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Triterpenoid glycosides from the stems of *Gordonia kwangsiensis*

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ABSTRACT

Eleven oleanane-type triterpenoid glycosides, named gordonsaponins A–K, were isolated from the stems of *Gordonia kwangsiensis*. Their structures were elucidated by spectroscopic and chemical methods. The cytotoxic activities of all eleven were evaluated against five human tumor cell lines (HCT-8, Bel-7402, BGC-823, A549, and A2780), with only one having activity against all tested cell lines, with IC_{50} values ranging from 0.1 to 2.41 μM.

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1. Introduction

The genus *Gordonia* (Theaceae) includes 40 species with ubiquitous distribution around the world. Of these *Gordonia kwangsiensis* chang is distributed widely in the Guangxi, Guizhou, and Yunnan Provinces of the People's Republic of China (Board Editorial Board, the Chinese Academy of Sciences, 1998). Previous phytochemical studies on *Gordonia* species showed that plants of this genus are rich in triterpenoids (Herath and Athukoralage, 1998, 2000; Hearth et al., 1999, 2000, 2001), steroids (Herath et al., 1999), tannins (Wang et al., 2001), and several other components (Athukoralage et al., 2001) were also isolated from these plants. Some of these substances exhibit apoptosis-inducing (Wang et al., 2001) and antifungal (Athukoralage et al., 2001) activities. In the course of a continuing search for new biologically active compounds from plant resources, the *n*-BuOH part of the 95% EtOH extract of the stems of *G. kwangsiensis* was found to exhibit selective cytotoxicities for HCT-8 and Bel-7402 cell lines. Until now, there were no reports on its chemical constituents and bioactivities. Studies focusing on biologically significant anticancer properties led to the isolation of 11 triterpenoid saponins. Reported herein are the isolation, structural elucidation, and biological activity of these compounds.

2. Results and discussion

The 95% EtOH extract of the stems of *G. kwangsiensis* was partitioned with $CHCl_3$, EtOAc, *n*-BuOH, successively. The *n*-BuOH-soluble portion showed selective cytotoxicities for HCT-8 (IC_{50} = 10.78 μM) and Bel-7402 (IC_{50} = 35.42 μM) cell lines. The *n*-BuOH-soluble portion was fractionated by silica gel column chromatography to give fractions A_1–A_{10}. Fraction A_5 eluted with EtOH–H_2O mixture from the D101 macroporous resin chromatography led to isolation of 11 triterpenoid saponins. Their structures were elucidated by extensive spectroscopic chemical methods including 1D (^1H and ^{13}C) and 2D NMR (HSQC, HMBC, TOCSY, and NOESY) experiments as well as ESIMS analysis.

Compound **1** was obtained as a white, amorphous powder. The IR spectrum of **1** showed hydroxy (3402 cm^{-1}), carbonyl (1678 cm^{-1}), and α,β-unsaturated carbonyl (1080 cm^{-1}) absorption signals. The molecular formula $C_{53}H_{86}O_{23}$ was determined by HRESIMS (*m*/*z* 1113.5473 $[M + Na]^+$, calcd. for 1113.5452) and supported by the NMR spectroscopic data. The ^1H NMR spectrum of **1** in pyridine-d_5 showed seven methyl signals (δ_H 0.80, 0.91, 1.03, 1.07, 1.10, 1.21, and 1.83). Additional resonances observed included those ascribed to an olefinic proton at δ_H 5.34 (1H, *br s*), two oxymethylene protons at δ_H 3.59 and 3.72 (1H each, *d*, *J* = 11.0 Hz), two oxymethine protons at δ_H 3.24 (1H, *dd*, *J* = 11.5, 4.5 Hz) and 4.61 (1H, *m*), and four anomeric proton signals at δ_H 4.85 (1H, *d*, *J* = 7.5 Hz), 5.05 (1H, *d*, *J* = 7.5 Hz), 5.70 (1H, *d*, *J* = 8.0 Hz), and 6.02 (1H, *d*, *J* = 8.0 Hz) correlated in the HSQC spectrum with four anomeric carbons at δ_C 105.4, 107.5, 101.9, and 102.2 in the ^{13}C NMR spectrum, respectively (Table 1). The ^{13}C NMR spectrum of **1** displayed 53 carbon signals, of which 23 were assigned to the sugar moieties and the remaining 30 to the aglycone. These data suggested that the aglycone part of **1** was likely to be a pentacyclic triterpene with two hydroxyl groups and a trisubstituted double bond. Comparison of the NMR spectroscopic data of **1** (Table 1) with those of primulagenin A (Akai et al., 1985) demonstrated that

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Table 1
NMR spectroscopic data (500 MHz, C_5D_5N) for compounds **1**, **2**, **9**, and **11**.

	1		**2**		**9**		**11**	
	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C
1		38.7		38.7		38.8		38.7
2		26.3		26.6		26.5		26.5
3	3.24, *dd* (11.5, 4.5)	89.3	3.24, *dd* (11.5, 4.5)	89.4	3.20, *br d* (11.5)	89.4	3.19, *dd* (11.5, 5.0)	89.6
4		39.8		39.5		39.5		39.5
5	0.74, *m*	55.5	0.79, *m*	55.5	0.80, *m*	55.4	0.79, *m*	55.7
6		18.2		18.7		18.7		18.4
7		33.3		30.9		36.9		35.7
8		39.8		38.9		39.4		40.0
9	1.70, *m*	46.8	1.69, *m*	47.2	1.68, *m*	47.0	1.69, *m*	46.8
10		36.6		36.9		36.6		36.2
11	1.83, *m*	23.6	1.84, *m*	23.9	1.78, *m*	23.9	1.86, *m*	23.8
12	5.34, *br s*	123.1[a]	5.44, *br s*	123.1	5.48, *br s*	125.3	5.42, *br s*	123.9
13		145.0		145.9		143.6		142.7
14		42.2		47.9		47.1		40.9
15	2.18, *m*	34.6	4.38, *m*	67.5	4.21, *m*	67.5	1.88, *m*	34.8
16	4.61, *m*	74.0	4.54, *m*	78.6	4.52, *m*	75.0	4.32, *m*	68.6
17		40.7		41.0		45.4		46.8
18	2.49, *br d* (13.0)	41.8	2.43, *br d* (12.0)	43.1	2.81, *br d* (11.5)	41.4	3.08, *m*	41.6
19a	2.72, *t* (13.0)	48.1	2.71, *m*	47.9	3.00, *t* (13.0)	47.6	3.08, *m*	47.1
19b	1.30, *m*		1.35, *m*		1.68, *m*		1.69, *m*	
20		31.1		31.2		33.1		36.7
21	1.22, *m*	36.9	1.31, *m*	36.7	6.58, *d* (10.0)	79.1	6.58, *d* (10.0)	79.3
22	2.27, *m*	30.3	2.27, *m*	31.0	6.15, *d* (10.0)	73.5	6.30, *d* (10.0)	73.4
23	1.10, *s*	24.6	1.21, *s*	27.9	1.31, *s*	27.9	1.25, *s*	28.0
24	1.07, *s*	16.5	1.08, *s*	17.5	1.10, *s*	16.7	1.09, *s*	16.7
25	0.80, *s*	15.5	0.83, *s*	15.8	0.80, *s*	15.7	0.80, *s*	15.6
26	0.91, *s*	16.8	1.04, *s*	16.7	0.98, *s*	17.5	0.84, *s*	16.8
27	1.83, *s*	27.2	1.82, *s*	20.9	1.84, *s*	20.6	1.83, *s*	27.5
28a	3.72, *d* (11.0)	69.9	3.79, *d* (10.5)	69.5	3.74, *d* (10.5)	63.6	3.67, *d* (10.0)	63.5
28b	3.59, *d* (11.0)		3.60, *d* (10.5)	33.4	3.49, *d* (10.5)		3.43, *d* (10.0)	
29	1.03, *s*	33.0	1.04, *s*	24.5	0.99, *s*	33.2	1.07, *s*	29.4
30	1.21, *s*	27.7	1.10, *s*		1.27, *s*	24.8	1.31, *s*	19.5
Ang								
1′						168.1		168.2
2′						129.0		129.2
3′					5.81, *q* (6.5)	136.5	5.93, *q* (7.0)	137.1
4′					2.02, *d* (6.5)	15.7	2.06, *d* (7.0)	15.8
5′					1.79, *s*	20.1	2.08, *s*	20.8
Sugar (C-3) GlcA								
1	4.85, *d* (7.5)	105.4	4.85, *d* (7.0)	105.6	4.88, *d* (7.5)	105.5	4.87, *d* (7.0)	105.4
2	4.67, *t* (8.5)	78.1	4.65, *t* (9.0)	78.3	4.65, *t* (8.5)	78.8	4.61, *t* (8.5)	78.9
3	4.43, *m*	84.7	4.45, *m*	84.9	4.45, *m*	84.8	4.40, *m*	83.8
4	4.38, *m*	70.9	4.46, *m*	71.1	4.53, *m*	71.0	4.54, *m*	71.3
5	4.11, *m*	76.8	4.49, *m*	77.0	4.50, *m*	76.9	4.55, *m*	77.3
6		171.7		171.9		171.9		176.1
Xyl (1 → 3) GlcA								
1	5.70, *d* (8.0)	101.9	5.70, *d* (7.5)	101.8	5.69, *d* (7.5)	101.8		
2	4.52, *dd* (8.0, 8.5)	83.7	4.50, *dd* (7.5, 8.5)	83.9	4.49, *m*	83.5		
3	4.24, *t* (8.5)	74.9	4.24, *t* (8.5)	75.1	4.09, *t* (8.0)	77.2		
4	4.50, *m*	70.3	4.37, *m*	70.5	4.27, *m*	70.7		
5	3.43, *t* (13.5)	67.4	3.44, *t* (13.0)	67.6	3.41, *t* (11.5)	67.5		
	4.39, *m*		4.48, *m*		4.24, *m*			
Glc (1 → 2) Xyl								
1	5.05, *d* (7.5)	107.5	5.05, *d* (8.0)	107.6	5.07, *d* (7.5)	107.4		
2	4.24, *t* (7.5)	74.9	4.24, *t* (8.0)	75.1	4.25, *dd* (7.5, 8.5)	75.0		
3	4.01, *t* (8.5)	78.2	4.04, *t* (8.5)	78.4	4.00, *t* (8.5)	78.3		
4	4.48, *m*	69.4	4.47, *m*	69.6	4.51, *m*	70.1		
5	4.32, *m*	76.3	4.31, *m*	76.5	4.24, *m*	76.0		
6	4.35, *m*	61.5	4.34, *m*	61.7	4.34, *m*	61.7		
Gal (1 → 2) GlcA								
1					5.86, *d* (7.5)	103.2	5.70, *d* (7.0)	103.4
2					4.49, *m*	73.7	4.49, *m*	73.7
3					4.47, *m*	78.3	4.53, *m*	75.0
4					4.47, *m*	69.6	4.55, *m*	70.1
5					4.35, *m*	76.3	4.27, *m*	76.4
6					4.44, *m*	61.9	4.43, *m*	61.8
Glc′ (1 → 2) GlcA								
1	6.02, *d* (8.0)	102.2	6.02, *d* (7.5)	102.4				
2	4.12, *dd* (8.0, 8.5)	72.6	4.10, *m*	72.8				

