Notes

Cytotoxic Acylated Triterpene Saponins from the Husks of *Xanthoceras sorbifolia*

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Four new oleanane-type triterpene saponins, xanifolia-Y_0 (**1**), xanifolia-Y_2 (**2**), xanifolia-Y_3 (**3**), and xanifolia-Y_7 (**4**), were isolated from the husks of *Xanthoceras sorbifolia* along with two known analogues, xanifolia-Y_8 (**5**) and xanifolia-Y_{10} (**6**). The structures of **1**−**4** were determined by spectroscopic data interpretation and chemical degradation. Compounds **1**−**6** were evaluated for their cell-growth inhibition activity toward human ovarian cancer cells (OVCAR3) by a MTT assay, and the IC_{50} values ranged from 4 to 13 μM. On the basis of the results obtained, it is concluded that a C-3 trisaccharide with a galactose and acylation with an angeloyl group at both C-21 and C-22 are important for cell inhibition activity for this class of compounds.

Xanthoceras sorbifolia Bunge (Sapindaceae) grows commonly in the Inner Mongolia region of mainland China and has been used as a folk medicine for various diseases, including rheumatism and enuresis in children. It has been shown that an extract from the husk of *X. sorbifolia* has cytotoxicity toward various human cancer cell lines.[1] A major active compound (xanifolia-Y) has been purified from this species and its chemical structure determined as an oleanane-type triterpenoid saponin with angeloyl groups attached to C-21 and C-22 and a trisaccharide unit attached to C-3. By comparing activities of compounds similar to xanifolia-Y and its acid- and alkaline-hydrolyzed derivatives, it was found that the angeloyl groups are necessary for cytotoxic activity.[2] Other functional groups that may contribute to the activity of this compound have not yet been investigated. The current study describes a series of related compounds (**1**−**6**) from the same plant, of which **1**−**4** are new, and investigates their structure−cytotoxic activity relationships.

From an active extract of *X. sorbifolia*, four new triterpene saponins (**1**−**4**) together with two known analogues were isolated. The known triterpene saponins were identified as 3-*O*-[β-D-glucopyranosyl-(1→2)]-α-L-arabinofuranosyl-(1→3)-β-D-glucuronopyranosyl-21β,22α-*O*-diangeloylprotoaescigenin (xanifolia-Y_8, **5**) and 3-*O*-[β-D-galactopyranosyl-(1→2)]-α-L-arabinofuranosyl-(1→3)-β-D-glucuronopyranosyl-21,22-*O*-diangeloyl-3β,16α,21β,22α,28-pentahydroxyolean-12-ene (xanifolia-Y_{10}, **6**), by comparing their spectroscopic data obtained with those reported in the literature.[3]

Compound **1** was obtained as an amorphous powder. It was assigned a molecular formula of $C_{55}H_{88}O_{23}$ on the basis of its HRMALDIMS at *m/z* 1151.5557 $[M + Na]^+$ (calcd 1151.5614), as well as its NMR spectroscopic data (Tables 1 and 2). In its MALDIMS, three quasimolecular ion peaks at *m/z* 1151 $[M + Na]^+$, 1173 $[M + 2Na - H]^+$, and 1189 $[M + Na + K - H]^+$ were displayed. The ^1H and ^{13}C NMR data of **1** revealed it to be a glycosidic derivative of R_1-barrigenol.[4] The NMR data indicated the presence of an angeloyl ester group and an isobutyryl ester group.[4,5] The angeloyl ester group and the isobutyryl ester group were located at C-21 and C-22, respectively, on the basis of the long-range proton−carbon correlations observed between signals at δ_H 6.67 (1H, d, J = 10.2 Hz, H-21) and δ_C 167.4 (Ang-1), as well as those between δ_H 6.24 (1H, d, J = 10.2 Hz, H-22) and δ_C 176.6 (i-Bu-1). The sugar part of **1** was found to consist of three monosaccharide residues, identified as β-glucuronic acid, β-galactose,[6] and α-arabinofuranose,[7] from its NMR spectroscopic data. In the HMBC spectrum, long-range correlations between δ_H 4.89 (GlcA-1) and δ_C 89.6 (C-3), between δ_H 5.36 (Gal-1) and δ_C 78.6 (Glc A-2), and between δ_H 6.06 (Ara-*f*-1) and δ_C 86.1 (Glc A-3) were observed. The absolute configuration of each monosaccharide was confirmed by acid hydrolysis and GC-MS analysis following conversion to the trimethylsilyl thiazolidine derivatives.[6,8] Thus, a trisaccharide unit of [β-D-galactopyranosyl-(1→2)]-α-L-arabinofuranosyl-(1→3)-β-D-glucuronopyranoside was attached to the C-3 position of R_1-barrigenol through a glycosidic linkage. On the basis of this evidence, compound **1** (xanifolia-Y_0) was characterized as 3-*O*-[β-D-galactopyranosyl-(1→2)]-α-L-arabinofuranosyl-(1→3)-β-D- glucuronopyranosyl-21-*O*-angeloyl-22-*O*-isobutyryl-3β,15α,16α,21β,22α,28-hexahydroxyolean-12-ene.

