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SPIROSTANOSIDES OF *ASPARAGUS SPRENGERI*

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Key Word Index—*Asparagus sprengeri*; Liliaceae; saponins; spirostanosides.

Abstract—Four new spirostanosides were isolated from the methanol extract of *Asparagus sprengeri* roots and characterized as 3-*O*-[β-D-xylo-(1 → 4)-β-D-gluco]-(25*R*)-spirost-5-en-3β-ol; 3-*O*-[α-L-rhamno-(1 → 6)-β-D-gluco]-(25*R*)-spirost-5-en-3β-ol; 3-*O*-{[α-L-rhamno-(1 → 2)] [β-D-xylo-(1 → 4)]-β-D-gluco}-(25*R*)-spirost-5-en-3β-ol and 3-*O*-{[α-L-rhamno-(1 → 2)] [α-L-rhamno-(1 → 6)]-β-D-gluco}-(25*R*)-spirost-5-en-3β-ol respectively.

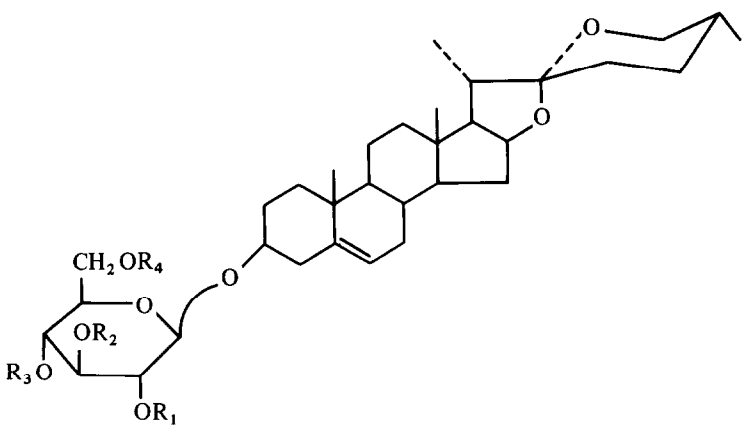
INTRODUCTION

The *Asparagus* species are well known for their medicinal uses [1]. *Asparagus sprengeri* is an ornamental small shrub and no phytochemical studies seem to have been done on this plant. Here we report the isolation and characterization of four new diosgenin spirostanosides from the methanol extract of roots of this plant.

RESULTS AND DISCUSSION

A crude saponin mixture obtained from an aqueous methanolic extract of the roots was found to be a mixture of eight components out of which four spirostanosides viz. sprengerinins A, B, C and D (**1**–**4**, characteristic spiroketal absorptions in their IR spectra) were crystallized.

Acid hydrolysis of all the four compounds, (**1**–**4**) separately furnished the same aglycone diosgenin (mmp, Co-TLC, superimposable IR spectrum with an authentic sample [2] and mass spectra). The aqueous hydrolysate of **1** contained D-glucose and D-xylose and the hydrolysate of **3** gave in addition L-rhamnose. The hydrolysates of **2** and **4** showed the presence of D-glucose and L-rhamnose (Co-PC). The configurations at the glycosidic bonds were established by the application of Klyne's rule [3] and by the ^{1}H NMR spectra to be β-D-glucose, β-D-xylose and α-L-rhamnose. All these sugars were found in the pyranose form. Sprengerinins A, B, C and D (**1**–**4**) were separately permethylated by Hakomori's method [4] to yield their permethylates **1a**, **2a**, **3a** and **4a** respectively. On methanolysis **1a** afforded a mixture of the methyl pyranosides of 2,3,4-tri-*O*-methyl-D-xylose and 2,3,6-tri-*O*-methyl-D-glucose (GC, 1:1) and **2a** gave a mixture of methyl



1 $R_1=R_2=R_4=H$, $R_3=\beta$-D-xyl
1a $R_1=R_2=R_4=Me$, $R_3=2,3,4$-tri-*O*-methyl-β-D-xyl
2 $R_1=R_2=R_3=H$, $R_4=\alpha$-L-rha
2a $R_1=R_2=R_3=Me$, $R_4=2,3,4$-tri-*O*-methyl-α-L-rha
3 $R_1=\alpha$-L-rha, $R_2=R_4=H$, $R_3=\beta$-D-xyl
3a $R_1=2,3,4$-tri-*O*-methyl-α-L-rha, $R_2=R_4=Me$
$R_3=2,3,4$-tri-*O*-methyl-β-D-xyl
4 $R_1=R_4=\alpha$-L-rha, $R_2=R_3=H$
4a $R_1=R_4=2,3,4$-tri-*O*-methyl-α-L-rha, $R_2=R_3=Me$