Table 1 (*continued*)

	1		**2**		**9**		**11**	
	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C
3	4.09, *t* (8.5)	77.0	4.09, *m*	77.2				
4	4.48, *m*	77.1	4.47, *m*	77.1				
5	4.47, *m*	78.0	4.44, *m*	78.2				
6	4.50, *m*	63.4	4.49, *m*	63.6				
	4.30, *m*		4.31, *m*					
Ara (1 → 3) GlcA								
1							5.70, *d* (7.0)	101.7
2							4.55, *m*	82.0
3							4.48, *m*	73.6
4							4.29, *m*	68.3
5							3.72, *t* (10.0)	65.6
							4.39, *m*	
Xyl (1 → 2) Ara								
1							5.02, *d* (7.5)	106.7
2							4.17, *m*	75.7
3							4.03, *m*	78.2
4							4.22, *m*	70.6
5							3.72, *t* (7.5)	67.4
							4.38, *m*	
21-OAc								
1						170.8		170.8
2					2.11, *s*	21.2	1.91, *s*	20.0

[a] Overlapped with other signals.

it belongs to the oleanane series. The assignment of hydroxyl group C-3 was confirmed from the HMBC correlations between H-1, H-2, H-23, H-24 and C-3. The two oxymethylene proton signals at δ_H 3.59 and 3.72, which correlated with the carbon resonance at δ_C 69.9 in the HSQC spectrum, showed HMBC correlations with C-16, C-17, C-18, and C-22, justifying its assignment to C-28. The HMBC correlations for H-9, H-10, H-18 with C-12, and H-10, H-18, H_3-27 with C-13 suggested the position of double bone in the triterpene core. A series of HMBC correlations from H_3-29 to C-19, C-20, C-21, and C-30, from H_3-30 to C-19, C-20, C-21, and C-29 allowed the connection of C-19, C-21, C-29, and C-30 to the quaternary carbon C-20 demonstrated that C-29 and C-30 were connected to the same carbon (C-20). From the foregoing evidences it was concluded that **1** possessed a 28-hydroxyolean-12-ene aglycone. In addition, the oxymethine proton signal at δ_H 4.61 (1H, *m*), which correlated with C-15 (δ_C 34.6) and C-17 (δ_C 40.7) in the HMBC spectrum, could be assigned to H-16. Comparison of the NMR spectroscopic data of **1** with those of aesculioside G1 (Yuan et al., 2012) established it to be a glycoside of an oxygenated 28-hydroxyolean-12-ene aglycone (Table 1).

Acid hydrolysis of **1** with 2 M HCl afforded monosaccharides, which were identified by GC analysis of their trimethylsilyl L-cysteine derivatives (Fu et al., 2011) as D-glucuronic acid, D-xylose, and D-glucose in a ratio of 1:1:2. On the basis of the coupling constants of anomeric protons and the chemical shifts of the anomeric carbons, the anomeric configurations of the sugar moieties were determined as β for glucuronic acid, xylcose, and glucose moieties. The sequence of the glycosidic chains in **1** was determined by the analysis of the 2D NMR spectroscopic data. The proton and protonated carbon signals in the NMR spectra of **1** were assigned unequivocally (Table 1) on the basis of TOCSY and HSQC spectroscopic analysis. HMBC correlation from GlcA-H1 (δ_H 4.85) to C-3 (δ_C 89.3) confirmed that the β-D-glucuronopyranosyl unit is located at C-3. Long-range correlations observed between the ^{1}H NMR resonances at δ_H 6.02 (Glc′-H-1) and the ^{13}C NMR signals at δ_C 78.1 (GlcA-C-2), between δ_H 5.70 (Xyl-H-1) and δ_C 84.7 (GlcA-C-3), and between δ_H 5.05 (Glc-H-1) and δ_C 83.7 (Xyl-C-2) indicated that the tetrasaccharide residue at C-3 of aglycone is β-D-glucopyranosyl-(1 → 2)-β-D-xylopyranosyl-(1 → 3)-[β-D-glucopyranosyl-(1 → 2)]-β-D-glucuronopyranoside. The relative configuration of **1** was deduced by analysis of the NOESY spectrum, which showed NOE correlations between the following proton pairs: H-3/H-5 and H-16/H-26. Thus, compound **1** was determined as 3-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-xylopyranosyl-(1 → 3)-[β-D-glucopyranosyl-(1 → 2)]-β-D-glucuronopyranosyl-olean-12-ene-16α,28-diol, and has been named gordonsaponin A.

Compound **2** was isolated as a white, amorphous powder. The HRESIMS peak at *m*/z 1129.5423 $[M + Na]^+$ indicated the molecular formula of **2** to be $C_{53}H_{86}O_{24}$, with one oxygen atom more than that of **1** (1113 $[M + Na]^+$). The structure of the sugar chain was determined to be the same as that of **1** by comparison of their ^{1}H and ^{13}C NMR spectroscopic data (Table 1). However, detailed comparison of the NMR data of **2** and **1** indicated that signals of an oxymethine (CH-15) of **2** replaced those of the methylene (CH_2-15) of **1** and that C-14 and C-16 of **2** were deshielded by $\Delta\delta_C$ 5.7 and 4.6 ppm as compared to those of **1**, respectively. These data suggested that **2** is a 15-oxygenated derivative of **1**, which was further confirmed by a HMBC experiment on **2**. In the HMBC spectrum of **2**, correlations from both H_3-27 and H-16 to C-15 (δ_C 67.5 ppm) confirmed that the additional hydroxyl group is located at C-15. In the NOESY spectrum of **2**, correlations between H-15 with H_3-26 and H_2-28, together with correlations between H-16 and H_2-28, were used to show that both hydroxyl groups at C-15 and C-16 have an α-oriented (Lu et al., 2000). Thus, compound **2** (gordonsaponin B) was elucidated as 3-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-xylopyranosyl-(1 → 3)-[β-D-glucopyranosyl-(1 → 2)]-β-D-glucuronopyranosyl-olean-12-ene-15α,16α,28-triol.

Compound **3** was isolated as a white, amorphous powder. Its molecular formula, $C_{58}H_{92}O_{26}$, was determined by HRESIMS (*m*/z 1227.5816 $[M + Na]^+$, calcd. for 1227.5823). The IR and NMR data of **3** were almost identical to those of **2** (see Section 4), except for signal corresponding to an additional angeloyl group [δ_H 1.82 (3H, *s*), 2.02 (3H, *d*, *J* = 7.0 Hz), and 5.83 (1H, *q*, *J* = 7.0 Hz); δ_C 167.9, 136.4, 129.3, 20.8, and 15.8] in the NMR spectrum of **3**. Additionally, HMBC correlations from H-22 (δ_H 6.19) to C-1′ (δ_C 167.9) indicated unambiguously that the angeloyloxy ester group is attached to C-22 of the aglycone. In the NOESY spectrum of **3**, a correlation between H-22 and H-18 indicated that the hydroxy

group at C-22 is an α-oriented. Thus, compound **3** (gordonsaponin C) was elucidated as 3-*O*-β-D-glucopyranosyl-(1 → 2)-α-L-xylopyranosyl-(1 → 3)-[β-D-glucopyranosyl-(1 → 2)]-β-D-glucuronopyranosyl-22α-angeloyloxyolean-12-ene-15α,16α,28-triol.

