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SAPONINS FROM *FAGONIA ARABICA*

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Key Word Index—*Fagonia arabica*; Zygophyllaceae; triterpene saponins.

Abstract – Seven new triterpenoid saponins were isolated and identified from the aerial parts of *Fagonia arabica*. They were characterized as 3-*O*-*β*-D-xylopyranosyl(1 → 2)-[*β*-D-glucopyranosyl(1 → 3)]-α-L-arabinopyranosyl oleanolic acid 28-*O*-*β*-D-glucopyranoside, 3-*O*-*β*-D-glucopyranosyl(1 → 2)-[*β*-D-glucopyranosyl(1 → 3)]-α-L-arabino pyranosyl oleanolic acid 28-*O*-*β*-D-glucopyranoside, 3-*O*-*β*-D-xylopyranosyl(1 → 2)-[*β*-D-glucopyranosyl (1 → 3)]-α-L-arabinopyranosyl oleanolic acid, 3-*O*-*β*-D-glucopyranosyl(1 → 2)-[*β*-D-glucopyranosyl(1 → 3)]-α-L-arabino pyranosyl oleanolic acid, 3-*O*-*β*-D-xylopyranosyl(1 → 2)-[*β*-D-glucopyranosyl (1 → 3)]-α-L-arabinopyranosyl 27-hydroxyoleanolic acid, 28-*O*-*β*-D-glucopyranoside, 3-*O*-*β*-D-xylopyranosyl(1 → 2)-[*β*-D-glucopyranosyl(1 → 3)]-α-L-arabinopyranosyl ursolic acid 28-*O*-*β*-D-glucopyranoside and 3-*O*-*β*-D-xylopyranosyl (1 → 2)-[*β*-D-glucopyranosyl (1 → 3)-α-L-arabinopyranosyl 27-hydroxyursolic acid 28-*O*-*β*-D-glucopyranoside. The structures of the saponins were established by analyses of their ^{1}H and ^{13}C NMR spectra with the aid of 2D experiments. The two genins, 27-hydroxyoleanolic acid and 27-ursolic acid, are new.

INTRODUCTION

As a part of our continuing studies on saponins from the genus *Fagonia* [1], we report on the structural elucidation of seven new saponins from the aerial parts of *F. arabica* grown in Egypt and used in traditional medicine.

RESULTS AND DISCUSSION

The crude saponin fraction was subjected to vacuum liquid chromatography (VLC) over TLC silica gel followed by HPLC, affording seven new saponins **1**–**7**. spectral analyses indicated that **3** and **4** were monodesmosides of 3-*O*-glycosides and **1**, **2** and **5**–**7** were bisdesmosides of 3,28-di-*O*-glycosides [2].

The major saponin **1** afforded, by mineral aid hydrolysis, the sugar components D-glucose, L-arabinose and D-xylose, identified by chromatographic analysis of their alditol acetate derivatives, in a molar ratio of 2:1:1. Its structure was determined by ^{1}H and ^{13}C NMR using H–H (COSY) and C–H (HSQC) and HMBC for long range C–H connectivities. The ^{13}C NMR data (Table 1) indicated that the genin portion was oleanolic acid substituted at positions C-3 and C-28 by sugar moieties [3]. The ^{1}H NMR spectrum displayed four anomeric proton signals at δ4.75, 5.26, 5.37 and 6.3. Their attached carbons were located at δ105.6, 105.1, 105.1 and 95.8, respectively. Spin decoupling and H–H COSY experiments allowed evaluation of the δ values, and spin–spin couplings of the remaining signals showed the presence of two *β*-glucopyranosyl, one *β*-xylopyranosyl and one α-arabinopyranosyl moieties. The lowfield shift of one of the glucose anomeric signals suggested the esterifying unit of C-28 aglycone. The assignment of the corresponding carbon shifts (Table 2) was followed from HSQC and HMBC spectra. The latter long range C–H correlation afforded the sequence of the sugar molecules and the position of attachment of the sugar chains to the aglycone from inter-moiety correlation over three bonds. Cross peaks observed between protons and carbons in adjacent systems were H-1 (Xyl) → C-2 (Ara), H-1 (ether Glc) → C-3 (Ara). These observations, confirmed by reverse correlations between a ring proton and C-1 of the next sugar moiety [H-2(Ara) → C-1 (Xyl), H-3 (Ara) → C-1 (ether Glc)], allowed linking of xylose and glucose moieties at positions C-2 and C-3 of the arabinose moiety. The cross peaks H-1 (Ara) → C-3 and H-1 (ester Glc) → C-28 indicated the points of attachment to the aglycone portion. Determination of the sequence of sugar residues and their linkage positions were further verified by NOE studies. Inter-residue NOEs between H-1 (Xyl) and H-2 (Ara), H-1 (ether Glc) and H-3 (Ara), H-1 (Ara) and H-3 aglycone, were observed. Intra-residue NOEs between each anomeric proton and H-3 (and H-5α) in pentoses,