Compound **2** was obtained as an amorphous powder with a molecular formula of $C_{57}H_{88}O_{24}$, as determined from its HRESIMS at *m/z* 1179.5548 $[M + Na]^+$ (calcd 1179.5558). The MALDIMS exhibited three quasimolecular ion peaks at *m/z* 1179 $[M + Na]^+$, 1201 $[M + 2Na - H]^+$, and 1217 $[M + Na + K - H]^+$. The ^{13}C NMR data of **2** were identical to those of 21,22-di-*O*-angeloyl-24-hydroxy-R_1-barrigenol except for the C-3 and the sugar moieties,[9] leading to its assignment as a glycoside of 21,22-di-*O*-angeloyl-24-hydroxy-R_1-barrigenol. The NMR data (Tables 1 and 2) indicated the presence of two angeloyl ester groups, and their locations at the C-21 and C-22 positions were confirmed by HMBC correlations observed between signals at δ_H 6.69 (d, J = 10.2 Hz, H-21) and δ_C 167.5 (21-*O*-Ang-1), as well as between resonance at δ_H 6.30 (d, J = 10.2 Hz, H-22) and δ_C 167.9 (22-*O*-Ang-1). The monosaccharide residues of the sugar part were identified as β-glucopyranose, α-arabinofuranose, and β-glucuronopyranose, by comparison of their NMR data with those reported in the literature.[10] Thus, three anomeric carbons at δ_C 104.5, 103.7, and 110.1 correlated with three anomeric protons at δ_H 4.87 (d, J = 7.2 Hz), 5.48 (d, J = 7.8 Hz), and 6.05 (brs) in the HMQC spectrum. The sequence of the sugars was established by application of the HMBC

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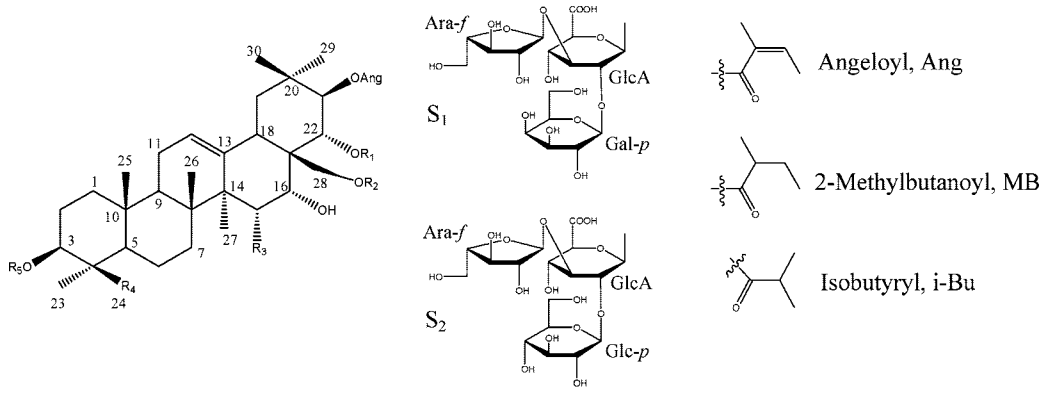