Compound **4** gave the same molecular formula as **1**, namely, $C_{53}H_{86}O_{23}$, as deduced by HRESIMS (*m*/z 1113.5466 $[M + Na]^+$, calcd. for 1113.5452). Acid hydrolysis of **4** afforded D-glucuronic acid, D-xylose, D-galactose, and D-glucose in a ratio of 1:1:1:1 through GC analysis. The NMR spectroscopic data of compound **4** were almost identical with those of **1** except that the glucose in **1** was replaced by a galactose moiety in **4** (see Section 4). The connectivity for the sugar residues was further confirmed from the following HMBC correlations: GlcA-H-1 (δ_H 4.87)/aglycone-C-3 (δ_C 89.5), Xyl-H-1 (δ_H 5.68)/GlcA-C-3 (δ_C 84.7), Glc-H-1 (δ_H 5.06)/Xyl-C-3 (δ_C 83.5), and Gal-H-1 (δ_H 5.85)/GlcA-C-2 (δ_C 78.9). Thus, compound **4** (gordonsaponin D) was elucidated as 3-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-xylopyranosyl-(1 → 3)-[β-D-galactopyranosyl-(1 → 2)]-β-D-glucuronopyranosyl-olean-12-ene-15α,16α,28-triol.

Compound **5** gave the same molecular formula as **2**, namely, $C_{53}H_{86}O_{24}$, as deduced by HRESIMS (*m*/z 1129.5411 $[M + Na]^+$, calcd. for 1129.5401). Acid hydrolysis of **5** afforded D-glucuronic acid, β-D-xylose, and β-D-galactose in a ratio of 1:1:2 through GC analysis. The NMR spectroscopic data of compound **5** were similar to those of **2** except that the glucose in **2** was replaced by a galactose in **5** (see Section 4). In addition, the D-galactose in **5** was assigned to C-2 of GlcA from the HMBC correlation between the H-1 (δ_H 5.85) of galactose and C-2 (δ_C 78.6) of GlcA. Thus, compound **5** (gordonsaponin E) was determined as 3-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-xylopyranosyl-(1 → 3)-[β-D-galactopyranosyl-(1 → 2)]-β-D-glucuronopyranosyl-olean-12-ene-16α,28-diol.

Compound **6** was isolated as a white, amorphous powder. The molecular formula $C_{55}H_{88}O_{25}$ was determined by HRESIMS (*m*/z 1171.5520 $[M + Na]^+$, calcd. for 1171.5507). Comparison of the ^1H and ^{13}C NMR spectroscopic data of **6** with those of **4** indicated that the signals of their sugar moieties were superimposable, suggesting the sugar structure at C-3 was the same as that in **4**. The ^1H and ^{13}C NMR spectroscopic data of the aglycone moiety in **6** were similar to those of **4** (see Section 4), except for additional resonances [δ_H 2.11 (3H, *s*); δ_C 169.7 and 21.8] assignable to an acetyl group in the NMR spectrum of **6**. In the HMBC spectrum of **6**, HMBC correlation from H-22 (δ_H 4.53) to C-1′ (δ_C 169.7) indicated unambiguously that the acetyl group is attached to C-22 of the aglycone. In the NOESY spectrum of **6**, a correlation between H-22 and H-18 indicated that the hydroxy group at C-22 is an α-oriented. Thus, compound **6** (gordonsaponin F) was determined as 3-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-xylopyranosyl-(1 → 3)-[β-D-galactopyranosyl-(1 → 2)]-β-D-glucuronopyranosyl-22α-acetoxyolean-12-ene-16α,28-diol.

Compound **7** had the molecular formula $C_{58}H_{92}O_{25}$, as deduced from the HRESIMS (*m*/z 1211.5805 $[M + Na]^+$, calcd. for 1211.5820). The NMR spectroscopic data of **7** resembled those of **6**, except that the acetyl group [δ_H 2.11 (3H, *s*); δ_C 169.7 and 21.8] in **6** was replaced by an angeloyl group [δ_H 1.94 (3H, *s*), 2.09 (3H, *d*, *J* = 6.5 Hz), and 5.87 (1H, *q*, *J* = 6.5 Hz); δ_C 168.0, 136.5, 129.3, 20.9, and 15.8] in **7** (see Section 4). In the HMBC spectrum of **7**, HMBC correlations from H-22 (δ_H 6.21) to C-1′ (δ_C 168.0) indicated unambiguously that the angeloyloxy ester group is attached to C-22 of the aglycone. In the NOESY spectrum of **7**, a correlation between H-22 and H-18 indicated that the hydroxy group at C-22 is an α-oriented. Thus, compound **7** (gordonsaponin G) was determined as 3-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-xylopyranosyl-(1 → 3)-[β-D-galactopyranosyl-(1 → 2)]-β-D-glucuronopyranosyl-22α-angeloyloxyolean-12-ene-16α,28-diol.

Compound **8** was isolated as a white, amorphous powder. The HRESIMS peak at *m*/z 1227.5795 $[M + Na]^+$ indicated the molecular formula of **8** to be $C_{58}H_{92}O_{26}$, with one oxygen atom more than that of **7** (1211 $[M + Na]^+$). The IR and NMR spectroscopic data of **8** were almost identical to those of **7** (see Section 4). However, detailed NMR analysies showed an additional hydroxy group at C-15 (δ_C 67.4 ppm). These data suggested that **8** is a 15-oxygenated derivative of **7**, which was further confirmed by HMBC and NOESY experiments on **8**. Thus, compound **8** (gordonsaponin H) was elucidated as 3-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-xylopyranosyl-(1 → 3)-[β-D-galactopyranosyl-(1 → 2)]-β-D-glucuronopyranosyl-22α-angeloyloxyolean 12-ene-15α,16α,28-triol.

Compound **9** was isolated as a white, amorphous powder. The molecular formula, $C_{60}H_{94}O_{28}$, was determined by HRESIMS (m/z 1285.5797 [M + Na]+, calcd. for 1285.5824). The IR and NMR spectroscopic data of 9 were almost identical to those of 8 (Table 1), except for an additional acetyl group [δ_H 2.11 (3H, s); δ_C 170.8 and 21.2] in the NMR spectrum of 9. These data suggested that 9 is an acetyl derivative of 8, which was confirmed by appropriate 2D NMR experiments on 9. In the 1H NMR spectrum of 9, H-21 was shielded by $\Delta\delta_H$ 3.79 ppm as compared to 8, indicating that the hydroxyl group is located at C-21 (δ_C 79.1) in 9. In the HMBC spectrum of 9, a long-range correlation from H-21 (δ_H 6.58) to the carbonyl carbon (δ_C 170.8) of the acetyl unit confirmed that the acetyl unit is attached to C-21. The vicinal coupling constant (10.0 Hz) between H-21 and H-22 indicated their trans-diaxial orientation, which was confirmed by NOESY cross-peaks of H-22/H2-28/H3-30 and H-21/H-19α/H3-27. Thus, compound 9 (gordonsaponin I) was elucidated as 3-O-β-D-glucopyranosyl-(1 → 2)-β-D-xylopyranosyl-(1 → 3)-[β-D-galactopyranosyl-(1 → 2)]-β-D-glucuronopyranosyl-21β-acetyl-22α-angeloyloxyolean 12-ene-15α,16α,28-triol.

Compound **10** was obtained as a white, amorphous power, and its positive-ion HRESIMS gave a quasimolecular ion peak at *m*/z 1327.5945 $[M + Na]^+$, which indicated the molecular formula to be $C_{62}H_{96}O_{29}$ (calcd. for $C_{62}H_{96}O_{29}Na$, *m*/z 1327.5929). The IR and NMR spectroscopic data of **10** were almost identical to those of **9** (see Section 4), except for an additional signals [δ_H 2.01 (3H, s); δ_C 170.3 and 20.7] assignable to an acetyl group in the NMR spectrum of **10**. These data suggested that **10** is an acetyl derivative of **9**, which was confirmed by appropriate 2D NMR experiments on **10**. In the HMBC spectrum of **10**, long-range correlations were observed between H-16 (δ_H 4.48) and acetyl carbonyl carbon (δ_C 170.3), between H-21 (δ_H 5.79) and acetyl carbonyl carbon (δ_C 170.8), and between H-22 (δ_H 6.23) and angeloyl carbonyl carbon (δ_C 167.5) indicated the two acetyl groups and the angeloyloxy ester group are attached to C-16, C-21, and C-22, respectively. In the NOESY spectrum of **10**, correlations between H-16 and H_2-28 and H_3-26 proved the acetyloxy at C-16 possesses an α-orientation. Thus, compound **10** (gordonsaponin J) was elucidated as 3-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-xylopyranosyl-(1 → 3)-[β-D-galactopyranosyl-(1 → 2)] -β-D-glucuronopyranosyl-16α,21β-diacetyl-22α-angeloyloxyolean 12-ene-15α,28-diol.

