JOURNAL OF NATURAL PRODUCTS

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Volume 72, Number 10 October 2009

Full Papers

Cytotoxic Acacic Acid Glycosides from the Roots of *Albizia coriaria*

Olivier Placide Noté,[†,‡] Anne-Claire Mitaine-Offer,[†] Tomofumi Miyamoto,[§] Thomas Paululat,[⊥] Jean-François Mirjolet,[▽] Olivier Duchamp,[▽] Dieudonné Emmanuel Pegnyemb,[‡] and Marie-Aleth Lacaille-Dubois*[,†]

Laboratoire de Pharmacognosie, UMIB, EA 3660, Faculté de Pharmacie, Université de Bourgogne, 7 Boulevard Jeanne D'Arc, BP 87900, 21079 Dijon Cedex, France, Laboratoire de Pharmacochimie, Département de Chimie Organique, Faculté des Sciences, Université de Yaoundé, BP 812, Yaoundé, Cameroon, Graduate School of Pharmaceutical Sciences, Kyushu University, Fukuoka 812-8582, Japan, and Universität Siegen FB8, OC-II (AK Ihmels), Adolf-Reichwein-Strasse 2, D-57068 Siegen, Germany, and Oncodesign, 20 Rue Jean Mazen, BP27627, 21076 Dijon Cedex, France

Received February 25, 2009

Two new oleanane-type saponins, coriariosides A (**1**) and B (**2**), along with a known saponin, gummiferaoside C (**3**), were isolated from the roots of *Albizia coriaria.* Their structures were established by extensive analysis of 1D and 2D NMR experiments (COSY, ROESY, TOCSY, HSQC, and HMBC) and mass spectrometry. Compounds **1** and **3** when tested for cytotoxicity against two colorectal human cancer cells showed activity against the HCT 116 (IC_{50} 4.2 μM for **1** and 2.7 μM for **3**) and HT-29 (IC_{50} 6.7 μM for **1** and 7.9 μM for **3**) cell lines.

Albizia coriaria Welw. ex Oliv. (Mimosaceae) is a tree widely distributed in Cameroon and Uganda, where it is harvested for timber or herbal medicine. The bark or root is used as a general tonic and for the treatment of syphilis, skin diseases, jaundice, eye diseases, cough, and sore throat.[1] It is also used to concentrate breast milk in humans.[1] Saponins have been isolated from the genus *Albizia*,[2,4−8] which most often possess acacic acid as aglycon with monoterpenoid glycosyl units at the 21-position and oligosaccharides at the 3- and 28-positions. Some of these compounds have exhibited interesting apoptosis-inducing properties.[4a] In our continuing search for new biologically active agents from Cameroonian medicinal plants,[9−14] chemical investigation of the roots of *A. coriaria* led to the isolation of two new triterpene saponins, coriariosides A (**1**) and B (**2**), together with one known saponin, gummiferaoside C (**3**), previously isolated from *Albizia gummifera*.[15]

* Corresponding author. Tel.: +33 3 80 39 32 29. Fax: +33 3 80 39 33 00. E-mail: m-a.lacaille-dubois@u-bourgogne.fr.
[†] Université de Bourgogne.
[‡] Université de Yaoundé.
[§] Kyushu University.
[⊥] Universität Siegen.
[▽] Oncodesign.

Results and Discussion

The *n*-BuOH fraction obtained from the MeOH extract of the roots of *A. coriaria* was submitted to vacuum-liquid chromatography (VLC) and repeated medium-pressure liquid chromatography (MPLC), affording two new triterpenoid saponins, coriariosides A (**1**) and B (**2**), and one known saponin (**3**), which was identified as gummiferaoside C, by comparison of its NMR data with literature values.[15]

Coriarioside A (**1**) was isolated as a white, amorphous powder. Its HRESIMS (positive-ion mode) exhibited a quasimolecular ion peak at *m/z* 2520.1796 $[M + Na]^+$ (calcd for $C_{119}H_{188}O_{55}Na$, 2520.1812), consistent with a molecular formula of $C_{119}H_{188}O_{55}Na$. By extensive analysis of 1D and 2D NMR spectra of **1**, and comparison with literature data, the aglycon part was identified as acacic acid (Table 1).[2−4,7] The ^1H NMR spectrum of **1** showed 10 anomeric protons at δ_H 4.82 (1H, d, J = 8.0 Hz), 4.87 (1H, d, J = 8.0 Hz), 4.89 (1H, d, J = 7.1 Hz), 6.05 (1H, d, J = 7.8 Hz), 5.91 (1H, brs), 6.25 (1H, brs), 5.32 (1H, d, J = 7.3 Hz), 4.87 (1H, d, J = 8.0 Hz), 4.95 (1H, d, J = 7.7 Hz), and 4.87 (1H, d, J = 8.0 Hz), which gave correlations in the HSQC spectrum with carbon atom resonances at δ_C 104.9, 105.5, 105.7, 107.0, 95.6, 101.8, 111.0, 99.3, 96.9, and 99.3, respectively (Tables 2 and 3). From the anomeric proton of each hexosyl unit and from the CH_3-proton doublet of each desoxy-

