New Triterpenoidal Saponins Acylated with Monoterpenic Acid from *Albizia adianthifolia*

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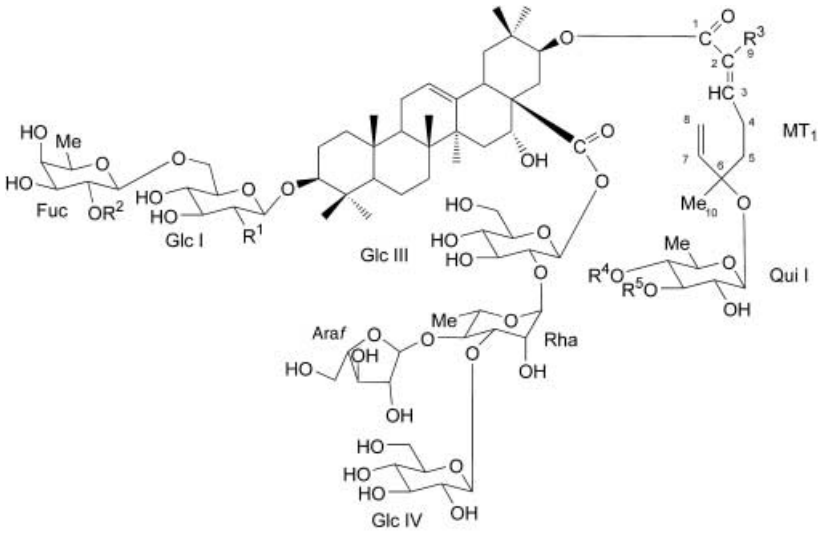
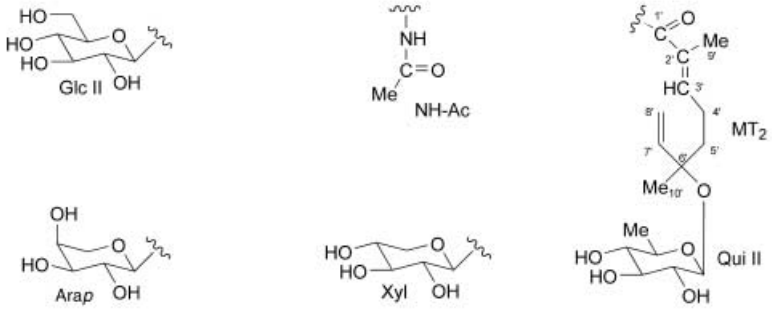
Four new triterpenoidal saponins acylated with monoterpenic acid, *i.e.*, adianthifoliosides C, D, E, and F (**1**–**4**), besides the two known julibroside III and the monodesmonoterpenyl elliptoside A, were isolated from the roots of *Albizia adianthifolia*. Their structures were elucidated on the basis of extensive 1D- and 2D-NMR studies and mass spectrometry as 3-*O*-{*O*-*α*-L-arabinopyranosyl-(1→2)-*O*-*β*-D-fucopyranosyl-(1→6)-*O*-[*β*-D-glucopyranosyl-(1→2)]-*β*-D-glucopyranosyl}-21-*O*-{(2*E*,6*S*)-6-{{4-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-(*β*-D-quinovopyranosyloxy)octa-2,7-dienoyl]-*β*-D-quinovopyranosyl}oxy}-2-(hydroxymethyl)-6-methylocta-2,7-dienoyl}acacic acid 28-{*O*-*α*-L-arabinofuranosyl-(1→4)-*O*-[*β*-D-glucopyranosyl-(1→3)]-*O*-*α*-L-rhamnopyranosyl-(1→2)-*β*-D-glucopyranosyl} ester (**1**), 21-*O*-{(2*E*,6*S*)-6-{{4-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-(*β*-D-quinovopyranosyloxy)octa-2,7-dienoyl]-*β*-D-quinovopyranosyl}oxy}-2-(hydroxymethyl)-6-methylocta-2,7-dienoyl}-3-*O*-{*O*-*β*-D-xylopyranosyl-(1→2)-*O*-*β*-D-fucopyranosyl-(1→6)-2-(acetylamino)-2-deoxy-*β*-D-glucopyranosyl}acacic acid 28-{*O*-*α*-L-arabinofuranosyl-(1→4)-*O*-[*β*-D-glucopyranosyl-(1→3)]-*O*-*α*-L-rhamnopyranosyl-(1→2)-*β*-D-glucopyranosyl} ester (**2**), 21-*O*-{(2*E*,6*S*)-6-{{3-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-(*β*-D-quinovopyranosyloxy)octa-2,7-dienoyl]-*β*-D-quinovopyranosyl}oxy}-2,6-dimethylocta-2,7-dienoyl}-3-*O*-{*O*-*β*-D-xylopyranosyl-(1→2)-*O*-*β*-D-fucopyranosyl-(1→6)-2-(acetylamino)-2-deoxy-*β*-D-glucopyranosyl}acacic acid 28-{*O*-*α*-L-arabinofuranosyl-(1→4)-*O*-[*β*-D-glucopyranosyl-(1→3)]-*O*-*α*-L-rhamnopyranosyl-(1→2)-*β*-D-glucopyranosyl} ester (**3**), and 3-*O*-{*O*-*α*-L-arabinopyranosyl-(1→2)-*O*-*β*-D-fucopyranosyl-(1→6)-*O*-[*β*-D-glucopyranosyl-(1→2)]-*β*-D-glucopyranosyl}-21-*O*-{(2*E*,6*S*)-2,6-dimethyl-6-(*β*-D-quinovopyranosyloxy)octa-2,7-dienoyl}acacic acid 28-{*O*-*α*-L-arabinofuranosyl-(1→4)-*O*-[*β*-D-glucopyranosyl-(1→3)]-*O*-*α*-L-rhamnopyranosyl-(1→2)-*β*-D-glucopyranosyl} ester (**4**).

Introduction. – Our previous phytochemical studies on the EtOH extract of *Albizia adianthifolia* (SCHUMACH.) W. F. WIGHT (Mimosaceae) have led to the isolation of two new biologically active triterpene saponins acylated with salicylic acid (adianthifoliosides A and B) [1] besides two new prosapogenins [2], isolated from the mild alkaline hydrolyzate of the roots. A further detailed investigation of the roots of this plant resulted in the isolation of the four additional major triterpene saponins **1**–**4**. Herein, we report the isolation and structure elucidation of these four new triterpene glycosides named adianthifoliosides C, D, E, and F (**1**–**4**).