The molecular formula of **11**, $C_{59}H_{92}O_{26}$, was indicated from the HRESIMS peak at *m*/z 1239.5761 $[M + Na]^+$. The NMR data (Table 1) analysis of **11** indicated that **11** contained the same aglycone, the structure of sugar chain, and angeloyloxy ester group as gordonoside I, which has been reported previously (Fu et al., 2011). The only difference between **11** and gordonoside I is that there is an additional signals [δ_H 1.91 (3H, *s*); δ_C 170.8 and 20.0] assignable to an acetyl group in the NMR spectrum of **11**. These data suggested that **11** is an acetyl derivative of gordonoside I, which was confirmed by appropriate 2D NMR experiments on **11**. Acid hydrolysis of **11** afforded D-glucuronic acid, L-arabinose, D-xylose, and D-galactose in a ratio of 1:1:1:1 through GC analysis. In the HMBC spectrum of **11**, long-range correlations were observed between H-21 (δ_H 6.58) and acetyl carbonyl carbon (δ_C 170.8), and between H-22 (δ_H 6.30) and angeloyl carbonyl carbon (δ_C 168.2) indicated the acetyl group and the angeloyloxy ester group are attached to

C-21 and C-22, respectively. The vicinal coupling constant (10.0 Hz) between H-21 and H-22 indicated their trans-diaxial orientation, which was confirmed by NOESY cross-peaks of H-22/H_2-28/H_3-30 and H-21/H-19α/H_3-27. Thus, compound **11** (gordonsaponin K) was elucidated as 3-*O*-β-D-xylopyranosyl-(1 → 2)-α-L-arabinopyranosyl-(1 → 3)-[β-D-galactopyranosyl-(1 → 2)]-β-D-glucuronopyranosyl-21β-acetyl-22α-angeloyloxyolean-12-ene-16α,28-diol.

Compounds **1**–**11** were evaluated for their cytotoxic activities against five human cancer cell lines (HCT-8, Bel-7402, BGC-823, A549, and A2780) with paclitaxel as a positive control. Compounds obtained in this study were inactive (IC_{50} > 10 μM) to HCT-8, Bel-7402, BGC-823, A549, and A2780 cell lines, except that compound **11** showed activity against all tested cell lines, with IC_{50} values ranging from 0.1 to 2.41 μM.

3. Concluding remarks

Based on the cytotoxic activity shown by the *n*-BuOH part of 95% EtOH extract of the stems of *G. kwangsiensis*, as a result, 11 new compounds were isolated and identified from *n*-BuOH part of *G. kwangsiensis*. All of the isolated triterpenoid glycosides possessed an olean-12-ene skeleton and oligosaccharidic chains were made up of four monosaccharide units linked to C-3. These compounds were devoide of cytotoxicity except for compound **11**.

4. Experimental

4.1. General experimental procedures

Optical rotations were measured on a Perkin-Elmer 241 automatic digital polarimeter. UV spectra were recorded using a Shimadzu UV-300 spectrophotometer. IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer by a transmission microscope method. 1D and 2D NMR spectra were obtained at 500 and 125 MHz for ^1H and ^{13}C, respectively, on an INOVA 500 MHz spectrometer in pyridine-d_5 with solvent peaks as references. ESIMS was obtained using an Agilent 1100 series LC/MSD Trap SL mass spectrometer. HRESIMS was determined by an Agilent 6520 Accurate-Mass Q-TOF LC/MS spectrometer. GC was conducted using an Agilent Technologies 7890A instrument (Agilent). Preparative HPLC was carried on a Shimadazu LC-6AD instrument with a SPD-20A detector, using a YMC-Pack ODS-A column (250 × 20 mm, 5 μM). Column chromatography (CC) was performed with silica gel (200–300 mesh, Qingdao Marine Chemical Inc., Qingdao, People's Republic of China) and ODS (50 μM, YMC, Japan). TLC was carried out with glass precoated silica gel GF_{254} plates. Spots were visualized under UV light or by spraying with 10% sulfuric acid in EtOH followed by heating.

4.2. Plant material

Stems of *G. kwangsiensis* were collected at Xishuangbanna, Yunnan Province, China, in May 2010 and identified by Prof. Jingyun Cui (Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences). A voucher specimen (No. 21798) was deposited at the Institute of Materia Medica, Chinese Academy of Medical Sciences, Beijing 100050.

4.3. Extraction and isolation

Air-dried stems of *G. kwangsiensis* (9.80 kg) were extracted with 95% EtOH (3 × 30 L) at reflux for 3 × 3 h, and the extract was evaporated under reduced pressure to yield a dark brown residue (220.2 g). The latter was suspended in H_2O (2000 mL) and then individually partitioned with $CHCl_3$ (5 × 2500 mL), EtOAc (5 × 2400 mL), and *n*-BuOH (5 × 2000 mL), respectively. After removing the solvent, the *n*-BuOH-soluble portion (50.5 g) was fractionated via silica gel CC, eluting with $CHCl_3$–MeOH–H_2O (7:3:0.5), to afford ten fractions A_1–A_{10} on the basis of TLC analysis. Fraction A_5 (34.2 g) was further passed through a D101 macroporous resin column eluted with H_2O, H_2O–EtOH (9:1, v/v), H_2O–EtOH (7:3, v/v), H_2O–EtOH (1:1, v/v) and H_2O–EtOH (3:7, v/v), respectively. The H_2O (1:1, v/v) EtOH fraction (4.0 g) was separated by silica gel column chromatography using $CHCl_3$–MeOH–H_2O gradient mixtures (8:2:0.2–5:5:0.5) to afford seven fractions (B_1–B_7). Fraction B_5 (1.3 g) was subjected to an ODS CC (50 μM, 10–50% CH_3CN–H_2O) to afford ten subfractions. Subfraction 3 (150 mg) was separated by reversed-phase HPLC with 28% CH_3CN–H_2O containing 0.05% TFA (28:72, v/v) as mobile phase to yield compounds **1** (8 mg) and **4** (6 mg). Subfraction 5 (200 mg) was subjected to preparative HPLC (YMC-ODS-A 5 μM, 250 mm × 20 mm, detection at 210 nm) using CH_3CN–H_2O containing 0.05% TFA (3:7, v/v, 7 mL/min) as mobile phase to yield compounds **2** (10 mg), **5** (12 mg), and **6** (15 mg). Subfraction 6 (80 mg) was subjected to preparative HPLC (YMC-ODS-A 5 μM, 250 mm × 20 mm, detection at 210 nm) using CH_3CN–H_2O containing 0.05% TFA (31:69, v/v, 7 mL/min) as mobile phase to yield compounds **3** (11 mg), **7** (14 mg), and **8** (12 mg). The EtOH–H_2O (7:3, v/v) fraction (300 mg) was purified by preparative HPLC (YMC-ODS-A 5 μM, 250 mm × 20 mm, detection at 210 nm) using CH_3CN–H_2O containing 0.05% TFA (36:64, v/v, 7 mL/min) as mobile phase to yield compounds **9** (25 mg), **10** (20 mg), and **11** (13 mg).

4.4. Acid hydrolysis and sugar analysis

The absolute configuration of the sugars in compounds **1**–**11** were determined as described previously (Fu et al., 2008, 2011).

4.5. Cytotoxicity assay

Compounds **1–11** were tested for cytotoxicity against HCT-8 (human colon cancer cell line), Bel-7402 (human hepatoma cancer cell line), BGC-823 (human gastric cancer cell line), A549 (human lung cancer cell line), and A2780 (human ovarian cancer cell line) by means of the MTT method as described previously (Li et al., 2008).

4.6. Gordonsaponin A (*1*)

White, amorphous powder; $[\alpha]_D^{20}$ −8.0 (*c* 0.09, MeOH); UV (MeOH) λ_{max} (log ε) 206 (3.87), 251 (3.39) nm; IR ν_{max} 3360, 2941, 1672, 1430, 1373, 1199, 1137, 1078, 1045 cm^{-1}; hν^1H NMR (pyridine-d_5, 500 MHz) and ^{13}C NMR (pyridine-d_5, 125 MHz) spectroscopic data, see Table 1; (+)-ESIMS *m*/*z* 1113 $[M + Na]^+$; (−)-ESIMS *m*/*z* 1089 $[M - H]^-$; HRESIMS *m*/*z* 1113.5473 $[M + Na]^+$ (calcd. for $C_{53}H_{86}O_{23}Na$, 1113.5452).

4.7. Gordonsaponin B (*2*)

White, amorphous powder; $[\alpha]_D^{20}$ −5.2 (*c* 0.09, MeOH); UV (MeOH) λ_{max} (log ε) 206 (4.07), 254 (3.57) nm; IR ν_{max} 3380, 2946, 1673, 1431, 1373, 1201, 1139, 1080, 1046 cm^{-1}; hν^1H NMR (pyridine-d_5, 500 MHz) and ^{13}C NMR (pyridine-d_5, 125 MHz) spectroscopic data, see Table 1; (+)-ESIMS *m*/*z* 1129 $[M + Na]^+$; (+)-ESIMS *m*/*z* 1105 $[M + H]^+$; HRESIMS *m*/*z* 1129.5423 $[M + Na]^+$ (calcd. for $C_{53}H_{86}O_{24}Na$, 1129.5401).