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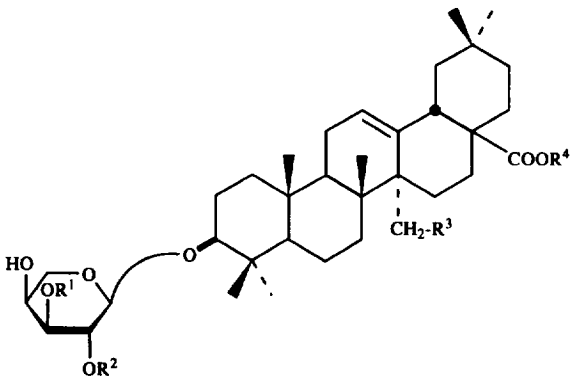
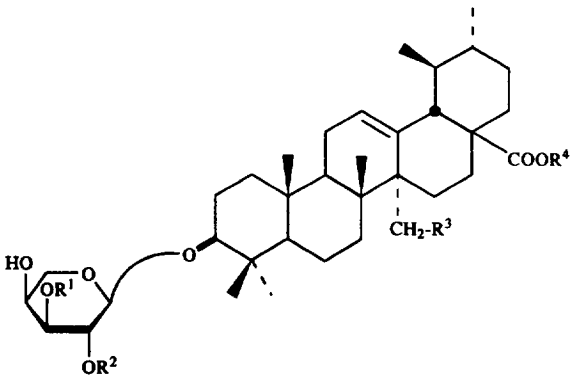


	R_1	R_2	R_3	R_4
1	Glc	Xyl	H	Glc
2	Glc	Glc	H	Glc
3	Glc	Xyl	H	H
4	Glc	Glc	H	H
5	Glc	Xyl	OH	Glc



	R_1	R_2	R_3	R_4
6	Glc	Xyl	H	Glc
7	Glc	Xyl	OH	Glc

and H-3 (and H-5) in hexoses, established another proof to the configuration of the sugar protons. The FAB mass spectrum of **1** was in agreement with the above conclusions and showed the molecular ion at *m/z* 1067 [$C_{52}H_{84}O_{21}$ + Na] along with a fragment ion at *m/z* 905 corresponding to [M^+ − hexose]. Thus, saponin **1** was assigned the structure of 3-*O*-*β*-D-xylopyranosyl(1 → 2)-[*β*-D-glucopyranosyl(1 → 3)]-α-L-arabinopyranosyl oleanolic 28-*O*-*β*-D-glucopyranoside.

Saponin **6** showed ^1H and ^{13}C NMR signals (Experimental and Tables 1 and 2) that closely resembled those of **1**, except the signals attributable to the aglycone moiety. The latter was identified as ursolic acid by considering the main differences from the aglycone of **1**, in the signal position of H-12, H-13, H-18 and ring E carbons [4]. The FAB mass spectrum exhibited [$M]^+$ at *m/z* 1067 [$C_{52}H_{84}O_{21}$ + Na] along with a fragment ion at *m/z* 905 due to the loss of a hexose unit. The structure of **6** was thus concluded to be 3-*O*-*β*-D-xylopyranosyl(1 → 2)-[*β*-D-glucopyranosyl(1 → 3)-α-L-arabinopyranosyl ursolic acid 28-*O*-*β*-D-glucopyranoside.