pyranosides of 2,3,4-tri-*O*-methyl-L-rhamnose and 2,3,4-tri-*O*-methyl-D-glucose (GC, 1:1) which on hydrolysis yielded the corresponding methylated sugars (PC). The mass spectra of **1a** and **2a** also supported these conclusions. In addition, methyl 2,3,6-tri-*O*-methyl glucopyranoside from **1a** and methyl 2,3,4-tri-*O*-methyl glucopyranoside from **2a** were isolated and identified (chromatographic techniques, mp and mmp). Therefore, **1** and **2** possess the structures 3-*O*-[β-D-xylopyranosyl-(1→4)β-D-glucopyranosyl]-(25*R*)-spirost-5-en-3β-ol and 3-*O*-[α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyl]-(25*R*)-spirost-5-en-3β-ol, respectively.

The field desorption mass spectrum of **3** showed a cationized cluster ion and other fragment ions at *m/z* 877 $[M+Na]^+$ (base peak), 745 $[(M+Na)-132]^+$, 731 $[(M+Na)-146]^+$, 147 (rhamnose-hydroxyl) and 133 (xylose-hydroxyl) which confirmed not only the purity of the compound but the presence of a branched chain trisaccharide pentosyl-(methyl pentosyl)-hexose (1:1:1) linked with an aglycone of MW 413 (diosgenin-H) [5, 6]. Compound **3a** on methanolysis furnished a mixture of the methyl pyranosides of 2,3,4-tri-*O*-methyl-L-rhamnose; 2,3,4-tri-*O*-methyl-D-xylose and 3,6-di-*O*-methyl-D-glucose (GC, 1:1:1). The mass peaks from **3a** at *m/z* 966 $[M]^+$, 775 [M − tri-*O*-methyl-xylose + H]$^+$, 761 [M − tri-*O*-methyl rhamnose + H]$^+$, 189 (terminal rhamnose) and 175 (terminal xylose) further confirmed the presence of D-xylose and L-rhamnose as the terminal sugars attached to D-glucose linked with the C-3 hydroxyl of diosgenin.

The peaks in the field desorption mass spectrum of **4** at *m/z* 891 $[M+Na]^+$ (base peak), 745 $[(M+Na)-146]^+$, 599 $[(M+Na)-292]^+$ and 413 proved its purity and the presence of a branched methyl pentosyl-(methyl pentosyl)-hexose (1:1:1) trisaccharide linked with a compound of MW 413 (diosgenin-H). Compound **4a** on methanolysis afforded a mixture of methyl pyranosides of 2,3,4-tri-*O*-methyl-L-rhamnose and 3,4-di-*O*-methyl-D-glucose (GC, 2:1). The mass spectrum of **4a** displayed peaks at *m/z* 980 $[M]^+$, 775 [M − tri-*O*-methyl-rhamnose + H]$^+$, 586 [M − 2(tri-*O*-methyl rhamnose) + H_2O]$^+$ and 189 (terminal rhamnose) confirming the presence of two terminal rhamnose units linked with a glucose molecule. Hydrolysis of the methyl pyranosides mixture of **3a** and **4a** (separately) yielded the corresponding methylated sugars (PC). 3,6-Di-*O*-methyl-D-glucose and 3,4-di-*O*-methyl-D-glucose obtained from **3a** and **4a**, respectively, were positive to Wallenfels' reagent [7]. These results indicated that in compounds **3** and **4** the aglycone diosgenin was glycosidated with C-1′ of D-glucose whose C-2′ was attached to a molecule of L-rhamnose. Compounds **3** and **4** differed only by the fact that the D-xylose formed a branching at C-4′ on the glucose in **3** whereas L-rhamnose formed a branching at C-6′ of the glucose in **4**.