	R_1	R_2	R_3	R_4	R_5
1	i-Bu	H	OH	H	S_1
2	Ang	H	OH	OH	S_2
3	Ang	H	OH	H	S_1
4	H	MB	OH	H	S_1
5	Ang	H	H	OH	S_2
6	Ang	H	H	H	S_1

Table 1. ^{1}H NMR Spectroscopic Data (600 MHz, pyridine-d_5) for Compounds **1**−**4**

position	**1**	**2**	**3**	**4**
1	0.85, 1.41	0.83, 1.36	0.83, 1.40	0.87, 1.45
2	1.86, 2.16	1.89, 2.25	1.81, 2.14	1.86, 2.15
3	3.27	3.39	3.25	3.25
5	0.77	0.87	0.78	0.88
6	1.39, 1.51	1.31, 1.57	1.55, 1.59	1.39, 1.52
7	2.05, 2.17	1.97, 2.12	2.00, 2.10	2.08, 2.16
9	1.65	1.63	1.69	1.73
11	1.68, 1.88	1.69, 1.89	1.74, 1.89	1.86, 1.92
12	5.50, br s	5.48, br s	5.49, br s	5.55, br s
15	4.23	4.18	4.21	4.28
16	4.46	4.43	4.45	4.65
18	3.05	3.06	3.07	2.88
19	1.42, 3.09	1.40, 3.08	1.41, 3.06	1.43, 3.12
21	6.67, d (10.2)	6.69, d (10.2)	6.71, d (10)	6.58, d (11.2)
22	6.24, d (10.2)	6.30, d (10.2)	6.32, d (10)	4.51, d (11.2)
23	1.30, s	1.29, s	1.26, s	1.28, s
24	1.12, s	3.28; 4.32	1.16, s	1.11, s
25	0.85, s	0.64, s	0.81, s	0.85, s
26	0.99, s	0.94, s	0.99, s	1.19, s
27	1.86	1.84, s	1.85, s	1.88, s
28	3.47, d (10.2); 3.75, d (10.2)	3.48, d (10.6); 3.72, d (10.6)	3.50, d (11.0); 3.76, d (11.0)	4.38
29	1.03, s	1.09, s	1.09, s	1.17, s
30	1.32, s	1.32, s	1.32, s	1.33, s
	21-*O*-Ang	21-*O*-Ang	21-*O*-Ang	21-*O*-Ang
3	6.06	5.95, q (7.2)	5.96, q (7.0)	5.92, q (7.2)
4	2.16, d (7.2)	2.08, d (7.2)	2.10, d (7.0)	2.07, d (7.2)
5	2.05, s	2.00, s	2.00, s	2.00, s
	i-Bu	22-*O*-Ang	22-*O*-Ang	MB
2	2.33, m			2.40, m
3	1.03, d (7.2)	5.76, q (7.2)	5.78, q (7.0)	1.46, 1.68
4	1.00, d (7.2)	1.95, d (7.2)	1.93, d (7.0)	0.87
5		1.74, s	1.74, s	1.10 d (7.2)
	GlcA-*p*	GlcA-*p*	GlcA-*p*	GlcA-*p*
1	4.89, d (7.2)	4.87, d (7.2)	4.89, d (7.8)	4.92, d (7.2)
2	4.32, m	4.31, m	4.38, m	4.41, m
3	4.23, m	4.23, m	4.20, m	4.20, m
4	4.46, m	4.45, m	4.42, m	4.45, m
5	4.54, m	4.53, m	4.52, m	4.51, m
	Gal-*p*	Glc-*p*	Gal-*p*	Gal-*p*
1	5.36, d (7.2)	5.48, d (7.8)	5.32, d (7.7)	5.35, d (7.8)
2	4.42, m	4.02, m	4.42, m	4.48, m
3	4.12, m	4.31, m	4.10, m	4.10, m
4	4.55, m	4.52, m	4.56, m	4.59, m
5	3.97, m	3.62, m	3.94, m	3.97, m
6	4.43, m; 4.55, m	4.33, m; 4.50, m	4.43, m; 4.52,m	4.45, m; 4.55, m
	Ara-*f*	Ara-*f*	Ara-*f*	Ara-*f*
1	6.06, br s	6.05, br s	6.03, br s	6.07, br s
2	4.97, m	4.97, m	4.94, m	4.96, m
3	4.80, m	4.74, m	4.78, m	4.55, m
4	4.85, m	4.84, m	4.82, m	4.82, m
5	4.18, m; 4.34, m	4.18, m; 4.33, m	4.12, m; 4.28, m	4.15, m; 4.33, m