The ^1H NMR spectrum and H–H COSY experiment on saponin **2** allowed identification of one α-arabinopyranosyl and three *β*-glucopyranosyl moieties exhibiting anomeric proton signals at *δ* 4.78 (*d*, *J* = 7.1 Hz), 5.28 (*d*, *J* = 7.8 Hz), 5.5 (*d*, *J* = 7.8 Hz) and 6.3 (*d*, *J* = 8.0 Hz). The ^{13}C NMR spectrum (Tables 1 and 2) indicated that **2** was bisdesmoside of 3,28-di-*O*-glycoside of oleanolic acid esterified at C-28 by D-glucose unit. It also showed, by comparison with that of **1**, signals due to the 3-*O*-sugar moieties, consistent with 2,3-disubstituted α-arabinopyranosyl and two terminal *β*-glycopyranosyl units. Although the two terminal glucose units need not be determined for their sequencing, the resonances of the unit linked to the C-3 position of the inner arabinose were taken as those closest to the values for the corresponding ones in saponin **1**. The FAB mass spectrum displayed [$M]^+$ at *m/z* 1097 [$C_{53}H_{86}O_{22}$ + Na] along with a fragment ion at *m/z* 935 [M^+-hexose], thus confirming that replacement of xylose in **1** by glucose to form **2**. Therefore, saponin **2** was considered to be 3-*O*-*β*-D-glucopyranosyl(1 → 2)-[*β*-D-glucopyranosyl(1 → 3)]-α-L-arabinopyranosyl oleanolic acid 28-*O*-*β*-D-glucopyranoside.

The FAB mass spectrum of saponin **3** exhibited [$M]^+$ at *m/z* 905 [$C_{46}H_{74}O_{16}$ + Na], less than that of **1** by one hexose unit. In the ^{13}C NMR spectrum (Table 2), the anomeric signals, due to sugar moieties, indicated the presence of three monosaccharide units [anomeric protons at *δ*4.75 (*d*, *J* = 7.1 Hz); 5.26 (*d*, *J* = 7.8 Hz); 5.37 (*d*, *J* = 7.6 Hz)] and all sugar carbon signals were almost identical to those of the 3-*O*-sugar moieties of **1**. The signals due to the aglycone moiety (Table 1) were in agreement with those of oleanolic acid glycosylated at the C-3 position [3]. Alkaline hydrolysis of **1** afforded glucose and a prosapogenin identical with **3**. These results led to the conclusion that **3** must be the 28-*O*-deglucosylated derivative of **1**. Its structure was then formulated as 3-*O*-*β*-D-xylopyranosyl(1 → 2)-[*β*-D glucopyranosyl (1 → 3)]-α-L-arabinopyranosyl oleanolic acid.

The FAB mass spectrum of **4** displayed [$M]^+$ at *m/z* 935 [$C_{47}H_{76}O_{17}$ + Na]; less than that of **2** by one hexose unit. In the ^{13}C NMR spectrum the signals due to the aglycone (Table 1) were in good agreement with the corresponding data for **3**, whereas the sugar signals (Table 2) showed similar chemical shifts to those of 3-*O*-sugar moieties of **2**. Thus, compound **4** must be the 28-*O*-deglucosylated derivative of **2** and was concluded to be 3-*O*-*β*-D-glucopyranosyl(1 → 2) [*β*-D-glucopyranosyl(1 → 3)]-α-L-arabinopyranosyl oleanolic acid.

The ^1H and ^{13}C NMR spectra (Tables 1 and 2) indicated that saponin **5** was a tetrasaccharide of an oleanane-type triterpene acid and showed signals due to sugar moieties almost superimposable on those of saponins **1** and **6**. The ^1H NMR spectrum demonstrated that the signal, due to H-12, appeared at *δ*5.8 and was located at lower field by 0.37 ppm relative to the

Table 1. ^{13}C NMR chemical shifts of aglycone moieties of saponin 1–7 in pyridine-d_5 (ppm)