10.1021/np900126r CCC: $40.75 © 2009 American Chemical Society and American Society of Pharmacognosy
Published on Web 09/24/2009

Table 1. ^{1}H and ^{13}C NMR Data of the Aglycon Moieties of **1** and **2** in Pyridine-d_5 (δ in ppm)[a]

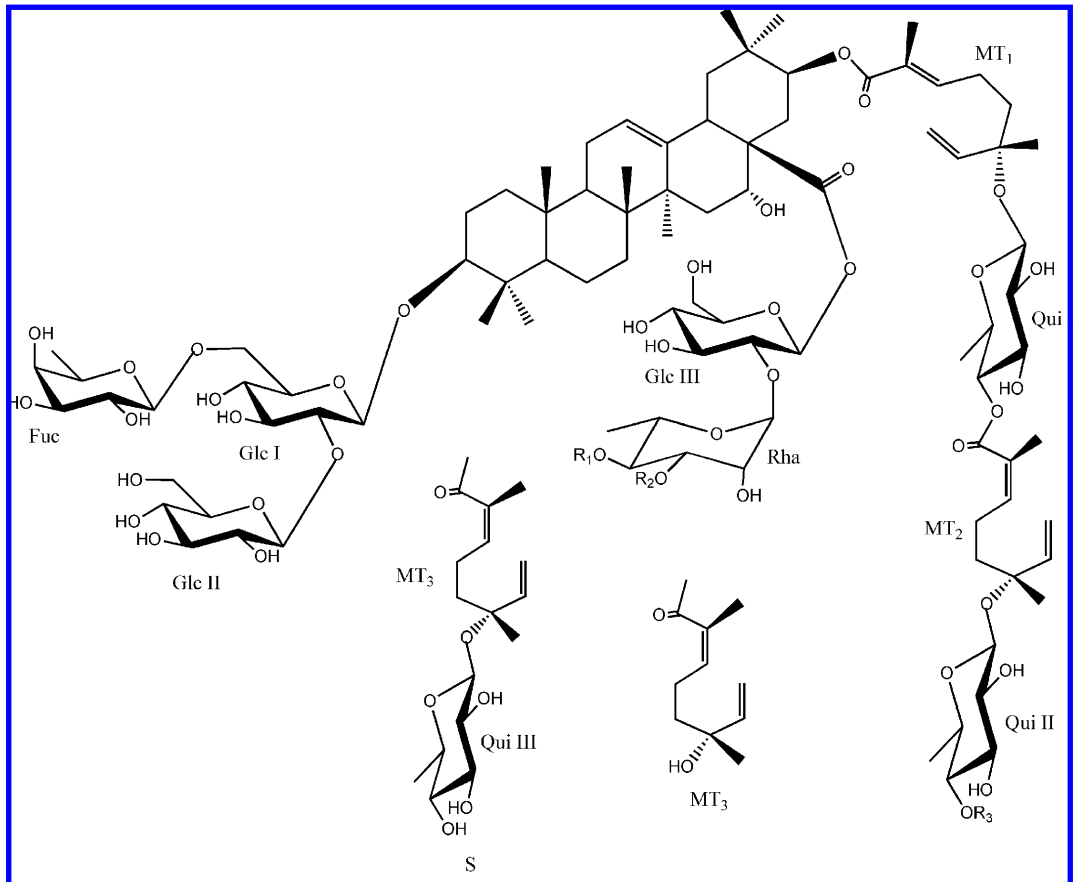
		1		**2**	
position	mult	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)
1	CH_2	38.9	1.52; nd[b]	38.9	nd; nd
2	CH_2	26.7	2.36; 0.92	26.8	1.79; nd
3	CH	89.2	3.24, dd (10.9, 4.4)	89.2	3.20, dd, (10.9, 4.0)
4	C	39.5		39.5	
5	CH	56.0	0.74, d (12.1)	55.9	0.66, d (12.1)
6	CH_2	18.6	nd; nd	18.4	nd; nd
7	CH_2	33.6	1.66; nd	33.5	1.60; nd
8	C	40.1		40.0	
9	CH	47.1	1.45	47.0	1.52
10	C	37.0		37.0	
11	CH_2	23.4	2.23; 2.42	23.6	2.24; 2.42
12	CH	123.1	5.65, brs	123.1	5.64, brs
13	C	143.3		143.1	
14	C	42.0		42.0	
15	CH_2	35.9	2.85, d (4.6); nd	36.0	2.87, d (4.4); 2.23
16	CH	73.8	5.24	73.5	5.33
17	C	51.7		51.7	
18	CH	40.1	1.78	41.1	1.78
19	CH_2	48.0	2.80; nd	48.0	1.50; nd
20	C	35.3		35.4	
21	CH	76.8	5.35	76.8	5.36
22	CH_2	36.4	nd; nd	36.5	nd; nd
23	CH_3	28.1	1.23, s	28.3	1.25, s
24	CH_3	16.9	1.15, s	16.9	1.12, s
25	CH_3	15.8	0.95, s	15.8	0.90, s
26	CH_3	17.3	1.18, s	17.3	1.10, s
27	CH_3	27.2	1.83, s	27.2	1.78, s
28	C	174.4		174.6	
29	CH_3	29.2	1.07, s	29.3	1.08, s
30	CH_3	19.2	1.13, s	19.3	1.14, s

