New Acylated Preatroxigenin Saponins from *Atroxima congolana*

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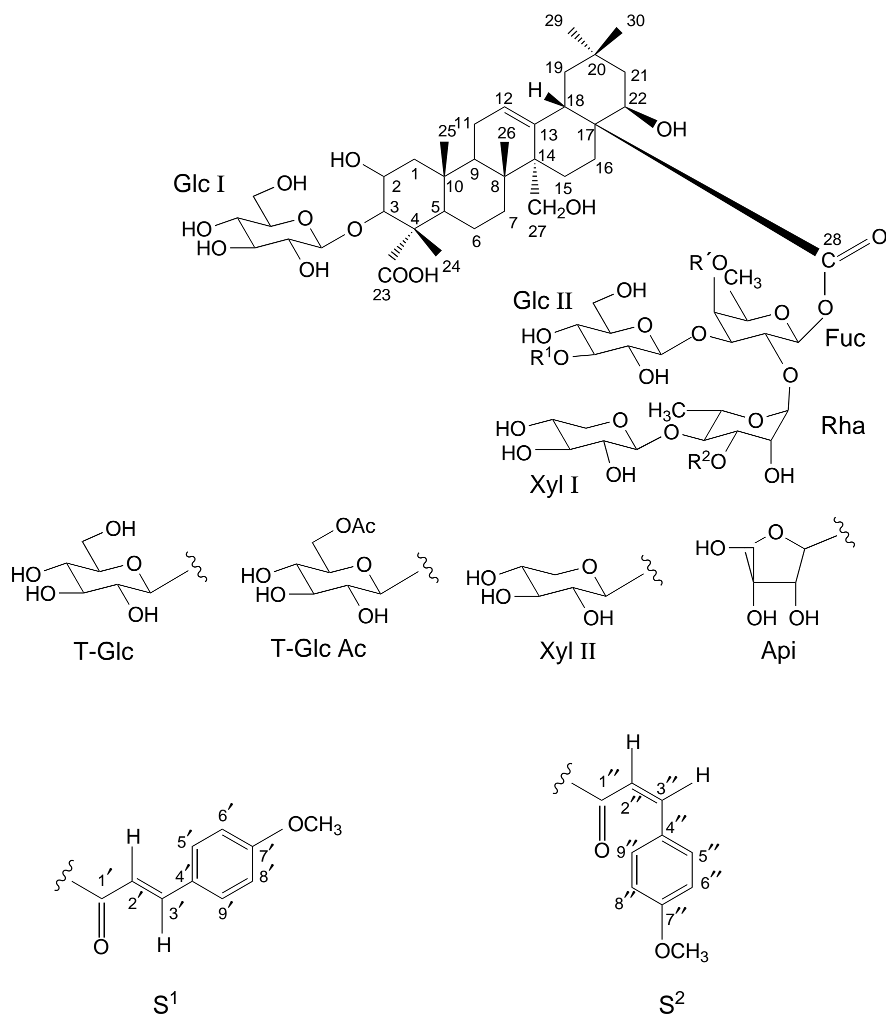
Eight new acylated preatroxigenin saponins **1**–**8** were isolated as four inseparable mixtures of the *trans*- and *cis*-4-methoxycinnamoyl derivatives, atroximasaponins A_1/A_2 (**1**/**2**), B_1/B_2 (**3**/**4**), C_1/C_2 (**5**/**6**) and D_1/D_2 (**7**/**8**) from the roots of *Atroxima congolana*. These compounds are the first examples of triterpene saponins containing preatroxigenin (=(2β,3β,4α,22β)-2,3,22,27-tetrahydroxyolean-12-ene-23,28-dioic acid as aglycone. Their structures were elucidated on the basis of extensive 1D- and 2D-NMR studies and FAB-MS as 3-*O*(β-D-glucopyranosyl)preatroxigenin 28-{*O*-β-D-xylopyranosyl-(1 → 4)-*O*-α-L-rhamnopyranosyl-(1 → 2)-*O*-[*O*-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 3)]-4-*O*-(*trans*-4-methoxycinnamoyl)-β-D-fucopyranoyl} ester (**1**) and its *cis*-isomer **2**, 3-*O*-(β-D-glucopyranosyl)preatroxigenin 28-{*O*-β-D-xylopyranosyl-(1 → 4)-*O*-α-L-rhamnopyranosyl-(1 → 2)-*O*-[*O*-6-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 3)]-4-*O*-(*trans*-4-methoxycinnamoyl)-β-D-fucopyranosyl} ester (**3**) and its *cis*-isomer **4**, 3-*O*-(β-D-glucopyranosyl)preatroxigenin 28-{*O*-β-D-xylopyranosyl-(1 → 4)-*O*-[β-D-apiofuranosyl-(1 → 3)]-*O*-α-L-rhamnopyranosyl-(1 → 2)-*O*-[*O*-6-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 3)]-4-*O*-(*trans*-4-methoxycinnamoyl)-β-D-fucopyranoyl} ester (**5**) and its *cis*-isomer **6**, 3-*O*-(β-D-glucopyranosyl)preatroxigenin 28-{*O*-β-D-xylopyranosyl-(1 → 4)-*O*-[β-D-apiofuranosyl-(1 → 3)]-*O*-α-L-rhamnopyranosyl-(1 → 2)-*O*-[*O*-β-D-xylopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 3)]-4-*O*-(*trans*-4-methoxycinnamoyl)-β-D-fucopyranosyl ester (**7**) and its *cis*-isomer **8**.

