Ac]<sup>-</sup>, 885 [M-rhamnosyl-Ac×3]<sup>-</sup>, 621 [M-rhamnosyl-Ac×3-xylosyl-arabinosyl]<sup>-</sup>; IR  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>: 3430 (OH), 2905 (CH), 1740 (C=O), 1450, 1370, 1235, 1135, 1040, 980; <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>):  $\delta$  6.55 (1H, *br s*, 1''-H), 6.10 (1H, *br d*, *J* = 3.5 Hz, 2''-H), 5.94 (1H, *dd*, *J* = 10.1, 3.5 Hz, 3''-H), 5.64 (1H, *dd*, *J* = 10.1, 10.1 Hz, 4''-H), 5.64 (overlapping, 6-H), 5.40 (1H, *d*, *J* = 7.9 Hz, 1'''-H), 5.20 and 5.03 (each 1H, *br s*, 27-H<sub>2</sub>), 5.02 (1H, *dq*, *J* = 10.1, 6.1 Hz, 5''-H), 4.90 and 4.00 (each 1H, *d*, *J* = 12.1 Hz, 26-H<sub>2</sub>), 4.80 (1H, *d*, *J* = 7.6 Hz, 1'''-H), 4.65 (1H, *d*, *J* = 7.6 Hz, 1'-H), 2.14, 2.04 and 1.88 (each 3H, *s*, Ac), 1.45 (3H, *d*, *J* = 6.1 Hz, 6'''-Me), 1.38 (3H, *s*, 19-Me), 1.08 (3H, *d*, *J* = 6.8 Hz, 21-Me), 1.01 (3H, *s*, 18-Me).

**Alkaline hydrolysis of 3–10.** Compounds **3** (3.0 mg) and **4–10** (each 5.0 mg) were subjected to alkaline hydrolysis with 4% KOH in EtOH (2 ml) at room temp. for 3 hr. Each reaction mixt. was neutralized by passing it through an Amberlite IR-120B (Organo) column, and purified by silica gel CC eluting with CHCl<sub>3</sub>–MeOH–H<sub>2</sub>O (30:10:1 for **3** and **4**; 20:10:1 for **5–10**). Compounds **3** and **4** yielded **1** (2.5 mg from **3**; 4.1 mg from **4**), **5–7** yielded **2** (4.0 mg from **5**; 3.6 mg from **6**; 3.2 mg from **7**), and **8–10** yielded **8a** (3.4 mg from **8**; 3.3 mg from **9**; 4.0 mg from **10**). Compound **8a**: amorphous solid,  $[\alpha]_D^{26} - 51.2^\circ$  (MeOH; *c* 0.29). Negative FAB-MS *m/z* 1015 [M-H]<sup>-</sup>; IR  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>: 3390 (OH), 2905 (CH), 1040; <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>):  $\delta$  6.29 (1H, *br s*, 1''-H), 5.57 (1H, *br d*, *J* = 5.4 Hz, 6-H), 5.23 and 5.08 (each 1H, *d*, *J* = 1.0 Hz, 27-H<sub>2</sub>), 5.14 (1H, *d*, *J* = 7.9, 1'''-H), 4.96 (1H, *d*, *J* = 7.4 Hz, 1'''-H), 4.83 and 3.98 (each 1H, *d*, *J* = 12.1 Hz, 26-H<sub>2</sub>), 4.76 (1H, *br d*, *J* = 3.5 Hz, 2''-H), 4.76 (overlapping, 5''-H), 4.71 (1H, *d*, *J* = 7.3 Hz, 1'-H), 4.57 (1H, *dd*, *J* = 9.4, 3.5 Hz, 3''-H), 4.25 (1H, *dd*, *J* = 9.4, 9.4 Hz, 4''-H), 1.70 (3H, *d*, *J* = 6.1 Hz, 6''-Me), 1.47 (1H, *d*, *J* = 6.4 Hz, 6'''-Me), 1.40 (3H, *s*, 19-Me), 1.07 (3H, *d*, *J* = 7.0 Hz, 21-Me), 0.93 (3H, *s*, 18-Me).

**Acid hydrolysis of 11 and 12.** A soln of **11** (1.0 mg) in 1 M HCl (dioxane–H<sub>2</sub>O, 1:1, 1 ml) was heated at 100° for 2 hr under an Ar atmosphere. After cooling, the reaction mixt. was neutralized by passing it through an Amberlite IRA-93ZU (Organo) column, and fractionated by Sep-Pak C<sub>18</sub> cartridge (Waters) eluting with H<sub>2</sub>O–MeOH (4:1) followed by MeOH to give a mixt. of monosaccharides (0.3 mg). The mixt. was diluted with H<sub>2</sub>O (1 ml) and treated with (–)- $\alpha$ -methylbenzylamine (5 mg) and Na[BH<sub>3</sub>CN] (8 mg) in EtOH (1 ml) at 40° for 4 hr, followed by acetylation with Ac<sub>2</sub>O (0.3 ml) in pyridine (0.3 ml). The reaction mixt. was passed through a Sep-Pak C<sub>18</sub> cartridge with H<sub>2</sub>O–MeCN (4:1, 10 ml; 1:1, 10 ml; 1:9, 10 ml). The H<sub>2</sub>O–MeOH (1:9) eluate fr. was further passed through a Toyopak IC-SP M cartridge (Tosoh) with EtOH (10 ml) to give a mixt. of 1-[(*S*)-*N*-acetyl- $\alpha$ -methylbenzylamino]-1-deoxyalditol acetate derivatives of the monosaccharides, which was then analysed by HPLC under the following conditions: solvent, MeCN–H<sub>2</sub>O (2:3); flow rate, 0.8 ml min<sup>-1</sup>; detection, UV 230 nm. The derivatives of L-arabinose, D-xylose and L-rhamnose were detected. *R<sub>f</sub>* (min): L-arabinose, 16.05; D-xylose, 16.90; L-rhamnose, 24.54. Compound **12** (1.0 mg) was subjected to acid hydrolysis as in the case of **11**. The monosaccharides obtained were converted to 1-[(*S*)-*N*-acetyl- $\alpha$ -methylbenzylamino]-1-deoxyalditol acetate derivatives and analysed by HPLC. The derivatives of L-arabinose, D-xylose, D-glucose and L-rhamnose were detected. *R<sub>f</sub>* (min): L-arabinose, 15.92; D-xylose, 17.04; D-glucose, 21.49; L-rhamnose, 24.24.

**Partial hydrolysis of 11 and 12.** A soln of **11** (2.0 mg) in 0.2 M HCl (dioxane–H<sub>2</sub>O, 1:1, 1 ml) was heated at 95° for 30 min under an Ar atmosphere. The reaction mixt. was neutralized by passing it through an Amberlite IRA-93ZU column and purified by ODS

silica-gel CC eluting with MeOH-H<sub>2</sub>O (2:1) to give a partial hydrolysate, **7** (0.8 mg) and L-rhamnose. L-Rhamnose: TLC, *R<sub>f</sub>* 0.64 (*n*-BuOH-Me<sub>2</sub>CO-H<sub>2</sub>O, 4:5:1). Compound **12** (1.0 mg) was subjected to partial acid hydrolysis as in the case of **11** to give **7** (0.4 mg) and D-glucose. D-Glucose: TLC, *R<sub>f</sub>* 0.38 (*n*-BuOH-MeOH-H<sub>2</sub>O, 4:5:1).

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