To determine the exact linkages of various sugars, **3** and **4** were subjected to partial hydrolysis. Compounds **3** and **4** afforded three prosapogenins, PS_1, PS_2 and PS_3 identical with sprengerinin A (**1**) (mmp; Co-TLC) whereas **4** gave PS_1, PS_2 and PS_4 identical with sprengerinin B (**2**) (mmp; Co-TLC). PS_1 and PS_2 on hydrolysis furnished diosgenin and glucose, PS_2 also gave additionally L-rhamnose. Hydrolysis of the PS_1 permethyl ether afforded 2,3,4,6-tetra-*O*-methyl-D-glucose only while PS_2 permethyl ether provided 2,3,4-tri-*O*-methyl-L-rhamnose and 3,4,6-tri-*O*-methyl-D-glucose (positive to Wallenfels' reagent, PC). The mass spectral studies of PS_2 permethyl ether also supported all these results. Thus, PS_1 and PS_2 were characterized as 3-*O*-[β-D-glucopyranosyl]-(25*R*)-spirost-5-en-3β-ol (trillin) and 3-*O*-[α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosly]-(25*R*)-spirost-5-en-3β-ol respectively.

Sodium periodate degradation of **4** yielded no free monosaccharide, whereas **3** furnished D-glucose and periodate treatment of **3a** methyl pyranosides gave methylpyranosides of 3,6-di-*O*-methyl-D-glucose, 2,3,4-tri-*O*-methyl-D-xylose and 2,3,4-tri-*O*-methyl-L-rhamnose (TLC) which established the 2,4-linkages in **3** and 2,6 linkages in **4**. From all the above studies the structures of sprengerinin C and sprengerinin D were established as 3-*O*-{[α-L-rhamnopyranosyl-(1→2)] [β-D-xylopyranosyl-(1→4)]-β-D-glucopyranosyl}-(25*R*)-spirost-5-en-3β-ol and 3-*O*-{[α-L-rhamnopyranosyl-(1 → 2)] [α-L-rhamnopyranosyl-(1→6)]β-D-glucopyranosyl}-(25*R*)-spirost-5-en-3β-ol, respectively.

EXPERIMENTAL

Mps are uncorr. CC was carried out over silica gel (60–120 mesh, BDH) with solvents in the order of increasing polarity. Homogeneity of fractions was tested on TLC (silica gel G, BDH) and spots were visualized by 10% H_2SO_4, followed by heating and on PC (descending technique on Whatman No. 1) by aniline hydrogen phthalate and triphenyl tetrazolium chloride (Wallenfels' reagent). The solvent systems used were: A, $CHCl_3$–MeOH–H_2O (65:25:10); B, $CHCl_3$–MeOH–H_2O (65:35:10); C, C_6H_6–EtOAc (9:1); D, *n*-BuOH–HOAc–H_2O (4:1:5); E, *n*-BuOH–EtOH–H_2O (5:1:4); F, C_6H_6–Me_2CO (10:1). GC of methyl methylated sugars: column 10% OV101, N_2 (40 ml/min), programmed at 220° at 4°/min.

Isolation of saponins. The roots of *Asparagus sprengeri* Regel collected from Meerut (U.P.) were well dried, powdered (3 kg) and defatted with petrol and then exhaustively extracted with 90% aq. MeOH (8 hr × 4). Removal of solvent gave a brown residue which was purified as usual for the isolation of saponins. The purified mass (20 g) was repeatedly chromatographed over silica gel (solvent A) to yield compounds **1**–**4** and four other unidentified compounds.

Sprengerinin A (**1**). Yield 1.0 g. Mp 240–242° (MeOH), $[\alpha]_D^{20}$ −90.4° (pyridine, *c* 1), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2850 (Δ^5), 1040, 981, 918, 898 (intensity 898 > 918, 25*R*-spiroketal), 855 and 810. (Found: C, 64.80; H, 8.70. $C_{38}H_{60}O_{12}$ requires C, 64.40; H, 8.47%.)

Sprengerinin B (**2**). Yield 1.5 g. Mp 245–247° (MeOH), $[\alpha]_D^{20}$ −88.9° (pyridine, *c* 1). IR ν_{max}^{KBr} cm^{-1}: 3395 (OH), 2845 (Δ^5), 980, 915, 896 (intensity 896 > 915, 25*R*-spiroketal) and 850. (Found: C, 65.0; H, 8.80. $C_{39}H_{62}O_{12}$ requires C, 64.80; H, 8.58%.)

