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3α-HYDROXY-OLEANENE TYPE TRITERPENE GLYCOSYL ESTERS FROM LEAVES OF *ACANTHOPANAX SPINOSUS**

MASAZUMI MIYAKOSHI, SUSUMU ISODA, HIROTOSHI SATO, YASUAKI HIRAI, JUNZO SHOJI and YOSHITERU IDA†

School of Pharmaceutical Sciences, Showa University, Hatanodai 1-5-8, Shinagawa-ku, Tokyo 142, Japan

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Key Word Index—*Acanthopanax spinosus*; Araliaceae; triterpenoid saponin; triterpene glycosyl ester; 3α,20α-dihydroxy-30-*nor*-olean-12-en-28-oic acid; 3α,20α-dihydroxy-23-oxo-30-*nor*-olean-12-en-28-oic acid; 3α,20α,23-trihydroxy-30-*nor*-olean-12-en-28-oic acid; 3α, 30-dihydroxy-23-oxo-olean-12-en-28-oic acid; spinogenin; spinoside.

Abstract—Four novel 3α-hydroxy-oleanane type triterpene oligoglycosyl esters, spinoside C2, C3, C6 and C7, were isolated from the leaves of *Acanthopanax spinosus*. The structures were established to be 28-*O*-α-L-rhamnopyranosyl(1 → 4)-β-D-glucopyranosyl(1 → 6)-β-D-glucopyranosyl esters of 3α,30-dihydroxy-23-oxo-olean-12-en-28-oic acid, 3α,20α-dihydroxy-30-*nor*-olean-12-en-28-oic acid, 3α,20α-dihydroxy-23-oxo-30-*nor*-olean-12-en-28-oic acid and 3α,20α,23-trihydroxy-30-*nor*-olean-12-en-28-oic acid. © 1997 Published by Elsevier Science Ltd

INTRODUCTION

In previous papers [1, 2], we reported on the isolation and the structure elucidation of six new 3α-hydroxy-oleanane type triterpene oligoglycosyl esters named spinosides D1, D2, D3, C1, C4 and C5 from the leaves of *Acanthopanax spinosus* MIQ. Further investigation led to the isolation of four new analogues. This paper deals with the structure elucidation of these four new saponins.

RESULTS AND DISCUSSION

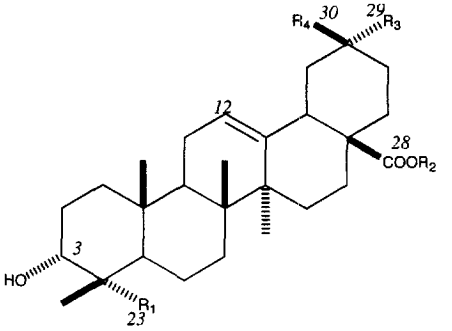
The crude saponin mixture obtained from the leaves as described in the Experimental was repeatedly subjected to chromatography to give seven compounds, **1**–**7**. Compounds **1**, **4** and **5** were identical with spinosides C1, C5 and C4 [2].

