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TRITERPENE GLYCOSIDES FROM *SCHEFFLERA BODINIERI* ROOTS

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Key Word Index—*Schefflera bodinieri*; Araliaceae; triterpene glycosides.

Abstract—Four novel triterpene glycosides were isolated from the roots of *Schefflera bodinieri*. The structures of the compounds have been determined as 28-*O*-[α-L-rhamopyranosyl-(1 → 4)-*O*-β-D-glucopyranosyl-(1 → 6)-]-β-D-glucopyranoside of 3β-hydroxy-isopolygalic-13(14)-ene-28-acid, 28-*O*-[α-L-rhamopyranosyl(1 → 4)-*O*-β-D-glucopyranosyl(1 → 6)-]-β-D-glucopyranoside of 3-oxo-isopolygalic-13(14)-ene-28-acid, 28-*O*-β-D-glucopyranosyl(1 → 6)-β-D-glucopyranoside of 3β-hydroxy-isopolygalic-13(14)-ene-28-acid and 28-*O*[α-L-rhamopyranosyl-(1 → 4)-*O*-β-D-glucopyranosyl-(1 → 6)-]-β-D-glucopyranoside of 3β-hydroxy-18-methyl-polygalic-13(14)-ene-28-acid. The structure elucidation is based on spectroscopic data, including ^{1}H–^{1}H COSY and ^{13}C–^{1}H COSY NMR.

INTRODUCTION

Some plants of *Schefflera* are recorded as folk remedies for the treatment of pain, rheumatic arthritis, and lumbago in China [1], and *Schefflera arboricola* is used clinically for trigeminal neuralgia and migraine in the southwest of the country [2]. Two selected species of *Schefflera* were screened by our ligand–receptor binding assays and the results showed that *Schefflera bodinieri* (Levi.) Rehd. root extract was able to bind to 5HT and GABA receptors. Guided by ligand–receptor binding assays, the chemical investigation was undertaken on this species. There is no previous phytochemical report on the plant and studies by other workers on the chemical components of *S. octophylla* and *S. capitata* indicated that the major ingredients of these two species were triterpene glycosides [3–13]. This communication is concerned with the isolation and structure identification of four novel triterpene glycosides from the root of *S. bodinieri*.

RESULTS AND DISCUSSION

The 70% EtOH extract was isolated by repeated flash chromatography and the further purification was conducted on sephadex columns and reverse phase HPLC. Four triterpene glycosides (**1–4**) were obtained and the structure identification was based on spectroscopic data.

The HR-FAB-mass spectrum of compound **1** established the molecular formula as $C_{47}H_{76}O_{17}$ and the molecular weight was found to be 912.5085 (requires 912.5083). The ^{1}H NMR spectrum indicated that it was a triterpene glycoside with three sugar moieties. The anomeric proton signals appeared at δ 5.36 (1H, *d*, J = 8 Hz), 4.41 (1H, *d*, J = 8 Hz), 4.86 (1H, *br s*), respectively. The ^{13}C NMR spectrum data confirmed the presence of the three sugar moieties (signals for anomeric C-atoms: δ 95.7, 102.9, 104.9, 104.3). (Table 1). Hydrolysis of the glycoside gave glucose and rhamnose as sugar residues as indicated by co-TLC (in three different solvent systems with glucose, rhamnose, arabinose, galactose, mannose and xylose as references). The three proton signal at δ 1.29 (3H, *d*, J = 6.5 Hz) and an anomeric signal at δ 4.86 (*br s*) showed the presence of only one rhamnose in the glycoside. The coupling constants of the anomeric protons in the ^{1}H NMR spectrum suggested the β-configuration of the glucoses (*d*, J = 8 Hz), and that the rhamnose had an α-orientation (*br s*) [14]. The ^{13}C–^{1}H COSY spectrum indicated that one of the glucose was linked to the genin via a carboxylic group since there was a cross peak between the proton at δ 5.36 (glucose-H_1) and the carbon at δ 95.7 (glucose-C_1) which was about 10 ppm downfield comparing with that of an anomeric carbon of glucose linked to the C-3 hydroxyl-group [15]. The FAB-MS data showed the peaks at *m/z* 935 $[M + Na]^+$, 789 $[M + Na - Rham]^+$, 604 $[M - Rham - Glc]^+$, and 442 $[M - Rham - Glc - Glc]^+$ which gave the possible link order of the sugar moieties. The ^{13}C NMR-DEPT spectrum suggested that the structure of the sugar moieties was α-D-rhamnopyranosyl (1 → 4)-*O*-β-D-glucopyranosyl(1 → 6)-*O*-β-D-glucopyranoside, because the chemical shift of C-6 of the glucose linked with genin and C-4 of the second glucose were both 7 ppm downfield [8]. Moreover, the sugar residue of compound **1** was found to be the same as those of other