C	1	2	3	4	5	6	7
1	39.0	38.9	38.9	38.8	38.8	39.1*	39.1*
2	26.8	26.6	26.8	26.7	26.7	26.8	26.8
3	89.3	89.0	89.3	89.0	89.1	89.3	89.1
4	39.9	39.7	39.9	39.8	39.8	39.2*	39.2*
5	56.1	56.0	56.1	56.0	55.9	56.1	56.0
6	18.6	18.6	18.6	18.5	18.6	18.6	18.7
7	33.2	33.2	33.4	33.2	33.7	33.6	34.5
8	40.0	40.0	39.9	39.8	40.7	40.2	41.1
9	48.2	48.1	48.2	48.1	48.7	48.1	48.1
10	37.1	37.1	37.1	37.1	37.2	37.0	37.2
11	23.9	23.9*	23.9*	23.9*	23.6*	23.7	23.2
12	123.0	123.0	122.5	122.5	128.0	126.2	130.2
13	144.2	144.1	145.0	145.0	139.2	138.5	n.d.
14	42.2	42.2	42.2	42.1	45.4	42.6	48.6
15	28.3	28.3	28.4	28.4	24.4	28.7	25.2
16	23.5	23.5*	23.8*	23.8*	23.6*	24.7	24.1
17	47.1	47.1	46.7	46.7	48.0	48.4	48.4
18	41.8	41.8	42.2	42.2	41.6	53.4	53.4
19	46.3	46.3	46.7	46.6	46.9	39.4*	39.3*
20	30.8	30.8	31.0	31.0	30.8	39.8*	39.8*
21	34.1	34.1	34.4	34.3	33.9	30.9	30.6
22	32.6	32.6	33.3	33.3	32.6	36.8	36.9
23	27.9	28.1	27.9	28.1	27.8	28.0	27.8
24	15.7	15.6	15.6	15.5	16.1	15.8	16.2
25	16.6	16.8	16.6	16.8	16.5	16.6	16.6
26	17.6	17.5	17.5	17.5	18.9	17.4	18.9
27	26.2	26.1	26.2	26.2	64.5	23.8	64.2
28	176.5	176.4	n.d.	n.d.	176.5	176.2	176.4
29	33.2	33.2	33.4	33.3	33.1	17.7	18.0
30	23.7	23.7*	23.9*	23.8*	23.8*	21.3	21.2

*Signals may be interchangeable in any column.
n.d., not detected signals.

corresponding value for **1**. The ^{13}C NMR spectrum (Table 1), in comparison with that of **1**, showed that the missing signal due to C-27 of the aglycone was replaced by signal at δ 64.5 assigned to a hydroxymethylene group. Furthermore, significant modifications of the chemical shift values of some ring C and D carbons were observed and allowed placement of the CH_2OH group at C-14, thus suggesting the structure of 27-hydroxyoleanolic acid for the aglycone. The C-12 (δ-position) and C-14 (β-position), which appeared at δ128.0 and 45.4, were deshielded by 5.0 and 3.2 ppm, respectively. The C-13 and C-15 (γ-position) appeared at δ139.2 and 24.4 and were shielded by 5.0 and 3.9 ppm, respectively. The FAB mass spectrum was consistent with the above conclusion and exhibited $[M]^+$ at *m/z* 1083 $[C_{53}H_{86}O_{21} + Na]$; 16 mass units more than that of **1** along with a fragment ion at *m/z* 921 $[M^+ -$ hexose]. Thus, the structure of compound **5** was proposed as 3-*O*-β-D-xylopyranosyl(1 → 2) [β-D-glucopyranosyl(1 → 3)]-α-L-arabinopyranosyl 27-hydroxy oleanolic acid 28-*O*-β-D-glucopyranoside.

Saponin **7** was shown to be a tetrasaccharide of an ursane-type triterpene by spectral analyses. In the ^{13}C NMR spectrum (Table 2), the signals due to the sugar moieties were in agreement with those of **1**, **5** and **6**. The signals due to the aglycone (Table 1) suggested the structure of 27-hydroxyursolic acid based on evidence similar to that established for the structure of 27-hydroxyoleanolic acid in **5**. The difference in δ values of some signals relative to the corresponding values for **6** and arising from introducing CH_2OH (δ 64.2) at C-14 were + 0.3 ppm (H-12), + 4.0 ppm (C-12), + 6.0 ppm (C-14) and − 3.5 ppm (C-15). The unlocated signal of C-13 was possibly hidden under the solvent signals because of its expected upfield position. The FAB mass spectrum displayed $[M]^+$ at *m/z* 1083 $[C_{53}H_{86}O_{21} + Na]$ along with a fragment ion at *m/z* 921 $[M^+ -$ hexose]. Thus, compound **7** must be the ursolic analogue of **5** and was concluded to be 3-*O*-β-D-xylopyranosyl(1 → 2)-[β-D-glucopyranosyl(1 → 3)]-α-L-arabinopyranosyl 27-hydroxyursolic aid 28-*O*-β-D-glucopyranoside.