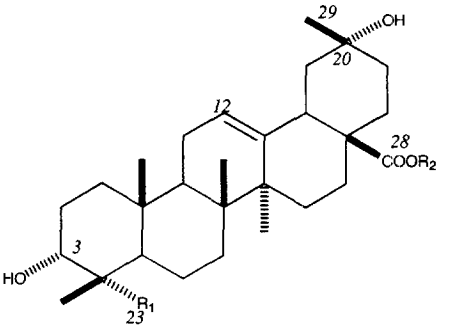
The new saponin **2** was named spinoside C2. Its molecular formula was established as $C_{48}H_{76}O_{19}$ by FAB mass spectroscopy and elemental analysis. On acid hydrolysis, **2** gave glucose (Glc) and rhamnose (Rha) (identified by TLC and GC) as sugar components. These properties of **2** were exactly the same as those of **5** (28-*O*-α-L-rhamnopyranosyl(1 → 4)-β-D-glucopyranosyl(1 → 6)-β-D-glucopyranosyl ester of 3α,29-dihydroxy-23-oxo-olean-12-en-28-oic acid). On comparison of the ^{13}C NMR spectrum of **2** with that of **5**, the only differences were those for the chemical shifts due to the carbons around C-20 in the E ring, although their multiplicities were still the same as those of **5**. In addition, the ^1H signal ascribable to H-18 (δ 3.31) in **2** showed *dd*, $J = 8.0$, 10.4 Hz. This suggested distortion of the E-ring due to the hydroxylation not of the equatorial methyl group (C-29) but of the axial methyl group (C-30). Thus **2** appeared to be the C-20 epimer of **5**. To simplify the structure elucidation, **2** was hydrolysed with crude hesperidinase to give spinogenin C2 (**2a**) as aglycone along with a partially hydrolysed product (spinogenin C2 monoglucosyl ester (**2b**)). The assumed substructure, a 30-hydroxy substituted oleanane-type triterpene, has been reported previously as queretaroic acid (3β,30-dihydroxy-olean-12-en-28-oic acid) [3]. The ^{13}C signals due to the CDE ring moiety of **2a** were superimposable on those of queretaroic acid. Since **2a** had the same ABC ring moiety as spinogenin (C4) (**5a**), the structure of **2a** was established to be 3α,30-dihydroxy-23-oxo-olean-12-en-28-oic acid. Thus spinoside C2 (**2**) was determined as 28-*O*-α-L-rhamnopyranosyl(1 → 4)-β-D-glucopyranosyl(1 → 6)-β-D-glucopyranosyl ester of 3α,30-dihydroxy-23-oxo-olean-12-en-28-oic acid.

Saponin **3** was named spinoside C3. Its M_r was shown to be 928 by FAB mass spectroscopy, and the molecular formula was established as $C_{47}H_{76}O_{18}$ by elemental analysis. It gave Glc and Rha on acid

* Part 3 in the series. For parts 1 and 2 see refs [1, 2].

† Author to whom correspondence should be addressed.





	R_1	R_2	R_3	R_4
1:	CH_3	S	CH_2OH	CH_3
2:	CHO	S	CH_3	CH_2OH
4:	CH_2OH	S	CH_2OH	CH_3
5:	CHO	S	CH_2OH	CH_3

S: α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl
Glc: β-D-glucopyranosyl

	R_1	R_2
3:	CH_3	S
3a:	CH_3	H
3b:	CH_3	Glc
6:	CH_2OH	S
6a:	CH_2OH	H
6b:	CH_2OH	Glc
7:	CHO	S
7a:	CHO	H

hydrolysis. The ^{13}C NMR spectrum of **3** was similar to that of **2**, indicating that **3** contained the same ester linked sugar chain, α-L-rhamnopyranosyl(1 → 4)-β-D-glucopyranosyl(1 → 6)-β-D-glucopyranosyl, as **2** and an oleanene type triterpenoid as the aglycone. On comparison of the ^{13}C NMR signals of **3** with those of **2**, they were found to be in good agreement for the oligoglycosyl moiety and the aglycone, except for the signals due to the E ring which included a signal due to a trisubstituted alcoholic carbon (δ 69.6, *s*). To establish the structure, **3** was hydrolysed in the same way as **2** to give spinogenin C3 (**3a**) and a partially hydrolysed product (**3b**). The molecular formula of **3a** was determined as $C_{29}H_{46}O_4$ by HR-FAB mass spectroscopy and **3a** was revealed to be a *nor*-triterpene carboxylic acid. The ^1H NMR spectrum of **3a** contained six tertiary methyl signals and the signals ascribable to H-3β (δ 3.59, *s*), H-12 (δ 5.54, *t*-like) and H-18 (δ 3.33, *dd*) [1]. The ^{13}C NMR spectrum of **3a** showed good agreement with that of **2a**, except for the signals due to the E ring carbons. The tertiary alcoholic carbon signal at δ 69.9 in the E ring was assigned to C-20 and the orientation of the hydroxyl group was α based on the following results. The ^{13}C NMR signal at δ 69.9 showed long range H-C correlation with one of the methylene proton signals at δ 2.39 (1H, *dd*) and a tertiary methyl proton signal at δ 1.55 (3H, *s*) in the HMBC spectrum; the ^1H NMR signal at δ 2.39 was assigned to H-19, which showed correlation with H-18 (δ 3.33) in the ^1H–^1H COSY spectrum. The tertiary methyl proton signal at δ 1.55 was assigned to H_3-29 since a long range H-C correlation was observed between this signal and the signal due to C-21 (δ 36.3, *t*) and C-19 (δ 47.9, *t*) in the HMBC spectrum. The orientation of this methyl group was determined to be β-axial since an NOE was shown between the H_3-29 signal and the H-18 signal. On the other hand, the ^{13}C NMR signals of the CDE ring moiety in **3a** were not superimposable on those of pfameric acid (3β,16β,20β-trihydroxy-30-*nor*-olean-12-en-28-oic acid) [4] but mubenoside A (3β,20α-dihydroxy-30-*nor*-olean-12-en-28-oic acid 3-*O*-[β-D-xylopyranosyl(1 → 2)-α-L-arabinopyranosyl (1 → 3)]β-D-glucopyranoside) [5]. Accordingly, **3a** was characterized as a 3α,20α-dihydroxy-30-*nor*-olean-12-en-28-oic acid and **3** as 28-*O*-α-L-rhamnopyranosyl(1 → 4)-β-D-glucopyranosyl(1 → 6)-β-D-glucopyranosyl ester of 3α,20α-dihydroxy-30-*nor*-olean-12-en-28-oic acid.