Table 1. ^{13}C NMR and ^{1}H NMR spectra assignments of compound **1**

Position	δ_C	δ_H	^{1}H–^{1}H COSY	^{13}C–^{1}H COSY
Aglycone				
1	32.7	1.35, 1.79	1.35 → 1.79, 1.55, 2.01	32.7 → 1.35, 1.79
2	23.1	1.55, 2.01	2.01 → 1.55, 1.35, 1.79	23.1 → 1.98, 1.55
3	76.6	3.33	3.33 → 1.55, 1.98	7.76 → 3.33
		overlapped with Glc$_1$-H$_2$		
4	38.3	—	—	—
5	48.8	1.50	1.50 → 1.60, 1.90	48.8 → 1.50
6	25.0	1.60, 1.90	1.60 → 1.90, 1.50, 1.27	25.0 → 1.60, 1.90
7	33.8	1.27, 1.18	1.27 → 1.18, 1.48, 1.60	33.8 → 1.18, 1.27
8	38.1	1.48	1.48 → 1.27, 1.18, 1.28	33.8 → 1.48
9	56.0	1.28	1.28 → 1.48	56.0 → 1.28
10	38.6	—	—	—
11	17.4	1.55, 1.50	1.55 → 1.50, 2.48, 1.20	17.4 → 1.55, 1.50
12	41.0	2.48 (*dd*, 10, 2), 1.20	2.48 → 1.20, 1.55	41.0 → 2.48, 1.20
13	130.0	—	—	—
14	137.0	—	—	—
15	30.7	2.18, 2.07	2.18 → 2.07, 1.90	30.7 → 2.18, 2.07
16	39.3	1.90, 1.62	—	—
17	53.7	—	—	—
18	46.0	—	—	—
19	40.9	1.58, 1.30	1.58 → 1.30	40.9 → 1.58, 1.30
20	30.2	—	—	—
21	31.5	1.52, 1.32	1.52 → 1.32, 1.78, 2.00	31.5 → 1.51, 1.32
22	20.2	2.00, 1.78	2.00 → 1.78, 1.52, 1.32	20.2 → 2.00, 1.78
23	31.6	0.87 (*s*)	—	31.6 → 0.87
24	15.7	0.83 (*s*)	—	15.7 → 0.83
25	16.5	0.99 (*s*)	—	16.5 → 0.99
26	—	—	—	—
27	25.0	0.91 (*s*)	—	25.0 → 0.91
28	178.0	—	—	—
29	27.6	0.80 (*s*)	—	27.6 → 0.80
30	19.9	0.75 (*s*)	—	19.9 → 0.75
Sugar				
Glcl*				
1	95.7	5.36 (*d*, 8)	5.36 → 3.33	95.7 → 5.36
2	73.7	3.33 (*m*)	3.33 → 5.36, 3.67	73.7 → 3.33
3	79.5	3.67 (*t*, 8)	3.67 → 3.33, 3.45	79.5 → 3.67
4	71.0	3.45 (*t*, 8)	3.45 → 3.67, 3.57	71.0 → 3.45
5	76.7	3.57 (*m*)	3.57 → 3.45, 3.85, 4.13	76.7 → 3.57
6	69.5	3.85, 4.13 (*m*)	3.85 → 4.13, 3.57	69.5 → 3.85, 4.13
Glc2				
1	104.3	4.41 (*d*, 8)	4.41 → 3.29	104.3 → 4.41
2	75.3	3.29 (*t*, 3)	3.29 → 4.41, 3.51	75.3 → 3.29
3	76.7	3.51 (*t*, 8)	3.51 → 3.29, 3.43	76.7 → 3.51
4	78.2	3.43 (*t*, 6)	3.43 → 3.51, 3.31	78.2 → 3.31
5	78.0	3.31 (*m*)	3.31 → 3.43, 3.83, 3.68	78.0 → 3.31
6	61.9	3.83, 3.68 (*m*)	3.83 → 3.68, 3.31	61.9 → 3.83, 3.68
Rham				
1	102.9	4.86 (*br s*)	4.86 → 3.88	102.9 → 4.86
2	72.5	3.88 (*br s*)	3.88 → 4.86, 3.67	72.5 → 3.88
3	72.2	3.67 (*dd*, 8, 2)	3.67 → 3.88, 3.43	72.2 → 3.67
4	73.9	3.43 (*t*, 3)	3.43 → 3.67, 4.03	73.9 → 3.43
5	70.7	4.03 (*m*)	4.03 → 3.43, 1.29	70.7 → 4.03
6	17.9	1.29 (*t*, 6.5)	1.29 → 4.03	17.9 → 1.29