Sprengerinin C (**3**). Yield 4.0 g. Mp 245–250° (MeOH), $[\alpha]_D^{20}$ −86.4° (pyridine, *c* 1), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2845 (Δ^5), 1040, 980, 916, 898 (intensity 898 > 916, 25*R*-spiroketal), 850. ^{1}H NMR (100 MHz, DMSO-d_6): δ5.28 (1H, *d*, *J* = 1.5 Hz, H-1 of Rha), 4.60 (1H, *d*, *J* = 6.5 Hz, H-1 of Glc), 4.20 (1H, *d*, *J* = 7 Hz, H-1 of Xyl). FDMS (silicone emitter 29–33 MA) *m/z* (rel. int.): 893 $[M+K]^+$ (30.0), 877 $[M+Na]^+$ (100), 855 $[M+H]^+$ (10), 854 $[M]^+$ (8), 745 $[(M+Na)-132]^+$ (18), 731 $[(M+Na)-146]^+$ (10), 599 $[(M+Na)-278]^+$ (4), 450 $[M+2Na]^{2+}$ (10), 147 [Rha-OH] (8), 133 [Xyl-OH] (6). (Found: C, 61.90; H, 8.25; $C_{44}H_{70}O_{16}$ requires C, 61.82; H, 8.19%.)

Sprengerinin D (**4**). Yield 3.0 g. Mp 250–255° (MeOH), $[\alpha]_D^{20}$ −85.2° (pyridine, *c* 1). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2840 (Δ^5), 1045, 986, 920, 898 (intensity 898 > 920, 25*R*-spiroketal) and 850. ^{1}H NMR (100 MHz, DMSO-d_6): δ5.25 (1H, *d*, *J* = 2.0 Hz, H-1

of Rha), 4.98 (1H, *br s*, H-1 of Rha), 4.85 (1H, *d*, $J = 6.5$ Hz, H-1 of Glc). FDMS (Silicone emitter 25.5–29 MA) *m/z* (rel. int.): 907 $[M+K]^+$ (92), 891 $[M+Na]^+$ (100), 869 $[M+H]^+$ (3), 868 $[M]^+$ (2), 745 $[(M+Na)-146]^+$ (11), 723 $[(M+H)-146]^+$ (20), 599 $[(M+Na)-292]^+$ (3.5), 577 $[(M+H)-292]^+$ (20), 457 $[M+2\,Na]^{2+}$ (19), 413 [genin]$^+$ (45), 397 [spirostadiene $+H]^+$ (20). (Found: C, 62.50; H, 8.70. $C_{45}H_{72}O_{16}$ requires C, 62.20; H, 8.4%.)

Acid hydrolysis of **1–4**. The glycosides (100 mg each) were separately refluxed with 7% HCl (20 ml, 3 hr) on a steam bath to give diosgenin mp 200–202° (MeOH), $[\alpha]_D^{20}$ −128° ($CHCl_3$, *c* 1). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 3020, 2845 (Δ^5), 980, 918, 898 (intensity 898 > 918, 25*R*-spiroketal), 860, 835 and 802. EIMS (probe) 70 eV, *m/z* (rel. int.): 414 $[M]^+$ (5.7), 396 (2.3), 345 (6.7), 300 (25.0), 282 (42.3), 271 (23.0), 253 (21.1), 139 (100), 115 (16.6). (Found: C, 78.15; H, 10.20. $C_{27}H_{42}O_3$ requires C, 78.21; H, 10.21%.) Monoacetate, mp 189–190° (MeOH), $[\alpha]_D^{20}$ −115°. IR ν_{max}^{KBr} cm^{-1}: 1730 (OAc). The neutralized (Ag_2CO_3) concd aq. hydrolysates showed the presence of the following sugars. From **1**: D-xylose (R_f 0.28) and D-glucose (R_f 0.18). From **3**: D-xylose, D-glucose and L-rhamnose (R_f 0.37). From **2** and **4**: L-rhamnose and D-glucose (PC, solvent D).

Permethylation of **1–4**. The glycosides (300 mg each) were separately permethylated by Hakomori's method to get the permethylated **1a** (285 mg), **2a** (275 mg), **3a** (280 mg) and **4a** (270 mg) respectively, purified by CC (solvent C).

Compound **1a**. Mp 79–80° (Et_2O–petrol). IR ν_{max}^{KBr} cm^{-1}: no OH. EIMS (probe) 48 eV, *m/z* (rel. int.): 792 $[M]^+$ (0.7), 616 (0.4), 601 $[M$ − 2,3,4-tri-*O*-methyl xylose $+H]^+$ (0.4), 397 [spirostadine $+H]^+$ (32), 379 (6), 283 (16), 282 (15), 253 (17), 175 (45), 147 (16), 143 (44), 139 (30), 111 (24), 101 (100), 88 (29), 75 (24), 71 (29), 69 (24), 45 (42). (Found: C, 66.70; H, 9.10. $C_{44}H_{72}O_{12}$ requires C, 66.66; H, 9.09%.)