The new saponins, **6** and **7**, were named spinoside C6 and C7, respectively. Their molecular compositions were determined to be $C_{47}H_{76}O_{19}$ and $C_{47}H_{74}O_{19}$, respectively, by elemental analysis and FAB mass spectroscopy. On comparison of the ^{13}C NMR spectra of **6** and **7** with those of **3**, **4** and **5**, the signals due to the C/D/E ring carbons and those of the sugar moiety were the same as those of **3**, and the signals due to A/B ring carbons were superimposable on those of **4** and **5**, respectively. On reduction with sodium borohydride in ethanol, **7** gave an alcohol which was identified as **6**, showing that **6** was the alcohol corresponding to the aldehyde **7**. In the ^{13}C NMR spectrum of the aglycone of **6** (**6a**), prepared in the same way as above, the signals due to the A/B rings were the same as those of 3-*epi*-hederagenin [1] and those due to the C/D/E rings were the same as those of **3a**. Therefore, **6** and **7** were characterized as 28-*O*-α-L-rhamnopyranosyl(1 → 4)-β-D-glucopyranosyl(1 → 6)-β-D-glucopyranosyl esters of 3α,23,20α-trihydroxy-30-*nor*-olean-12-ene-28-oic acid and

3α,20α-dihydroxy-23-oxo-30-*nor*-olean-12-en-28-oic acid, respectively. The names, spinogenins C6 (**6a**) and C7 (**7a**) are now proposed for the aglycones of **6** and **7**, respectively. Saponins **6** and **7** are the C-23 oxidation products of **3**.

It has been shown that the leaves of *A. spinosus* are abundant in 3α-hydroxy-oleanane type triterpene glycosyl esters having no sugar chain at the C-3 hydroxyl group. Recently, saponins having a β-hydroxyl group at C-3 in their aglycone have been obtained in small amounts from the leaves of this plant.

EXPERIMENTAL

General. ^{1}H NMR: 500 MHz; ^{13}C NMR: 125 MHz; GC (TMSi derivatives with FID; glass column (3 mm × 2.1 m) packed with 5% OV-17 at 155°); TLC: silica gel $60F_{254}$ (Merck), developed by $CHCl_3$–MeOH–H_2O (6:4:1). The solvents used for spectral determination were: C_5D_5N–TMS (NMR); MeOH ($[\alpha]_D$); unless otherwise stated. CC: silica gel 60 (Merck), Chromatorex ODS (Fuji-Silysia) and Sephadex LH-20 (Pharmacia). The solvent systems for CC were all homogeneous.

Plant material. The plant was collected at Fujiyoshida City (Yamanashi Pref.), Japan, in May 1994 and was identified by one of the authors (S. Isoda). A specimen has been deposited in the Herbarium of this Institute.