Results and Discussion. – The 95% EtOH extract of the roots of *A. adianthifolia* was purified by precipitation with Et_2O, yielding a crude saponin mixture, which was then dialyzed for two days. The powder obtained was submitted to column chromatography (*Sephadex LH-20*) and was separated by repeated medium-pressure liquid chromatography (MPLC; normal silica gel and reversed phase), yielding compounds **1**–**4**.





	R^1	R^2	R^3	R^4	R^5
1 adianthifolioside C	O-Glc II	Ara*p*	CH_2OH	MT_2-Qui II	H
2 adianthifolioside D	NH-Ac	Xyl	CH_2OH	MT_2-Qui II	H
3 adianthifolioside E	NH-Ac	Xyl	CH_3	H	MT_2-Qui II
4 adianthifolioside F	O-Glc II	Ara*p*	CH_3	H	H

Structure elucidation of the compounds was mainly achieved by extensive spectroscopic mass and 1D- and 2D-NMR experiments (^{1}H, ^{13}C, COSY, TOCSY, NOESY, HSQC, and HMBC, see *Tables 1–5*). All the compounds were isolated as amorphous powders. The sugars obtained from aqueous acid hydrolysis of **1**–**4** were identified by comparison with authentic samples (TLC) as glucose, arabinose, fucose

(=6-deoxygalactose), rhamnose (=6-deoxymannose), and quinovose (=6-deoxyglucose) (in the case of **1** and **4**) and as glucose, xylose, fucose, 2-(acetylamino)-2-deoxy-β-D-glucopyranose [2], rhamnose, arabinose, and quinovose (in the case of **2** and **3**). Alkaline hydrolysis with a 5% KOH aqueous solution of **1** and **4** afforded the same prosapogenin, whereas another prosapogenin, was obtained in the case of **2** and **3**. By further acid hydrolysis, the prosapogenin furnished glucose, fucose, and arabinose in the case of **1** and **4** and glucose, fucose, xylose, and *N*-acetylglucosamine in the case of **2** and **3** (co-TLC with a reference compound), and acacic acid lactone (the 21,28-lactone derivative of acacic acid obtained under the experimental conditions used) in the case of **1**–**4**, by comparison of its NMR data with literature values [1][2]. The native aglycone was characterized as acacic acid (=(3β,16α,21β)-3,16,21-trihydroxyolean-12-en-28-oic acid) from the 2D-NMR spectra from **1**–**4**.

The ESI-TOF-MS (positive-ion mode) of **1** showed a quasi-molecular-ion peak at *m/z* 2380 ($[M+2+2Na]^{++}$), which was consistent with its relative molecular mass as calculated for $C_{108}H_{172}O_{54}$. The full assignment of all the ^{1}H- and ^{13}C-NMR signals by 2D-NMR experiments of **1** resulted in the establishment of the structure as 3-*O*-{*O*-α-L-arabinopyranosyl-(1→2)-*O*-β-D-fucopyranosyl-(1→6)-*O*-[β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl}-21-*O*-{(2*E*,6*S*)-6-{{4-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-(β-D-quinovopyranosyloxy)octa-2,7-dienoyl]-β-D-quinovopyranosyl}oxy}-2-(hydroxymethyl)-6-methylocta-2,7-dienoyl}acacic acid 28-{*O*-α-L-arabinofuranosyl-(1→4)-*O*-[β-D-glucopyranosyl-(1→3)]-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl} ester (**1**), a new natural compound [1–21].

The ^{1}H- and ^{13}C-NMR signals of the aglycone of **1** (*Table 1*) obtained from 2D-NMR spectra of **1** (see *Table 1–5*) were almost superimposable on those of acacic acid [1][2]. In addition, the ^{13}C-NMR spectrum of **1** showed one ester carbonyl C-atom (δ 174.3), two α,β-unsaturated ester carbonyl C-atoms (δ 167.7, 167.8), two trisubstituted olefinic C=C bonds (δ 146.0, 132.5, 143.0, 127.3), and two monosubstituted olefinic C=C bonds (δ 143.1, 115.0, 143.2, 115.0), which corresponded to the two monoterpene moieties (*Table 5*). The ^{1}H-NMR spectrum of **1** displayed signals for ten anomeric protons at δ(H) 6.08 (br. *s*), 5.86 (d, *J* = 7.5 Hz), 5.72 (br. *s*), 5.22 (*d*, *J* = 7.5 Hz), 5.14 (*d*, *J* = 7.5 Hz), 5.03 (*d*, *J* = 6.2 Hz), 4.80 (*d*, *J* = 8.0 Hz), 4.76 (*d*, *J* = 7.3 Hz), 4.74 (*d*, *J* = 7.5 Hz), and 4.71 (*d*, *J* = 7.3 Hz) (*Tables 2* and *4*), which correlated in the HSQC spectrum with ^{13}C-NMR signals at δ(C) 110.0, 94.9, 101.3, 104.0, 104.8, 105.0, 102.7, 98.6, 104.2, and 98.4, respectively (*Tables 3* and *5*). The ring protons of the monosaccharide residues were assigned starting from the anomeric protons by means of the COSY, TOCSY, HSQC, and HMBC NMR plots (*Table 2*), and the sequence of the oligosaccharide chains was obtained from the HMBC and NOESY experiments. Evaluation of spin-spin couplings and chemical shifts allowed the identification of four β-glucopyranosyl (Glc), one β-fucopyranosyl (Fuc), one α-arabinopyranosyl (Ara*p*), one α-arabinofuranosyl (Ara*f*), one α-rhamnopyranosyl (Rha), and two β-quinovopyranosyl (Qui) units, respectively. The common D-configuration for Qui, Fuc, and Glc and the L-configuration for Rha, Ara*p*, and Ara*f* were assumed, according to those most often encountered among plant glycosides in each case.

A comparative study of the ^{13}C-NMR data of **1** with adianthifoliosides A and B [1] led to the observation of glycosylation- and acylation-induced shifts for δ(C) 89.1 (downfield shift of C(3)), 77.1 (downfield shift of C(21)), and 174.3 (upfield shift of C(28)), suggesting that **1** should be a 3,28-*O*-bisdesmosidic structure having a third substituent linked at C(21) *via* an ester bond.