Table 2. ^{13}C NMR Spectroscopic Data (150 MHz, pyridine-d_5) for Compounds **1**−**4**

position	**1**	**2**	**3**	**4**
1	38.7, CH_2	38.4, CH_2	38.7, CH_2	38.8, CH_2
2	26.5, CH_2	26.4, CH_2	26.4, CH_2	26.4, CH_2
3	89.6, CH	91.3, CH	89.6, CH	89.7, CH
4	39.4, qC	43.4, qC	39.4, qC	39.4, qC
5	55.4, CH	56.7, CH	55.3, CH	55.4, CH
6	18.6, CH_2	18.6, CH_2	18.5, CH_2	18.6, CH_2
7	36.5, CH_2	36.3, CH_2	36.5, CH_2	36.4, CH_2
8	42.2, qC	40.7, qC	41.2, qC	41.2, qC
9	46.9, CH	46.7, CH	47.0, CH	47.0, CH
10	36.9, qC	36.6, qC	37.2, qC	36.7, qC
11	23.7, CH_2	23.9, CH_2	23.7, CH_2	23.9, CH_2
12	125.1, CH	125.1, CH	125.2, CH	125.3, CH
13	143.5, qC	143.4, qC	143.4, qC	143.4, qC
14	47.5, qC	47.5, qC	47.5, qC	47.3, qC
15	67.3, CH	67.1, CH	67.3, CH	67.2, CH
16	72.6, CH	73.2, CH	73.6, CH	71.9, CH
17	48.2, qC	48.1, qC	48.3, qC	47.7, qC
18	40.7, CH	41.4, CH	40.8, CH	41.0, CH
19	46.6, CH_2	46.6, CH_2	46.8, CH_2	46.7, CH_2
20	36.1, qC	36.1, qC	36.2, qC	35.9, qC
21	78.2, CH	78.3, CH	79.3, CH	80.9, CH
22	73.2, CH	73.1, CH	73.5, CH	70.4, CH
23	27.7, CH_3	22.0, CH_3	27.7, CH_3	27.7, CH_3
24	16.5, CH_3	62.9, CH_2	16.5, CH_3	16.5, CH_3
25	15.5, CH_3	15.6, CH_3	16.0, CH_3	15.7, CH_3
26	17.3, CH_3	17.1, CH_3	17.3, CH_3	17.5, CH_3
27	21.0, CH_3	20.8, CH_3	21.0, CH_3	21.0, CH_3
28	63.0, CH_2	63.1, CH_2	62.9, CH_2	65.0, CH_2
29	29.2, CH_3	29.3, CH_3	29.2, CH_3	29.6, CH_3
30	20.0, CH_3	20.0, CH_3	20.0, CH_3	20.0, CH_3
	21-*O*-Ang	21-*O*-Ang	21-*O*-Ang	21-*O*-Ang
1	167.4, qC	167.5	167.7	168.3
2	128.5, qC	128.7	129.6	129.3
3	137.9, CH	137.2	137.2	135.9
4	15.4, CH_3	16.7	15.5	15.6
5	20.8, CH_3	20.6	20.8	20.8
	i-Bu	22-*O*-Ang	22-*O*-Ang	MB
1	176.6, qC	167.9	167.9	175.7, qC
2	35.3, CH	128.9	129.8	41.1, CH
3	18.8, CH_3	136.3	136.3	26.9, CH_2
4	19.0, CH_3	15.6	15.5	11.4, CH_3
5		20.4	20.5	16.4, CH_3
	GlcA-*p*	Glc A-*p*	GlcA-*p*	GlcA-*p*
1	104.6, CH	104.5	104.9	104.9
2	78.6, CH	78.6	79.1	78.6
3	86.1, CH	86.5	86.1	86.1
4	71.5, CH	71.6	71.5	71.5
5	77.0, CH	77.4	78.0	77.0
6	171.9, qC	171.9	171.9	171.9
	Gal-*p*	Glc-*p*	Gal-*p*	Gal-*p*
1	104.6, CH	103.7, CH	104.6	104.6
2	73.2, CH	75.3, CH	73.6	73.3
3	74.7, CH	78.0, CH	74.9	74.9
4	69.5, CH	69.3, CH	69.5	69.5
5	76.4, CH	78.2, CH	76.4	76.4
6	61.5, CH_2	61.5, CH_2	61.6	61.6
	Ara-*f*	Ara-*f*	Ara-*f*	Ara-*f*
1	110.0, CH	110.1	110.6	110.9
2	83.4, CH	83.5	83.4,	83.4
3	77.5, CH	77.8	78.3	77.4
4	85.2, CH	85.0	85.2	85.2
5	62.1, CH_2	62.2	62.2	62.1