Extraction and separation. The dried leaves (3.0 kg) were extracted with MeOH. After removal of the solvent by evapn, the combined extracts (456 g, 15.2%) were chromatographed on highly porous polymer resin (DIAION HP-20, Mitsubishi Chem. Ind. Co. Ltd.) eluted with H_2O, MeOH and Me_2CO, successively. The MeOH eluate (185 g, 6.2%) was chromatographed on silica gel CC ($CHCl_3$–MeOH–H_2O 10:5:1) to give four frs, I (86.7 g, 2.9%), II (44.8 g, 1.5%), III (12.8 g, 0.04%) and IV (31.6 g, 1.1%), in order of elution. Fr. II (20 g) was chromatographed on LH-20 CC to give two frs, IIa (13.2 g, 0.99%) and IIb (6.0 g, 0.45%). Fr. IIa was chromatographed on silica gel CC ($CHCl_3$–MeOH–H_2O 10:5:1) to give four frs, IIa-1 (0.73 g, 0.05%), IIa-2 (6.36 g, 0.47% = spinoside C fr.), IIa-3 (4.32 g, 0.32% = spinoside D fr.) and IIa-4 (1.63 g, 0.12%). Fr. IIa-2 was chromatographed on ODS CC (MeOH–H_2O 1:1 and 3:2) to give 17 frs (Fr. 1–17) in order of elution. Frs 12, 10 and 8 gave **1** (1.12 g, 0.08%), **5** (458 mg, 0.034%) and **4** (350 mg, 0.026%) by evapn of solvents, respectively. Fr. 11 (952 mg, 0.071%) was sepd by ODS CC (32% and 28% aq. MeCN) to give **2** (216 mg, 0.016%) and **3** (670 mg, 0.05%). Fr. 9 (151 mg, 0.011%) was composed of **4** and **5**. Fr. 7 (457 mg, 0.034%) was sepd by ODS CC (26% aq. MeCN) to give **6** (170 mg, 0.013%). Fr. 6 (179 mg) was purified with ODS CC (24% aq. MeCN) to give **7** (107 mg, 0.0080%). The purity of all compounds was checked by HPLC with UV detection (210 nm) as follows. Condition A; Column: L-column ODS (4.6 mm I.D. × 250 mm: Chemical Inspection and Testing Institute), Mobile phase: MeOH–H_2O 3:2, 0.7 ml min^{-1}, R_t s: **1** (19.3 min), **2** (15.0 min), **3** (13.0 min), **4** (10.6 min), **5** (9.4 min), **6** (8.2 min), **7** (7.5 min). Condition B; Column: ODS 80TM (7.6 mm I.D. × 300 mm: TOSOH), Mobile phase: 32% aq. MeCN, 2.5 ml min^{-1}, R_t s: **2** (14.1 min), **3** (12.8 min), **6** (6.7 min).

*Spinoside C*2 (**2**). Powder; $[\alpha]_D^{25}$ −17.8° (*c* 1.00); FABMS (negative) *m/z*: 955 $[M-H]^-$, 485 [M-(Glc-Glc-Rha)-H]$^-$; $C_{48}H_{76}O_{19} \cdot 3H_2O$ requires C, 57.02, H, 8.17, Found C, 57.13, H, 8.20; ^{1}H NMR δ: 0.91 (3H, *s*, H-25), 1.08 (3H, *s*, H-24), 1.11 (3H, *s*, H-26), 1.12 (3H, *s*, H-30), 1.18 (3H, each *s*, H-27), 1.67 (3H, *d*, *J* = 6.1 Hz, Rha H-6), 3.31 (1H, *dd*, *J* = 8.0, 10.4 Hz, H-18), 3.99 (1H, *s*, H-3), 4.95 (1H, *d*, *J* = 7.9 Hz, outer Glc H-1), 5.42 (1H, *t-like*, H-12), 5.83 (1H, *s*, Rha H-1), 6.21 (1H, *d*, *J* = 8.2 Hz, inner Glc H-1), 9.95 (1H, *s*, H-23); ^{13}C NMR: Table 1.