Introduction. – In the course of our studies on the saponins of the family of Polygalaceae [1][2], we have investigated the cortex of the roots of *Atroxima congolana* STAPF. This genus is distributed in the forests of Western and Central Africa [3]. Although the presence of preatroxigenin (=(2β,3β,4α,22β)-2,3,22,27-tetrahydroxyolean-12-ene-23,28-dioic Acid) was reported in *Atroxima afzeliana*, there is no saponin previously elucidated containing this aglycone [4]. This paper describes the isolation and structure elucidation of eight new triterpene glycosides named atroximasaponins A_1, A_2, B_1, B_2, C_1, C_2, D_1, and D_2 (**1**–**8**) respectively, which were obtained as four inseparable mixtures of the *trans*- and *cis*-acylated derivatives from the EtOH extract of the roots of *A. congolana.*

Results and Discussion. – The EtOH extract of the cortex of the roots of *A. congolana* was suspended in MeOH and purified by precipitation with Et_2O to yield a crude saponin mixture [3]. This extract was further fractionated by column chromatography (*Sephadex LH-20*) and repeated medium-pressure liquid chromatography (MPLC) with normal silica gel, followed by semi-prep. reversed-phase HPLC yielding atroximasaponins A_1/A_2, B_1/B_2, C_1/C_2, and D_1/D_2 as four inseparable mixtures, each one of them giving only one spot by HPTLC but two peaks by HPLC.



	R[1 a)]	R^2	R´[b)]
Atroximasaponin A_1 (**1**)	T-Glc	H	S^1
Atroximasaponin A_2 (**2**)	T-Glc	H	S^2
Atroximasaponin B_1 (**3**)	T-Glc Ac	H	S^1
Atroximasaponin B_2 (**4**)	T-Glc Ac	H	S^2
Atroximasaponin C_1 (**5**)	T-Glc Ac	Api	S^1
Atroximasaponin C_2 (**6**)	T-Glc Ac	Api	S^2
Atroximasaponin D_1 (**7**)	Xyl II	Api	S^1
Atroximasaponin D_2 (**8**)	Xyl II	Api	S^2

[a]) T stands for terminal. [b]) Arbitrary numbering.

Saponin structures were established mainly by spectroscopic 1D and 2D NMR experiments (^{1}H, ^{13}C, COSY, TOCSY, NOESY, HSQC, HMBC, see *Tables 1–3* and below) and FAB-MS. Atroximasaponins A_1/A_2 (**1/2**), B_1/B_2 (**3/4**), C_1/C_2 (**5/6**) and D_1/D_2 (**7/8**) were isolated as amorphous powders, which gave fluorescence-quenching zones under 254-nm and violet-blue fluorescence under 365-nm UV light on TLC without chemical treatment. On acid hydrolysis, **1**–**8** afforded the same artifactual aglycone. TLC of the hydrolyzates and comparison with standard sugars allowed the identification of the monosaccharide units as glucose, fucose, rhamnose, and xylose in the case of **1**–**4**, and as glucose, fucose, rhamnose, xylose, and apiose in the case of **5**–**8**. Alkaline hydrolysis of **1**–**8** gave the same prosapogenin, which is a little more polar than tenuifolin (= 3-*O*-(β-D-glucopyranosyl)presenegenin) (TLC) obtained from *Muraltia heisteria* [1]. The mild alkaline hydrolysis of **1**–**8** with 1% KOH solution

Table 1. *^{13}C-* (150 MHz)[a]) *and ^{1}H-NMR* (600 MHz) *Spectral Data of the Aglycone Parts of* **1**–**8** *in* (D_5) *Pyridine from 1D- and 2D-NMR Experiments.* δ in ppm.