Comparison of the NMR spectra of **1** with those of adianthifolioside B [2] showed that the ^{1}H- and ^{13}C-NMR data of **1** due to the aglycone part and the sugar moieties at C(3) and C(28) (*Tables 1–5*) were almost superimposable to those of adianthifolioside B with only one difference. Compound **1** was shown to possess a terminal Ara*p* unit at C(2) of the Fuc of the oligosaccharide part at C(3) of the aglycone instead of a terminal Xyl at this position in adianthifolioside B. Consequently, the structure of the sugar moieties at C(3) and at C(28) were determined to be an *O*-α-L-arabinopyranosyl-(1→2)-*O*-β-D-fucopyranosyl-(1→6)-*O*-[β-D-glucopyranosyl-(1→2)]-β-D-glucopyranoside and an *O*-α-L-arabinofuranosyl-(1→4)-*O*-[β-D-glucopyranoside-(1→3)]-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside, resp.

Table 1. *^{13}C-* (150 MHz)[a]) *and ^{1}H-NMR* (600 MHz) *Data of the Aglycone Parts of* **1**–**4** *in (D_5)Pyridine from 1D- and 2D-NMR Experiments.* δ in ppm.

	1		**2**		**3**		**4**	
	δ(C)	δ(H)[b])	δ(C)	δ(H)[b])	δ(C)	δ(H)[b])	δ(C)	δ(H)[b])
CH_2(1)	36.4	0.96, 1.52	38.5	1.02, 1.56	38.0	0.94, 1.52	37.5	0.98, 1.55
CH_2(2)	26.0	[c]), [c])	26.2	[c]), [c])	25.9	[c]), [c])	26.0	[c]), [c])
CH(3)	89.1	3.30	88.8	3.36	89.0	3.30	88.1	3.40
C(4)	39.5		39.0		38.5		39.5	
CH(5)	55.2	0.78	55.8	0.84	55.4	0.84	54.8	0.78
CH_2(6)	18.0	[c]), [c])	18.1	1.18, [c])	18.0	1.20, 1.23	15.5	1.38, 1.40
CH_2(7)	33.0	[c]), 1.60	33.3	1.66, [c])	32.9	[c]), 1.64	32.3	[c]), 1.62
C(8)	39.9		40.1		39.8		39.5	
CH(9)	46.5	1.75	46.9	1.78	46.5	1.72	46.8	1.72
C(10)	33.4		36.8		36.5		37.0	
CH_2(11)	23.0	[c]), 1.98	23.4	[c]), 2.10	23.0	[c]), 1.97	22.1	[c]), 1.97
CH(12)	123.0	5.56	122.7	5.57	122.2	5.55	122.0	5.55
C(13)	143.3		143.0		143.3		143.0	
C(14)	40.8		41.2		41.2		40.7	
CH_2(15)	35.1	1.92, 2.10	35.1	1.98	35.0	[c]), 1.94	34.0	[c]), 1.94
CH(16)	73.1	5.07	73.4	5.12	72.8	5.07	72.2	5.08
C(17)	51.3		51.4		51.3		51.0	
CH(18)	40.2	3.32	40.5	3.38	40.4	[c])	40.2	[c])
CH_2(19)	47.5	1.31, 2.82	47.6	1.34, 2.87	47.0	1.32, 2.81	46.5	1.32, 2.83
C(20)	35.0		35.2		34.9		35.0	
CH(21)	77.1	6.07	77.0	6.18	76.8	6.04	76.0	6.06
CH_2 (22)	35.7	2.16, 2.65	35.1	2.16, 2.68	35.1	2.10, 2.64	34.9	2.16, 2.64
Me(23)	27.7	1.15	27.9	1.14	27.1	1.09	26.5	1.16
Me(24)	15.9	0.90	16.9	0.94	16.3	0.88	15.6	0.88
Me(25)	15.5	0.87	15.5	0.89	15.1	0.82	14.3	0.86
Me(26)	16.1	1.05	17.1	1.12	16.6	1.04	16.0	1.04
Me(27)	26.7	1.74	26.9	1.80	26.5	1.74	25.6	1.74
C(28)	174.3		174.4		174.5		175.0	
Me(29)	28.8	0.92	28.9	0.95	28.8	0.92	27.5	0.92
Me(30)	18.9	1.05	18.9	1.07	18.8	1.03	18.0	1.12

[a]) Multiplicities were assigned from DEPT spectra. [b]) Overlapped ^{1}H-NMR signals are reported without designated multiplicity. [c]) Not determined.

In addition, the observation of an acylation shift for C(21) of the aglycone permitted to locate the monoterpene units. The ^{1}H-NMR spectrum of **1** showed the presence of two anomeric protons remaining at δ(H) 4.76 (d, $J = 7.3$ Hz) and 4.71 (d, $J = 7.3$ Hz), together with two secondary Me groups at δ(H) 1.23 and 1.45 (*Table 4*), which correlated in the HSQC spectrum with δ(C) 98.6, 98.4, 18.0, and 18.6 (*Table 5*) indicating the presence of two β-D-quinovopyranosyl units. Furthermore, the HMBC correlations between δ(H) 4.76 (d, $J =$ 7.3 Hz, Qui I H–C(1)) and δ(C) 79.9 (MT_1 C(6)) and between δ(H) 4.71 (d, $J = 7.3$ Hz, Qui II H–C(1)) and δ(C) 79.4 (MT_2 C(6)) established that Qui I and Qui II were attached to MT_1 and MT_2, respectively. The NMR data of the MT part of **1**, especially for H–C(7), Me(10), C(5), and C(8) of the inner monoterpene, and H–C(7′), H–C(10′), C(5′), and C(8′) of the outer monoterpene more closely resembled those of julibroside J_9 (configuration (6*S*, 6′*S*)) [3] rather than those of julibroside J_1 (configuration (6*S*,6′*R*)), indicating the absolute (*S*) configuration at both C(6) of the inner and C(6′) of the outer monoterpene. Thus the structure of the moiety at C(21) of the aglycone was established to be an ester of (2*E*,6*S*)-6-{{4-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-(β-D-quinovopyranosyloxy)octa-2,7-dienoyl]-β-D-quinovopyranosyl}oxy}-2-(hydroxymethyl)-6-methylocta-2,7-dienoic acid.