*Spinoside C*3 (**3**). Powder; $[\alpha]_D^{25}$ −21.6° (*c* 1.00); FABMS (negative) *m/z*: 927 $[M-H]^-$, 457 [M-(Glc-Glc-Rha)-H]$^-$; $C_{47}H_{76}O_{18} \cdot \frac{1}{2}H_2O$ requires C, 60.17; H, 8.27, Found C, 60.20; H, 8.59; ^{1}H NMR δ: 0.86 (3H, *s*, H-24), 0.93 (3H, *s*, H-25), 1.08 (3H, *s*, H-26), 1.12 (3H, *s*, H-27), 1.17 (3H, *s*, H-23), 1.42 (3H, *s*, H-30), 1.67 (3H, *d*, *J* = 6.1 Hz, Rha H-6), 3.20 (1H, *dd*, *J* = 14.3, 4.3 Hz, H-18), 3.64 (1H, *s*, H-3), 4.94 (1H, *d*, *J* = 7.6 Hz, outer Glc H-1), 5.47 (1H, *t-like*, H-12), 5.82 (1H, *s*, Rha H-1), 6.22 (1H, *d*, *J* = 8.3 Hz, inner Glc H-1); ^{13}C NMR: Table 1.

*Spinoside C*6 (**6**). Powder; $[\alpha]_D^{27}$ −16.7° (*c* 0.75); FABMS (negative) *m/z*: 943 $[M-H]^-$, 473 [M-(Glc-Glc-Rha)-H]$^-$; $C_{47}H_{76}O_{19} \cdot 2H_2O$ requires C, 57.53, H, 8.22, Found C, 57.50, H, 8.22; ^{1}H NMR δ: 0.73 (3H, *s*, H-24), 0.93 (3H, *s*, H-25), 1.10 (6H, *s*, H-26 and H-27), 1.42 (3H, *s*, H-30), 1.64 (3H, *d*, *J* = 6.1 Hz, Rha H-6), 3.18 (1H, *dd*, *J* = 14.4, 3.7 Hz, H-18), 3.88 (1H, *s*, H-3), 4.93 (1H, *d*, *J* = 8.0 Hz, outer Glc H-1), 5.45 (1H, *t-like*, H-12), 5.77 (1H, *s*, Rha H-1), 6.19 (1H, *d*, *J* = 7.9 Hz, inner Glc H-1); ^{13}C NMR: Table 1.

*Spinoside C*7 (**7**). Powder; $[\alpha]_D^{27}$ −25.2° (*c* 1.03); FABMS (negative) *m/z*: 941 $[M-H]^-$, 471 [M-(Glc-Glc-Rha)-H]$^-$; $C_{47}H_{74}O_{18} \cdot 2\frac{1}{2}H_2O$ requires C, 57.13, H, 7.97, Found C, 57.26, H, 8.06; ^{1}H NMR δ: 0.93 (3H, *s*, H-25), 1.08 (3H, *s*, H-24), 1.11 (3H, *s*, H-26), 1.12 (3H, *s*, H-27), 1.43 (3H, *s*, H-30), 1.66 (3H, *d*, *J* = 6.1 Hz, Rha H-6), 3.21 (1H, *dd*, *J* = 14.1, 4.3 Hz, H-18), 3.98 (1H, *s*, H-3), 4.95 (1H, *d*, *J* = 7.9 Hz, outer Glc H-1), 5.48 (1H, *t-like*, H-12), 5.83 (1H, *s*, Rha H-1), 6.23 (1H, *d*, *J* = 8.3 Hz, inner Glc H-1), 9.94 (1H, *s*, H-23); ^{13}C NMR: Table 1.

$NaBH_4$ reduction of **7**. A soln of **7** (23 mg) and $NaBH_4$ (30 mg) in EtOH (5 ml) was stirred for 17 hr at room temp. After decomposition of excess of the reagent with Me_2CO (1 ml), the mixt. was deionized with Amberlite MB-3 and concd *in vacuo* to give the reduction product (13 mg) which was identical to **6** by co-TLC and NMR spectra.

Enzymatic hydrolysis of **2**, **3** *and* **6**. A soln of **2** (109 mg) and crude hesperidinase (105 mg, Sigma Co. Ltd.)

