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OLEANANE SAPONINS FROM *POLYSCIAS FRUTICOSA*

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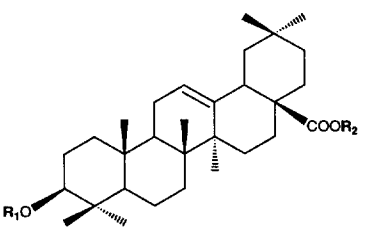
Key Word Index—*Polyscias fruticosa*; Araliaceae; oleanolic acid saponins; polysciosides A–H.

Abstract—From the leaves and roots of *Polyscias fruticosa*, eight new oleanolic acid saponins named polysciosides A to H were isolated together with three known saponins. The structures of the saponins were established by means of spectral data, particularly NMR, which included COSY, HSQC, HMBC, HOHAHA and ROESY techniques. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Polyscias fruticosa (L.) Harms. [syn. *Panax fruticosum* L., *Nothopanax fruticosum* Miq.] (family Araliaceae) is widely cultivated in several countries of south-eastern Asia and the tropical islands of the Pacific region. In Asian countries, the leaves are used as a tonic, anti-inflammatory, antitoxin, antibacterial, and are good for digestion. The root is also used as a diuretic, febrifuge, anti-dysentery, and is employed for neuralgia and rheumatic pains [1]. Alongside with medicinal purposes, *Polyscias fruticosa* is also used as an ornamental plant and a spice. Recent studies on the constituents of the leaves of this plant afforded two known oleanolic acid saponins [2, 3], while the roots afforded polyacetylenes which showed antibacterial and antifungal activities [4–6]. The volatile leaf oils were also studied [7]. The present paper describes the isolation and structural elucidation of eight new saponins named polysciosides together with the identification of three known saponins from leaves and roots of this plant.



	R_1	R_2
1	GlcA(4→)Glc	H
2	GlcA(2→)Glc	H
3	GlcA(2→)[Glc(4→)]	H
4	GlcA(2→)[Glc(4→)]Ara(p)	H
5	GlcA(2→)[Glc(3→)]Gal	H
6	GlcA(4→)Glc	Glc
7	GlcA(2→)[Glc(4→)]Glc	Glc
8	GlcA(2→)[Glc(4→)]Ara(p)	Glc
9	GlcA(2→)[Glc(3→)]Gal	Glc
10	GlcA(4→)Glc	Glc(3→)Rha
11	GlcA(2→)[Glc(4→)]Glc	Glc(3→)Rha

RESULTS AND DISCUSSION

The methanol extracts of the leaves and roots of *P. fruticosa* were worked-up as described in the Experimental to give compounds **1–3**, **6**, **7**, **10** and **11** from the leaves, and **1** and **3–9** from the roots. On acid hydrolysis, these compounds afforded oleanolic acid as a common aglycone.

By comparison of the physical and spectroscopic data with those of the reported data, **1** and **2** were identified as ladyginoside A and zingibroside R1 which were isolated from *Ladyginia bucharica* [8] and *Panax zingiberensis* [9], respectively, and **6** was identified as 3-*O*-[β-D-glucopyranosyl (1-4)-β-D-glucuronopyranosyl] oleanolic acid 28-*O*-β-D glucopyranosyl ester which was isolated from *Swartzia simplex* [10].

Compound **3** had the molecular formula $C_{48}H_{76}O_{19}$ based on high-resolution FAB mass spectrometry. The ^1H and ^{13}C NMR spectra demonstrated that **3** had one β-glucuronopyranosyl and two β-glucopyranosyl moieties. On acid hydrolysis, glucuronic acid and glucose were identified in the hydrolysate. Comparison of the ^{13}C NMR spectra of **3** with its aglycone showed

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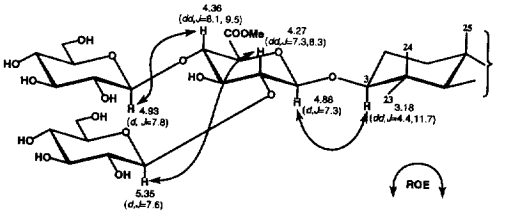

Fig. 1. ROE of the sugar moiety of **3a**.

glycosylation shifts for the signals due to C-2 and C-3, indicating that **3** was a 3-*O*-glycoside of oleanolic acid.