Table 2. *^{1}H-NMR* (600 MHz) *Chemical Shifts δ of the Sugar Moieties of* **1**–**4** *in (D_5)Pyridine from 1D- and 2D-NMR Experiments. δ* in ppm. *J* in Hz.

		1	**2**	**3**	**4**
3-*O*-Sugars: Glc I or	H–C(1)	4.74 (*d*, *J* = 7.5)	4.97 (*d*, *J* = 7.5)	4.92 (*d*, *J* = 7.5)	4.78 (*d*, *J* = 7.5)
Glc I-NH-Ac	H–C(2)	4.22	4.51	4.41	4.20
	H–C(3)	3.88	4.30	4.30	3.86
	H–C(4)	3.91	3.98	3.98	3.95
	H–C(5)	4.04	4.01	3.90	3.99
	CH_2(6)	4.21, 4.51	4.33, 4.60	4.20, 4.51	4.20, 4.54
	NH		8.91	9.00	
	Me				
Glc II	H–C(1)	5.22 (*d*, *J* = 7.5)			5.32 (*d*, *J* = 7.5)
	H–C(2)	3.94			3.93
	H–C(3)	3.85			3.84
	H–C(4)	4.05			4.10
	H–C(5)	4.08			3.90
	CH_2(6)	4.04, 4.34			4.07, 4.32
Fuc	H–C(1)	4.80 (*d*, *J* = 8.0)	4.88 (*d*, *J* = 8.0)	4.81 (*d*, *J* = 8.0)	4.84 (*d*, *J* = 8.0)
	H–C(2)	4.30	4.38	4.30	4.31
	H–C(3)	4.04	4.10	4.04	4.04
	H–C(4)	3.98	3.92	3.95	3.95
	H–C(5)	3.64	3.68	3.68	3.68
	Me(6)	1.40	1.40	1.38	1.38
Xyl	H–C(1)		4.97 (*d*, *J* = 7.8)	4.90 (*d*, *J* = 7.8)	
	H–C(2)		4.02	3.90	
	H–C(3)		4.04	4.02	
	H–C(4)		4.12	4.04	
	CH_2(5)		3.52, 4.42	3.48, 4.33	
Ara*p*	H–C(1)	5.03 (*d*, *J* = 6.2)			5.04 (*d*, *J* = 6.2)
	H–C(2)	4.37			4.39
	H–C(3)	4.17			4.25
	H–C(4)	4.00			4.00
	CH_2(5)	3.60, 4.40			3.62, 4.36
28-*O*-Sugars: Glc III	H–C(1)	5.86 (*d*, *J* = 7.5)	5.99 (*d*, *J* = 7.5)	5.81 (*d*, *J* = 7.5)	5.87 (*d*, *J* = 7.5)
	H–C(2)	3.83	3.96	3.87	3.87
	H–C(3)	3.96	4.11	3.85	3.81
	H–C(4)	4.04	4.17	3.93	3.94
	H–C(5)	3.84	3.90	3.84	3.84
	CH_2(6)	4.05, 4.20	4.10, 4.27	4.05, 4.20	4.06, 4.23
Rha	H–C(1)	5.72 (br. *s*)	5.82 (br. *s*)	5.72 (br. *s*)	5.73 (br. *s*)
	H–C(2)	5.00	5.08	4.99	5.00
	H–C(3)	4.71	4.80	4.69	4.70
	H–C(4)	4.35	4.45	4.35	4.35
	H–C(5)	4.36	4.46	4.36	4.36
	Me(6)	1.67	1.74	1.66	1.69
Ara*f*	H–C(1)	6.08 (br. *s*)	6.11 (br. *s*)	6.10 (br. *s*)	6.09 (br. *s*)
	H–C(2)	4.81	4.90	4.81	4.83
	H–C(3)	4.61	4.72	4.60	4.62
	H–C(4)	4.60	4.68	4.60	4.61
	CH_2(5)	4.12, 4.36	4.20, 4.40	4.12, 4.32	4.12, 4.33
Glc IV	H–C(1)	5.14 (*d*, *J* = 7.5)	5.20 (*d*, *J* = 7.5)	5.13 (*d*, *J* = 7.5)	5.15 (*d*, *J* = 7.5)
	H–C(2)	3.90	3.98	3.90	3.94
	H–C(3)	4.05	4.10	4.05	4.04
	H–C(4)	4.06	4.00	4.05	4.04
	H–C(5)	3.87	3.90	3.84	3.86
	CH_2(6)	4.05, 4.30	4.10, 4.40	4.07, 4.32	4.13, 4.22

Table 3. *^{13}C-NMR* (150 MHz) *Chemical Shifts δ of the Sugar Moieties of* **1**–**4** *in (D_5)Pyridine from 1D- and 2D-NMR Experiments. δ* in ppm. Multiplicities were assigned from DEPT spectra.

		1	**2**	**3**	**4**
3-*O*-Sugars: Glc I or Glc I-NH-Ac	CH(1)	104.2	104.2	103.5	103.2
	CH(2)	80.0	57.4	56.5	80.0
	CH(3)	77.9	75.0	74.5	77.2
	CH(4)	71.2	72.5	73.3	71.0
	CH(5)	77.1	76.0	76.0	76.5
	CH_2(6)	68.8	69.5	68.8	68.8
	C=O		170.9	171.3	
	Me		23.3	22.8	
Glc II	CH(1)	104.0			103.0
	CH(2)	75.8			75.8
	CH(3)	77.4			77.5
	CH(4)	70.2			70.0
	CH(5)	77.1			76.5
	CH_2(6)	61.5			61.0
Fuc	CH(1)	102.7	103.0	102.2	101.6
	CH(2)	79.9	81.6	80.8	80.8
	CH(3)	74.1	74.9	74.0	74.5
	CH(4)	72.8	71.5	71.4	71.0
	CH(5)	71.0	71.2	70.5	70.5
	Me(6)	18.0	16.9	16.2	17.1
Xyl	CH(1)		106.3	105.5	
	CH(2)		74.5	74.1	
	CH(3)		77.0	77.0	
	CH(4)		70.9	70.6	
	CH_2(5)		66.7	66.0	
Ara*p*	CH(1)	105.0			103.9
	CH(2)	72.0			71.0
	CH(3)	74.5			73.5
	CH(4)	70.1			69.9
	CH_2(5)	66.0			65.0
28-*O*-Sugars: Glc III	CH(1)	94.9	95.2	94.6	93.8
	CH(2)	77.2	77.0	77.0	76.5
	CH(3)	76.5	78.5	76.8	77.0
	CH(4)	70.7	71.0	70.5	71.0
	CH(5)	77.0	78.6	77.0	77.0
	CH_2(6)	61.2	61.5	61.0	60.8
Rha	CH(1)	101.3	101.5	100.9	100.2
	CH(2)	70.0	70.3	69.9	69.0
	CH(3)	81.5	81.7	81.0	80.0
	CH(4)	78.0	76.3	77.6	79.0
	CH(5)	68.9	68.9	68.2	69.6
	Me(6)	18.2	18.9	18.2	18.0
Ara*f*	CH(1)	110.0	110.5	109.6	108.9
	CH(2)	83.2	83.8	82.9	82.2
	CH(3)	77.5	77.9	77.2	76.5
	CH(4)	84.5	84.9	84.1	83.3
	CH_2(5)	62.0	62.2	61.4	61.0
Glc IV	CH(1)	104.8	105.2	104.5	103.7
	CH(2)	75.7	75.5	76.0	75.5
	CH(3)	77.0	77.5	77.0	76.5
	CH(4)	70.1	71.8	70.0	70.0
	CH(5)	77.0	77.6	77.4	77.2
	CH_2(6)	61.8	62.2	61.2	61.1