Table 1. ^{13}C NMR signals of the compounds in pyridine-d_5

C	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**2a**	**2b**	**3a**	**3b**	**6a**
1	33.6	32.8	33.6	33.5	32.8	33.3	32.8	32.8	32.8	33.6	33.6	33.4
2	26.3	26.4	26.3	26.5	26.5	26.3	26.4	26.5	26.4	26.3	26.3	26.5
3	75.1	72.6	75.1	75.6	72.6	75.0	72.6	72.7	72.7	75.2	75.2	75.7
4	37.9	52.3	37.8	40.8	52.4	40.5	52.3	52.4	52.4	37.9	37.9	40.7
5	49.3	43.9	49.3	43.8	43.9	43.5	43.8	43.9	43.9	49.3	49.3	53.6
6	18.7	21.1	18.6	18.5	21.1	18.3	21.0	21.1	21.1	18.6	18.6	18.4
7	33.1	32.7	33.1	32.9	32.9	32.7	32.7	32.8	32.7	33.3	33.2	32.7
8	40.1	40.5	40.1	40.1	40.5	39.9	40.5	40.4	40.5	40.0	40.1	39.9
9	47.9	47.8	47.9	48.2	47.8	47.9	47.7	47.8	47.8	48.1	47.9	48.0
10	37.5	36.7	37.5	37.4	36.8	37.2	36.7	36.8	36.7	37.5	37.5	37.3
11	23.8	23.7	23.7	24.0	23.8	23.7	23.7	23.7	23.7	23.9	23.8	23.8
12	123.0	122.9	123.1	123.1	122.8	123.0	122.9	122.5	122.8	122.8	123.1	122.7
13	144.3	144.1	143.6	144.4	144.4	143.6	143.7	144.9	144.2	144.4	143.6	144.4
14	42.2	42.3	42.1	42.3	42.3	42.1	42.3	42.4	42.3	42.2	42.2	43.2
15	28.3	28.2	28.2	28.4	28.3	28.1	28.2	28.3	28.2	28.3	28.2	28.3
16	23.4	23.7	23.5	23.5	23.5	23.4	23.5	24.1	23.7	23.8	23.6	23.8
17	47.5	47.1	47.1	47.6	47.5	47.0	47.1	46.7	47.0	46.8	47.1	46.7
18	41.1	41.3	44.0	41.2	41.2	43.9	44.1	41.7	41.4	44.4	44.2	44.4
19	41.0	41.6	47.8	41.1	41.0	47.6	47.7	42.0	41.6	47.9	47.9	48.1
20	36.4	35.7	69.6	36.4	36.4	69.6	69.5	35.9	35.7	69.9	69.6	69.9
21	28.9	29.4	35.9	28.9	28.9	35.7	35.9	29.6	29.4	36.3	36.0	36.2
22	32.0	32.3	34.4	32.1	32.0	34.3	34.5	33.0	32.3	35.2	34.5	35.2
23	29.3	209.4	29.3	71.3	209.5	71.0	209.3	209.3	209.3	29.3	29.3	71.3
24	22.7	14.8	22.7	18.3	14.9	18.0	14.8	14.8	14.8	22.7	22.7	18.2
25	15.6	15.6	15.5	16.1	15.7	15.8	15.6	15.5	15.6	15.4	15.5	15.8
26	17.6	17.7	17.6	17.7	17.8	17.5	17.7	17.6	17.7	17.5	17.6	17.5
27	26.0	26.0	25.9	26.2	26.2	25.8	25.9	26.2	26.1	26.0	25.9	26.0
28	176.6	176.6	176.4	176.8	176.7	176.4	176.4	180.3	176.5	180.0	176.3	180.0
29	73.6	28.2	25.6	73.8	73.7	25.4	25.6	28.4	28.3	25.7	25.6	25.7
30	19.7	65.4	—	19.8	19.7	—	—	65.6	65.4	—	—	—
Glc-1	95.6	95.7	95.7	95.7	95.7	95.6	95.7		95.7		95.8	
2	73.8	73.8	73.8	74.0	73.8	73.6	73.7		74.1		74.1	
3	78.7	78.8	78.7	78.7	78.7	78.4	78.6		78.9		78.9	
4	70.7	70.9	70.8	70.7	70.7	70.5	70.7		71.1		71.2	
5	77.9	77.9	77.9	78.0	78.0	77.8	77.9		79.3		79.3	
6	69.2	69.4	69.3	69.2	69.2	69.1	69.3		62.2		62.3	
Glc-1	104.8	105.1	104.9	104.8	104.8	104.7	105.0					
2	75.3	75.3	75.3	75.4	75.3	75.3	75.2					
3	76.5	76.5	76.5	76.5	76.5	76.3	76.4					
4	78.2	78.4	78.3	78.2	78.3	78.3	78.4					
5	77.1	77.2	77.1	77.2	77.1	77.0	77.2					
6	61.2	61.3	61.3	61.3	61.3	61.1	61.2					
Rha-1	102.7	102.8	102.7	102.7	102.7	102.6	102.7					
2	72.5	72.8	72.7	72.6	72.7	72.4	72.5					
3	72.7	72.7	72.5	72.7	72.7	72.3	72.4					
4	73.9	74.0	74.0	73.8	74.0	73.7	73.9					
5	70.3	70.3	70.3	70.4	70.4	70.5	70.3					
6	18.5	18.5	18.5	18.6	18.6	18.4	18.5					