[a] Multiplicities were assigned from DEPT spectra. Assignments were based on the HMBC, HSQC, COSY, TOCSY, ROESY, and DEPT experiments. Overlapped ^{1}H NMR signals are reported without designated multiplicity. [b] nd: not determined.

hexosyl unit, all the protons within each spin system were assigned using COSY, TOCSY, and ROESY experiments. With the aid of HSQC and HMBC experiments, these sugar units were identified as four β-glucopyranosyl (Glc I, Glc II, Glc III, and Glc IV), one β-fucopyranosyl (Fuc), three β-quinovopyranosyl (Qui I, Qui II, and Qui III), one α-rhamnopyranosyl (Rha), and one α-arabinofuranosyl (Ara_f) (Tables 2 and 3). The absolute configuration was determined to be D for Glc, Fuc, and Qui and L for Rha and Ara_f (see Experimental Section). The sequencing of the glycosidic chains was achieved by analysis of HMBC and ROESY experiments (Figure 1). The observation of glycosylation- and acylation-induced shifts in the ^{13}C NMR spectrum at δ_C 89.2 (downfield shift of C-3 of the aglycon), δ_C 76.8 (downfield shift of C-21 of the aglycon), and δ_C 174.4 (upfield shift of C-28 of the aglycon) suggested that compound **1** is a 21-acyl 3,28-bidesmoside of acacic acid. The FABMS of **1** revealed a fragment ion at m/z 1893 $[(M - H) - 602]^-$, in which 602 mass units were accounted for the mass of the C-28-linked oligosaccharidic chain consisting of one pentosyl, one desoxyhexosyl, and two hexosyl units. The carbon and proton NMR signals observed for the sugar moiety linked at C-28 in the ^{1}H and ^{13}C NMR spectra of **1** were almost superimposable on those of julibroside J_5.[5b] Thus, the tetrasaccharide residue at C-28 of the aglycon was determined to be α-L-arabinofuranosyl-(1→4)-[β-D-glucopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl (Figure 1). On the other hand, the HMBC correlation observed between the anomeric proton signal at δ_H 4.82 (Glc I H-1) and δ_C 89.2 (Agly C-3) suggested that this sugar was directly attached to C-3 of the aglycon. This was supported by the ROESY correlation observed between δ_H 4.82 (Glc I H-1) and δ_H 3.24 (Agly H-3) (Figure 1). The HMBC correlation observed between δ_H 4.87 (Fuc H-1) and δ_C 70.2 (Glc I C-6) allowed us to suggest that the fucose is linked at position-6 of Glc I. Moreover, in the ROESY spectrum, a correlation was observed between the anomeric proton at δ_H 4.89 (Glc II H-1) and the signal at δ_H 4.13. This signal showed a HSQC correlation with δ_C 83.2 (Glc I C-2) (Table 2), suggesting that Glc II is linked at position-2 of Glc I. Thus, the trisaccharide moiety attached to C-3 of the aglycone was determined to be β-D-fucopyranosyl-(1→6)-[β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl (Figure 1). At this stage we characterized the 3,28-bidesmoside of acacic acid of compound **1**. After subtraction of the NMR data of the bidesmosidic part from the whole spectra of compound **1**, the remaining signals assigned from 2D NMR experiments corresponded to the acyl part of the molecule at C-21 (three quinovose, Qui I, Qui II, and Qui III, and three monoterpenyl moieties, MT_1, MT_2, and MT_3) (Table 3). The NMR data of the monoterpene moieties were in accordance with those described in the literature[4a] for a (2*E*,6*S*)-2,6-dimethyl-6-hydroxyocta-2,7-dienoyl unit in acylated saponins from the genus *Albizia*.[2a,4a,7,15,16] The ^{13}C NMR data of compound **1** showed that the signals of C-5 and C-10 of the monoterpene moieties in **1** were similar to those of the outer monoterpene moiety of julibroside III,[4b] confirming the C-6 (*S*) configurations of the three monoterpene moieties. Moreover, the observation of an acylation shift for C-21 (δ_C 76.8) of the aglycon permitted the location of the monoterpene units. The linkage modes for the above structural units (aglycon, Qui I, Qui II, Qui III, MT_1, MT_2, and MT_3) were established by HMBC experiments. HMBC correlations were observed between δ_H 5.35 (Agly H-21) and δ_C 167.7 (MT_1 C-1), between δ_H 4.87 (Qui I H-1) and δ_C 79.4 (MT_1 C-6), between δ_H 5.34 (Qui I H-4) and δ_C 167.7 (MT_2 C-1), between δ 4.95 (Qui II H-1) and δ_C 79.4 (MT_2 C-6), between δ_H 5.63 (Qui II H-4) and δ_C 167.2 (MT_3 C-1), and between δ 4.87 (Qui III H-1) and δ_C 79.4 (MT_3 C-6) (Figure 1). Thus, the moiety containing three MT-Qui units attached to C-21 was determined to be {(2*E*,6*S*)-6-*O*-{4-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-*O*-(β-D-quinovopyranosyl)octa-2,7-dienoyl]-4-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-*O*-(β-D-quinovopyranosyl) octa-2,7-dienoyl]-β-D-quinovopyranosyl}-2,6-dimethylocta-2,7-dienoyl}. Therefore, the structure of compound **1** (coriaroside A) was determined as 3-*O*-{β-D-fucopyranosyl-(1→6)-[β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl}-21-*O*-{(2*E*,6*S*)-6-*O*-{4-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-*O*-(β-D-quinovopyranosyl)octa-2,7-dienoyl]-4-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-*O*-(β-D-quinovopyranosyl)octa-2,7-dienoyl]-β-D-quinovopyranosyl}-2,6-dimethylocta-2,7-dienoyl}acacic acid 28-*O*-α-L-arabinofuranosyl-(1→4)-[β-D-glucopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl ester.