	1/2		**3/4**		**5/6**		**7/8**	
	δ(C)	δ(H)[b])[c])	δ(C)	δ(H)[b])[c])	δ(C)	δ(H)[b])[c])	δ(C)	δ(H)[b])[c])
CH_2(1)	43.2	1.42, 2.20	43.5	1.40, 2.22	43.9	1.45, 2.30	43.9	1.32, 2.25
CH(2)	69.7	4.62	69.9	4.60	70.0	4.60	69.8	4.68
CH(3)	86.1	4.47	86.5	4.52	86.7	4.52	85.8	4.54
C(4)	52.5		52.5		52.1		52.3	
CH(5)	51.8	2.01	52.1	2.13	51.8	2.10	51.8	2.12
CH_2(6)	20.7	n.d.	21.0	n.d.	21.0	n.d.	21.0	n.d.
CH_2(7)	32.9	n.d.	33.3	n.d.	33.6	n.d.	33.6	1.87, 2.27
C(8)	40.2		40.3		40.4		40.8	
CH(9)	48.5	2.03	48.8	2.10	48.7	2.10	49.0	2.20
C(10)	36.0		36.1		36.1		36.6	
CH_2(11)	23.0	1.82, 1.87	23.1	n.d.	23.1	n.d.	23.5	2.07, 2.15
CH(12)	127.0	5.73	126.9	5.77	126.9	5.83	126.9	5.88
C(13)	138.5		139.1		139.0		139.6	
C(14)	47.7		48.2		48.0		48.2	
CH_2(15)	23.8	1.95, 2.00	24.1	n.d.	23.9	1.95, 2.00	23.8	2.09, 2.18
CH_2(16)	23.7	n.d., 1.92	24.0	n.d.	23.8	n.d., 1.96	23.7	n.d., 2.18
C(17)	53.1		53.3		53.3		53.3	
CH(18)	38.3	3.31	38.4	3.37	39.2	3.45	39.2	3.54
CH_2(19)	45.1	1.25, 1.62	45.9	1.30, 1.70	45.5	1.35, 1.75	45.5	1.43, 1.86
C(20)	29.6		29.8		30.0		30.2	
CH_2(21)	40.3	n.d., 1.50	40.4	1.30, 1.51	40.8	1.43, 1.55	41.3	1.46, 1.55
CH(22)	70.4	4.56	70.2	4.64	70.2	4.72	71.3	4.68
C(23)	181.1		181.5		182.0		182.0	
Me(24)	14.0	1.68 (*s*)	14.3	1.76 (*s*)	14.4	1.85 (*s*)	14.0	1.88 (*s*)
Me(25)	17.2	1.27 (*s*)	17.0	1.37 (*s*)	17.2	1.45 (*s*)	17.2	1.50 (*s*)
Me(26)	18.1	0.92 (*s*)	18.3	0.98 (*s*)	18.0	1.20 (*s*)	18.4	1.18 (*s*)
CH_2(27)	63.4	3.65, 4.0	63.9	3.72, 4.07	63.4	3.84, 4.14	63.9	3.88, 4.11
C(28)	175.5		174.7		174.4		174.5	
Me(29)	33.4	0.77 (*s*)	33.7	0.78 (*s*)	33.7	0.79 (*s*)	33.9	0.84 (*s*)
Me(30)	26.7	1.20 (*s*)	26.8	1.22 (*s*)	26.8	1.28 (*s*)	27.3	1.35 (*s*)

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

Table 2. *^{13}C- (150 MHz) Spectral Data of the Sugar Moieties of **1**–**8** in (D_5)Pyridine from 1D- and 2D-NMR Experiments*[a]). δ in ppm.