Multiplicities were established by DEPT experiments.

Assignments were confirmed by the combination of the 2D NMRs (^1H-^1H-COSY, HMBC, HMQC and NOESY) and the corresponding ref.

in H_2O (15 ml) was incubated for 14 days at 37°. The reaction mixt. was passed through an ODS CC eluted with H_2O and MeOH successively. The MeOH eluate (73 mg) was purified over silica gel CC eluted with $CHCl_3$–MeOH–H_2O (30:10:1) to give **2a** (28 mg) and **2b** (16 mg). In the same way, **3** (112 mg) gave **3a** (35 mg) and **3b** (12 mg), and **6** (93 mg) gave **6a** (37 mg) and **6b** (trace).

Spinogenin C2 (**2a**). Powder; $[\alpha]_D^{24}$ +22.1° (*c* 0.31, C_5H_5N); FABMS (positive) *m/z*: 525.2968 $[M+K]^+$, $C_{30}H_{46}O_5K$ requires: 525.2982, 487 $[M+H]^+$, ^1H NMR δ: 0.89 (3H, *s*, H-25), 1.02 (3H, *s*, H-24), 1.08

(3H, *s*, H-26), 1.19 (3H, *s*, H-29), 1.24 (3H, *s*, H-27), 2.47 (1H, *d*, $J = 11.3$ Hz, H-5), 3.43 (1H, *dd*, $J = 12.2$, 6.1 Hz, H-18), 3.89 (1H, *d*, $J = 10.4$ Hz, H-30a), 3.98 (1H, *d*, $J = 10.4$ Hz, H-30b), 4.00 (1H, *s*, H-3), 5.50 (1H, *t-like*, H-12), 9.98 (1H, *s*, H-23); ^{13}C NMR: Table 1.

Spinogenin C2 monoglucosyl ester (**2b**). Powder; $[\alpha]_D^{27}$ −1.0° (*c* 0.80); FABMS (negative) *m/z*: 647 $[M-H]^-$, 485 [M-Glc-H]$^-$; ^{1}H NMR δ: 0.90 (3H, *s*, H-25), 1.07 (3H, *s*, H-24), 1.12 (3H, *s*, H-26), 1.14 (3H, *s*, H-29), 1.19 (3H, *s*, H-27), 3.34 (1H, *dd*, $J = 9.5$, 9.2 Hz, H-18), 3.78 (1H, *d*, $J = 11.0$ Hz, H-30a), 3.81 (1H, *d*, $J = 11.0$ Hz, H-30b), 4.00 (1H, *s*, H-3), 4.01 (1H, *ddd*, $J = 2.5$, 4.3, 9.5 Hz, Glc H-5), 4.17 (1H, *dd*, $J = 8.3$, 8.9 Hz, Glc H-2), 4.25 (1H, *dd*, $J = 9.2$, 8.9 Hz, Glc H-3), 4.34 (1H, *dd*, $J = 9.2$, 9.5 Hz, Glc H-4), 4.38 (1H, *dd*, $J = 4.3$, 12.2 Hz, Glc H-6a), 4.43 (1H, *dd*, $J = 2.5$, 12.0 Hz, Glc H-6b), 5.44 (1H, *t-like*, H-12), 6.30 (1H, *d*, $J = 8.3$ Hz, Glc H-1), 9.95 (1H, *s*, H-23); ^{13}C NMR: Table 1.