To the best of our knowledge, the two genins 27-hydroxyoleanolic acid and 27-hydroxyursolic acid are new. Structurally related saponins, with α-L-arabino pyranosyl as the inner glycosyl unit at C-3 of oleanolic acid or hederagenin and β-D-glucopyranosyl as the ester glucosyl unit at C-28, were previously isolated from *F. cretica* [1].

Table 2. ^{13}C NMR chemical shifts of sugar moieties of saponins 1–7 in pyridine-d_5 (ppm)

C	1	2	3	4	5	6	7
3-*O*-Arabinose inner							
1	105.6	105.4	105.7	105.5	105.6	105.6	105.6
2	77.5	77.5	77.5	77.5	77.5	77.5	77.5
3	83.7	83.3	83.7	83.3	83.7	83.7	83.7
4	68.9	68.8	68.9	68.8	68.9	68.9	68.9
5	66.1	65.9	66.1	65.9	66.1	66.1	66.1
3-*O*-Xylose							
1	105.1		105.1		105.1	105.1	105.1
2	76.0		76.0		76.0	76.0	76.0
3	78.5		78.5		78.5	78.5	78.5
4	71.6		71.6		71.6	71.6	71.6
5	67.1		67.2		67.1	67.1	67.1
3-*O*-Glucose							
1	105.1	105.0	105.1	105.0	105.1	105.1	105.2
2	75.3	75.3	75.3	75.3	75.3	75.3	75.3
3	78.9	78.7*	79.0	78.7*	79.0*	78.9*	78.9*
4	71.3	71.6	71.4	71.6	71.3	71.3	71.4
5	78.4	78.4	78.4	78.4	78.4	78.3	78.4
6	62.6	62.6	62.6	62.7	62.6	62.6	62.6
3-*O*-Glucose							
1		104.4		104.4			
2		76.2		76.2			
3		78.5*		78.5*			
4		72.5		72.5			
5		77.4		77.4			
6		63.3		63.3			
28-*O*-Glucose							
1	95.8	95.8			95.8	95.7	95.8
2	74.2	74.2			74.2	74.1	74.2
3	79.3	79.3			79.3*	79.1*	79.2*
4	71.4	71.3			71.4	71.3	71.4
5	79.0	78.7*			79.0*	79.0*	79.0*
6	62.3	62.3			62.3	62.4	62.4

*Signals may be interchangeable in any column.

EXPERIMENTAL

Optical rotations were measured with a JASCO DIP-1000 digital polarimeter. MS were measured on a JEOL JMS-SX102 mass spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on JEOL α-400 (399.65 and 100.40 MHz) NMR spectrometers. Chemical shifts are given on the δ scale with TMS as int. standard. HPLC was performed on a JASCO system 800 instrument.

Plant material. Fagonia arabica was collected from Sinai peninsula, Egypt, in March 1993 and identified by Dr M. El-Gibaly at the taxonomy department, N.R.C., where a voucher specimen was deposited.

Extraction and isolation. Air dried powdered of *F. arabica* (2 kg) were defatted by *n*-hexane, then extracted by 60% aq. EtOH. After removal of solvent by evapn, the residue (51 g) was dissolved in the minimum amount of MeOH and the soln was diluted with Me_2CO to ppt the crude saponin fr. (30 g). The later afforded **1** (125 mg), **2** (10 mg), **3** (21 mg), **4** (7 mg), **5** (5 mg), **6** (72 mg) and **7** (4 mg) after VLC [300 g Silica gel G; $CHCl_3$–MeOH (9:1–4:1)] [5] and prep. HPLC (ODS and Ph A; MeCN–H_2O system).