The structure of the trisaccharide moiety was deduced from the ROE experiment of its dimethyl ester (**3a**) which was obtained by methylation of **3** with CH_2N_2. The NOE were observed between (δ 4.93) H-1 of glucose and (δ 4.36) H-4 of glucuronic acid, and (δ 5.35) H-1 of glucose and (δ 4.27) H-2 of glucuronic acid (Fig. 1). Based on this, the trisaccharide moiety was characterized as β-D-glucopyranosyl (1-2)-[β-D-glucopyranosyl (1-4)]-β-D-glucuronopyranose. Thus, the structure of compound **3** was established as shown.

The ^1H and ^{13}C NMR spectra showed that compounds **4**, $C_{47}H_{74}O_{18}$, and **5**, $C_{48}H_{76}O_{19}$, were the 3-*O*-glycosides of oleanolic acid having three monosaccharide units. On acid hydrolysis, both compounds afforded glucuronic acid and glucose as the common sugar components. Furthermore, arabinose and galactose were detected from the hydrolysate of compounds **4** and **5**, respectively. Detailed analyses of the ^1H and ^{13}C NMR spectra of both compounds suggested that all of these sugars were of the pyranose type, and their anomeric configurations were as follows: glucuronic acid, glucose and galactose were β and arabinose was α (Tables 1, 2 and 3). The structures of both sugar moieties were investigated by the ROE experiment, and were deduced as the same as in the case of **3**. Based on these experiments, the structures of compounds **4** and **5** were characterized as shown.

Compounds **7**, $C_{54}H_{86}O_{24}$, **8**, $C_{53}H_{84}O_{23}$, and **9**, $C_{54}H_{86}O_{24}$, were bidesmosides having four monosaccharide units. Alkaline hydrolysis yielded compound **3** from **7**, **4** from **8**, and **5** from **9** as their prosapogenins, together with 1,6-anhydroglucose. These results led to the formulation of the structures of compounds, **7**, **8** and **9** as shown.

Compound **10**, $C_{54}H_{86}O_{23}$, and **11**, $C_{60}H_{96}O_{28}$, were bidesmosides having four and five monosaccharide units, respectively (Tables 1 and 2). Both compounds liberated glucuronic acid, glucose and rhamnose on acid hydrolysis. The FAB mass spectra suggested the presence of each one of terminal rhamnose and glucose units in **10** and a terminal rhamnose and two terminal glucose units in **11**. Alkaline hydrolysis of **10** and **11** afforded **1** and **3** as the prosapogenin, respectively. The ROESY spectra of monomethyl esters **10a** and **11a** showed in both cases a cross-peak between (δ 6.55) H-1 of the rhamnose and (δ 4.30) H-3 of the ester linked glucose at C-28. On the basis of these observations, the structures of **10** and **11** were established as shown.

EXPERIMENTAL

General. OR were measured with a Union PM-101 automatic digital polarimeter. NMR spectra were recorded on JEOL JNM A400 spectrometers in C_5D_5N using TMS as an int. standard. MS were obtained on a JEOL JMS-SX102 spectrometer by the direct inlet method at an ionizing voltage of 70 eV. HPLC was carried out using a D-ODS-5 (20 mm i.d. × 25 cm YMC) column with a TOSOH HLC 803D pump and a TOYO SODA RI-8000 differential refractometer as detector. For CC, Kieselgel 60 (70–230 mesh, Merck), LiChroprep RP-18 (Merck) and Diaion HP-20 (Mitsubishi Chem. Ind. Co, Ltd.) were used. For TLC, silica gel 60 precoated plates F254 (Merck) and RP-18 precoated plates F-254 (Merck) were used. The spots on TLC were visualized by spraying 10% H_2SO_4 followed by heating.

Plant material. The plant was collected in Thu duc District, Ho Chi Minh City, Vietnam. A voucher specimen was deposited in the Herbarium of The Science-Production Union of Ginseng and Medicinal Plants, Ho Chi Minh City, Vietnam.