		δ(C)							
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
3-*O*-Glc I	CH(1)	103.5	103.5	103.6	103.6	103.6	103.6	103.9	103.9
	CH(2)	74.3	74.3	74.2	74.2	74.5	74.5	74.2	74.2
	CH(3)	76.3	76.3	76.4	76.4	76.7	76.7	77.0	77.0
	CH(4)	69.4	69.4	69.4	69.4	69.0	69.0	70.3	70.3
	CH(5)	76.9	76.9	76.7	76.7	77.2	77.2	77.7	77.7
	CH_2(6)	61.2	61.2	61.4	61.4	61.4	61.4	61.9	61.9
28-*O*-Sugars									
Fuc	CH(1)	93.7	93.7	93.8	93.8	94.2	94.2	94.4	94.2
	CH(2)	71.0	71.0	71.0	71.0	71.0	71.0	71.2	71.1
	CH(3)	82.9	82.9	82.9	82.9	82.8	82.8	82.7	82.7
	CH(4)	73.6	73.3	74.0	73.7	73.5	73.5	74.1	74.0
	CH(5)	70.4	70.2	70.6	70.5	70.4	70.4	70.7	70.6
	Me(6)	15.7	15.6	15.7	15.6	16.3	16.3	16.1	16.0
Rha	CH(1)	100.2	100.0	100.2	100.0	100.5	100.4	101.0	100.9
	CH(2)	70.5	70.4	70.9	70.6	71.2	71.2	71.1	71.0
	CH(3)	71.7	71.7	71.3	71.3	80.5	80.5	80.6	80.6
	CH(4)	83.8	83.8	83.9	84.0	78.1	78.1	78.1	78.1
	CH(5)	67.5	67.4	67.6	67.5	67.7	67.7	67.9	67.7
	Me(6)	17.6	17.6	17.8	17.7	18.1	18.1	17.6	17.6
Api	CH(1)	–	–	–	–	110.6	110.6	111.0	111.0
	CH(2)	–	–	–	–	77.6	77.6	77.5	77.5
	C(3)	–	–	–	–	79.1	79.1	79.5	79.5
	CH_2(4)	–	–	–	–	74.1	74.1	74.3	74.3
	CH_2(5)	–	–	–	–	64.0	64.0	64.6	64.6
Xyl I	CH(1)	106.0	106.0	106.0	106.0	104.6	104.6	105.0	105.0
	CH(2)	75.0	75.0	75.2	75.2	74.7	74.7	74.7	74.7
	CH(3)	76.2	76.2	76.4	76.4	76.9	76.9	77.4	77.4
	CH(4)	70.1	70.1	70.4	70.4	70.6	70.6	70.1	70.1
	CH_2(5)	65.9	65.9	66.2	66.2	65.9	65.9	65.9	65.9
Glc II	CH(1)	104.8	104.8	105.0	105.0	105.4	105.4	105.3	105.3
	CH(2)	74.0	74.0	75.2	75.2	74.7	74.7	75.0	75.0
	CH(3)	86.3	86.3	86.0	86.0	86.7	86.7	87.3	87.3
	CH(4)	70.2	70.2	70.4	70.4	70.4	70.4	69.3	69.3
	CH(5)	76.5	76.5	76.8	76.8	77.2	77.2	77.7	77.7
	CH_2(6)	61.6	61.6	61.5	61.5	61.5	61.5	62.0	62.0
T-Glc	CH(1)	103.6	103.6	103.7	103.7	103.9	103.9	–	–
	CH(2)	74.0	74.0	74.0	74.0	74.1	74.1	–	–
	CH(3)	76.5	76.5	76.4	76.4	77.0	77.0	–	–
	CH(4)	68.8	68.8	69.3	69.3	70.0	70.0	–	–
	CH(5)	76.8	76.8	77.3	77.3	77.6	77.6	–	–
	CH_2(6)	61.1	61.1	63.4	63.4	63.1	63.1	–	–
	Ac-O–C(6)	–	–	20.4, 171.8	20.3, 171.4	20.4, 171.6	20.3, 170.6	–	–
Xyl II	CH(1)	–	–	–	–	–	–	104.6	104.6
	CH(2)	–	–	–	–	–	–	74.8	74.8
	CH(3)	–	–	–	–	–	–	78.0	78.0
	CH(4)	–	–	–	–	–	–	71.1	71.1
	CH_2(5)	–	–	–	–	–	–	66.7	66.7
Acid	C(1′,1″)	167.8	166.6	167.8	166.7	166.7	166.0	167.6	166.6
	CH(2′,2″)	114.4	115.5	114.6	115.7	115.1	116.0	115.3	116.2
	CH(3′,3″)	146.0	144.5	145.9	144.5	145.0	144.0	145.7	144.4
	CH(4′,4″)	126.3	126.6	126.8	126.8	126.3	126.6	126.4	126.6
	CH(5′,9′), CH(5″,9″)	130.0	132.4	130.0	132.5	130.0	132.6	130.3	132.8
	CH(6′,8′), CH(6″,8″)	114.3	113.5	114.3	113.5	114.3	113.6	114.5	113.8
	MeO–*C*(7′,7″)	161.5	160.5	161.4	160.4	161.4	160.4	161.8	160.8
	*Me*O–C(7′,7″)	55.2	55.0	55.2	55.0	55.2	55.0	55.3	55.2

[a]) Multiplicities were assigned from DEPT spectra

Table 3. *¹H-NMR* (600 MHz) *Spectral Data of the Sugar Moieties of* **1**–**8** *in (D₅)Pyridine from 1D- and 2D-NMR Experiments*[a]). *J* in Hz.