Methanolysis of **1a**. Compound **1a** (150 mg) in 1 N HCl–MeOH (15 ml) was refluxed (4 hr), neutralized (Ag_2CO_3), filtered and the filtrate was concd *in vacuo*. GC R_t (min): 1.26 (methyl-2,3,4-tri-*O*-methyl-β-D-xylopyranoside), 1.42 (methyl-2,3,6-tri-*O*-methyl-β-D-glucopyranoside), ratio 1:1. Usual hydrolysis of this mixture liberated 2,3,4-tri-*O*-methyl-D-xylose R_G 0.94) and 2,3,6-tri-*O*-methyl-D-glucose (R_G 0.83, PC; solvent E). Methyl-2,3,6-tri-*O*-methyl-D-glucopyranoside was also isolated by prep. TLC (solvent F) using I_2 as visualizing agent; mp 98–99°.

Compound **2a**. Mp 88–91° (Et_2O–petrol), IR ν_{max}^{KBr} cm^{-1}: no OH. EIMS (probe) 70 eV, *m/z* (rel. int): 806 $[M]^+$ (0.8), 601 $[M$ − 2,3,4-tri-*O*-methyl rhamnose $+H]^+$ (0.8), 397 [spirostadiene $+H]^+$ (42), 282 (9), 275 (17), 253 (10), 205 (3), 189 (70), 173 (6), 157 (20), 139 (20), 125 (8), 101 (24), 88 (100), 75 (18), 59 (12), 45 (16). (Found: C, 67.10; H, 9.25; $C_{45}H_{74}O_{12}$ requires C, 67.0; H, 9.18%.)

Methanolysis of **2a**. Compound **2a** (150 mg) was subjected to methanolysis as described for **1a**. GC R_t (min): 0.88 (methyl-2,3,4-tri-*O*-methyl-α-L-rhamnopyranoside), 1.37 (methyl-2,3,4-tri-*O*-methyl-β-D-glucopyranoside), ratio 1:1. Hydrolysis gave 2,3,4-tri-*O*-methyl-L-rhamnose (R_G 1.01) and 2,3,4-tri-*O*-methyl-D-glucose (R_G 0.85, PC, solvent E). Methyl-2,3,4-tri-*O*-methyl-β-D-glucopyranoside was also isolated (as above), mp 100–101°.

Compound **3a**. Mp 89–92° (Et_2O–petrol), IR ν_{max}^{KBr} cm^{-1}: no-OH. EIMS (probe) 48 eV, *m/z* (rel. int.): 966 $[M]^+$ (0.18), 775 (0.16), 761 (0.15), 569 (0.36), 553 (0.68), 397 (32), 282 (10), 253 (8), 189 (100), 175 (23), 157 (27), 143 (21), 139 (10), 111 (13), 101 (27), 88 (68), 75 (20), 45 (6). (Found: C, 64.76; H, 8.98. $C_{52}H_{86}O_{16}$ requires C, 64.6; H, 8.9%.)

Methanolysis of **3a**. Compound **3a** (200 mg) was treated as above for **1a** and the products examined by GC. R_t (min): 0.81 (methyl-2,3,4-tri-*O*-methyl-α-L-rhamnopyranoside), 1.28 (methyl-2,3,4-tri-*O*-methyl-β-D-xylopyranoside) and 1.36 (methyl-3,6-di-*O*-methyl-β-D-glucopyranoside), ratio 1:1:1. Usual hydrolysis of this mixture yielded 2,3,4-tri-*O*-methyl-L-rhamnose (R_G 1.01), 2,3,4-tri-*O*-methyl-D-xylose (R_G 0.94) and 3,6-di-*O*-methyl-D-glucose (R_G 0.51, pink colour with Wallenfels' reagent, PC, solvent E).

Compound **4a**. Mp 90–93° (Et_2O–petrol), IR ν_{max}^{KBr} cm^{-1}: no-OH. EIMS (probe) 70 eV, *m/z* (rel. int.): 980 $[M]^+$ (0.2), 775 (0.4), 602 (1.2), 586 (0.6), 413 (3), 397 (36), 282 (26), 253 (14), 189 (83), 157 (25), 139 (29), 116 (28), 101 (54), 88 (100), 75 (34), 45 (46). (Found: C, 64.98; H, 9.10. $C_{53}H_{88}O_{16}$ requires C, 64.89; H, 8.97%.)