Extraction and Isolation. Dried leaves of *Polyscias fruticosa* (860 g) were extracted with MeOH, and the MeOH extract was concd to dryness. The residue (147 g) was suspended in H_2O, washed with Et_2O and then extracted with *n*-BuOH. The *n*-BuOH layer was evapd to give a residue (25 g). A part of the *n*-BuOH extract (15 g) was submitted to silica gel column using CH_2Cl_2–MeOH–H_2O (13:7:2 to 13:14:2) as solvents and then by repeated LiChroprep RP-18 CC (MeOH: 50–70%) to give seven saponins **1** (135 mg), **2** (18 mg), **3** (136 mg), **6** (250 mg), **7** (15 mg), **10** (106 mg) and **11** (15 mg).

Dried roots (1850 g) of the same plant were extracted with MeOH. After removal of the solvent, the MeOH extract (230 g) was chromatographed on a column of highly porous polymer (Diaion HP-20) and eluted with H_2O, 50% MeOH, 80% MeOH, MeOH and Me_2CO, successively. The fr. eluted with MeOH (16.29 g) was subjected to chromatography on silica gel using CH_2Cl_2–MeOH–H_2O (30:15:1 to 6:4:1) followed by reversed-phase column chromatography using LiChroprep RP-18 (MeOH: 60%) and purified by HPLC (75–80% MeOH with 0.05% TFA) to give four saponins **1** (18 mg), **3** (64 mg), **4** (83 mg) and **5** (103 mg). The fr. eluted with 80% MeOH (6.89 g) was chromatographed on a silica gel column using CH_2Cl_2–MeOH–H_2O (30:20:1 to 15:10:1) and then purified by HPLC (70–75% MeOH with 0.05% TFA)

Table 1. ^{13}C NMR spectral data of the aglycone moieties of saponins (**1–11**) (100 MHz, pyridine-d_5)