Table 4. *^{1}H-NMR* (600 MHz) *Chemical Shifts δ of the Monoterpene Quinovosyl Moieties of* **1**–**4** *in (D$_5$)Pyridine from 1D- and 2D-NMR Experiments.* δ in ppm, *J* in Hz.

		Inner monoterpene						Outer monoterpene		
		1	**2**	**3**	**4**			**1**	**2**	**3**
MT_1	CH(3)	7.00	7.00	6.80	6.98	MT_2	CH(3′)	6.94	6.96	6.93
	CH_2(4)	2.60, [a])	2.62, [a])	2.32, [a])	2.60, [a])		CH_2(4′)	2.30, [a])	2.36, [a])	2.32, [a])
	CH_2(5)	1.78, [a])	1.56, [a])	1.74, [a])	1.73, [a])		CH_2(5′)	1.55, 1.70	1.55, [a])	1.68, [a])
	CH(7)	6.14	6.15	6.10	6.12		CH(7′)	6.18	6.18	6.08
	CH_2(8)	5.18, 5.32	5.18, 5.36	5.28, 5.32	5.17, 5.32		CH_2(8′)	5.20, 5.36	5.20, 5.38	5.21, 5.34
	CH_2(9) or Me(9)	4.60, [a])	4.63, [a])	1.74	1.74		Me(9′)	1.80	1.82	1.78
	Me(10)	1.50	1.48	1.38	1.39		Me(10′)	1.47	1.48	1.44
Qui I	H–C(1)	4.76	4.78	4.79	4.71	Qui II	H–C(1)	4.71	4.78	4.71
		(*d*, *J* = 7.3)	(*d*, *J* = 7.3)	(*d*, *J* = 7.3)	(*d*, *J* = 7.3)			(*d*, *J* = 7.3)	(*d*, *J* = 7.3)	(*d*, *J* = 7.3)
	H–C(2)	3.82	3.89	3.93	3.87		H–C(2)	3.90	3.97	3.85
	H–C(3)	4.10	4.15	5.41	4.00		H–C(3)	4.10	4.08	4.04
	H–C(4)	5.15	5.22	3.90	3.58		H–C(4)	3.61	3.61	3.80
	H–C(5)	3.52	3.68	3.62	3.56		H–C(5)	3.52	3.68	3.60
	Me(6)	1.23	1.28	1.23	1.45		Me(6)	1.45	1.53	1.43

[a]) Not determined.

Table 5. *^{13}C-NMR* (150 MHz) *Chemical Shifts δ of the Monoterpene Quinovosyl Moieties of* **1**–**4** *in (D$_5$)Pyridine from 1D- and 2D-NMR Experiments.* δ in ppm. Multiplicities were assigned from DEPT spectra.

		Inner monoterpene						Outer monoterpene		
		1	**2**	**3**	**4**			**1**	**2**	**3**
MT1	C(1)	167.7	167.5	167.7	167.6	MT_2	C(1′)	167.8	167.7	167.2
	C(2)	132.5	133.2	127.7	127.0		C(2′)	127.3	127.6	127.5
	CH(3)	146.0	145.3	142.9	142.0		CH(3′)	143.0	143.4	143.3
	CH_2(4)	23.1	23.4	22.9	22.1		CH_2(4′)	23.1	23.4	22.9
	CH_2(5)	40.1	40.5	40.1	40.2		CH_2(5′)	39.8	40.5	40.0
	C(6)	79.9	79.6	78.9	79.8		C(6′)	79.4	79.4	79.0
	CH(7)	143.1	143.5	142.7	142.0		CH(7′)	143.2	143.5	143.0
	CH_2(8)	115.0	115.1	114.8	114.0		CH_2(8′)	115.0	114.8	115.0
	CH_2(9) or Me(9)	55.6	55.8	12.0	12.1		Me(9′)	12.1	12.4	12.0
	Me(10)	23.0	23.4	23.1	22.3		Me(10′)	23.2	23.4	23.0
Qui I	CH(1)	98.6	98.8	96.1	97.0	Qui II	CH(1)	98.4	98.8	98.1
	CH(2)	75.6	75.1	74.1	74.0		CH(2)	75.4	75.0	75.5
	CH(3)	75.0	74.9	74.5	76.5		CH(3)	77.5	77.8	77.0
	CH(4)	76.7	77.0	75.0	75.0		CH(4)	76.0	76.4	76.8
	CH(5)	69.9	69.9	71.7	70.8		CH(5)	72.0	72.4	72.0
	Me(6)	18.0	17.1	18.0	17.3		Me(6)	18.6	18.8	18.0

The ESI-TOF-MS (positive-ion mode) of **2** showed a quasi-molecular-ion peak at *m/z* 2257 ($[M+2+2\mathrm{Na}]^{++}$), which was consistent with its relative molecular mass as calculated for $C_{104}H_{163}NO_{49}$. This was confirmed by the high-resolution (HR) ESI-MS (positive-ion mode) which exhibited a quasi-molecular-ion peak at *m/z* 2255.0106