4.8. Gordonsaponin C (*3*)

White, amorphous powder; $[\alpha]_D^{20}$ −2.2 (*c* 0.08, MeOH); UV (MeOH) λ_{max} (log ε) 206 (4.10) nm; IR ν_{max} 3378, 2926, 1681,

1458, 1378, 1246, 1201, 1142, 1077, 1043 cm^{-1}; ^1H NMR (pyridine-d_5, 500 MHz): Aglycone δ 0.73 (1H, *m*, H-5), 0.82 (3H, *s*, H-25), 1.01 (3H, *s*, H-26), 1.05 (3H, *s*, H-29), 1.06 (3H, *s*, H-24), 1.19 (3H, *s*, H-23), 1.27 (3H, *s*, H-30), 1.38 (1H, *m*, H-19b), 1.70 (1H, *m*, H-9), 1.81 (1H, *m*, H-11), 1.86 (3H, *s*, H-27), 2.04 (1H, *m*, H-21b), 2.78 (1H, *t*, *J* = 12.0 Hz, H-21a), 2.86 (1H, *t*, *J* = 14.5 Hz, H-19a), 3.02 (1H, *br d*, *J* = 14.5 Hz, H-18), 3.22 (1H, *br d*, *J* = 11.0 Hz, H-3), 3.62 (1H, *d*, *J* = 10.5 Hz, H-28b), 3.78 (1H, *d*, *J* = 10.5 Hz, H-28a), 4.25 (1H, *m*, H-15), 4.54 (1H, *m*, H-16), 5.46 (1H, *br s*, H-12), 6.19 (1H, *dd*, *J* = 5.0/12.0 Hz, H-22); Ang δ 1.82 (1H, *s*, H-5′), 2.02 (1H, *q*, *J* = 7.0 Hz, H-4′), 5.83 (1H, *q*, *J* = 7.0 Hz, H-3′); *Sugars:* GlcA δ 4.45 (1H, *m*, H-3), 4.48 (1H, *m*, H-4), 4.52 (1H, *m*, H-5), 4.65 (1H, *t*, *J* = 8.5 Hz, H-2), 4.83 (1H, *d*, *J* = 6.5 Hz, H-1), Xyl δ 3.41 (1H, *t*, *J* = 11.0 Hz, H-5b), 4.25 (1H, *t*, *J* = 8.0 Hz, H-3), 4.31 (1H, *m*, H-5a), 4.47 (1H, *m*, H-4), 4.51 (1H, *m*, H-2), 5.74 (1H, *br s*, H-1), Glc δ 4.01 (1H, *t*, *J* = 8.5 Hz, H-3), 4.31 (1H, *m*, H-5), 4.32 (1H, *m*, H-2), 4.36 (1H, *m*, H-6), 4.53 (1H, *m*, H-4), 5.02 (1H, *br s*, H-1), Glc′ δ 4.09 (1H, *t*, *J* = 9.0 Hz, H-3), 4.10 (1H, *dd*, *J* = 8.0/9.0 Hz, H-2), 4.33 (1H, *m*, H-6b), 4.45 (1H, *m*, H-6a), 4.46 (1H, *m*, H-5), 4.47 (1H, *m*, H-4), 6.00 (1H, *d*, *J* = 7.0 Hz, H-1); Aglycone δ 15.8 (C-25), 16.7 (C-24), 17.5 (C-26), 18.7 (C-6), 21.3 (C-27), 23.9 (C-11), 25.1 (C-30), 26.6 (C-2), 27.8 (C-23), 32.0 (C-20), 32.5 (C-7), 33.4 (C-29), 36.7 (C-10), 38.9 (C-1), 39.5 (C-8), 39.5 (C-4), 41.4 (C-18), 41.7 (C-21), 45.2 (C-17), 47.0 (C-9), 47.1 (C-14), 47.7 (C-19), 55.4 (C-5), 63.6 (C-28), 67.5 (C-15), 72.8 (C-22), 75.0 (C-16), 89.4 (C-3), 123.1 (C-12), 144.4 (C-13); Ang δ 15.8 (C-4′), 20.8 (C-5′), 129.3 (C-2′), 136.4 (C-3′), 167.9 (C-1′); *Sugars:* GlcA δ 71.1 (C-4), 76.9 (C-5), 78.7 (C-2), 84.5 (C-3), 105.5 (C-1), 172.5 (C-6), Xyl δ 67.6 (C-5), 70.5 (C-4), 76.4 (C-3), 83.7 (C-2), 101.8 (C-1), Glc δ 61.7 (C-6), 69.8 (C-4), 75.0 (C-2), 75.9 (C-5), 78.2 (C-3), 107.6 (C-1), Glc′ δ 62.9 (C-6), 72.7 (C-2), 77.1 (C-4), 77.2 (C-3), 78.4 (C-5), 102.4 (C-1); (+)-ESIMS *m*/z 1227 $[M + Na]^+$; (+)-ESIMS *m*/z 1205 $[M + H]^+$; HRESIMS *m*/z 1227.5816 $[M + Na]^+$ (calcd. for $C_{58}H_{92}O_{26}Na$, 1227.5823).

4.9. Gordonsaponin D (**4**)

White, amorphous powder; $[\alpha]_D^{20}$ −3.6 (*c* 0.12, MeOH); UV (MeOH) λ_{max} (log ε) 206 (3.92), 253 (3.77) nm; IR ν_{max} 3345, 2931, 1672, 1457, 1387, 1201, 1140, 1078, 1046 cm^{-1}; ^1H NMR (pyridine-d_5, 500 MHz): Aglycone δ 0.73 (1H, *m*, H-5), 0.80 (3H, *s*, H-25), 0.89 (3H, *s*, H-26), 1.02 (3H, *s*, H-29), 1.10 (6H, *s*, H-23, H-24), 1.27 (3H, *s*, H-30), 1.28 (1H, *m*, H-19b), 1.40 (1H, *m*, H-21), 1.68 (1H, *m*, H-9), 1.80 (3H, *s*, H-27), 1.82 (1H, *m*, H-11), 2.18 (1H, *m*, H-15), 2.24 (1H, *m*, H-22), 2.46 (1H, *br d*, *J* = 13.5 Hz, H-18), 2.70 (1H, *t*, *J* = 13.5 Hz, H-19a), 3.24 (1H, *dd*, *J* = 13.0 Hz, H-3), 3.58 (1H, *d*, *J* = 10.5 Hz, H-28b), 3.70 (1H, *d*, *J* = 10.5 Hz, H-28a), 4.60 (1H, *m*, H-16), 5.33 (1H, *br s*, H-12); *Sugars:* GlcA δ 4.42 (1H, *m*, H-3), 4.47 (1H, *m*, H-4), 4.47 (1H, *m*, H-5), 4.64 (1H, *t*, *J* = 8.5 Hz, H-2), 4.87 (1H, *d*, *J* = 7.5 Hz, H-1), Xyl δ 3.41 (1H, *t*, *J* = 12.0 Hz, H-5b), 4.08 (1H, *t*, *J* = 8.0 Hz, H-3), 4.25 (1H, *m*, H-4), 4.31 (1H, *m*, H-5a), 4.49 (1H, *dd*, *J* = 7.5/8.5 Hz, H-2), 5.68 (1H, *d*, *J* = 7.5 Hz, H-1), Glc δ 4.00 (1H, *t*, *J* = 8.5 Hz, H-3), 4.22 (1H, *dd*, *J* = 7.5/8.5 Hz, H-2), 4.32 (1H, *m*, H-6), 4.34 (1H, *m*, H-5), 4.47 (1H, *m*, H-4), 5.06 (1H, *d*, *J* = 7.5 Hz, H-1), Gal δ 4.36 (1H, *m*, H-5), 4.42 (1H, *m*, H-6), 4.48 (1H, *m*, H-3), 4.49 (1H, *m*, H-2), 4.52 (1H, *m*, H-4), 5.85 (1H, *d*, *J* = 7.5 Hz, H-1); Aglycone δ 15.6 (C-25), 16.7 (C-24), 16.9 (C-26), 18.4 (C-6), 23.7 (C-11), 24.7 (C-23), 26.3 (C-2), 27.3 (C-27), 28.0 (C-30), 30.5 (C-22), 31.3 (C-20), 33.1 (C-29), 33.4 (C-7), 34.7 (C-15), 36.7 (C-10), 37.1 (C-21), 38.7 (C-1), 39.5 (C-4), 39.9 (C-8), 40.9 (C-17), 41.9 (C-18), 42.4 (C-14), 46.9 (C-9), 48.3 (C-19), 55.7 (C-5), 69.6 (C-28), 74.2 (C-16), 89.5 (C-3), 123.1 (C-12), 145.1 (C-13); *Sugars:* GlcA δ 71.1 (C-4), 76.9 (C-5), 78.9 (C-2), 84.7 (C-3), 105.5 (C-1), 172.0 (C-6), Xyl δ 67.5 (C-5), 70.6 (C-4), 77.1 (C-3), 83.5 (C-2), 101.7 (C-1), Glc δ 61.6 (C-6), 70.1 (C-4), 75.0 (C-2), 76.0 (C-5), 78.2 (C-3), 107.4 (C-1), Gal δ 61.9 (C-6), 70.1 (C-4), 73.7 (C-2), 75.0 (C-3), 76.3 (C-5), 103.2 (C-1); (+)-ESIMS *m*/z 1113 $[M + Na]^+$; (-)-ESIMS *m*/z 1089 $[M - H]^-$; HRESIMS *m*/z 1113.5466 $[M + Na]^+$ (calcd. for $C_{53}H_{86}O_{23}Na$, 1113.5452).