C	1	1a	2	3	3a	4	4a	5	5a	6	7	8	9	10	10a	11a
1	38.7	38.5	38.6	38.5	38.6	38.6	38.7	38.5	38.5	38.7	38.5	39.0	38.6	38.7	38.7	38.7
2	26.2	26.5	26.6	26.4	26.5	26.5	26.5	26.5	26.5	26.5	26.4	26.5	26.5	26.5	26.5	26.4
3	89.3	89.2	89.2	89.4	89.5	89.2	89.4	89.6	89.6	89.3	89.4	89.3	89.6	89.1	89.3	89.5
4	39.5	39.5	39.5	39.5	39.5	39.5	39.5	39.4	39.4	39.5	39.4	39.5	39.6	39.5	39.5	39.4
5	55.9	55.7	55.8	55.7	55.8	55.7	55.9	55.7	55.7	55.8	55.7	55.8	55.7	55.8	55.9	55.9
6	18.5	18.4	18.4	18.4	18.5	18.4	18.5	18.4	18.4	18.5	18.4	18.5	18.5	18.5	18.5	18.5
7	33.3	33.1	33.3	33.2	33.2	33.3	33.2	33.2	33.2	33.1	33.1	33.1	33.1	33.3	33.3	33.3
8	39.8	39.6	39.7	39.6	39.7	39.7	39.7	39.7	39.7	40.0	39.8	39.9	39.6	39.9	40.0	40.0
9	48.0	47.9	48.0	47.9	47.9	48.0	47.9	47.9	47.9	48.1	47.9	48.0	47.8	48.0	48.1	48.1
10	37.0	36.9	36.9	36.8	36.9	36.9	37.0	36.9	36.9	37.0	36.8	36.9	36.9	36.9	37.0	36.9
11	23.8	23.7	23.7	23.7	23.7	23.9	23.7	23.7	23.7	23.8	23.7	23.8	23.6	23.8	23.8	23.8
12	122.6	122.8	122.5	122.5	122.9	122.5	122.5	122.5	122.5	122.9	122.8	122.9	122.9	122.9	122.9	122.6
13	144.9	144.1	144.8	144.8	144.2	144.8	144.2	144.8	144.8	144.2	144.1	144.1	144.1	144.3	144.2	144.3
14	42.2	41.9	42.1	42.1	42.0	42.1	42.0	42.1	42.1	42.2	42.1	42.2	42.1	42.3	42.3	42.3
15	28.3	28.1	28.3	28.2	28.1	28.3	28.1	28.3	28.3	28.3	28.2	28.3	28.2	28.1	28.1	28.2
16	23.8	23.6	23.7	23.6	23.7	23.7	23.7	23.6	23.6	23.7	23.6	23.6	23.6	23.6	23.7	23.7
17	46.7	46.9	46.6	46.6	47.0	46.6	47.0	46.6	46.6	47.0	46.9	47.0	47.0	47.0	47.2	46.9
18	42.1	41.8	42.0	41.9	41.9	42.0	41.9	41.9	41.9	41.8	41.7	41.7	41.7	42.1	42.1	41.7
19	46.6	46.1	46.4	46.4	46.2	46.4	46.2	46.4	46.4	46.3	46.2	46.2	46.2	46.3	46.4	46.2
20	31.0	30.8	30.9	30.9	30.8	30.9	30.8	30.9	30.9	30.8	30.7	30.8	30.7	30.8	30.7	30.7
21	34.3	33.9	34.2	34.2	34.0	34.2	34.0	34.2	34.0	34.1	33.9	34.0	34.0	34.0	34.1	33.9
22	33.3	33.0	33.2	33.1	33.1	33.2	33.1	33.2	33.1	33.1	33.1	33.1	33.1	33.1	33.1	33.1
23	28.3	28.0	28.1	28.0	28.1	28.3	27.9	28.0	28.1	28.2	28.0	27.9	28.0	28.1	28.7	28.0
24	17.0	16.9	16.7	16.6	16.7	16.4	16.5	16.7	16.7	17.0	16.6	16.4	16.7	16.9	16.9	16.6
25	15.5	15.4	15.4	15.3	15.4	15.4	15.5	15.4	15.5	15.5	15.4	15.5	15.5	15.5	15.5	15.4
26	17.5	17.1	17.4	17.3	17.2	17.5	17.2	17.3	17.2	17.5	17.4	17.5	17.4	17.4	17.4	17.4
27	26.2	26.1	26.2	26.1	26.1	26.2	26.2	26.2	26.2	26.1	26.0	26.1	26.1	26.1	25.9	26.0
28	180.3	178.0	180.1	180.1	178.0	180.1	178.0	180.1	178.0	176.4	176.4	176.4	176.4	176.4	176.3	176.4
29	33.3	32.8	33.3	33.2	32.8	33.3	32.8	33.2	32.8	32.6	32.5	32.5	32.5	33.1	33.1	32.5
30	23.8	23.4	23.7	23.7	23.5	23.7	23.5	23.6	23.5	23.5	23.4	23.4	23.4	23.4	23.4	23.4
OMe		51.5			51.6		51.6		51.6							

Table 2. ^{13}C NMR spectral data of the sugar moieties of saponins (**1**–**11**) (100 MHz, pyridine-d_5)