*Glcl: the first glucose linked with the aglycone, Glc2: the second glucose linked with Glc1, Rham rhamnose linked with Glc2.

The data obtained from ^{1}H NMR (CD_3OD, 500 MHz), ^{13}C NMR (CD_3OD, 125.7 MHz), ^{1}H–^{1}H COSY and ^{13}C–^{1}H COSY.

triterpene glucosides isolated from species of *Schefflera* [7, 9].

The EI-mass spectrum of compound **1** showed the M^+ of the aglycone at *m/z* 442. The ^{13}C NMR-DEPT spectrum exhibited the presence of two double bond quaternary carbons (δ 130.0, 137.0), one carboxyl

carbon (δ 178.0) and a total of 29 aglycone carbon atoms including six methyl, eleven methylene, three methine, and five quaternary carbons (in addition to -C = C, -COOH). These data suggested the molecular formula of the aglycone as $C_{29}H_{46}O_3$ and the structure can be established as a pentacyclic triterpene skeleton with a double bond in the ring system. In the EI-mass spectrum, the major fragments came from allylic cleavage showing peaks at *m/z* 275 (ion *a*), 207 (ion *b*), and 234 (ion *c*) whch suggested that the double bond might be located at C-13/C-14, because the double bond carbons had no associated olefinic protons (Scheme 1). There was a methyl group on C-18 as indicated by ion *c*. Based on the ^1H–^1H COSY spectrum, the proton signal at δ 3.33 in ^1H NMR was assigned to C-3. The C-3 hydroxy group was β-equatorially oriented as indicated by the chemical shift of H-3 (δ 3.33) and in comparsion with the corresponding signal of the α-axial isomer (δ 3.67 for H_{eq}-3) [16]. The assignment of all protons and carbons of compound **1** (Table 1) was made from the ^1H NMR, ^1H–^1H COSY, ^{13}C–^1H COSY, ^{13}C NMR-DEPT spectral data and by comparsion with the related data in the literatures [17, 18]. The structure of the new compound (**1**) is thus represented by 28-*O*-[α-L-rhamnopyranosyl (1 → 4)-*O*-β-D-glucopyranosyl (1 → 6)-]-β-D-glucopyranoside of 3β-hydroxy-isopolygalic-13(14)-ene-28-acid.

The HR-FAB mass spectrum of compound **2** exhibited the molecular formula as $C_{47}H_{74}O_{17}$ and the molecular weight at 910.4929 (requires 910.4926). The ^1H NMR spectrum showed that compound **2** had a similar structure to compound **1** and also with three sugar moieties. The signals of the anomeric protons at δ 5.35, 4.85, 4.40 in the ^1H NMR spectrum and the signals of anomeric carbons at δ 95.56, 104.24, 102.86 in the ^{13}C NMR spectrum suggested the presence of the same trisaccharide residue as compound **1**. Hydrolysis products of **2** were glucose and rhamnose as indicated by co-TLC. The difference between **2** and **1** was in the aglycone. In the EI-mass spectrum, the M^+ of the aglycone was at *m/z* 440 and a series of peaks which had **2** mass units less than those of compound **1** showed clearly. The major fragments of **2** are shown in Scheme 1 and the fragmentation suggested the presence of a carbonyl group at C-3 (ion *a* and ion *b*). The ^{13}C NMR spectrum of **2** further substantiated the presence of a carbonyl group (compared with **1**, absence of one C-OH carbon and presence of a carbonyl carbon signal at δ 220.96). From these data, the structure of this new glycoside was established as 28-*O*-[α-L-rhamnopyranosyl (1 → 4)-*O*-β-D-glucopyranosyl(1-6)-β-D-glucopyranoside of 3-oxo-isopolygalic -13(14)-ene-28-acid.