([$M+2$Na]$^{++}$; calc. 2255.0089), consistent with a molecular formula of $C_{104}H_{163}NNa_2O_{49}$. The assignments of all the ^{1}H- and ^{13}C-NMR signals of **2** were successfully carried out with 2D-NMR experiments (*Tables 1–5*). Thus, the structure of **2** was determined as 21-*O*-{(2*E*,6*S*)-6-{{4-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-(*β*-D-quinovopyranosyloxy)octa-2,7-dienoyl]-*β*-D-quinovopyranosyl}oxy}-2-(hydroxymethyl)-6-methylocta-2,7-dienoyl}-3-*O*-{*O*-*β*-D-xylopyranosyl-(1 → 2)-*O*-*β*-D-fucopyranosyl-(1 → 6)-2-(acetylamino)-2-deoxy-*β*-D-glucopyranosyl}acacic acid 28-{*O*-*α*-L-arabinofuranosyl-(1 → 4)-*O*-[*β*-D-glucopyranosyl-(1 → 3)]-*O*-*α*-L-rhamnopyranosyl-(1 → 2)-*β*-D-glucopyranosyl} ester (**2**), a new natural compound [1–21].

The ^{1}H- and ^{13}C-NMR data obtained from 2D-NMR spectra of **2** allowed the identification of acacic acid as an aglycone (*Table 1*). The presence of nine monosaccharide units was suggested by the nine anomeric protons at δ(H) 6.11 (br. *s*), 5.99 (*d*, *J* = 7.5 Hz), 5.82 (br. *s*), 5.20 (*d*, *J* = 7.5 Hz), 4.97 (*d*, *J* = 7.8 Hz), 4.97 (*d*, *J* = 7.5 Hz), 4.88 (*d*, *J* = 8.0 Hz), 4.78 (*d*, *J* = 7.3 Hz), and 4.78 (*d*, *J* = 7.3 Hz) (*Tables 2* and *4*), which correlated in the HSQC spectrum with nine C-atoms at δ(C) 110.5, 95.2, 101.5, 105.2, 106.3, 104.2, 103.0, 98.8, and 98.8, resp. (*Tables 3* and *5*).

Comparison of the 2D-NMR signals of **2** and **1**, as well as the results of their acid and alkaline hydrolysis indicated the loss of the signals of Glc II at C(2) of Glc I of **1**. This was confirmed by the observation of the ^{1}H- and ^{13}C-NMR data (*Tables 2* and *3*) of **2**. In addition, the presence of an acetamido group (IR: 1640 and 1569 cm^{-1}; ^{1}H-NMR: δ(H) 2.10 (*s*, MeCO) and 9.05 (*d*, *J* = 8.8 Hz, NH); ^{13}C NMR: δ(C) 23.3 (*Me*CO) and 170.9 (Me*C*O)) together with the ^{1}H- and ^{13}C-NMR data of C(2) of Glc I of **1** (δ(H) 4.51 and δ(C) 57.4) suggested the presence of one 2-(acetylamino)-2-deoxyglucose (Glc I-NH-Ac) in **2** instead of Glc I in **1**. Furthermore, comparison of the 2D-NMR spectra of **2** and **1** revealed that the sugar linked at C(2) of Fuc is Xyl (δ(H) 4.97, *d*, *J* = 7.8 Hz, Xyl H–C(1)) in the case of **2** instead of an Ara*p* (δ(H) 5.03 *d*, *J* = 6.2 Hz, Ara*p* H–C(1)) in the case of **1**, from their assigned δ(H) and δ(C).

The ESI-TOF-MS (positive-ion mode) of **3** showed a quasi-molecular-ion peak at *m/z* 2241 ([$M+2+2$Na]$^{++}$), which was consistent with its relative molecular mass as calculated for $C_{104}H_{163}NO_{48}$. The assignments of all the ^{1}H- and ^{13}C-NMR signals of **3** were successfully carried out with 2D-NMR experiments (*Tables 1–5*). Thus, the structure of **3** was determined as 21-*O*-{(2*E*,6*S*)-6-{{3-*O*-[(2*E*,6*S*)-2,6-dimethyl-6-(*β*-D-quinovopyranosyloxy)octa-2,7-dienoyl]-*β*-D-quinovopyranosyl}oxy}-2,6-dimethylocta-2,7-dienoyl}-3-*O*-{*O*-*β*-D-xylopyranosyl-(1 → 2)-*O*-*β*-D-fucopyranosyl-(1 → 6)-2-(acetylamino)-2-deoxy-*β*-D-glucopyranosyl}acacic acid 28-{*O*-*α*-L-arabinofuranosyl-(1 → 4)-*O*-[*β*-D-glucopyranosyl-(1 → 3)]-*O*-*α*-L-rhamnopyranosyl-(1 → 2)-*β*-D-glucopyranosyl} ester (**3**), a new natural compound [1–21].

The ^{1}H-NMR spectrum of **3** displayed signals for nine anomeric protons at δ(H) 6.10 (br. *s*), 5.81 (*d*, *J* = 7.5 Hz), 5.72 (br. *s*), 5.13 (*d*, *J* = 7.5 Hz), 4.92 (*d*, *J* = 7.5 Hz), 4.90 (*d*, *J* = 7.8 Hz), 4.81 (*d*, *J* = 8.0 Hz), 4.79 (*d*, *J* = 7.3 Hz), and 4.71 (*d*, *J* = 7.3 Hz), which correlated in the HSQC spectrum with ^{13}C-NMR signals at δ(C) 109.6, 94.6, 100.9, 104.5, 103.5, 105.5, 102.2, 96.1, and 98.1, resp. The ^{1}H- and ^{13}C-NMR signals of **3** were almost superimposable on those of julibroside III [9], except for the linkage between MT_2 and Qui I. The observation of the ^{13}C-NMR spectra of **3** and julibroside III suggested that in **3**, this is a (1 → 3) linkage between MT_2 and Qui I, (C(3) at δ 74.5 and C(4) at δ 75.0) instead of a (1 → 4) linkage (C(3) at δ 75.5 and C(4) at δ 77.1) in the case of julibroside III. This result was confirmed by another comparison of the ^{1}H- and ^{13}C-NMR spectra of **3** and **2**. In the case of **2**, this is also a (1 → 4) linkage (H–C(3)/C(3) at δ 4.15/74.9 and H–C(4)/C(4) at δ 5.22/77.0) instead of a (1 → 3) linkage between MT_2 and Qui I (H–C(3)/C(3) at δ 5.41/74.5 and H–C(4)/C(4) at δ 3.90/75.0) in the case of **3**. Furthermore, comparison of the NMR data of the MT part of **3** with those of julibroside J_9 and J_1 [3], especially for H–C(7), Me(10), C(5), and C(8) of the inner monoterpene, and H–C(7′), H–C(10′), C(5′), and C(8′) of the outer monoterpene, indicated the absolute (*S*) configuration at both C(6) of the inner and C(6′) of the outer monoterpene.