Coriarioside B (**2**) was isolated as an amorphous powder. Its HRESIMS (positive-ion mode) exhibited a quasimolecular ion peak at m/z 2212.0680 $[M + Na]^+$ (calcd for $C_{107}H_{168}O_{46}Na$, 2212.0704), consistent with a molecular formula of $C_{107}H_{168}O_{46}Na$. The ^{1}H NMR spectrum of **2** showed eight anomeric protons at δ_H 4.84 (1H, d, J = 8.0 Hz), 4.88 (1H, d, J = 8.0 Hz), 5.30 (1H, d, J = 7.3 Hz), 6.12 (1H, d, J = 7.7 Hz), 6.36 (1H, brs), 5.25 (1H, d, J = 7.6 Hz), 4.88 (1H, d, J = 8.0 Hz), and 4.94 (1H, d, J = 8.1 Hz), which gave correlations in the HSQC spectrum with eight carbon atom resonances at δ_C 105.0, 105.5, 106.2, 95.3, 101.2, 106.5, 99.3, and 99.3, respectively (Tables 2 and 3). The sugars were characterized in the same way as for compound **1**. Hence, three β-glucopyranosyl (Glc I, Glc II, and Glc III), one β-fucopyranosyl (Fuc), two β-quinovopyranosyl (Qui I and Qui II), one β-xylopyranosyl (Xyl), and one α-rhamnopyranosyl (Rha) unit were identified (Tables 2 and 3). The sugar unit absolute configurations were determined to be D for Glc, Fuc, Qui, and Xyl and L for Rha (see Experimental Section). The observation of connectivities in the COSY, TOCSY, ROESY, HSQC, and HMBC spectra revealed that the aglycon part and the glycosidic chain at C-3 in **2** and in **1** were almost superimposable, suggesting 3-*O*-{β-D-fucopyranosyl-(1→6)-[β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl}acacic acid as prosa-