		δ(H)							
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
3-*O*-Glc I	H-C(1)	4.85 (*d*, *J* = 7.0)	4.85 (*d*, *J* = 7.0)	4.89 (*d*, *J* = 7.0)	4.89 (*d*, *J* = 7.0)	4.90 (*d*, *J* = 7.0)	4.90 (*d*, *J* = 7.0)	4.92 (*d*, *J* = 7.0)	4.92 (*d*, *J* = 7.0)
	H−C(2)	3.78	3.78	3.82	3.82	4.84	4.84	3.98	3.98
	H−C(3)	4.00	4.00	4.08	4.08	4.11	4.11	4.04	4.04
	H−C(4)	3.96	3.96	4.05	4.05	3.95	3.95	4.13	4.13
	H−C(5)	3.84	3.84	3.82	3.82	3.82	3.82	3.88	3.88
	CH_2(6)	3.95, 4.25	3.95, 4.25	4.01, 4.22	4.01, 4.22	4.08, 4.24	4.08, 4.24	4.11, 4.33	4.11, 4.33
28-O-Sugars									
Fuc	H−C(1)	5.98 (*d*, *J* = 8.0)	5.91 (*d*, *J* = 8.0)	5.97 (*d*, *J* = 8.0)	5.91 (*d*, *J* = 8.0)	6.00 (*d*, *J* = 8.0)	6.00 (*d*, *J* = 8.0)	6.13 (*d*, *J* = 8.0)	6.10 (*d*, *J* = 8.0)
	H−C(2)	4.62	4.48	4.73	4.60	4.74	4.74	4.78	4.77
	H−C(3)	4.44	4.39	4.32	4.32	4.30	4.30	4.48	4.48
	H−C(4)	5.88	5.85	5.90	5.88	5.78	5.78	5.98	5.97
	H−C(5)	4.23	4.18	4.23	4.18	4.18	4.18	4.20	4.18
	Me(6)	1.17 (*d*, *J* = 6.0)	1.11 (*d*, *J* = 6.0)	1.21 (*d*, *J* = 6.0)	1.16 (*d*, *J* = 6.0)	1.20 (*d*, *J* = 6.0)	1.20 (*d*, *J* = 6.0)	1.16 (*d*, *J* = 6.0)	1.15 (*d*, *J* = 6.0)
Rha	H−C(1)	6.13 (br. *s*)	6.09 (br. *s*)	6.30 (br. *s*)	6.28 (br. *s*)	6.22 (br. *s*)	6.22 (br. *s*)	6.35 (br. *s*)	6.33 (br. *s*)
	H−C(2)	4.56	4.53	4.63	4.61	4.81	4.81	4.90	4.88
	H−C(3)	4.32	4.32	4.37	4.37	4.44	4.44	4.55	4.55
	H−C(4)	4.02	4.02	4.05	4.04	4.32	4.32	4.41	4.41
	H−C(5)	4.27	4.23	4.32	4.28	4.49	4.49	4.59	4.51
	Me(6)	1.61 (*d*, *J* = 6.0)	1.56 (*d*, *J* = 6.0)	1.63 (*d*, *J* = 6.0)	1.60 (*d*, *J* = 6.0)	1.63 (*d*, *J* = 6.0)	1.63 (*d*, *J* = 6.0)	1.70 (*d*, *J* = 6.0)	1.66 (*d*, *J* = 6.0)
Api	H−C(1)					5.98 (br. *s*)	5.98 (br. *s*)	6.04 (br. *s*)	6.04 (br. *s*)
	H−C(2)					4.62	4.62	4.72	4.72
	CH_2(4)					4.14, 4.43	4.14, 4.43	4.23, 4.54	4.23, 4.54
	CH_2(5)					4.00, 4.01	4.00, 4.01	4.01, 4.02	4.01, 4.02
Xyl I	H−C(1)	4.78 (*d*, *J* = 7.0)	4.78 (*d*, *J* = 7.0)	4.77 (*d*, *J* = 7.0)	4.77 (*d*, *J* = 7.0)	5.11 (*d*, *J* = 7.0)	5.11 (*d*, *J* = 7.1)	5.20 (*d*, *J* = 7.0)	5.20 (*d*, *J* = 7.0)
	H−C(2)	3.76	3.76	3.87	3.87	3.90	3.90	3.94	3.94
	H−C(3)	4.00	4.00	4.07	4.07	4.01	4.01	4.09	4.09
	H−C(4)	3.84	3.84	3.86	3.86	3.90	3.90	4.04	4.04
	CH_2(5)	3.38, 4.03	3.38, 4.03	3.35, 4.05	3.35, 4.05	3.35, 4.04	3.35, 4.04	3.40, 4.11	3.40, 4.11
Glc II	H−C(1)	4.99 (*d*, *J* = 7.2)	4.99 (*d*, *J* = 7.2)	5.02 (*d*, *J* = 7.2)	5.02 (*d*, *J* = 7.2)	5.02 (*d*, *J* = 7.1)	5.02 (*d*, *J* = 7.1)	5.02 (*d*, *J* = 7.1)	5.02 (*d*, *J* = 7.1)
	H−C(2)	3.75	3.75	3.74	3.74	3.91	3.91	3.95	3.95
	H−C(3)	4.07	4.07	4.15	4.15	4.10	4.10	4.12	4.12
	H−C(4)	3.76	3.76	3.85	3.85	3.94	3.94	3.98	3.98
	H−C(5)	3.81	3.81	3.81	3.81	3.81	3.81	3.86	3.86
	CH_2(6)	3.93, 4.24	3.93, 4.24	3.98, 4.34	3.98, 4.34	4.02, 4.38	4.02, 4.38	4.19, 4.44	4.19,4.44
T-Glc	H−C(1)	5.02 (*d*, *J* = 7.0)	5.02 (*d*, *J* = 7.0)	5.07 (*d*, *J* = 7.0)	5.07 (*d*, *J* = 7.0)	5.07 (*d*, *J* = 7.0)	5.07 (*d*, *J* = 7.0)		
	H−C(2)	3.76	3.76	3.75	3.75	3.88	3.88		
	H−C(3)	3.96	3.96	4.08	4.08	4.01	4.01		
	H−C(4)	3.82	3.82	3.96	3.96	3.92	3.92		
	H−C(5)	3.80	3.80	3.86	3.86	3.84	3.84		
	CH_2(6)	4.00,4.16	4.00,4.16	4.57,4.78	4.57,4.78	4.50,4.80	4.50,4.80		
	AcO−C(6)			1.92 (*s*, 1 H)	1.96 (*s*, 1 H)	1.99 (*s*, 1 H)	2.02 (*s*, 1 H)		
Xyl II	H−C(1)							5.12 (*d*, *J* = 8.0)	5.12 (*d*, *J* = 8.0)
	H−C(2)							3.88	3.88
	H−C(3)							4.02	4.02
	H−C(4)							4.08	4.08
	CH_2(5)							3.53,4.13	3.53,4.13
Acid	H−C(2′,2″)	6.32 (*d*, *J* = 16.0)	5.87 (*d*, *J* = 12.0)	6.30 (*d*, *J* = 16.0)	5.83 (*d*, *J* = 12.1)	6.27 (*d*, *J* = 16.1)	5.80 (*d*, *J* = 12.2)	6.43 (*d*, *J* = 15.8)	5.87 (*d*, *J* = 12.0)
	H−C(3′,3″)	7.73 (*d*, *J* = 16.0)	6.82 *d*, *J* = 12.0)	7.72 (*d*, *J* = 16.0)	6.82 (*d*, *J* = 12.1)	7.70 (*d*, *J* = 16.1)	6.70 (*d*, *J* = 12.2)	7.85 (*d*, *J* = 15.8)	6.85 (*d*, *J* = 12.0)
	H−(5′,9′), H−C(5″,9″)	7.27 (*d*, *J* = 8.0)	7.74 (*d*, *J* = 8.0)	7.26 (*d*, *J* = 8.8)	7.77 (*d*, *J* = 8.8)	7.27 (*d*, *J* = 8.4)	7.83 (*d*, *J* = 8.4)	7.37 (*d*, *J* = 8.0)	7.90 (*d*, *J* = 8.0)
	H−C(6′,8′), H−C(6″,8″)	6.89 (*d*, *J* = 8.0)	6.88 (*d*, *J* = 8.0)	6.90 (*d*, *J* = 8.8)	6.88 (*d*, *J* = 8.8)	6.92 (*d*, *J* = 8.4)	6.90 (*d*, *J* = 8.4)	6.99 (*d*, *J* = 8.0)	6.97 (*d*, *J* = 8.0)
	MeO−C(7′,7″)	3.76 (*s*, 3 H)	3.71 (*s*, 3 H)	3.73 (*s*, 3 H)	3.67 (*s*, 3 H)	3.70 (*s*, 3 H)	3.67 (*s*, 3 H)	3.74 (*s*, 3 H)	3.69 (*s*, 3 H)