Compound **1**. Amorphous powder; $[\alpha]_D^{25}$ + 20.4° (MeOH; *c* 1.67); FABMS *m/z*: 1067 [M + Na]$^+$, 905, 860, 467, 440, 391, 287, 248, 203; ^{1}H NMR (pyridine-d_5): δ 0.88, 0.89, 0.92, 1.09, 1.09, 1.26, 1.27 (3H, *s*, 7 × Me), 3.19 (1H, *dd*, *J* = 14.5, 2.6 Hz, H-18), 3.35 (1H, *dd*, *J* = 12, 4.5 Hz, H-3), 3.43 (1H, *br t*, *J* = 10 Hz, Xyl H-5), 3.66 (1H, *d*, *J* = 11 Hz, Ara H-5), 3.91 (1H, *m*, Glc H-5), 3.98 (1H, *t*, *J* = 8 Hz, Glc H-2), 4.0 (1H, *t*, *J* = 8 Hz, Xyl H-2), 4.01 (1H, *m*, ester Glc H-5), 4.08 (1H, *t*, *J* = 8 Hz, Xyl H-3), 4.16 (overlapped, Ara H-5′), 4.18 (1H, *t*, *J* = 8 Hz, ester Glc H-2), 4.2 (overlapped, Xyl H-4, Glc H-3), 4.24 (overlapped, Glc H-6), 4.26 (overlapped, ester Glc H-3), 4.27 (overlapped, Ara H-3), 4.30 (overlapped, Glc H-4, ester Glc H-4), 4.38 (*dd*, *J* = 12, 4.5 Hz, ester Glc H-6), 4.44 (overlapped, Glc H-6′, ester Glc H-6′), 4.48 (1H, *m*, Ara

H-4), 4.64 (1H, *dd*, $J = 9$, 7 Hz, Ara H-2), 4.75 (1H, *d*, $J = 7.5$ Hz, Ara H-1), 5.26 (1H, *d*, $J = 8$ Hz, Glc H-1), 5.37 (1H, *d*, $J = 7.5$ Hz, Xyl H-1), 5.43 (1H, *t*, $J = 3$ Hz, H-12), 6.3 (1H, *d*, $J = 8$ Hz, ester Glc H-1); ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

Compound **2**. Amorphous powder; $[\alpha]_D^{25} + 25.4°$ (MeOH; *c* 0.59); FABMS *m/z*: 1097 $[M + Na]^+$, 935, 890, 740, 497, 439, 393, 317, 189; ^{1}H NMR (pyridine-d_5): δ 0.85, 0.90, 0.92, 1.09, 1.09, 1.25, 1.26 (3H, *s*, 7 × Me), 3.20 (1H, *dd*, $J = 14.5$, 2.5 Hz, H-18), 3.24 (1H, *dd*, $J = 12$, 4.5 Hz, H-3), 3.66 (1H, *d*, $J = 10.7$ Hz, Ara H-5), 3.70 (1H, *m*, Glc′ H-5), 3.92 (1H, *m*, Glc H-5), 3.99 (1H, *t*, $J = 8$ Hz, Glc H-2), 4.01 (1H, *m*, ester Glc H-5), 4.04 (1H, *t*, $J = 8$Hz, Glc′ H-2), 4.15 (1H, *t*, $J = 8$Hz, ester Glc H-2), 4.17 (overlapped, Ara H-5, Glc′ H-6), 4.18 (overlapped, Glc′ H-3), 4.19 (overlapped, Glc H-6), 4.20 (overlapped, Glc H-3), 4.27 (overlapped, Glc′ H-4), 4.29 (overlapped, ester Glc H-3), 4.31 (overlapped, ester Glc H-4, Ara H-3), 4.32 (overlapped, Glc H-4), 4.35 (overlapped, Glc′ H-6′), 4.39 (overlapped, ester Glc H-6), 4.46 (overlapped, ester Glc H-6′), 4.47 (overlapped, Glc H-6′), 4.48 (overlapped, Ara H-4), 4.71 (1H, *dd*, $J = 7.1$, 8.5 Hz, Ara H-2), 4.78 (1H, *d*, $J = 7.1$, Ara H-1), 5.28 (1H, *d*, $J = 7.8$ Hz, Glc H-1), 5.43 (1H, *t*, $J = 3$ Hz, H-12), 5.50 (1H, *d*, $J = 7.8$ Hz, Glc′ H-1), 6.30 (1H, *d*, $J = 8$ Hz, ester Glc H-1), ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