The ^1H NMR spectrum of compound **3** indicated that the compound had a similar structure to compound **1**, but no rhamnose unit was present (absence of the signals of anomeric proton at δ 4.85 and the methyl group at δ 1.29). The chemical shifts of the aglycone protons were the same as compound **1** (e.g. H-12 at δ 2.48, H-3α at δ 3.33). The FAB-mass spectrum gave the M_r at *m/z* 766 and EI-mass spectrometry showed the M^+ of the aglycone at *m/z* 442. The major fragments in the EI-mass spectrum were the same as compound **1** (Scheme 1). Based on these data, the new structure (**3**) was determined as the 28-*O*-β-D-glucopyranosyl(1 → 6)-β-D-glucopyranoside of 3β-hydroxy-isopolygalic-13(14)-ene-28-acid.

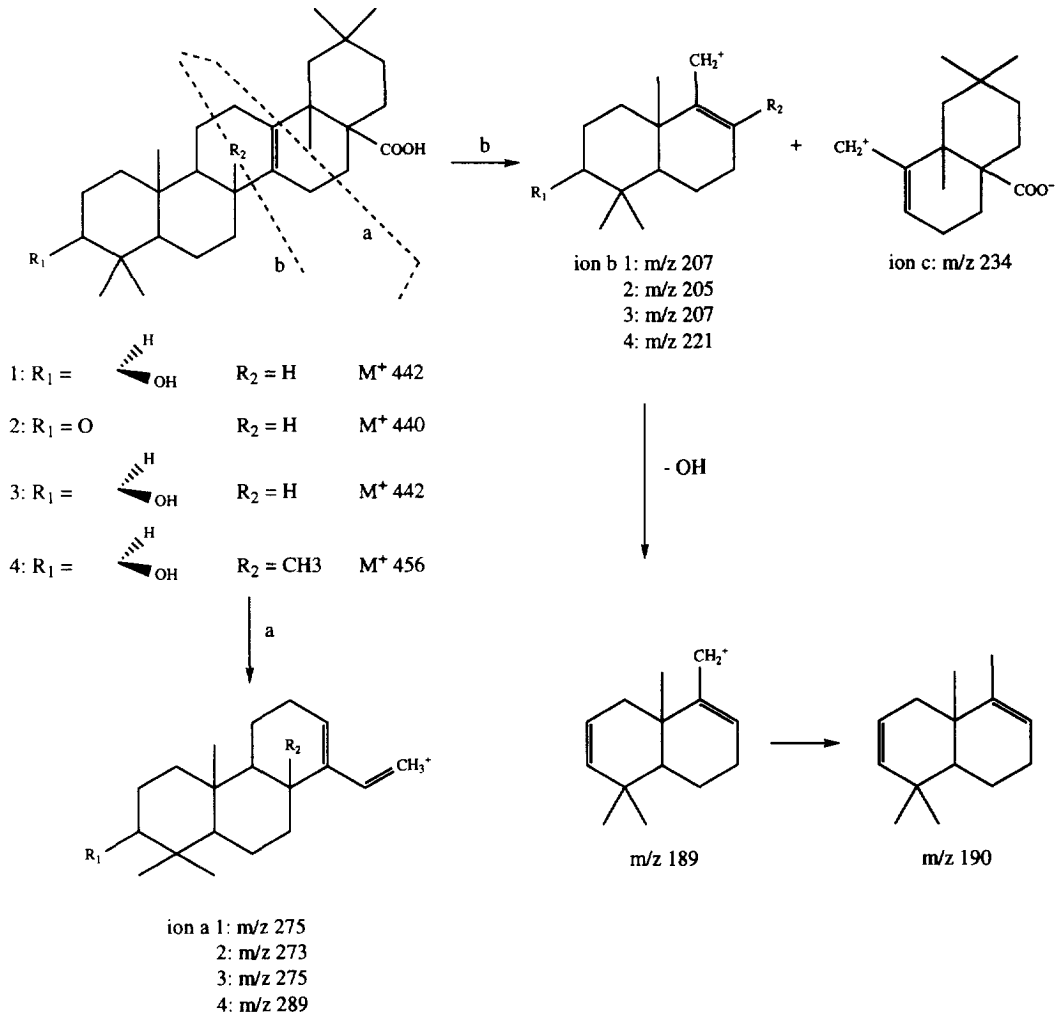
Compared with **1**, compound **4** had the same sugar moieties as indicated by the ^1H NMR spectrum. The anometric proton signals appeared at δ 5.35 (1H, *d*, *J* = 8 Hz), H-1 of Glc-1), 4.40 (1H, *d*, *J* = 8 Hz, H-1 of Glc-2), 4.85 (1H, *br s*, H-1 of Rham). Hydrolysis of the compound gave glucose and rhamnose as sugar residues as revealed by co-TLC. The EI-mass spectrum gave the M^+ of the aglycone at *m/z* 456 and the CI-mass spectrum gave the molecular ion at *m/z* 926. The compound had a similar parent skeleton to compound **1** except for having one extra methyl group exhibiting a signal in the ^1H NMR spectrum. This methyl group was assigned to C-8 due to a diagnostic peak at *m/z* 289 (ion *a*) in the EI-mass spectrum (Scheme 1). The compound had a lower R_f value than that of compound **1** on TLC and showed a different colour after spraying with the vanillin–sulphuric acid reagent. Based on these data, the new structure (**4**) is represented by 28-*O*[α-L-rhamnopyranosyl-(1 → 4)-*O*-β-D-glucopyranosyl(1 → 6)-]-β-D-glucopyranoside of 3β-hydroxy-18-methyl-polyalic-13(14)-ene-28-acid.