[a]) Overlapped signals are reported without designated multiplicity.

(60 min at room temperature) yielded *trans*- and *cis*-4-methoxycinnamic acid (TLC) and deacylated saponins, which were homogeneous for each inseparable mixture according to TLC and HPLC.

The full assignment of all the ^{1}H- and ^{13}C-NMR signals by 2D NMR experiments of **1/2** resulted in the establishment of their structures as 3-*O*-(*β*-D-glucopyranosyl)preatroxigenin 28-{*O*-*β*-D-xylopyranosyl-(1 → 4)-*O*-*α*-L-rhamnopyranosyl-(1 → 2)-*O*-[*O*-*β*-D-glucopyranosyl-(1 → 3)-*β*-D-glucopyranosyl-(1 → 3)]-4-*O*-(*trans*-4-*methoxycinnamoyl*-*β*-D-fucopyranosyl} ester (**1**) and its *cis*-isomer **2**, two new natural compounds [1][5–10].

The ^{1}H,^{1}H-COSY experiments indicated that **1/2** is a mixture of *trans*- and *cis*-4-methoxycinnamoyl-substituted triterpenoic acid glycosyl esters (2:1, from relative NMR and HPLC intensivities). This mixture was homogeneous by HPTLC but was separated into *trans*- and *cis*-isomers by HPLC. All attempts to separate **1/2** by semi-prep. HPLC were unsuccessful. This phenomenon of isomerization referred to the effect of light on the 4-methoxycinnamoyl group in aqueous MeOH solution. Under these conditions, isomeric structures of the 4-methoxycinnamoyl groups in **1** and **2** showed tautomer-like behavior. This phenomenon has already been observed in (*E*)/(*Z*) mixtures of senegasaponins from *Polygala senega* [11], in Jenissensosides from *Silene jenisseensis* [12], and in the acylated saponins from *Muraltia heisteria* [1].