Chart 1



	R_1	R_2	R_3
Coriarioside A (**1**)	Ara*f*	Glc	S
Coriarioside B (**2**)	Xyl	H	MT_3
Gummiferaoside C (**3**)	Xyl	H	S

pogenin (Tables 1 and 2). Comparison of the NMR data (Tables 1 and 2) of **1** and **2** indicated that the oligosaccharide moiety at C-28 is a trisaccharide constituted by one Glc, one Rha, and one Xyl. Extensive analysis of 1D and 2D NMR spectra revealed that this moiety was identical to that of gummiferaoside C[15] and of grandibracteosides A.[2d] Hence, the trisaccharide moiety at C-28 of **2** was determined to be a β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl unit (Table 2). A detailed ^{13}C NMR data comparison of the acyl moiety at C-21 in **2** and **1** showed small differences of the ^{13}C NMR spectroscopic data of the outer monoterpene (MT_3) in **2** compared to **1**. The ^{13}C NMR data of MT_3 in compound **2** were almost superimposable to those of the outer monoterpene of proceraoside A,[16] indicating this outer monoterpene (MT_3) to be free at its C-6 hydroxy group in **2** instead of being substituted by a quinovopyranosyl moiety in **1**. The connectivities of the units present in the C-21 acyl group of compound **2** were determined by the same methodology used in the elucidation of the C-21 acyl moiety of compound **1**. Hence, the structure of compound **2** (coriarioside B) was determined as 3-*O*-{β-D-fucopyranosyl-(1→6)-[β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl}-21-*O*-{(2*E*,6*S*)-6-*O*-{4-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-*O*-(β-D-quinovopyranosyl)octa-2,7-dienoyl]-4-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-*O*-(β-D-quinovopyranosyl)octa-2,7-dienoyl]}-2,6-dimethyl-6-hydroxyocta-2,7-dienoyl}acacic acid 28-*O*-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl ester.

Compound **3**, isolated as an amorphous powder, was identified as 3-*O*-{β-D-fucopyranosyl-(1→6)-[β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl}-21-*O*-{(2*E*,6*S*)-6-*O*-{4-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-*O*-(β-D-quinovopyranosyl)octa-2,7-dienoyl]-4-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-*O*-(β-D-quinovopyranosyl)octa-2,7-dienoyl]-β-D-quinovopyranosyl}-2,6-dimethylocta-2,7-dienoyl}acacic acid 28-*O*-β-D-xylopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl ester, recently isolated from *Albizia gummifera*, and was given the name gummiferaoside C.[15]

Since acacic acid glycosides from the genus *Albizia* have been reported to be cytotoxic to cancer cell lines,[4,5,15] compounds **1** and **3** were tested for cytotoxicity against the HCT 116 and HT-29 human colon cancer cell lines, using paclitaxel as a positive control. The tested compounds showed significant (HCT 116: IC_{50} 4.2 μM for **1** and 2.7 μM for **3**) to moderate (HT-29: IC_{50} 6.7 μM for **1** and 7.9 μM for **3**) cytotoxic activity, as determined by the MTT assay.[17] The only difference between compounds **1** and **3** lies in the oligosaccharide moiety at C-28 of the acacic acid aglycone, with a tetrasaccharide moiety at C-28 in **1**, instead of a trisaccharide moiety in **3**. Since **1** and **3** showed a similar cytotoxicity, these results are in good agreement with previous observations pointing out the crucial role of acacic acid with the presence of an ester substituent at C-21 in mediating cytotoxicity.[2a,d,4b,15]

Experimental Section

General Experimental Procedures. Optical rotations were measured with a AA-10R automatic polarimeter. NMR spectra were obtained on a Varian UNITY INOVA-600 spectrometer.[14] Chemical shifts are reported as δ values (ppm), referenced with respect to the residual

Table 2. NMR Spectroscopic Data (600 MHz for ^{1}H and 150 MHz for ^{13}C) for the Sugar Moieties at C-3 and C-28 of Compounds **1** and **2** in Pyridine-d_5 (δ in ppm, J in Hz)[a]

	1		**2**			**1**		**2**	
position	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	position	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)
		3-O-sugars							
Glc I 1	104.9	4.82, d (8.0)	105.0	4.84, d (7.8)	Rha 1	101.8	5.91, brs	101.2	6.36, brs
2	83.1	4.13, d (8.1)	83.5	4.15	2	70.6	5.15	71.4	4.81
3	78.0	3.92	78.1	3.90	3	82.0	4.90	72.1	4.74
4	71.4	4.16	71.1	4.16	4	79.0	4.47	83.2	4.44
5	76.4	4.04	76.8	4.04	5	69.1	4.54	68.4	4.55
6	70.2	4.85; 4.28	70.1	4.87; 4.25	6	18.6	1.78, d (6.3)	18.5	1.76, d (6.5)
Fuc 1	105.5	4.87, d (8.0)	105.5	4.88, d (8.0)	Xyl 1			106.5	5.25, d (7.8)
2	72.6	4.03	72.1	4.05	2			75.2	4.08
3	75.6	3.98	75.2	4.00	3			78.6	4.10
4	71.4	4.04	72.6	4.04	4			71.1	4.15
5	71.9	3.82, m	71.4	3.82	5			67.4	3.52, t (10.7);
6	17.3	1.53, d (6.0)	17.3	1.54, d (6.1)					4.25
Glc II 1	105.7	4.89, d (7.1)	106.2	5.30, d (7.4)	Ara$_f$ 1	111.0	6.25, brs		
2	75.6	4.07	75.2	4.08	2	84.4	4.98		
3	78.0	4.22, d (8.9)	78.1	4.22	3	78.0	4.78		
4	71.9	4.27	71.4	4.30	4	85.4	4.74		
5	77.0	3.90	77.9	3.92	5	62.8	4.16; 4.24		
6	62.8	4.47; 4.45	62.8	4.47; 4.49	Glc IV 1	105.9	5.32, d (7.3)		
		28-O-sugars			2	75.5	3.98		
Glc III 1	95.6	6.05, d (7.8)	95.3	6.12, d (7.7)	3	78.4	4.21		
2	76.2	4.02	75.6	4.29	4	71.9	4.08		
3	78.0	4.16	77.1	4.22	5	78.0	3.89		
4	71.4	4.16	71.4	4.30	6	62.8	4.49; 4.21		
5	78.4	3.95	79.0	4.00					
6	62.1	4.32;	61.2	4.25					
		4.21, d (3.6)		4.35					