Compound **3**. Amorphous powder; $[\alpha]_D^{25} + 21.2°$ (MeOH; *c* 2.1); FABMS *m/z*: 905 $[M + Na]^+$, 860, 772, 578, 439, 391, 289, 248, 203; ^{1}H NMR (pyridine-d_5): δ 0.86, 0.96, 0.99, 1.02, 1.09, 1.28, 1.30 (3H, *s*, 7 × Me), 3.26 (overlapped, H-3, H-18), 3.44 (1H, *t*, $J = 10$ Hz, Xyl H-5), 3.66 (1H, *br d*, $J = 11$ Hz, Ara H-5), 3.91 (1H, *m*, Glc H-5), 3.98 (1H, *t*, $J = 8.5$ Hz, Glc H-2), 4.0 (1H, *t*, $J = 8$ Hz, Xyl H-2), 4.09 (1H, *t*, $J = 8$ Hz, Xyl H-3), 4.31 (1H, *t*, $J = 8$ Hz, Glc H-4), 4.45 (1H, *dd*, $J = 12$, 2.5 Hz, Glc H-6), 4.48 (1H, *m*, Ara H-4), 4.65 (1H, *dd*, $J = 9$, 7 Hz, Ara H-2), 4.75 (1H, *d*, $J = 7.1$ Hz, Ara H-1), 5.26 (1H, *d*, $J = 7.8$ Hz, Glc H-1), 5.37 (1H, *d*, $J = 7.6$ Hz, Xyl H-1), 5.46 (1H, *t*, $J = 2.5$ Hz, H-12); ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

Compound **4**. Amorphous powder; $[\alpha]_D^{25} + 31.7°$ (MeOH; *c* 0.52); FABMS *m/z*; 935 $[M + Na]^+$, 890, 802, 688, 477, 439, 391, 317, 261, 189; ^{1}H NMR (pyridine-d_5): δ 0.83, 0.96, 0.99, 1.02, 1.08, 1.27, 1.29 (3H, *s*, 7 × Me), 3.26 (overlapped, H-3 and H-18), 3.66 (1H, *br d*, $J = 11.7$ Hz, Ara H-5), 3.70 (1H, *m*, Glc′ H-5), 3.92 (1H, *m*, Glc H-5), 3.99 (1H, *t*, $J = 8$ Hz, Glc H-2), 4.04 (1H, *t*, $J = 8$ Hz, Glc′ H-2), 4.72 (1H, *dd*, $J = 6.8$, 8.8 Hz, Ara H-2), 4.78 (1H, *d*, $J = 7.5$ Hz, Ara H-1), 5.29 (1H, *d*, $J = 7.8$ Hz, Glc H-1), 5.46 (1H, *t*, $J = 2.5$ Hz, H-12), 5.50 (1H, *d*, $J = 7.8$ Hz, Glc′ H-1); ^{13}C NMR (pyridine-d_5); see Tables 1 and 2.

Compound **5**. Amorphous powder; $[\alpha]_D^{25} + 16.0°$ (MeOH; *c* 0.50); FABMS *m/z*: 1083 $[M + Na]^+$, 921, 840, 664, 576, 532, 437, 391, 307; ^{1}H NMR (pyridine-d_5): δ 0.85, 0.88, 0.91, 1.09, 1.11, 1.23 (3H, *s*, 6 × Me), 3.13 (1H, *dd*, $J = 12$, 4.5 Hz, H-3), 3.44 (1H, *br t*, $J = 10$ Hz, Xyl H-5), 3.69 (1H, *br d*, $J = 11$ Hz, Ara H-5), 3.92 (1H, *m*, Glc H-5), 3.99 (1H, *t*, $J = 7.8$ Hz, Glc H-2), 4.02 (1H, *m*, ester Glc H-5), 4.09 (1H, *t*, $J = 8.0$ Hz, Xyl H-3), 4.18 (1H, *t*, $J = 8$ Hz, ester Glc H-2), 4.38 (1H, *dd*, $J = 12$, 4.5 Hz, ester Glc H-6), 4.48 (1H, *m*, Ara H-4), 4.64 (1H, *dd*, $J = 7$, 8.8 Hz, Ara H-2), 4.70 (1H, *d*, $J = 7.1$ Hz, Ara H-1), 5.26 (1H, *d*, $J = 7.8$ Hz, Glc H-1), 5.37 (1H, *d*, $J = 7.6$ Hz, Xyl H-1), 5.80 (1H, *t*, $J = 3$ Hz, H-12), 6.34 (1H, *d*, $J = 8.1$ Hz, ester Glc H-1); ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