The HSQC spectrum of **1/2** displayed signals of five tertiary Me groups at $\delta_{(H)}$ 1.68 (*s*, Me(24)), 1.27 (*s*, Me(25)), 1.20 (*s*, Me(30)), 0.92 (*s*, Me(26)), and 0.77 (*s*, Me(29)) and one trisubstituted olefinic proton at *δ* 5.73 (br. *s*), which correlated with five sp^3 C-atoms at *δ*(C) 14.0, 17.2, 26.7, 18.1, and 33.4 and one sp^2 olefinic C-atom at *δ* 127.0, respectively. These data together with the presence of a quaternary C-atom observed in the ^{13}C-NMR spectrum at *δ* 138.5, indicated that the aglycone possessed an olean-12-ene skeleton. Further, its ^{1}H-NMR spectrum showed three oxygenated methine moieties at *δ*(H) 4.62 (H–C(2)), 4.56 (H–C(22)), and 4.47 (H–C(3)) and one CH_2 group at *δ*(H) 4.00, 3.65 (CH_2(27)), which gave correlations in the HSQC spectrum with ^{13}C-NMR signals at *δ* 69.7, 70.4, 86.1, and 63.4, respectively. Comparison of ^{1}H- and ^{13}C-NMR spectra of the aglycone of **1/2** with those of presenegenin (=(2*β*,3*β*,4*α*)-2,3,27-trihydroxyolean-12-ene-23,28-dioic acid) showed that the only difference between the two aglycones was an additional oxymethine proton at C(22) in **1/2** [1]. After extensive 2D NMR studies, the aglycone was identified as preatroxigenin (=(2*β*,3*β*,4*α*,22*β*)-2,3,22,27-tetrahydroxyolean-12-ene-23,28-dioic acid) (*Fig.*). Most of the signals were in good agreement with literature data [3][4]. Furthermore, the fragment ion peak at *m/z* 533 ([$M - H - 162 - 162 - 132 - 2 \times 146 - 160 - 162]^-$) in the FAB-MS corresponds to the peak of the aglycone (preatroxigenin).

The negative-ion FAB-MS of **1/2** showed a quasi-molecular ion peak at *m/z* 1603 ([$M - H]^-$), indicating a molecular mass of 1604, compatible with a molecular formula $C_{75}H_{112}O_{37}$. Other significant ion peaks appeared at *m/z* 1441 ([$M - H - 162]^-$), 1279 ([$M - H - 2 \times 162]^-$), and 695 ([$M - H - 2 \times 162 - 132 - 2 \times 146 - 160]^-$), corresponding to the loss of two hexosyl, one pentosyl, two deoxyhexosyl, and one 4-methoxycinnamoyl moiety, respectively.

The ^{1}H,^{1}H-COSY experiment of **1/2** permitted us to identify the *trans*-olefinic protons of the 4-methoxycinnamoyl moiety at *δ*(H) 6.32 (*d*, *J* = 16.0 Hz, H–C(2′)) and 7.73 (*d*, *J* = 16.0 Hz, H–C(3′)), the *cis*-olefinic protons at *δ* 5.87 (*d*, *J* = 12.0 Hz, H–C(2″)) and 6.82 (*d*, *J* = 12.0 Hz, H–C(3″)), and the disubstituted benzene ring protons at *δ* 7.27 (*d*, *J* = 8.0 Hz, H–C(5′) and H–C(9′)) and 6.89 (*d*, *J* = 8.0 Hz, H–C(6′) and H–C(8′)) for the *trans*- and *δ* 7.74 (*d*, *J* = 8.0 Hz, H–C(5″) and H–C(9″)) and 6.88 (*d*, *J* = 8.0 Hz, H–C(6″) and H–C(8″)) for the *cis*-derivatives.

The ^{1}H-NMR spectrum of **1/2** showed six anomeric signals at *δ* 6.13 (br.*s*), 5.98 (*d*, *J* = 8.0 Hz), 5.02 (*d*, *J* = 7.0 Hz), 4.99 (*d*, *J* = 7.2 Hz), 4.85 (*d*, *J* = 7.0 Hz), and 4.78 (*d*, *J* = 7.0 Hz), which correlated in the HSQC spectrum with ^{13}C-NMR signals at *δ* 100.2, 93.7, 103.6, 104.8, 103.5, and 106.0, respectively. 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 3*), 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 one *α*-rhamnopyranosyl (Rha), one *β*-fucopyranosyl (Fuc), three *β*-glucopyranosyl (Glc), and one *β*-xylopyranosyl (Xyl) units. The common D-configuration for Fuc, Glc, and Xyl and the

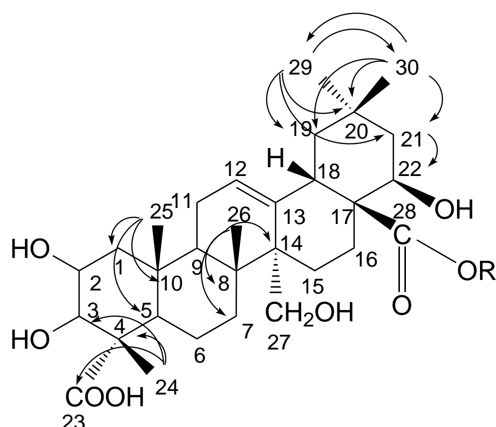


Figure. *HMBC Correlations of the aglycone of* **1**–**8**.