Oleananes form the largest group of triterpenoids and occur widely in the plant kingdom often as glycosides [19]. In the Araliaceae, oleanane triterpene glycosides are one of the major components in the plants, and they usually have a C-12 double bond in the molecule. *Schefflera bodinieri*, a species of Araliaceae, also has oleanane type glycosides as major ingredients. However, the double bond position of the four novel glycosides was found between C-13 and C-14, which is unusual and this skeleton has only been found so far in the plants of *Polygala* and *Bredemeyera* [19]. This is the first time that oleanane triterpenes with a Δ^{13}-double bond have been found in the Araliaceae.

EXPERIMENTAL

General experimental procedures. ^1H NMR, ^1H–^1H COSY and ^{13}C–^1H COSY spectra were measured at 500 MHz and the ^{13}C NMR spectra (DEPT) were measured at 125.7 MHz on an AMX-500, at room temp. with d_4-methanol soln and TMS as int. standard. EI-MS (70 ev), CI-MS, FAB-MS and HR-FAB were taken with a direct probe on an Analytical ZAB-2F (VG, Micromass Ltd). The isolation was conducted on the following chromatographic columns: silica gel C60 (40-60A, May and Baker); Sephadex LH-20 (Sigma); reverse phase ODS column (dp 5μ, 2.5 cm × 4.6 mm, Beckman) in HPLC Waters 991, photodiode array detector.

Plant material. Schefflera bodinieri was collected on Jinfo Mountain, Sichuan province, P.R. China in



Scheme 1. Fragment ions of the aglycones of compounds **1**–**4** observed: see EI-mass spectrum.

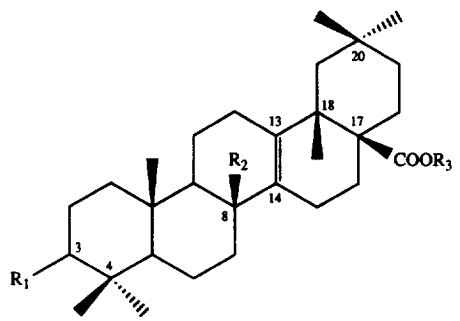
November, 1990 and identified by Professor Z. Liu of that institute. The voucher specimens are kept in the herbarium of the Institute of Medicinal Plant Cultivation, Sichuan province, P. R. China.