data. HMBC correlations between δ_H 5.48 (Glc-1) and δ_C 78.6 (Glc A-2), as well as between δ_H 6.05 (Ara-*f*-1) and δ_C 86.5 (Glc A-3), suggested a trisaccharide structure of [β-D-glucopyranosyl-(1→2)]-α-L-arabinofuranosyl(1→3)-β-D-glucuronopyranoside. The HMBC correlation between the δ_H 4.87 (Glc A-1) and δ_C 91.3 (C-3) signals, as well as the downfield shift value of C-3 (δ_C 91.3), suggested the trisaccharide moiety was attached to the C-3 position of 21,22-di-*O*-angeloyl-24-hydroxy-R_1-barrigenol through a glycosidic linkage. The absolute configuration of D-glucose, L-arabinose, and D-glucuronic acid were confirmed by acid hydrolysis and GC-MS analysis following conversion to the trimethylsilyl thiazolidine derivatives.[6,8] Consequently, compound **2** (xanifolia-Y_2) was determined as 3-*O*-[β-D-glucopyranosyl-(1→2)]-α-L-arabinofuranosyl-(1→3)-β-D-glucuronopyranosyl-21,22-*O*-diangeloyl-3β,15α,16α,21β,22α,24β,28-heptahydroxyolean-12-ene.

Compound **3** was obtained as a white, amorphous powder. Its molecular formula was established as $C_{57}H_{88}O_{23}$, on the basis of the HRESIMS at *m/z* 1163.5615 $[M + Na]^+$ (calcd 1163.5609). The MALDIMS exhibited three quasimolecular ion peaks at *m/z* 1163 $[M + Na]^+$, 1185 $[M + 2Na - H]^+$, and 1201 $[M + Na + K - H]^+$. The ^{13}C NMR data of **3** were identical with those of 21,22-di-*O*-angeloyl-R_1-barrigenol except for the C-3 and the sugar moieties,[4,11] leading to its assignment as a glycoside of 21,22-di-*O*-angeloyl-R_1-barrigenol. The presence of two angeloyl ester groups in **3** was suggested by the characteristic ^1H and ^{13}C NMR data (Tables 1 and 2).[4] Their locations at the C-21 and C-22 positions were determined on the basis of long-range proton−carbon correlations observed between δ_H 6.71 (1H, d, J = 10 Hz, H-21) and δ_C 167.7 (21-*O*-Ang-1), as well as between signals at δ_H 6.32 (1H, d, J = 10 Hz, H-22) and δ_C 167.9 (22-*O*-Ang-1). From the ^1H and ^{13}C NMR data (Tables 1 and 2), it was evident that the sugar structure at C-3 was the same as that in **1**, and acid hydrolysis afforded the same compounds. The linkages were established on the basis of a HMBC experiment. On the basis of the available evidence, compound **3** (xanifolia-Y_3) was determined to be 3-*O*-[β-D-galactopyranosyl-(1→2)]-α-L-arabinofuranosyl-(1→3)-β-D-glucuronopyranosyl-21,22-*O*-diangeloyl-3β,15α,16α, 21β,22α,28-hexahydroxyolean-12-ene.