C	1	1a	2	3	3a	4	4a	5	5a	6	7	8	9	10	10a	11a
3-*O*-GlcA 1	106.6	106.9	106.0	104.6	104.9	104.6	104.8	105.3	105.3	106.8	104.6	104.6	105.3	106.8	106.8	105.1
2	74.9	74.8	82.9	80.9	80.9	82.0	81.8	79.4	79.2	74.9	80.9	82.0	79.4	74.9	74.9	81.0
3	76.7	76.1	77.1	75.9	75.8	75.8	75.6	87.5	87.5	76.4	76.0	75.6	87.7	76.4	75.1	75.8
4	82.7	82.6	73.2	81.9	81.9	81.8	81.7	71.5	71.6	82.5	81.9	81.8	71.5	82.6	82.5	81.9
5	74.9	75.1	77.4	74.8	74.8	74.8	74.8	76.6	76.3	75.8	74.8	74.8	76.6	75.9	75.5	74.8
6	171.6	170.0	172.5	172.1	169.6	172.1	169.7	172.0	170.0	172.3	172.1	172.1	171.9	172.5	170.0	169.6
OMe		52.4			52.5		52.5		52.1						52.4	52.5
Glc or Gal 1			105.4	105.2	105.3			104.6	104.6		105.2		104.6			105.4
2			77.7	76.9	76.9			73.7	73.7		76.9		73.7			74.9
3			77.9	77.8	77.9			75.3	75.4		77.8		75.3			77.9
4			71.7	71.7	71.9			69.7	69.9		71.7		69.8			71.9
5			78.3	78.2	78.2			77.0	76.6		78.2		77.2			78.2
6			62.7	62.7	62.9			61.6	61.7		62.7		61.7			62.9
Glc 1	104.6	105.1		105.0	105.1	105.0	105.0	104.7	104.7	104.7	105.0	105.0	104.7	104.8	105.0	104.9
2	73.6	74.4		75.5	74.5	75.5	74.4	75.4	75.4	74.9	75.5	75.4	75.4	74.9	74.5	74.5
3	77.7	78.2		78.0	78.1	78.0	78.2	78.5	78.6	78.1	78.0	78.0	78.6	78.0	78.2	78.2
4	71.5	71.6		71.5	71.6	71.5	71.6	71.9	71.7	71.7	71.4	71.5	71.9	71.6	71.7	71.6
5	78.4	78.5		78.3	78.4	78.4	78.4	78.5	78.6	78.5	78.3	78.4	78.5	78.5	78.4	78.4
6	62.5	62.5		62.3	62.4	62.4	62.4	62.2	62.4	62.7	62.3	62.4	62.3	62.6	62.6	62.4
Ara(p) 1						106.3	106.2					106.3				
2						73.8	73.8					73.8				
3						74.1	74.1					74.2				
4						69.1	69.2					69.1				
5						67.0	67.0					67.0				
28-*O*-Glc 1										95.8	95.7	95.8	95.7	94.9	94.9	94.9
2										74.1	74.1	74.1	74.1	75.5	76.1	75.8
3										79.2	79.2	79.3	79.2	79.9	79.7	79.8
4										71.3	71.1	71.1	71.1	71.3	71.5	71.5
5										78.9	78.8	78.9	78.9	79.0	78.9	78.9
6										62.4	62.2	62.2	62.1	62.0	62.2	62.2
Rha 1														101.4	101.4	101.4
2														72.3	72.3	72.3
3														72.6	72.6	72.6
4														73.9	73.9	73.9
5														69.7	69.7	69.8
6														18.7	18.7	18.7

Table 3. ^{1}H NMR spectra data of the sugar moieties of **1a**, **3a**, **4a**, **5a**, **10a** and **11a** (400 MHz, pyridine-d_5)