Methanolysis of **4a**. Compound **4a** (180 mg) was subjected to methanolysis as for **1a**. GC R_t (min): 0.80 (methyl-2,3,4-tri-*O*-methyl-α-L-rhamnopyranoside) and 1.39 (methyl-3,4-di-*O*-methyl-β-D-glucopyranoside), ratio 2:1. Hydrolysis of a portion of this sugar mixture in the usual way liberated 2,3,4-tri-*O*-methyl-L-rhamnose (R_G 1.01) and 3,4-di-*O*-methyl-D-glucose (R_G 0.52, pink colour with Wallenfels' reagent, PC, solvent E).

$NaIO_4$ *oxidation*. Compounds **3** and **4** (25 mg each in 10 ml H_2O) were separately treated with $NaIO_4$ (250 mg) for 48 hr in the dark. Ethylene glycol (1 ml) was added to decompose excess $NaIO_4$ and the solns were hydrolysed with 10% HCl–MeOH (45 min), filtered, neutralized (Ag_2CO_3), concd and examined by PC (solvent D). Compound **3** showed only D-glucose while no sugars were detected in **4**. A portion of the mixture of methyl pyranosides, obtained by the methanolysis of **3a** was treated with $NaIO_4$, worked up as usual and the products showed the presence of methyl 3,6-di-*O*-methyl-D-glucopyranoside along with other methyl pyranosides (solvent F).

Partial hydrolysis of **3** *and* **4**. The glycosides **3** and **4** (2 g each) were separately refluxed on a steam bath with 5% aq. HCl–MeOH (1:1, 150 ml, 40 min), neutralized (Ag_2CO_3) and filtered. The filtrates were dried *in vacuo* and chromatographed separately (solvent A). Compounds **3** and **4** gave diosgenin (30 and 40 mg), PS_1 (200 and 150 mg) and PS_2 (250 and 225 mg respectively). **3** additionally gave PS_3 (300 mg) which was identical with sprengerinin A (**1**) (mmp, Co-TLC, permethylation and methanolysis results), while **4** gave PS_4 (275 mg) identical with sprengerinin B (**2**) (mmp, Co-TLC, permethylation and methanolysis results).

Compound PS_1. Mp 254–259° (MeOH), $[\alpha]_D^{20}$ −94.2° ($CHCl_3$, *c* 1) IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 981, 916, 896 (intensity 896 > 916 25*R*-spiroketal), 855. (Found: C, 68.20; H, 9.15. $C_{33}H_{52}O_8$ requires C, 68.77; H, 9.08%.) On acid hydrolysis PS_1 afforded diosgenin and D-glucose (PC, R_f 0.18, solvent D). PS_1 permethylate on hydrolysis released 2,3,4,6-tetra-*O*-methyl-D-glucose (PC, R_G 1.0, solvent E). PS_1 tetra-acetate mp 208–209° $[\alpha]_D^{20}$ −89.5° ($CHCl_3$, *c* 1.0).

Compound PS_2. Mp 242–244° (MeOH), $[\alpha]_D^{20}$ −89.0° (pyridine, *c*1). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2845 (Δ^5) 980, 915, 898 (intensity 898 > 915, 25*R*-spiroketal) and 850. On acid hydrolysis it afforded diosgenin (mmp, Co-TLC) and D-glucose (R_f 0.18) and L-rhamnose (R_f 0.37) as sugars (Co-PC, solvent D). PS_2 permethylate mp 87–89°. IR ν_{max}^{KBr} cm^{-1}: no-OH. EIMS (probe) 70 eV, *m/z* (rel. int.): 806 $[M]^+$ (0.7), 601 $[M-2,3,4$-tri-*O*-methyl rhamnose $+H]^+$ (0.6), 397 [spirostadiene $+H]^+$ (30), 189 (78), 157 (22), 139 (15), 88 (100). On acid hydrolysis it afforded 2,3,4-tri-*O*-methyl-L-rhamnose (R_G 1.01) and 3,4,6-tri-*O*-methyl-D-glucose (R_G 0.84; pink colour with Wallenfels' reagent, PC, solvent E).

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