4.10. Gordonsaponin E (**5**)

White, amorphous powder; $[\alpha]_D^{20}$ −6.4 (*c* 0.05, MeOH); UV (MeOH) λ_{max} (log ε) 206 (4.12), 252 (3.62) nm; IR ν_{max} 3392, 2945, 1672, 1431, 1374, 1201, 1139, 1080, 1047 cm^{-1}; ^1H NMR (pyridine-d_5, 500 MHz): Aglycone δ 0.76 (1H, *m*, H-5), 0.80 (3H, *s*, H-25), 1.03 (6H, *s*, H-26, H-29), 1.09 (3H, *s*, H-30), 1.11 (3H, *s*, H-24), 1.25 (3H, *s*, H-23), 1.31 (1H, *m*, H-19b), 1.80 (3H, *s*, H-27), 1.68 (1H, *m*, H-9), 1.81 (1H, *m*, H-21b), 1.83 (1H, *m*, H-11), 2.06 (1H, *m*, H-21a), 2.25 (1H, *m*, H-22), 2.43 (1H, *m*, H-18), 2.68 (1H, *m*, H-19a), 3.25 (1H, *dd*, *J* = 3.5/11.5 Hz, H-3), 3.59 (1H, *d*, *J* = 10.5 Hz, H-28b), 3.78 (1H, *d*, *J* = 10.5 Hz, H-28a), 4.46 (1H, *m*, H-15), 4.53 (1H, *m*, H-16), 5.42 (1H, *br s*, H-12); *Sugars:* GlcA δ 4.41 (1H, *m*, H-3), 4.48 (1H, *m*, H-5), 4.50 (1H, *m*, H-4), 4.64 (1H, *t*, *J* = 9.0 Hz, H-2), 4.87 (1H, *d*, *J* = 7.0 Hz, H-1), Xyl δ 3.41 (1H, *t*, *J* = 11.0 Hz, H-5b), 4.06 (1H, *t*, *J* = 8.0 Hz, H-3), 4.25 (1H, *m*, H-4), 4.31 (1H, *m*, H-5a), 4.53 (1H, *dd*, *J* = 6.5/8.5 Hz, H-2), 5.68 (1H, *d*, *J* = 6.5 Hz, H-1), Glc δ 4.00 (1H, *t*, *J* = 8.5 Hz, H-3), 4.22 (1H, *dd*, *J* = 7.5/8.5 Hz, H-2), 4.32 (1H, *m*, H-6), 4.38 (1H, *m*, H-5), 4.50 (1H, *m*, H-4), 5.07 (1H, *d*, *J* = 7.5 Hz, H-1), Gal δ 4.36 (1H, *m*, H-5), 4.42 (1H, *m*, H-6), 4.46 (1H, *m*, H-4), 4.47 (1H, *m*, H-2), 4.48 (1H, *m*, H-3), 5.85 (1H, *d*, *J* = 7.5 Hz, H-1); Aglycone δ 15.8 (C-25), 16.8 (C-24), 17.5 (C-26), 18.7 (C-6), 20.9 (C-27), 23.9 (C-11), 24.5 (C-30), 26.5 (C-2), 28.0 (C-23), 31.0 (C-22), 31.2 (C-20), 33.4 (C-7), 33.4 (C-29), 36.7 (C-10), 36.9 (C-21), 38.7 (C-1), 38.9 (C-8), 39.5 (C-4), 41.0 (C-18), 43.2 (C-17), 47.2 (C-9), 47.8 (C-19), 47.9 (C-14), 55.5 (C-5), 67.5 (C-15), 78.3 (C-16), 69.4 (C-28), 89.5 (C-3), 123.1 (C-12), 145.9 (C-13); *Sugars:* GlcA δ 71.0 (C-4), 76.3 (C-5), 78.6 (C-2), 84.9 (C-3), 105.5 (C-1), 172.0 (C-6), Xyl δ 67.3 (C-5), 70.8 (C-4), 77.1 (C-3), 83.7 (C-2), 101.8 (C-1), Glc δ 61.7 (C-6), 70.1 (C-4), 75.1 (C-2), 76.3 (C-5), 78.9 (C-3), 107.5 (C-1), Gal δ 62.0 (C-6), 69.5 (C-4), 73.5 (C-2), 74.8 (C-3), 76.1 (C-5), 103.2 (C-1); (+)-ESIMS *m*/z 1105 $[M + H]^+$; HRESIMS *m*/z 1129.5411 $[M + Na]^+$ (calcd. for $C_{53}H_{86}O_{24}Na$, 1129.5401).

4.11. Gordonsaponin F (**6**)

White, amorphous powder; $[\alpha]_D^{20}$ −8.6 (*c* 0.14, MeOH); UV (MeOH) λ_{max} (log ε) 206 (3.84), 253 (3.65) nm; IR ν_{max} 3361, 2975, 1658, 1530, 1438, 1179, 1152, 1080, 1046 cm^{-1}; ^1H NMR (pyridine-d_5, 500 MHz): Aglycone δ 0.65 (1H, *m*, H-5), 0.73 (3H, *s*, H-25), 1.00 (3H, *s*, H-29), 1.06 (3H, *s*, H-30), 1.08 (3H, *s*, H-24), 1.25 (3H, *s*, H-23), 1.22 (1H, *m*, H-19b), 1.45 (3H, *s*, H-27), 1.48 (3H, *s*, H-26), 1.56 (1H, *m*, H-9), 1.80 (1H, *m*, H-11), 1.80 (1H, *m*, H-21b), 2.05 (1H, *m*, H-21a), 2.14 (1H, *m*, H-18), 2.21 (1H, *m*, H-15), 2.43 (1H, *m*, H-19a), 3.22 (1H, *br d*, *J* = 11.5 Hz, H-3), 3.61 (1H, *d*, *J* = 11.0 Hz, H-28b), 4.00 (1H, *d*, *J* = 11.0 Hz, H-28a), 4.51 (1H, *m*, H-16), 4.53 (1H, *m*, H-22), 5.31 (1H, *br s*, H-12); *Sugars:* GlcA δ 4.48 (1H, *m*, H-3), 4.48 (1H, *m*, H-4), 4.49 (1H, *m*, H-5), 4.65 (1H, *t*, *J* = 8.5 Hz, H-2), 4.82 (1H, *d*, *J* = 7.5 Hz, H-1), Xyl δ 3.77 (1H, *t*, *J* = 10.5 Hz, H-5b), 4.05 (1H, *t*, *J* = 8.0 Hz, H-3), 4.28 (1H, *m*, H-4), 4.31 (1H, *m*, H-5a), 4.48 (1H, *m*, H-2), 5.71 (1H, *d*, *J* = 7.5 Hz, H-1), Glc δ 4.00 (1H, *t*, *J* = 8.5 Hz, H-3), 4.22 (1H, *m*, H-5), 4.23 (1H, *dd*, *J* = 8.0/8.5 Hz, H-2), 4.23 (1H, *m*, H-4), 4.36 (1H, *m*, H-6), 5.04 (1H, *d*, *J* = 8.0 Hz, H-1), Gal δ 4.35 (1H, *m*, H-5), 4.44 (1H, *m*, H-4), 4.44 (1H, *m*, H-6), 4.48 (1H, *m*, H-2), 4.49 (1H, *m*, H-3), 5.85 (1H, *d*, *J* = 7.5 Hz, H-1); 22-OAc δ 2.11 (3H, *s*); Aglycone δ 15.3 (C-25), 16.4 (C-24), 18.0 (C-26), 18.0 (C-6), 23.4 (C-11), 25.0 (C-30), 26.6 (C-27), 26.8 (C-2), 27.6 (C-23), 30.8 (C-7), 31.2 (C-20), 32.6 (C-15), 33.5 (C-29), 36.4 (C-10), 38.4 (C-1), 39.7 (C-8), 39.3 (C-4), 41.4 (C-18), 41.4 (C-14), 43.6 (C-17), 44.1 (C-21), 46.5 (C-9), 47.1 (C-19), 55.3 (C-5), 68.7 (C-28), 69.8 (C-16), 72.2 (C-22), 89.3

(C-3), 125.3 (C-12), 142.1 (C-13); *Sugars:* GlcA δ 71.6 (C-4), 76.8 (C-5), 78.6 (C-2), 84.3 (C-3), 105.3 (C-1), 171.8 (C-6), Xyl δ 67.2 (C-5), 70.8 (C-4), 76.9 (C-3), 83.3 (C-2), 101.5 (C-1), Glc δ 61.5 (C-6), 70.4 (C-4), 74.8 (C-2), 75.8 (C-5), 78.0 (C-3), 107.2 (C-1), Gal δ 61.8 (C-6), 69.4 (C-4), 73.5 (C-2), 74.8 (C-3), 76.1 (C-5), 102.9 (C-1), 22-OAc δ 21.8 (C-2), 169.7 (C-1); (+)-ESIMS *m*/*z* 1171 $[M + Na]^+$; HRESIMS *m*/*z* 1171.5520 $[M + Na]^+$ (calcd. for $C_{55}H_{88}O_{25}Na$, 1171.5507).