[a] Assignments were based on the HMBC, HSQC, COSY, TOCSY, ROESY, and DEPT experiments. Overlapped ^{1}H NMR signals are reported without designated multiplicity.

Table 3. NMR Data of the Monoterpene-Quinovosyl Units of **1** and **2** in Pyridine-d_5 (δ in ppm, J in Hz)[a]

	1		**2**			**1**		**2**	
monoterpenes	δ_C	δ_H	δ_C	δ_H	quinovoses	δ_C	δ_H	δ_C	δ_H
MT$_1$ 1	167.7		167.6		Qui I 1	99.3	4.87, d (8.0)	99.3	4.88, d (7.7)
2	128.5		128.6		2	75.5	4.02	75.2	4.04
3	142.3	6.91, t (6 0.9)	142.2	6.92	3	75.6	4.21	75.6	4.20
4	23.4	2.43	23.6	2.43	4	76.9	5.34	76.8	5.36
5	40.5	1.78; nd	41.0	1.76; nd[b]	5	70.8	3.70	70.2	3.70
6	79.4		79.4		6	18.4	1.36, d (6.0)	18.5	1.36, d (6.0)
7	144.0	6.21	142.8	6.25	Qui II 1	96.9	4.95, d (7.7)	99.3	4.94, d (8.1)
8	114.8	5.25; 5.47	114.8	5.22; 5.45	2	75.5	3.97	75.2	3.98
9	12.6	1.86, s	12.7	1.86, s	3	78.0	4.20	77.9	4.22
10	23.8	1.56, s	23.7	1.56, s	4	76.8	5.63	76.8	5.64
MT$_2$ 1	167.7		167.2		5	72.6	3.72	72.6	3.72
2	128.1		128.1		6	18.6	1.58, d (5.27)	18.7	1.60, d (5.28)
3	142.9	6.99, t (7.5)	143.1	7.07, t (7.3)	Qui III 1	99.3	4.87, d (8.0)		
4	23.6	2.48; nd	23.8	2.46; nd	2	75.6	3.98		
5	41.0	1.59; nd	40.5	1.76; 1.79	3	78.4	4.10		
6	79.4		79.4		4	76.8	3.70		
7	143.9	6.23	143.4	6.25	5	72.6	3.70		
8	115.0	5.28; 5.43	115.0	5.27; 5.48	6	18.8	1.60, d (5.28)		
9	12.6	1.95, s	12.7	1.94, s					
10	23.7	1.50, s	23.7	1.56, s					
MT$_3$ 1	167.2		167.6						
2	128.2		127.9						
3	143.1	6.99, t (7.5)	143.6	6.26, t (9.7)					
4	23.6	2.45; nd	24.1	2.03; nd					
5	40.5	1.78	41.5	1.60					
6	79.4		72.1						
7	143.9	6.26	146.6	6.15					
8	115.4	5.28; 5.37	111.6	5.16; 5.18					
9	12.6	1.93, s	12.6	1.90, s					
10	23.6	1.57, s	28.6	1.47, s					

[a] Assignments were based on the HMBC, HSQC, COSY, TOCSY, ROESY, and DEPT experiments. Overlapped ^{1}H NMR signals are reported without designated multiplicity. [b] nd: not determined.