H	**1a**	**3a**	**4a**	**5a**	**10a**	**11a**
3-*O*-GlcA 1	4.95 *d* (7.8)	4.88 *d* (7.3)	4.95 *d* (7.8)	4.90 *d* (7.5)	4.93 *d* (6.9)	4.87 *d* (6.9)
2	4.07 *dd* (7.8, 8.7)	4.27 *dd* (7.3, 8.3)	4.19 *dd* (7.8, 8.5)	4.38 *dd* (7.5, 8.7)	4.05 *dd* (6.9, 7.8)	4.28 *dd* (6.9, 7.8)
3	4.25 *dd* (8.7, 8.7)	4.28 *dd* (8.3, 8.1)	4.24 *dd* (8.5, 8.5)	4.26 *dd* (8.7, 8.5)	4.24 *dd* (7.8, 8.7)	4.29 *dd* (7.8, 9.0)
4	4.44 *dd* (8.7, 9.7)	4.36 *dd* (8.1, 9.5)	4.41 *dd* (8.5, 9.3)	4.31 *dd* (8.5, 9.5)	4.43 *dd* (8.7, 9.8)	4.38 *dd* (9.0, 9.6)
5	4.62 *d* (9.7)	4.49 *d* (9.5)	4.48 *d* (9.3)	4.37 *d* (9.5)	4.60 *d* (9.8)	4.49 *d* (9.6)
OMe	3.85 *s*	3.85 *s*	3.84 *s*	3.70 *s*	3.85 *s*	3.85 *s*
Glc or Gal 1		5.35 *d* (7.6)		5.52 *d* (7.6)		5.34 *d* (7.6)
2		4.00 *dd* (7.6, 9.0)		4.45 *dd* (7.6, 9.6)		4.01 *dd* (7.6, 8.5)
3		4.18 *dd* (9.0, 8.8)		4.14 *dd* (9.6, 3.5)		4.18 *dd* (8.5, 9.0)
4		4.23 *dd* (8.8, 9.3)		4.56 *dd* (3.5, 1.1)		4.24 *dd* (9.0, 9.8)
5		3.86 *ddd* (9.3, 3.2, 4.4)		3.93 *dd* (1.1, 5.5, 7.0)		3.86 *ddd* (9.8, 5.6, 5.0)
6		4.45 *dd* (3.2, 11.5)		4.46 *dd* (7.0, 10.7)		4.44 *dd* (5.0, 10.4)
		4.38 *dd* (4.4, 11.5)		4.36 *dd* (5.5, 10.7)		4.41 *dd* (5.6, 10.4)
Glc 1	5.01 *d* (8.0)	4.93 *d* (7.8)	4.92 *d* (7.6)	5.28 *d* (7.8)	5.00 *d* (8.0)	4.94 *d* (7.8)
2	3.95 *dd* (8.0, 8.5)	3.91 *dd* (7.8, 9.0)	3.90 *dd* (7.6, 8.5)	4.00 *dd* (7.8, 8.7)	3.95 *dd* (8.0, 8.5)	3.91 *dd* (7.8, 8.9)
3	4.13 *dd* (8.5, 8.7)	4.09 *dd* (9.0, 7.8)	4.12 *dd* (8.5, 7.6)	4.14 *dd* (8.7, 8.7)	4.10 *dd* (8.5, 8.1)	4.12 *dd* (8.9, 8.7)
4	4.11 *dd* (8.7, 8.5)	4.10 *m*	4.10 *dd* (7.6, 8.8)	4.09 *dd* (8.7, 9.3)	4.07 *dd* (8.1, 8.5)	4.10 *dd* (8.7, 8.6)
5	3.95 *ddd* (8.5, 2.2, 5.6)	3.91 *m*	3.90 *m*	3.95 *ddd* (6.2, 2.2, 9.3)	3.95 *ddd* (8.5, 2.2, 5.3)	3.93 *dd* (8.6, 2.8, 5.7)
6	4.50 *dd* (2.2, 11.4)	4.46 *dd* (2.7, 11.4)	4.43 *dd* (2.0, 11.9)	4.47 *dd* (2.2, 11.4)	4.47 *dd* (2.2, 11.4)	4.43 *dd* (2.8, 10.7)
	4.21 *dd* (5.6, 11.4)	4.22 *dd* (5.6, 11.4)	4.21 *dd* (4.2, 11.9)	4.20 *dd* (6.2, 11.4)	4.22 *dd* (5.3, 11.4)	4.22 *dd* (5.7, 10.7)
Ara(p) 1			5.14 *d* (6.6)			
2			4.44 *dd* (6.6, 8.8)			
3			4.12 *dd* (8.8, 3.9)			
4			4.25 *ddd* (3.9, 3.2, 1.7)			
5			4.33 *dd* (3.2, 12.2)			
			3.72 *dd* (1.7, 12.2)			
28-*O*-Glc 1					6.17 *d* (8.1)	6.17 *d* (7.8)
2					4.45 *dd* (8.1, 9.0)	4.46 *m*
3					4.29 *dd* (9.0, 8.3)	4.30 *m*
4					4.26 *dd* (8.3, 8.7)	4.26 *m*
5					3.96 *ddd* (8.7, 3.2, 5.6)	3.95 *ddd* (5.0, 2.9, 9.2)
6					4.49 *dd* (3.2, 11.5)	4.45 *dd* (5.0, 11.4)
					4.30 *dd* (5.6, 11.5)	4.28 *dd* (2.9, 11.4)
Rha 1					6.55 *s*	6.55 *s*
2					4.76 *dd* (1.5, 3.4)	4.76 overlapped
3					4.52 *dd* (3.4, 9.0)	4.51 *dd* (3.8, 8.1)
4					4.29 *m*	4.29 *m*
5					4.52 *m*	4.52 *m*
6					1.75 *d* (6.3)	1.74 *d* (6.1)

to give four saponins **6** (20 mg), **7** (16 mg), **8** (11 mg) and **9** (29 mg).