Compound **4** was obtained as an amorphous powder, and a quasimolecular ion peak at *m/z* 1165.5750 $[M + Na]^+$ (calcd 1165.5765) was evident by HRESIMS, establishing a molecular formula of $C_{57}H_{90}O_{23}$. Detailed NMR data analysis indicated the aglycon to be R_1-barrigenol (Tables 1 and 2).[4,11] The presence of an angeloyl ester group and a 2-methylbutanoyl group in **4** was suggested by the characteristic ^1H and ^{13}C NMR data and HMBC results.[9] These functional groups were located at the C-21 and C-28 positions, respectively, on the basis of HMBC correlations observed between signals at δ_H 6.58 (d, J = 11.2 Hz) and δ_C 168.3 (Ang-1), as well as between those at δ_H 4.38 (H-28) and δ_C 175.7 (MB-1). Compound **4** contains the same trisaccharide at C-3 as in **1** and **3** (Tables 1 and 2), and **4** (xanifolia-Y_7) was determined to be 3-*O*-[β-D-galactopyranosyl-(1→2)]-α-L-arabinofuranosyl-(1→3)-β-D-glucuronopyranosyl-21-*O*-angeloyl-28-*O*-2-methylbutanoyl-3β,15α,16α,21β,22α,28-hexahydroxyolean-12-ene.

Compounds **1**−**6** exhibited cell-growth inhibition activity as determined by a MTT assay toward human ovarian cancer cells (OVCAR3) and exhibited IC_{50} values of 4.2 ± 0.7, 10.7 ± 0.2, 4.0 ± 0.5, 13.1 ± 0.5, 8.9 ± 1.3, and 4.8 ± 0.2 μM, respectively. On the basis of their growth inhibition activities, these compounds may be categorized into two groups: group A (**1**, **3**, and **6**) had IC_{50} values of 4−5 μM, while group B (**2**, **4**, and **5**) was less potent, having IC_{50} values of 9−13 μM. These results suggested that, for this class of compounds, acylation at both C-21 and C-22 is important for cytotoxicity, and analogues with a C-24 methyl group (instead of CH_2OH) and a galactose (instead of glucose) in the trisaccharide moiety attached to C-3 exhibit higher potency. However, hydroxylation at C-15 has no apparent effect.

Experimental Section

General Experimental Procedures. Optical rotations were measured with a JASCO P-1020 polarimeter. IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer. ^1H and ^{13}C NMR spretra were acquired with a Bruker Avance 600 MHz NMR spectrometer with a QXI probe ($^1H/^{13}C/^{15}N/^{31}P$) at 298 K. Each pure compound was dissolved in pyridine-d_5 with 0.05% v/v TMS (tetramethylsilane). HRESIMS and MALDIMS were obtained on a ThermoFinnigan MAT 95 XL mass spectrometer and Applied Biosystems MALDI-TOF Voyager DE-STR mass spectrometer, respectively. GC-MS analysis was performed on an Agilent Technologies 6890N15973N GC/MS.

Plant Material. The husks of *Xanthoceras sorbifolia* Bunge (Sapindaceae) were collected in September 2004 from Inner Mongolia, People's Republic of China, and authenticated by Professor Yun Wang (Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang, People's Republic of China). A voucher specimen (No. CUSCM2008-

02) has been deposited in the School of Chinese Medicine, the Chinese University of Hong Kong.

Extraction and Isolation. The dried husks of *Xanthoceras sorbifolia* (10 kg) were extracted three times with 70% aqueous ethanol (30 L) at 40 °C. The solution was filtered and evaporated to dryness under reduced pressure to yield a powered extract (140 g). The extract was purified by passing through an octadecyl-functionalized silica gel column (2 cm × 28 cm) equilibrated with 10% acetonitrile−0.005% trifluoroacetic acid (TFA). Elution with a gradient of 10−80% acetonitrile afforded 100 fractions (10 mL each). The active fraction (fractions 55−66)[2] was further separated by HPLC on a C_{18} column (Waters Delta Pak C_{18}-300A). Isocratic elution with a mixture of 45% acetonitrile−0.005% TFA led to the isolation of **1** (t_R 35.0 min, 190 mg), **2** (t_R 40.2 min, 700 mg), **3** (t_R 44.5 min, 1.35 g), **4** (t_R 54.2 min, 130 mg), **5** (t_R 61.5 min, 280 mg), and **6** (t_R 73.5 min, 500 mg). Solvents used in the final purification of compounds are HPLC grade.