solvent signal of C_5D_5N, and coupling constants (J) were measured in Hz. HRESIMS (positive-ion mode) was obtained on a Q-TOF1-micromass spectrometer, and FABMS (negative-ion mode) was obtained on a JEOL-SX-102 instrument.[14] Thin-layer chromatography (TLC) and high-performance thin-layer chromatography (HPTLC) were performed on precoated silica gel plates (60 F_{254}, Merck).[14] Vacuum-liquid chromatography (VLC) was carried out using RP-18 silica gel 60 (25−40 and 63−200 μm). Medium-pressure liquid chromatography

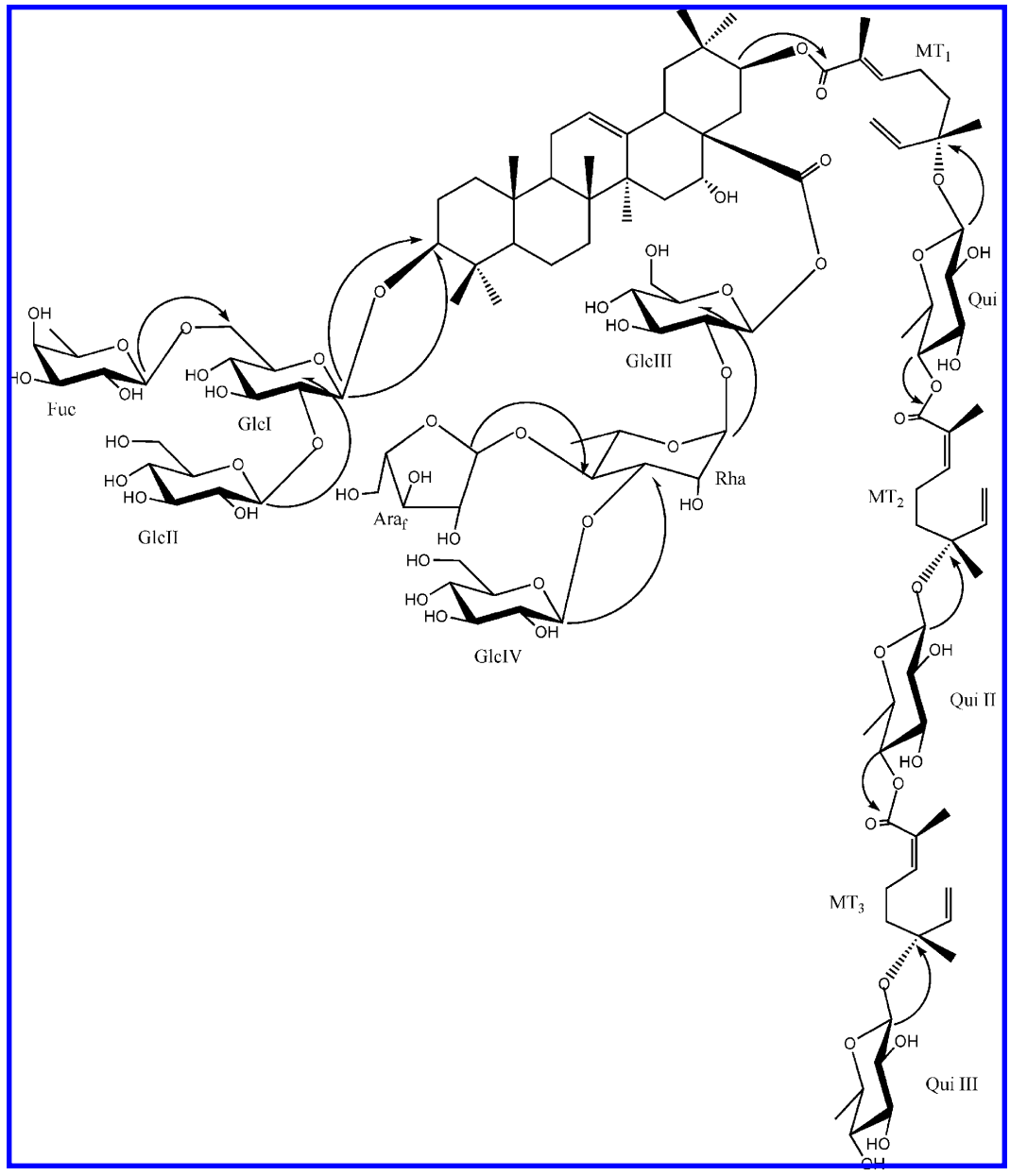


Figure 1. Important HMBC (→) and ROESY (⇀) correlations observed for **1**.

(MPLC) was carried out using silica gel 60 (15−40 μm) with a M-305 Gilson pump, a Büchi column (46 × 2.5 and 46 × 1.5 cm), and RP-18 silica gel 60 (25−40 μm) with a C-605 Büchi pump manager, with two pumps (2× Büchi pump module C-601) and one Büchi fraction collector C-660 for purification.