The negative-ion FAB-MS of **4** showed a quasi-molecular-ion peak at *m/z* 2003 ($[M-H]^-$), indicating a relative molecular mass of 2004, which suggested a molecular formula $C_{92}H_{148}O_{47}$. The assignments of all the ^{1}H- and ^{13}C-NMR signals of **4** were successfully carried out with 2D-NMR experiments (*Tables 1–5*). Thus, the structure of **4** was determined as 3-*O*-{*O*-α-L-arabinopyranosyl-(1→2)-*O*-β-D-fucopyranosyl-(1→6)-*O*-[β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl}-21-*O*-{(2*E*,6*S*)-2,6-dimethyl-6-(β-D-quinovopyranosyloxy)octa-2,7-dienoyl}acacic acid 28-{*O*-α-L-arabinofuranosyl-(1→4)-*O*-[β-D-glucopyranosyl-(1→3)]-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl} ester (**4**).

The ^{1}H-NMR spectrum of **4** displayed signals for nine anomeric protons at δ(H) 6.09 (br. *s*), 5.87 (*d*, *J* = 7.5 Hz), 5.73 (br. *s*), 5.32 (*d*, *J* = 7.5 Hz), 5.15 (*d*, *J* = 7.5 Hz), 5.04 (*d*, *J* = 6.2 Hz), 4.84 (*d*, *J* = 8.0 Hz), 4.78 (*d*, *J* = 7.5 Hz), and 4.71 (*d*, *J* = 7.3 Hz), which correlated in the HSQC spectrum with δ(C) 108.9, 93.8, 100.2, 103.0, 103.7, 103.9, 101.6, 103.2, and 97.0, resp. Comparison of the 2D-NMR spectra of **4** and **1**, as well as the results of their acid and alkaline hydrolysis revealed that the only difference between these compounds is due to the disappearance of the signals of the Qui II and MT_2 moieties and the replacement of $CH_2(9)OH$ at MT_1 by Me(9).

The known compounds were identified by comparing their MS and ^{1}H- and ^{13}C-NMR data obtained from 2D-NMR experiments with published data as julibroside III [9] and monodesmonoterpenyl elliptoside A [18].

Experimental Part

General. Column Chromatography (CC): *Sephadex LH-20* (*Pharmacia*). Medium-pressure liquid chromatography (MPLC): silica gel *60* (*Merck,* 15–40 μm), *Gilson* pump *M 305*, *Büchi* column (460 × 25 mm and 460 × 15 mm), *Büchi* precolumn (110 × 15 mm). TLC and HPTLC: silica gel *60* F_{254} (*Merck*); eluents: for saponins, $CHCl_3$/MeOH/AcOH/H_2O 15:8:3:2 (*a*); for sapogenins, $CHCl_3$/MeOH 9:1 (*b*); for monosaccharides, $CHCl_3$/MeOH/H_2O 8:5:1 (*c*); spray reagents: for saponins, *Komarowsky* reagent, a 5:1 mixture of 2% 4-hydroxybenzaldehyde in MeOH and 50% H_2SO_4 soln.; for sugars, diphenylamine/phosphoric acid reagent. IR Spectra (KBr): *Perkin-Elmer-281*-IR spectrophotometer; in cm^{-1}. 1D- and 2D-NMR Spectra (^{1}H,^{1}H, COSY, TOCSY, NOESY, HSQC, and HMBC); *Unity-600* spectrometer, *Varian-Inova-600* instrument equipped with a *Sun-4-L-X* computer system, at 600 (^{1}H) and 150 MHz (^{13}C); conventional pulse sequences for COSY, HSQC, and HMBC; TOCSY, standard MLEV17 spin-locking sequence and 90 ms mixing time; NOESY, 500 ms mixing time; C multiplicities by DEPT experiments; chemical shifts δ in ppm, *J* in Hz; (D_5)pyridine solns. (δ(C) 150.3, 155.9, 123.9). Fast-atom bombardment (FAB) MS: negative-ion mode; *Jeol SX 102*. ESI-MS and HR-ESI-MS: positive-ion mode; *Q-TOF-1-Micromass* spectrometer.

Plant Material. The roots of *Albizia adianthifolia* (SCHUMACH.) W. F. WIGHT (Mimosaceae) were collected in April 1990 in Lamto, Ivory Coast, and identified by Mr. *N. Konan*, Tropical Ecology Station, Lamto. A voucher specimen (No. 16–90) is deposited in the Herbarium of the Laboratory of Pharmacognosy, Faculty of Pharmacy, University of Burgundy, France.

Extraction and Isolation. Dried, powdered roots (200 g) were macerated for 4 h with 3 l of 95% EtOH and further refluxed for 24 h (3 × 3 l). After cooling, the EtOH soln. was filtered and evaporated: EtOH extract (20 g). This extract was suspended in H_2O (400 ml) and submitted to a partition against BuOH sat. with H_2O (3 × 400 ml). Evaporation of the solvent gave the BuOH extract (7 g). This was solubilized in MeOH (10 ml) and precipitated in Et_2O (3 × 250 ml): 2.5 g of a crude saponin fraction. The latter was suspended in H_2O, dialyzed for two days, and lyophilized, yielding a crude saponin mixture. An aliquot (1.8 g) of this mixture was fractionated by CC (*Sephadex LH-20*, MeOH) and submitted to successive MPLC (silica gel *60* (15–40 μm), $CHCl_3$/MeOH/H_2O 8:5:1 and 6:4:1): **1** (10 mg), **2** (15 mg), **3** (11 mg), and **4** (12 mg).