Polyscioside A (**3**). White powder, $[\alpha]_D^{18}+1.36°$ (MeOH; *c* 1.47). HRFABMS (negative) *m/z*: 955.4878 $[C_{48}H_{76}O_{19}-H]^-$, requires 955.4903. FABMS (negative) *m/z*: 955 $[M-H]^-$, 793 $[M-Glc-H]^-$, 455 $[M-GlcA-2Glc-H]^-$. ^1H NMR: δ 4.95 (1H, *d*, *J* = 7.3 Hz, GlcA H-1), 5.13 (1H, *d*, *J* = 7.8 Hz, Glc H-1), 5.37 (1H, *d*, *J* = 7.8 Hz, Glc H-1), ^{13}C NMR: see Tables 1 and 2.

Polyscioside B (**4**). White powder, $[\alpha]_D^{27}+9.48°$ (MeOH; *c* 0.63) HRFABMS (negative) *m/z*: 925.4705 $[C_{47}H_{74}O_{18}-H]^-$, requires 925.4735. FABMS (negative) *m/z*: 925 $[M-H]^-$, 793 $[M-Ara-H]^-$, 763 $[M-Glc-H]^-$. 455 $[M-GlcA-Glc-Ara-H]^-$. ^1H NMR: δ 4.97 (1 H, *d*, *J* = 7.6 Hz, GlcA H-1), 5.18 (1H, *d*, *J* = 7.1 Hz, Glc H-1), 5.44 (1H, *s*, Ara H-1), ^{13}C NMR: see Tables 1 and 2.

Polyscioside C (**5**). White powder, $[\alpha]_D^{27}+18.57°$ (MeOH; *c* 1.40) HRFABMS (negative) *m/z*: 955.4890 $[C_{48}H_{76}O_{19}-H]^-$, requires 955.4902. FABMS (negative) *m/z*: 955 $[M-H]^-$, 793 $[M-Hexose-H]^-$, 455 $[M-GlcA-Glc-Gal-H]^-$. ^1H NMR: δ 4.94 (1H, *d*, *J* = 7.1 Hz, GlcA H-1), 5.35 (1H, *d*, *J* = 7.3 Hz, Glc H-1), 5.54 (1H, *d*, *J* = 7.6 Hz, Gal H-1), ^{13}C NMR: see Tables 1 and 2.

Polyscioside D (**7**). White powder, $[\alpha]_D^{25}-3.85°$ (MeOH; *c* 1.56) HRFABMS (negative) *m/z*: 1117.5450 $[C_{54}H_{86}O_{24}-H]^-$, requires 1117.5437. FABMS (negative) *m/z*: 1117 $[M-H]^-$, 955 $[M-Glc-H]^-$, 793 $[M-2Glc-H]^-$, 455 $[M-GlcA-3Glc-H]^-$. ^1H NMR: δ 4.70 (1H, *d*, *J* = 6.8 Hz, GlcA H-1), 4.93 (1H, *d*, *J* = 7.8 Hz, Glc H-1), 5.18 (1H, *d*, *J* = 7.3 Hz, Glc H-1), 6.09 (1H, *d*, *J* = 8.4 Hz, Glc H-1), ^{13}C NMR: see Tables 1 and 2.

Polyscioside E (**8**). White powder, $[\alpha]_D^{21}+3.13°$ (MeOH; *c* 0.32) HRFABMS (negative) *m/z*: 1087.5310 $[C_{53}H_{84}O_{23}-H]^-$, requires 1087.5323. FABMS (negative) *m/z*: 1087 $[M-H]^-$, 955 $[M-Ara-H]^-$, 925 $[M-Glc-H]^-$, 763 $[M-2Glc-H]^-$, 455 $[M-GlcA-2Glc-Ara-H]^-$. ^1H NMR: δ 4.94 (1H, *d*, *J* = 7.1 Hz, GlcA H-1), 5.18 (1H, *d*, *J* = 6.4 Hz, Glc H-1), 5.40 (1H, *s*, Ara H-1), 6.32 (1H, *d*, *J* = 8.0 Hz, Glc H-1), ^{13}C NMR: see Tables 1 and 2.