Xanifolia-Y_0 (1): amorphous powder; $[\alpha]^{20}_D$ −16.3 (*c* 0.19, MeOH); IR (KBr) ν_{max} 3401, 2931, 1712, 1602, 1431, 1388, 1142, 1075, 1040 cm^{-1}; ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2; HRMALDIMS *m/z* 1151.5557 $[M + Na]^+$ (calcd 1151.5614); MALDIMS *m/z* 1151 $[M + Na]^+$, 1173 $[M + 2Na - H]^+$, 1189 $[M + Na + K - H]^+$.

Xanifolia-Y_2 (2): amorphous powder; $[\alpha]^{20}_D$ −12.5 (*c* 0.21, MeOH); IR (KBr) ν_{max} 3389, 2954, 1683, 1456, 1380, 1159, 1075, 1041 cm^{-1}; ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2; HRESIMS *m/z* 1179.5548 $[M + Na]^+$ (calcd 1179.5558); MALDIMS *m/z* 1179 $[M + Na]^+$, 1201 $[M + 2Na - H]^+$, and 1217 $[M + Na + K - H]^+$.

Xanifolia-Y_3 (3): amorphous powder; $[\alpha]^{20}_D$ −24.5 (*c* 0.20, MeOH); IR (KBr) ν_{max} 3398, 2954, 1702, 1458, 1388, 1163, 1075, 1042 cm^{-1}; ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2; HRESIMS *m/z* 1163.5615 $[M + Na]^+$ (calcd 1163.5609); MALDIMS *m/z* 1163 $[M + Na]^+$, 1185 $[M + 2Na - H]^+$, and 1201 $[M + Na + K - H]^+$.

Xanifolia-Y_7 (4): amorphous powder; $[\alpha]^{20}_D$ +4.7 (*c* 0.19, MeOH); IR (KBr) ν_{max} 3406, 2959, 1680, 1644, 1409, 1388, 1148, 1082, 1040 cm^{-1}; ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2; HRESIMS *m/z* 1165.5750 $[M + Na]^+$ (calcd 1165.5765); MALDIMS *m/z* 1063 $[M + Na - 102]^+$, 1165 $[M + Na]^+$.

Acid Hydrolysis and Determination of the Absolute Configuration of the Monosaccharides. A solution of each saponin (**1**−**4**; 5−10 mg) in 1 M HCl (dioxane−H_2O, 1:1, 4 mL) was heated at 100 °C for 1 h. The mixture was evaporated to dryness under reduced pressure. The residue was suspended in deionized water (2 mL) and extracted with EtOAc (1 mL × 3). The water layer was neutralized by passing through an ion-exchange resin (Ionac NM-65) column (0.5 mL of bed volume) and evaporated to dryness to furnish a monosaccharide residue. The residue was dissolved in pyridine (0.2 mL) to which 0.08 M L-cysteine methyl ester hydrochloride (Aldrich, Milwaukee, WI) in pyridine (0.3 mL) was added. The mixture was kept at 60 °C for 2 h, dried under reduced pressure, and trimethylsilylated with 1-trimethylsilylimidazole (Fluka, Buchs, Switzerland) (0.2 mL) for 2 h. The mixture was partitioned between *n*-hexane and water (1.0 mL each), and the *n*-hexane extract was analyzed by GC-MS under the following conditions: capillary column, HP-5MS (30 m × 0.25 mm × 0.25 μm, Agilent); column temperature, 230 °C; injection temperature, 250 °C; carrier, He gas; split ratio, 10:1; flow rate, 0.8 mL/min; MS scan range 50−500. In the acid hydrolysates of **1**−**4**, D-glucose, L-arabinose, D-galactose, and D-glucuronic acid were confirmed by comparison of the retention times of their derivatives with those of L-arabinose, D-arabinose, D-glucuronic acid, D-glucose, L-glucose, D-galactose, and L-galactose derivatives prepared in a similar way, which showed retention times of 5.89, 6.43, 8.18, 9.85, 10.78, 11.29, and 12.09 min, respectively.

MTT Assay. Inhibition of cell-growth activity was determined by a MTT assay using human ovarian carcinoma cells (OVCAR-3) as previously described.[2,12] Experiments were repeated two times to obtain the average IC_{50} (±SD) values. Paclitaxel was used as a positive control and showed an IC_{50} value of 1.0 ± 0.2 nM.

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