*(3β,16α,21β)-3-{[*O*-α-L-Arabinopyranosyl-(1→2)*-O*-6-deoxy-β-D-galactopyranosyl-(1→6)*-O*-[β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl}oxy}-21-{[(2*E*,6*S*)-6-{[6-deoxy-4-*O*-[(2*E*,6*S*)-6-(6-deoxy-β-D-glucopyranosyloxy)-2,6-dimethyl-1-oxoocta-2,7-dienyl]-β-D-glucopyranosyl}oxy}-2-(hydroxymethyl)-6-methyl-1-*

*oxoocta-2,7-dienyl}oxy}-16-hydroxyolean-12-en-28-oic Acid 28-{*O*-α-*L*-Arabinofuranosyl-(1 → 4)-*O*-[β-*D*-glucopyranosyl-(1 → 3)]-*O*-6-deoxy-α-*L*-mannopyranosyl-(1 → 2)-β-*D*-glucopyranosyl} Ester* (= *Adianthifolioside A*; **1**): White amorphous powder. R_f 0.29. $[\alpha]_D^{25} = -30$ ($c = 0.1$, MeOH). IR (KBr): 3500–3300, 2928, 1735, 1718, 1580, 1260, 1090. ^{1}H- and ^{13}C-NMR ((D_5)pyridine): *Tables 1–5.* ESI-TOF-MS (pos.): 2380 ($[M + 2 + 2Na]^{++}$).

*(3β,16α,21β)-21-{{(2E,6S)-6-{{6-Deoxy-4-*O*-[(2E,6S)-6-(6-deoxy-β-*D*-glucopyranosyloxy)-2,6-dimethyl-1-oxoocta-2,7-dienyl]-β-*D*-glucopyranosyl}oxy}-2-(hydroxymethyl)-6-methyl-1-oxoocta-2,7-dienyl}oxy}-16-hydroxy-3-{[*O*-β-*D*-xylopyranosyl-(1 → 2)-*O*-6-deoxy-β-*D*-galactopyranosyl-(1 → 6)-2-(acetylamino)-2-deoxy-β-*D*-glucopyranosyl]oxy}olean-12-en-28-oic Acid 28-{*O*-α-*L*-Arabinofuranosyl-(1 → 4)-*O*-[β-*D*-glucopyranosyl-(1 → 3)]-*O*-6-deoxy-α-*L*-mannopyranosyl-(1 → 2)-β-*D*-glucopyranosyl} Ester* (= *Adianthifolioside B*; **2**): White amorphous powder. R_f 0.39. $[\alpha]_D^{25} = -40$ ($c = 0.1$, MeOH). IR (KBr): 3500–3300, 2926, 1735, 1718, 1570, 1639, 1260, 1090. ^{1}H- and ^{13}C-NMR ((D_5)pyridine): *Tables 1–5.* HR-ESI-MS (pos.): 2255.0106 ($[M + 2Na]^+$; calc. 2255.0089).

*(3β,16α,21β)-21-{{(2E,6S)-6-{{6-Deoxy-3-*O*-(2E,6S)-6-(6-deoxy-β-*D*-glucopyranosyloxy)-2,6-dimethyl-1-oxoocta-2,7-dienyl]-β-*D*-glucopyranosyl}oxy}-2,6-dimethyl-1-oxoocta-2,7-dienyl}oxy}-16-hydroxy-3-{[*O*-β-*D*-xylopyranosyl-(1 → 2)-*O*-6-deoxy-β-*D*-galactopyranosyl-(1 → 6)-2-(acetylamino)-2-deoxy-β-*D*-glucopyranosyl]oxy}olean-12-en-28-oic Acid 28-{*O*-α-*L*-Arabinofuranosyl-(1 → 4)-*O*-[β-*D*-glucopyranosyl-(1 → 3)]-*O*-6-deoxy-α-*L*-mannopyranosyl-(1 → 2)-β-*D*-glucopyranosyl} Ester* (= *Adianthifolioside E*; **3**): White amorphous powder. R_f 0.45. $[\alpha]_D^{25} = -43$ ($c = 0.1$, MeOH). IR (KBr): 3500–3300, 2926, 1735, 1718, 1570, 1639, 1260, 1090. ^{1}H- and ^{13}C-NMR ((D_5)pyridine): *Tables 1–5.* ESI-TOF-MS (pos.): 2241 ($[M + 2 + 2Na]^{++}$).

*(3β,16α,21β)-3-{[*O*-α-*L*-Arabinopyranosyl-(1 → 2)-*O*-6-deoxy-β-*D*-galactopyranosyl-(1 → 6)-*O*-[β-*D*-glucopyranosyl-(1 → 2)]-β-*D*-glucopyranosyl}oxy}-21-{[(2E,6S)-6-(6-deoxy-β-*D*-glucopyranosyloxy)-2,6-dimethyl-1-oxoocta-2,7-dienyl]oxy}-16-hydroxyolean-12-en-28-oic Acid 28-{*O*-α-*L*-Arabinofuranosyl-(1 → 4)-*O*-[β-*D*-glucopyranosyl-(1 → 3)]-*O*-6-deoxy-α-*L*-mannopyranosyl-(1 → 2)-β-*D*-glucopyranosyl} Ester* (= *Adianthifolioside F*; **4**): White amorphous powder. R_f 0.22. $[\alpha]_D^{25} = -10$ ($c = 0.1$, MeOH). IR (KBr): 3500–3300, 2927, 1735, 1720, 1570, 1639, 1260, 1090. ^{1}H- and ^{13}C-NMR ((D_5)pyridine): *Tables 1–5.* FAB-MS (neg.): 2003 ($[M - H]^-$).

Acid Hydrolysis. A soln. of saponin (5 mg) in H_2O (2 ml) and 2N aq. CF_3COOH (5 ml) was refluxed on a water bath for 3 h. After extraction with $CHCl_3$ (3 × 5 ml), the aq. layer was repeatedly evaporated with MeOH until neutral and then analyzed by TLC by comparison with standard sugars (solvent system *c*).

Alkaline Hydrolysis. The saponin (5 mg) was refluxed in 5% aq. KOH soln. (10 ml) for 2 h. The mixture was adjusted to pH 6 with dil. HCl soln. and then extracted with H_2O-sat. BuOH (3 × 10 ml). The combined BuOH extracts were washed with H_2O and evaporated: prosapogenin.

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