Compound **6**. Amorphous powder; $[\alpha]_D^{25} + 14.8°$ (MeOH; *c* 1.32); FABMS *m/z*: 1067 $[M + Na]^+$, 905, 860, 740, 678, 439, 392, 307, 248; ^{1}H NMR (pyridine-d_5): δ0.89, 1.09, 1.13, 1.21, 1.28 (3H, *s*, 5 × Me), 0.91, 0.95 (3H, *d*, $J = 6.3$ Hz, 2 × Me), 2.52 (1H, *d*, $J = 11$ Hz, H-18), 3.26 (1H, *dd*, $J = 10$, 4 Hz, H-3), 3.43 (1H, *t*, $J = 9.5$ Hz, Xyl H-5), 3.66 (1H, *d*, $J = 11.2$ Hz, Ara H-5), 3.91 (1H, *m*, Glc H-5), 4.08 (1H, *t*, $J = 8$ Hz, Xyl H-3), 4.48 (1H, *m*, Ara H-4), 4.64 (1H, *dd*, $J = 9$,7 Hz, Ara H-2), 4.75 (1H, *d*, $J = 7.0$ Hz, Ara H-1), 5.25 (1H, *d*, $J = 7.8$ Hz, Glc H-1), 5.35 (1H, *d*, $J = 7.5$, Xyl H-1), 5.44 (1H, *t*, $J = 3$ Hz, H-12), 6.24 (1H, *d*, $J = 8$ Hz, ester Glc H-1); ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

Compound **7**. Amorphous powder; $[\alpha]_D^{25} + 6.3°$ (MeOH; *c* 0.4); FABMS *m/z*: 1083 $[M + Na]^+$, 921, 796, 664, 620, 532, 488, 487, 308; ^{1}H NMR (pyridine-d_5): δ0.83, 1.09, 1.17, 1.21 (3 H, *s*, 4 × Me), 0.92, 1.05 (3H, *d*, $J = 6$ Hz, 2 × Me), 2.64 (1H, *d*, $J = 11$ Hz, H-18), 3.16 (1H, *dd*, $J = 10$, 4 Hz, H-3), 3.44 (1H, *t*, $J = 9.5$ Hz, Xyl H-5), 3.66 (1H, *d*, $J = 11$ Hz, Ara H-5), 3.91 (1H, *m*, Glc H-5), 4.09 (1H, *t*, $J = 8$ Hz, Xyl H-3), 4.48 (1H, *m*, Ara H-4), 4.64 (1H, *dd*, $J = 7$, 9 Hz, Ara H-2, 4.70 (1H, *d*, $J = 7.1$ Hz, Ara H-1), 5.26 (1H, *d*, $J = 7.8$ Hz, Glc H-1), 5.37 (1H, *d*, $J = 7.8$ Hz, Xyl H-1), 5.74 (1H, *t*, $J = 3$ Hz, H-12), 6.30 (1H, *d*, $J = 8$ Hz, ester Glc H-1; ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

Alkaline hydrolysis of saponins **1** and **2**. A soln of saponin (**1**, **2**) (2 mg) in 5% aq. KOH (3 ml) was heated at 100° for 30 min. The reaction mixture was neutralized with 5% HCl and then extracted with *n*-BuOH (satd with H_2O). The *n*-BuOH layer was concd to dryness to give prosapogenin. By this process, **1** and **2** afforded **3** and **4** respectively. Identification was based on comparison by co-TLC with authentic samples.

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