Polyscioside F (**9**). White powder, $[\alpha]_D^{27}-18.76°$ (MeOH; *c* 0.69) HRFABMS (negative) *m/z*: 1117.5430 $[C_{54}H_{86}O_{24}-H]^-$, requires 1117.5400. FABMS (negative) *m/z*: 1117 $[M-H]^-$, 955 $[M-Hexose-H]^-$, 793 $[M-2Hexose-H]^-$, 455 $[M-GlcA-3Hexose-H]^-$. ^1H NMR: δ 4.92 (1H, *d*, *J* = 7.6 Hz, GlcA H-1), 5.33 (1H, *d*, *J* = 7.8 Hz, Glc H-1), 5.53 (1H, *d*, *J* = 7.8 Hz, Gal H-1), 6.28 (1H, *d*, *J* = 8.1 Hz, Glc H-1), ^{13}C NMR: see Tables 1 and 2.

Polyscioside G (**10**). White powder, $[\alpha]_D^{26}-12.12°$ (MeOH; *c* 0.33) HRFABMS (negative) *m/z*: 1101.5470 $[C_{54}H_{86}O_{23}-H]^-$, requires 1101.5484. FABMS (negative) *m/z*: 1101 $[M-H]^-$, 939 $[M-Glc-H]^-$, 793 $[M-Glc-Rha-H]^-$, 631 $[M-2Glc-Rha-H]^-$, 455 $[M-GlcA-2Glc-Rha-H]^-$. ^1H NMR: δ 5.00 (1H, *d*, *J* = 7.6 Hz, GlcA H-1), 5.23 (1H, *d*, *J* = 7.8 Hz, Glc H-1), 6.19 (1H, *d*, *J* = 8.0 Hz, Glc H-1), 6.66 (1H, *s*, Rha H-1), ^{13}C NMR: see Tables 1 and 2.

Polyscioside H (**11**). White powder, $[\alpha]_D^{18}+24.00°$ (MeOH; *c* 1.00), HRFABMS (negative) *m/z*: 1263.6496 $[C_{60}H_{96}O_{28}-H]^-$, requires 1263.6553. FABMS (negative) *m/z*: 1263 $[M-H]^-$, 1101 $[M-Glc-H]^-$, 955 $[M-Glc-Rha-H]^-$, 793 $[M-2Glc-Rha-H]^-$, 455 $[M-GlcA-3Glc-Rha-H]^-$.

Alkaline hydrolysis. Compounds **6–9** (a few mg) were hydrolysed by heating with 1 M NaOH aq. (2 ml) in a sealed tube at 70° for 2 hr. The reaction mixt. was neutralized with Amberlite MB-3 resin and then partitioned between H_2O and *n*-BuOH. The *n*-BuOH layer was concd to dryness. The prosapogenins and 1,6-anhydroglucose were identified by TLC analysis with authentic samples. By the same procedure, **10** and **11** were worked-up as described above for identification of the prosapogenins.

Acid hydrolysis. The compounds (a few mg) were heated with aq. 10% HCl (2 ml) in a sealed tube at 80° for 4 hr. The sapogenin was extracted with Et_2O and identified as oleanolic acid (Co-TLC). The aq. layer was neutralized with Amberlite MB-3 resin and dried. Sugars were identified by comparison with authentic ones on TLC using CH_2Cl_2–MeOH–H_2O (10:6:1) as solvent system.

Methylation. A soln of **1** (78 mg) in MeOH was treated with excess ethereal CH_2N_2 and the product was purified by HPLC using 95% MeOH to give a methyl ester **1a** (33 mg). By the same procedure, **3** (73 mg), **4** (65 mg), **5** (50 mg), **10** (15 mg) and **11** (15 mg), gave **3a** (28 mg), **4a** (26 mg), **5a** (19 mg), **10a** (7 mg) amd **11a** (9 mg), respectively.

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