Extraction and isolation. The air-dried root of *Schefflera bodinieri* (1 kg) was extracted by 70% EtOH at room temp. to yield an extract (70 g). The extract (20 g) was subjected to a flash column of silica gel eluted with solvents of increasing polarity. The MeOH fraction (3 g) was purified by a Sephadex LH-20 column and reverse-phase HPLC to give compound **1** (100 mg), compound **2** (10 mg), compound **3** (6 mg), and compound **4** (5 mg).

Hydrolysis of the glycosides. Glycoside (2 mg) was dissolved in 10 ml MeOH with 10% HCl and heated at 80° for 1 hr. The reaction sol was diluted with H_2O and extracted with $CHCl_3$. This extract was dried over anhydrous Na_2SO_4 and filtered. Removal of the organic solvent resulted in the aglycone. The aq. layer was neutralized by NaOH and dried *in vacuo* to give the sugar moieties of the glycoside. The dry material was dissolved in MeOH and identified by co-TLC with authentic samples. TLC examination was carried out with silica gel 60 F254 plates (Merck). Spray reagent: vanillin–H_2SO_4 for glycosides, aglycones and sugars. Solvent systems for examining sugars: $CHCl_3$–MeOH–HOAc (2:2:1); *n*-BuOH–HOAc–H_2O (5:1:2); EtOAc–MeOH–HOAc (3:2:1). Reference compounds for sugar detection included glucose, rhamnose, arabinose, galatose, mannose, and xylose.

Compound **1**. Amorphous powder, soluble in MeOH. TLC (silica gel): R_f 0.53 ($CHCl_3$–MeOH–H_2O 8:2:0.1). Found: M_r 912.5085, $C_{47}H_{76}O_{17}$, requires 912.5083. ^1H NMR and ^{13}C NMR: see Table 1. EI-MS *m/z* (rel. int.): 442 (20), 427 (40), 409 (17), 381 (15), 363 (33), 275 (31), 261 (13), 234 (6), 227 (28), 219 (11), 207 (48), 189 (46), 191 (73), 190 (95), 175 (45), 161 (21), 147 (27), 135 (85), 55 (100). FAB-MS *m/z*: 935 $[M + Na]^+$, 789 $[M + Na - rhamnose]^+$, 604 $[M - rhamnose - glucose]^+$.

Compound **2**. Amorphous powder, soluble in MeOH. TLC (silica gel): R_f 0.55 ($CHCl_3$–MEOH–H_2O 8:2:0.1). Found: M_r 910.4929, $C_{47}H_{74}O_{17}$, requires 910.4926. ^1H NMR (CD_3OD-d_4, 500 MHz): δ 0.90,



	R_1	R_2	R_3
1		H	-Glc-Glc-Rham
2	=O	H	-Glc-Glc-Rham
3		H	-Glc-Glc
4		CH3	-Glc-Glc-Rham