Spinogenin C3 (**3a**). Powder; $[\alpha]_D^{26}$ +1.3° (*c* 0.20, C_5H_5N); FABMS (negative) *m/z*: 457 $[M-H]^-$ (positive) *m/z*: 497.3022 $[M+K]^+$, $C_{29}H_{46}O_4K$ requires: 497.3034; ^{1}H NMR δ: 0.87 (3H, *s*, H-24), 0.90 (3H, *s*, H-25), 1.03 (3H, *s*, H-26), 1.13 (3H, *s*, H-27), 1.21 (3H, *s*, H-23), 1.55 (3H, *s*, H-29), 2.39 (1H, *dd*, $J = 13.7$, 14.4 Hz, H-19α), 3.33 (1H, *dd*, $J = 14.4$, 4.6 Hz, H-18), 3.59 (1H, *s*, H-3), 5.54 (1H, *t-like*, H-12); ^{13}C NMR: Table 1.

Spinogenin C3 monoglucosyl ester (**3b**). Powder; $[\alpha]_D^{27}$ +5.8° (*c* 0.84); FABMS (negative) *m/z*: 619 $[M-H]^-$, 457 [M-Glc-H]$^-$; ^{1}H NMR δ: 0.86 (3H, *s*, H-24), 0.92 (3H, *s*, H-25), 1.10 (3H, *s*, H-26), 1.14 (3H, *s*, H-27), 1.19 (3H, *s*, H-23), 1.42 (3H, *s*, H-29), 2.35 (1H, *dd*, $J = 13.8$, 14.1 Hz, H-19α), 3.24 (1H, *dd*, $J = 13.8$, 4.0 Hz, H-18), 3.59 (1H, *s*, H-3), 4.03 (1H, *ddd*, $J = 2.2$, 4.0, 9.2 Hz, Glc H-5), 4.19 (1H, *dd*, $J = 8.9$, 8.0 Hz, Glc H-2), 4.27 (1H, *dd*, $J = 8.9$, 8.9 Hz, Glc H-3), 4.34 (1H, *dd*, $J = 9.2$, 8.9 Hz, Glc H-4), 4.40 (1H, *dd*, $J = 4.0$, 11.9 Hz, Glc H-6a), 4.47 (1H, *dd*, $J = 2.2$, 11.9 Hz, Glc H-6b), 5.50 (1H, *t-like*, H-12), 6.33 (1H, *d*, $J = 8.0$ Hz, Glc H-1); ^{13}C NMR: Table 1.

Spinogenin C6 (**6a**). Powder; $[\alpha]_D^{26}$ +24.6° (*c* 0.71, C_5H_5N); FABMS (negative) *m/z*: 473 $[M-H]^-$ (positive) *m/z*: 513.2959 $[M+K]^+$, $C_{29}H_{46}O_5K$ requires: 513.2982; ^{1}H NMR δ: 0.76 (3H, *s*, H-24), 0.92 (3H, *s*, H-25), 1.04 (3H, *s*, H-26), 1.16 (3H, *s*, H-27), 1.54 (3H, *s*, H-29), 2.38 (1H, *dd*, $J = 14.1$, 14.1 Hz, H-19α), 3.35 (1H, *dd*, $J = 14.1$, 4.0 Hz, H-18), 3.66 (1H, *d*, $J = 11.0$ Hz, H-23a), 3.85 (1H, *d*, $J = 11.0$ Hz, H-23b), 3.91 (1H, *s*, H-3), 5.55 (1H, *t-like*, H-12); ^{13}C NMR: Table 1.

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