Plant Material. The roots of *A. coriaria* were harvested at Eloundem, Yaoundé peripheral quarter, in Cameroon in September 2007, under the guidance of Dr. Paul Nana, botanist of the National Herbarium of Cameroon (NHC), where a voucher specimen (No. 09565/07) was deposited.

Extraction and Isolation. Air-dried, finely powdered roots (300 g) of *A. coriaria* were extracted with MeOH in a Soxhlet apparatus. The methanolic solution was then evaporated to dryness under reduced pressure and gave 26 g of a dark residue. This residue was suspended in 200 mL of water and partitioned against H_2O−saturated *n*-BuOH (3 × 200 mL). The *n*-BuOH-soluble phase was evaporated to dryness, affording 9.52 g of a brown gum, which was taken up in a minimum of water (10 mL) and submitted to VLC, using RP-18 (25−40 μm), eluting with H_2O, 50% MeOH, and 100% MeOH. The 100% MeOH eluant was evaporated to dryness, affording 4.45 g of a crude saponin mixture. This saponin mixture was then submitted to medium-pressure liquid chromatography (MPLC), using silica gel 60 (15−40 μm), eluted with $CHCl_3$−MeOH−H_2O (60:32:6.5), to give 19 fractions (Fr1−Fr19). Fraction Fr14 (16.0 mg) was purified by repeated MPLC, using normal-phase silica gel 60 (15−40 μm) eluted with $CHCl_3$−MeOH−H_2O (60:32:7) to give compound **2** (4.8 mg). Fr15 and Fr17 were submitted to MPLC with normal-phase silica gel 60 (15−40 μm), eluted with $CHCl_3$−MeOH−H_2O (60:32:6.5), to give subfractions Fr15.1 (22.3 mg) and Fr17.3 (12.3 mg), respectively. These subfractions were purified by further MPLC, using RP-18 (25−40 μm), eluted with a gradient of MeOH−H_2O (70:30 → 100:0), to afford **1** (5.6 mg) and gummiferaoside C (3.5 mg).

Coriarioside A (1): amorphous, white powder; $[\alpha]^{25}_D$ −41 (*c* 0.12, MeOH); ^{1}H NMR (C_5D_5N, 600 MHz) and ^{13}C NMR (C_5D_5N, 150 MHz), see Tables 1−3; FABMS (negative-ion mode) *m*/*z* 1893 [(M − H) − 602]$^-$; HRESIMS (positive-ion mode) *m*/*z* 2520.1796 (calcd for $C_{119}H_{188}O_{55}Na$, 2520.1812).

Coriarioside B (2): amorphous powder; $[\alpha]^{25}_D$ −30 (*c* 0.31, MeOH); ^{1}H NMR (C_5D_5N, 600 MHz) and ^{13}C NMR (C_5D_5N, 150 MHz), see Tables 1−3; FABMS (negative-ion mode) *m*/*z* 1876 [(M − H) − 166 − 146]$^-$, 1709 [(M − H) − 166 − 146 − 167]$^-$, 1563 [(M − H) − 166 − 146 − 167 − 146]$^-$; HRESIMS (positive-ion mode) *m*/*z* 2212.0680 (calcd for $C_{107}H_{168}O_{46}Na$, 2212.0704).

Acid Hydrolysis and GC Analysis. Compounds **1** and **2** (2 mg) were each hydrolyzed with 2 N aqueous CF_3COOH (5 mL) for 3 h at 95 °C. After extraction with CH_2Cl_2 (3 × 5 mL), the aqueous layer

was repeatedly evaporated to dryness with MeOH until neutral and then analyzed by TLC over silica gel ($CHCl_3$−MeOH−H_2O, 8:5:1), by comparison with authentic samples. The trimethylsilyl thiazolidine derivative of the sugar residue of each compound was prepared and analyzed by GC.[2a] The absolute configurations were determined by comparing the retention times with thiazolidine derivatives prepared in a similar way from standard sugars (Sigma-Aldrich). The following sugars were detected: D-glucose, D-quinovose, L-rhamnose, L-arabinose for **1**; D-glucose, D-xylose, D-quinovose, and L-rhamnose for **2**.

MTT Cytotoxicity Assay. The bioassay was carried out according to a previously described method, with two human colorectal cancer cell lines (HCT 116 and HT-29). Paclitaxel was used as positive control and exhibited IC_{50} values of 3.5 nM (HCT 116) and 3.4 nM (HT-29).[17]

Acknowledgment. The authors are grateful to Dr. Paul Nana of the National Herbarium of Cameroon (NHC) for the identification and collection of plant.

Supporting Information Available: NMR spectra for compounds **1** and **2**. This information is available free of charge via the Internet at http://pubs.acs.org.

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NP900126R