0.95, 0.95, 1.00, 1.05, 1.10 (3H, each, *s*, *tert*-Me), 2.48 (1H, *dd*, $J = 10$, 2 Hz, H-12), 5.35 (1H, *d*, $J = 8$ Hz, H-1 of Glc-1), 4.40 (1H, *d*, $J = 8$ Hz, H-1 of Glc -2), 4.85 (1H, *br.s*, H-1 of Rham). 1.28 (3H, *d*, $J = 6.5$ Hz, H-6 of Rham) 3.28-4.15 (16H, sugar protons). ^{13}C NMR (DMSO-d_6, 125.7 MHz): aglycone δ 35.0 (*t*, C-1), 34.9 (*t*, C-2), 221.0 (*s*, C-3), 38.0 (*s*, C-4), 55.7 (*d*, C-5), 21.5 (*t*, C-6), 35.1 (*t*, C-7), 40.1 (*d*, C-8), 56.7 (*d*, C-10), 38.7 (*s*, C-10), 19.3 (*t*, C-11), 42.3 (*t*, C-12), 131.4 (*s*, C-13), 137.3 (*s*, C-14), 32.0 (*t*, C-15), 39.6 (*t*, C-16), 49.6 (*s*, C-17), 46.5 (*s*, C-18), 40.1 (*t*, C-19), 34.9 (*s*, C-20), 32.6 (*t*, C-21), 20.8 (C-22), 33.0 (*q*, C-23), 21.4 (*q*, C-24), 16.8 (*q*, C-25), 25.1 (*q*, C-27), 178.1 (*s*, C-28), 27.2 (*q*, C-29), 20.7 (*q*, C-30); sugar moieties: Glc-1 95.56 (C-1), 73.61 (C-2), 78.73 (C-3), 70.85 (C-4), 76.66 (C-5), 69.42 (C-6); Glc-2: 104.24 (C-1), 75.11 (C-2), 76.57 (C-3), 79.60 (C-4), 77.77 (C-5), 61.80 (C-6); Rham: 102.86 (C-1), 72.27 (C-2), 72.07 (C-3), 73.78 (C-4), 70.58 (C-5), 17.82 (C-6), EI-MS *m/z* (rel. int.): 440 (3), 425 (92) 394 (17), 379 (78), 273 (29), 261 (9), 248 (12), 234 (5), 227 (26), 219 (8), 205 (30), 201 (32), 189 (40), 190 (35), 177 (68), 81 (100). FAB-MS *m/z*: 993 $[M + Na]^+$, 787 $[M + Na - Rham]^+$, 603 [aglycone + Glc + 1], 441 [agylcone + 1].

Compound **3**. Amorphous powder, soluble in MeOH. TLC (silica gel): R_f 0.70 ($CHCl_3$–MeOH–H_2O 8:2:0.1). Found: M_r 766.4505, $C_{41}H_{66}O_{13}$, requires 766.4503. ^{1}H NMR (CD_3OD-d_4, 500 MHz): δ 0.80, 0.85, 0.93, 0.94, 0.97, 0.98 (3H, each *s*, *tert*-Me); 3.33 (1H, *br.s*. H-3α), 2.48 (1H, *dd*, $J = 10$, 2 Hz, H-12), 5.35 (1H, *d*, $J = 8$ Hz, H-1 of Glc-1), 4.40 (1H, *d*, $J = 8$ Hz, H-1 of Glc-2), 3.28-4.12 (12H, sugar protons), 1.28, (3H, *d*, $J = 6.5$ Hz, Rham-Me). EI-MS *m/z* (rel. int.): 443 (12), 428 (23), 410 (13), 397 (5), 382 (8), 364 (25), 289 (3), 275 (32), 273 (28), 234 (8), 229 (38), 207 (13), 190 (37), 189 (39), 94 (100). FAB-MS *m/z* 789 $[M + Na]^+$, 627 $[M + Na - Glc]^+$.

Compound **4**. Amorphous powder, soluble in MeOH. TLC (silica gel): R_f 0.50 ($CHCl_3$–MeOH–H_2O 8:2:0.1). Found: M_r 926.5242, $C_{48}H_{78}O_{17}$, requires 926.5239. ^{1}H NMR (CD_3OD-d_4, 500 MHz): δ 0.75, 0.83, 0.87, 0.91, 0.93, 0.95, 0.95 (3H, each *s*, *tert*-Me), 3.33 (1H, *br.s*. H-3α); 2.48 (1H, *dd*, $J = 10$, 2 Hz, H-12), 5.35 (1H, *d*, $J = 8$ Hz, H-1 of Glc-1) 4.40 (1H, *d*, $J = 8$ Hz, H-1 of Glc-2), 4.85 (1H, *br.s*. H-1 of Rham), 1.28 (3H, *s*, H-6 of Rham), 3.28–4.15 (16H, sugar protons). EI-MS *m/z* (rel. int.): 456 (5), 442 (5), 428 (10), 409 (7), 396 (7), 382 (6), 289 (3), 275 (8), 273 (10), 234 (8), 229 (9), 227 (6), 221 (5), 207 (21), 190 (7). FAB-MS *m/z*: 949 $[M + Na]^+$, 803 $[M + Na - Rham]^+$, 618 $[M + Glc]^+$.

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