4.12. Gordonsaponin G (**7**)

White, amorphous powder; $[\alpha]_D^{20}$ −2.9 (*c* 0.10, MeOH); UV (MeOH) λ_{max} (log ε) 206 (3.80) nm; IR ν_{max} 3395, 2928, 1728, 1679, 1433, 1376, 1203, 1142, 1079, 1046 cm^{-1}; ^1H NMR (pyridine-d_5, 500 MHz): Aglycone δ 0.72 (1H, *m*, H-5), 0.77 (3H, *s*, H-25), 0.85 (3H, *s*, H-26), 1.04 (3H, *s*, H-29), 1.12 (3H, *s*, H-24), 1.28 (6H, *s*, H-23, H-30), 1.31 (1H, *m*, H-19b), 1.70 (1H, *m*, H-9), 1.84 (1H, *m*, H-11), 1.87 (3H, *s*, H-27), 2.04 (1H, *m*, H-21b), 2.31 (1H, *m*, H-15), 2.82 (1H, *m*, H-21a), 2.89 (1H, *t*, *J* = 13.5 Hz, H-19a), 3.04 (1H, *br d*, *J* = 13.5 Hz, H-18), 3.25 (1H, *br d*, *J* = 11.5 Hz, H-3), 3.42 (1H, *d*, *J* = 10.5 Hz, H-28b), 4.36 (1H, *d*, *J* = 10.5 Hz, H-28a), 4.64 (1H, *m*, H-16), 5.38 (1H, *br s*, H-12), 6.21 (1H, *dd*, *J* = 5.5/11.5 Hz, H-22); Ang δ 1.94 (1H, *s*, H-5′), 2.09 (1H, *q*, *J* = 6.5 Hz, H-4′), 5.87 (1H, *q*, *J* = 6.5 Hz, H-3′); *Sugars:* GlcA δ 4.47 (1H, *m*, H-3), 4.48 (1H, *m*, H-4), 4.49 (1H, *m*, H-5), 4.66 (1H, *m*, H-2), 4.86 (1H, *br s*, H-1), Xyl δ 3.42 (1H, *t*, *J* = 10.5 Hz, H-5b), 4.08 (1H, *t*, *J* = 8.5 Hz, H-3), 4.36 (1H, *m*, H-4), 4.36 (1H, *m*, H-5a), 4.52 (1H, *dd*, *J* = 7.0/8.5 Hz, H-2), 5.72 (1H, *d*, *J* = 7.0 Hz, H-1), Glc δ 4.02 (1H, *t*, *J* = 8.5 Hz, H-3), 4.25 (1H, *dd*, *J* = 7.5/8.5 Hz, H-2), 4.25 (1H, *m*, H-5), 4.27 (1H, *m*, H-4), 4.36 (1H, *m*, H-6), 5.08 (1H, *d*, *J* = 7.5 Hz, H-1), Gal δ 4.37 (1H, *m*, H-5), 4.45 (1H, *m*, H-6), 4.47 (1H, *m*, H-3), 4.51 (1H, *m*, H-2), 4.53 (1H, *m*, H-4), 5.87 (1H, *d*, *J* = 6.5 Hz, H-1); Aglycone δ 15.6 (C-25), 16.7 (C-24), 16.8 (C-26), 18.4 (C-6), 23.8 (C-11), 25.2 (C-30), 26.5 (C-2), 27.6 (C-27), 28.0 (C-23), 32.1 (C-20), 33.1 (C-7), 33.5 (C-29), 35.1 (C-15), 36.7 (C-10), 38.7 (C-1), 39.6 (C-4), 40.1 (C-8), 40.9 (C-18), 41.6 (C-14), 41.7 (C-21), 44.8 (C-17), 46.9 (C-9), 47.4 (C-19), 55.7 (C-5), 63.6 (C-28), 70.1 (C-16), 89.5 (C-3), 73.0 (C-22), 123.1 (C-12), 143.7 (C-13); Ang δ 15.8 (C-4′), 20.9 (C-5′), 129.3 (C-2′), 136.5 (C-3′), 168.0 (C-1′); *Sugars:* GlcA δ 71.1 (C-4), 76.9 (C-5), 79.0 (C-2), 84.7 (C-3), 105.5 (C-1), 172.5 (C-6), Xyl δ 67.6 (C-5), 70.7 (C-4), 77.1 (C-3), 83.7 (C-2), 101.8 (C-1), Glc δ 61.7 (C-6), 70.2 (C-4), 75.0 (C-2), 76.0 (C-5), 78.3 (C-3), 107.3 (C-1), Gal δ 62.0 (C-6), 69.8 (C-4), 73.8 (C-2), 75.1 (C-3), 76.3 (C-5), 103.2 (C-1); (+)-ESIMS *m*/*z* 1187 $[M + Na]^+$; (−)-ESIMS *m*/*z* 1211 $[M - H]^-$; HRESIMS *m*/*z* 1211.5805 $[M + Na]^+$ (calcd. for $C_{58}H_{92}O_{25}Na$, 1211.5820).

4.13. Gordonsaponin H (**8**)

White, amorphous powder; $[\alpha]_D^{20}$ −0.5 (*c* 0.13, MeOH); UV (MeOH) λ_{max} (log ε) 206 (3.64); IR ν_{max} 3396, 2933, 1679, 1432, 1377, 1201, 1141, 1079, 1045 cm^{-1}; ^1H NMR (pyridine-d_5, 500 MHz): Aglycone δ 0.78 (1H, *m*, H-5), 0.81 (3H, *s*, H-25), 1.00 (3H, *s*, H-26), 1.04 (3H, *s*, H-29), 1.08 (3H, *s*, H-24), 1.27 (6H, *s*, H-23, H-30), 1.30 (1H, *m*, H-19b), 1.69 (1H, *m*, H-9), 1.78 (1H, *m*, H-11), 1.85 (3H, *s*, H-27), 2.04 (1H, *m*, H-21b), 2.79 (1H, *m*, H-21a), 2.86 (1H, *t*, *J* = 13.0 Hz, H-19a), 3.01 (1H, *br d*, *J* = 13.5 Hz, H-18), 3.24 (1H, *br d*, *J* = 11.5 Hz, H-3), 3.62 (1H, *d*, *J* = 10.0 Hz, H-28b), 3.76 (1H, *d*, *J* = 10.0 Hz, H-28a), 4.33 (1H, *m*, H-15), 4.53 (1H, *m*, H-16), 5.48 (1H, *br s*, H-12), 6.18 (1H, *dd*, *J* = 5.5/11.5 Hz, H-22); Ang δ 1.82 (1H, *s*, H-5′), 2.02 (1H, *q*, *J* = 7.0 Hz, H-4′), 5.83 (1H, *q*, *J* = 7.0 Hz, H-3′); *Sugars:* GlcA δ 4.47 (1H, *m*, H-5), 4.50 (1H, *m*, H-3), 4.51 (1H, *m*, H-4), 4.66 (1H, *t*, *J* = 8.0 Hz, H-2), 4.86 (1H, *d*, *J* = 5.5 Hz, H-1), Xyl δ 3.42 (1H, *t*, *J* = 10.0 Hz, H-5b), 4.07 (1H, *t*, *J* = 8.0 Hz, H-3), 4.26 (1H, *m*, H-5a), 4.28 (1H, *m*, H-4), 4.50 (1H, *m*, H-2), 5.68 (1H, *d*, *J* = 6.0 Hz, H-1), Glc δ 4.00 (1H, *t*, *J* = 8.5 Hz, H-3), 4.23 (1H, *dd*, *J* = 6.0/8.5 Hz, H-2), 4.24 (1H, *m*, H-5), 4.34 (1H, *m*, H-6), 4.51 (1H, *m*, H-4), 5.09 (1H, *d*, *J* = 6.0 Hz, H-1), Gal δ 4.35 (1H, *m*, H-5), 4.44 (1H, *m*, H-6), 4.47 (1H, *m*, H-3), 4.47 (1H, *m*, H-4), 4.49 (1H, *m*, H-2), 5.86 (1H, *d*, *J* = 7.5 Hz, H-1); Aglycone δ 15.8 (C-25), 16.8 (C-24), 17.5 (C-26), 18.8 (C-6), 21.3 (C-27), 23.9 (C-11), 25.1 (C-30), 26.6 (C-2), 28.0 (C-23), 32.0 (C-20), 33.4 (C-29), 36.7 (C-7), 36.7 (C-10), 38.9 (C-1), 39.5 (C-4), 39.5 (C-8), 41.4 (C-18), 41.7 (C-21), 45.2 (C-17), 47.0 (C-9), 47.1 (C-14), 47.7 (C-19), 55.5 (C-5), 62.9 (C-28), 67.4 (C-15), 72.7 (C-22), 75.0 (C-16), 89.4 (C-3), 123.1 (C-12), 144.4 (C-13); Ang δ 15.8 (C-4′), 20.8 (C-5′), 129.3 (C-2′), 136.4 (C-3′), 167.9 (C-1′); *Sugars:* GlcA δ 71.0 (C-4), 76.9 (C-5), 79.0 (C-2), 84.8 (C-3), 105.2 (C-1), 172.1 (C-6), Xyl δ 67.5 (C-5), 70.7 (C-4), 77.1 (C-3), 83.4 (C-2), 101.9 (C-1), Glc δ 61.7 (C-6), 70.2 (C-4), 75.0 (C-2), 76.3 (C-5), 78.3 (C-3), 107.4 (C-1), Gal δ 62.0 (C-6), 69.8 (C-4), 73.8 (C-2), 75.1 (C-3), 76.2 (C-5), 103.2 (C-1); (+)-ESIMS *m*/*z* 1227 $[M + Na]^+$; (−)-ESIMS *m*/*z* 1203 $[M - H]^-$; HRESIMS *m*/*z* 1227.5795 $[M + Na]^+$ (calcd. for $C_{58}H_{92}O_{26}$ Na, 1227.5823).

4.14. Gordonsaponin I (**9**)

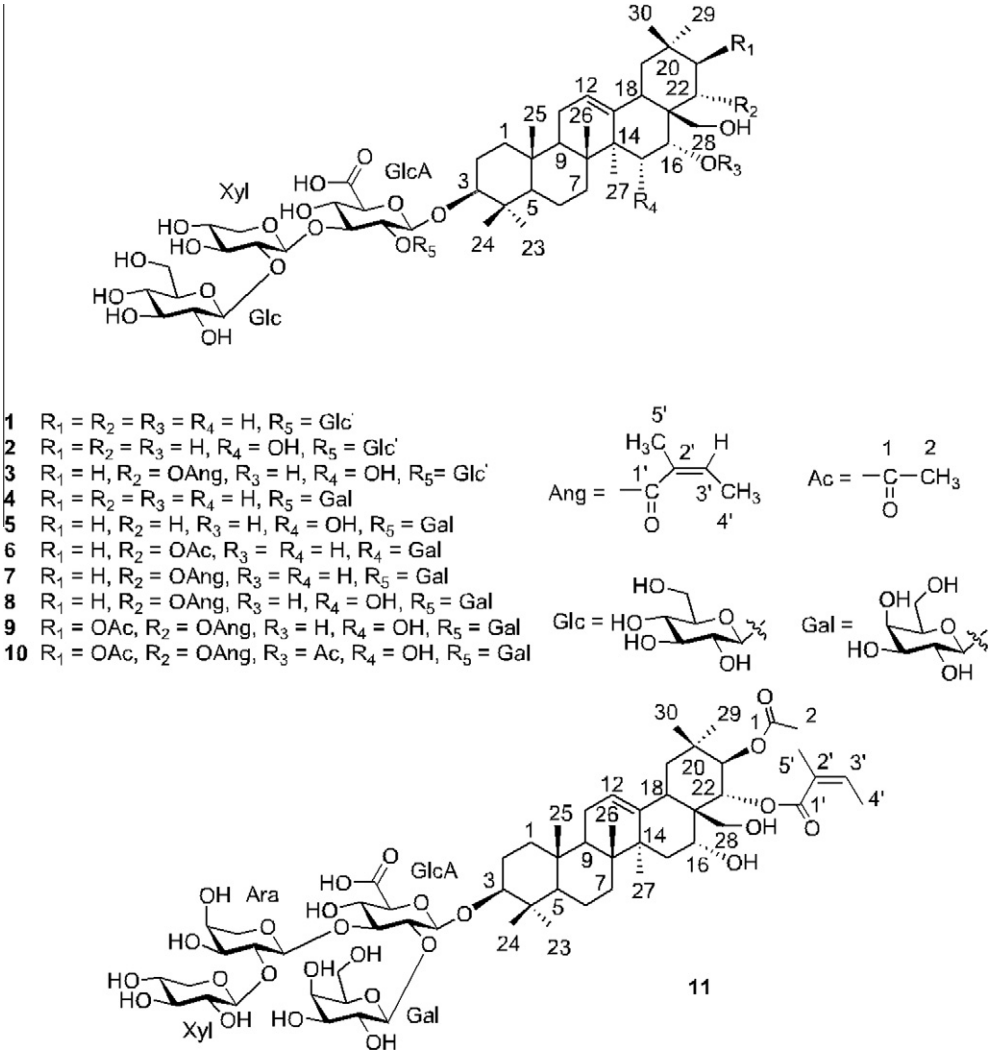
White, amorphous powder; $[\alpha]_D^{20}$ −13.8 (*c* 0.13, MeOH); UV (MeOH) λ_{max} (log ε) 206 (4.04), 251 (3.71) nm; IR ν_{max} 3359, 2947, 1676, 1432, 1375, 1202, 1139, 1080, 1047 cm^{-1}; ^1H NMR (pyridine-d_5, 500 MHz) and ^{13}C NMR (pyridine-d_5, 125 MHz) are given in Table 1; (+)-ESIMS *m*/*z* 1285 $[M + Na]^+$; (−)-ESIMS *m*/*z* 1261 $[M - H]^-$; HRESIMS *m*/*z* 1285.5797 $[M + Na]^+$ (calcd. for $C_{60}H_{94}O_{28}Na$, 1285.5824).

4.15. Gordonsaponin J (**10**)

White, amorphous powder; $[\alpha]_D^{20}$ −24.8 (*c* 0.05, MeOH); UV (MeOH) λ_{max} (log ε) 204 (4.08) nm; IR ν_{max} 2975, 1655, 1531, 1438, 1179, 1152, 1131, 1015 cm^{-1}; ^1H NMR (pyridine-d_5, 500 MHz): Aglycone δ 0.74 (3H, *s*, H-25), 0.78 (1H, *m*, H-5), 0.94 (3H, *s*, H-26), 1.05 (3H, *s*, H-29), 1.13 (3H, *s*, H-24), 1.25 (6H, *s*, H-23, H-30), 1.47 (1H, *m*, H-19b), 1.74 (1H, *m*, H-9), 1.79 (3H, *s*, H-27), 1.85 (1H, *m*, H-11), 2.37 (1H, *m*, H-18), 2.68 (1H, *m*, H-19a), 3.28 (1H, *br d*, *J* = 11.5 Hz, H-3), 3.53 (1H, *d*, *J* = 10.0 Hz, H-28b), 3.74 (1H, *d*, *J* = 10.0 Hz, H-28a), 4.38 (1H, *m*, H-15), 4.48 (1H, *m*, H-16), 5.51 (1H, *br s*, H-12), 5.79 (1H, *d*, *J* = 10.5 Hz, H-21), 6.23 (1H, *d*, *J* = 10.5 Hz, H-22); Ang δ 2.00 (1H, *s*, H-5′), 2.09 (1H, *q*, *J* = 7.0 Hz, H-4′), 5.86 (1H, *q*, *J* = 7.5 Hz, H-3′); *Sugars:* GlcA δ 4.38 (1H, *m*, H-3), 4.49 (1H, *m*, H-5), 4.50 (1H, *m*, H-4), 4.68 (1H, *t*, *J* = 8.5 Hz, H-2), 4.87 (1H, *d*, *J* = 7.5 Hz, H-1), Xyl δ 3.54 (1H, *t*, *J* = 10.5 Hz, H-5b), 4.08 (1H, *t*, *J* = 8.5 Hz, H-3), 4.28 (1H, *m*, H-4), 4.38 (1H, *m*, H-5a), 4.50 (1H, *m*, H-2), 5.70 (1H, *d*, *J* = 8.0 Hz, H-1), Glc δ 4.00 (1H, *t*, *J* = 8.5 Hz, H-3), 4.23 (1H, *m*, H-5), 4.23 (1H, *dd*, *J* = 7.5/8.5 Hz, H-2), 4.37 (1H, *m*, H-6), 4.48 (1H, *m*, H-4), 5.07 (1H, *d*, *J* = 7.5 Hz, H-1), Gal δ 4.35 (1H, *m*, H-5), 4.44 (1H, *m*, H-6), 4.46 (1H, *m*, H-4), 4.47 (1H, *m*, H-3), 4.49 (1H, *m*, H-2), 5.86 (1H, *d*, *J* = 7.5 Hz, H-1); 16-OAc δ 2.44 (3H, *s*), 21-OAc δ 2.01 (3H, *s*); Aglycone δ 15.7 (C-25), 16.7 (C-24), 17.5 (C-26), 18.7 (C-6), 19.5 (C-30), 21.7 (C-27), 23.9 (C-11), 26.6 (C-2), 28.0 (C-23), 29.4 (C-29), 36.0 (C-7), 36.7 (C-10), 36.7 (C-20), 38.9 (C-1), 39.4 (C-8), 39.5 (C-4), 41.6 (C-18), 45.4 (C-17), 47.0 (C-14), 47.2 (C-19), 47.5 (C-9), 55.3 (C-5), 63.3 (C-28), 66.8 (C-15), 72.0 (C-22), 75.1 (C-16), 78.3 (C-21), 89.4 (C-3), 126.4 (C-12), 142.3 (C-13); Ang δ 15.8 (C-4′), 20.9 (C-5′), 129.0 (C-2′), 137.7 (C-3′), 167.5 (C-1′); *Sugars:* GlcA δ 71.0 (C-4), 77.0 (C-5), 78.9 (C-2), 84.5 (C-3), 105.5 (C-1), 172.0 (C-6), Xyl δ 67.8 (C-5), 70.7 (C-4), 77.2 (C-3), 83.6 (C-2), 101.8 (C-1), Glc δ 61.7 (C-6), 70.2 (C-4), 75.1 (C-2), 76.1 (C-5), 79.2 (C-3), 107.5 (C-1), Gal δ 62.0 (C-6), 69.7 (C-4), 73.8 (C-2), 76.3 (C-3), 78.3 (C-5), 103.2 (C-1), 16-OAc δ 21.9 (C-2), 170.8 (C-1), 21-OAc δ 20.7 (C-2), 170.3 (C-1); (+)-ESIMS *m*/*z* 1327 $[M + Na]^+$; HRESIMS *m*/*z* 1327.5945 $[M + Na]^+$ (calcd. for $C_{62}H_{96}O_{29}Na$, 1327.5929).

4.16. Gordonsaponin K (**11**)

White, amorphous powder; $[\alpha]_D^{20}$ −9.0 (*c* 0.08, MeOH); UV (MeOH) λ_{max} (logε) 206 (4.02) nm; IR ν_{max} 3400, 2928, 1679, 1443, 1374, 1205, 1144, 1079, 1047 cm^{-1}; hν^{1}H NMR (pyridine-d_5, 500 MHz) and ^{13}C NMR (pyridine-d_5, 125 MHz) spectroscopic data see Table 1; (+)-ESIMS *m*/*z* 1239 $[M + Na]^+$; HRESIMS *m*/*z* 1239.5761 $[M + Na]^+$ (calcd. for $C_{59}H_{92}O_{26}Na$, 1239.5769).



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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.phytochem.2012.08.019.

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