L-configuration for Rha were assumed, according to those most encountered among the plant glycosides in each case.

On the basis of extensive 1D and 2D NMR experiments, it can be concluded that **1/2** were bisdesmosidic saponins with one Glc at C(3) (δ(C) 86.1) of the aglycone and the other five monosaccharides linked at C(28) (δ(C) 175.5) through an ester bond.

The NOESY correlation observed between the anomeric proton of Glc I (Glc I H−C(1)) at δ 4.85 (*d*, *J* = 7.0 Hz) and H−C(3) of the aglycone (Agly H−C(3)) at δ 4.47 indicated that the glucopyranosyl moitey was linked to the preatroxigenin unit at C(3). Further confirmation was obtained by the HMBC correlation between δ(H) 4.85 (*d*, *J* = 7.0 Hz, Glc I H−C(1)) and δ(C) 86.1 (Agly, C(3)). It was concluded to be a terminal Glc (Glc I) by its ^{1}H- and ^{13}C-NMR data (*Tables 2* and *3*). In addition, the fragment ions at *m/z* 695 ($[M - H - 162 - 162 - 132 - 2 \times 146 - 160]^-$) and 533 ($[M - H - 162 - 162 - 132 - 2 \times 146 - 160 - 162]^-$), showed the elimination of one hexosyl unit from the fragment-ion peak of the aglycone. The sequence of the sugars at C(28) of the aglycone was based on HMBC and NOESY experiments. The HMBC between δ(H) 5.98 (*d*, *J* = 8.0 Hz) (Fuc H−C(1)) and δ(C) 175.5 (Agly C(28)) confirmed the Fuc to be linked at C(28) of the aglycone. The location of the 4-methoxycinnamoyloxy group at C(4) of Fuc (δ(H) 5.88, Fuc H−C(4)) was determined by the TOCSY and COSY plots, starting from the anomeric ^{1}H-NMR signal of Fuc at δ 5.98 (*d*, *J* = 8.0 Hz). The downfield shifts observed in the HSQC spectrum for the Fuc H−C(4)/C(4) resonances at δ(H) 5.88/δ(C) 73.6 established that the secondary-alcohol function OH−C(4) of Fuc was acylated. The HMBC between δ(H) 4.62 (Fuc H−C(2)) and δ(C) 100.2 (Rha C(1)) indicated that the Rha was linked to the Fuc by a 1 → 2 linkage. This was confirmed by a NOESY cross-peak between δ(H) 6.13 (br. *s*) (Rha H−C(1)) and δ(H) 4.62 (Fuc H−C(2)). Other HMBCs observed between δ(H) 4.78 (*d*, *J* = 7.0 Hz, Xyl I H−C(1)) and δ(C) 83.8 (Rha C(4)) showed that Xyl I was linked to C(4) of Rha. This was also confirmed by a NOESY cross-peak between δ(H) 4.78 (*d*, *J* = 7.0 Hz, Xyl I H−C(1)) and δ(H) 4.02 (Rha H−C(4)). Furthermore, fragment ions at *m/z* 1279 ($[M - H - 2 \times 162]^-$) and 695 ($[M - H - 2 \times 162 - 132 - 2 \times 146 - 160]^-$) showed the successive elimination of one pentosyl, two deoxyhexosyl, and one 4-methoxycinnamoyl moiety, according to the second fragment-ion peak. The HMBC between δ(H) 4.99 (*d*, *J* = 7.2 Hz, Glc II H−C(1)) and δ(C) 82.9 (Fuc C(3)) indicated that Glc II was linked to C(3) of Fuc. Further confirmation was obtained by a NOESY cross-peak between $\delta_{(H)}$ 4.99 (*d*, *J* = 7.2 Hz, Glc II H−C(1)) and δ(H) 4.44 (Fuc H−C(3)). The HMBCs between δ(H) 5.02 (*d*, *J* = 7.0 Hz, T-Glc H−C(1)) and δ(C) 86.3 (Glc II C(3)) and another HMBC between δ(H) 4.07 (Glc II H−C(3)) and δ(C) 103.6 (T-GlcC(1)) established that T-Glc was attached to C(3) of Glc II. This was confirmed by a NOESY cross-peak between δ(H) 5.02 (*d*, *J* = 7.0 Hz, T-Glc H−C(1)) and δ(H) 4.07 (Glc II H−C(3)). Furthermore, fragment ions at *m/z* 1441 ($[M - H - 162]^-$) and 1279 ($[M - H - 2 \times 162]^-$) showed successive elimination of two hexosyl moieties.

The negative-ion FAB-MS of **3/4** showed a quasi-molecular-ion peak at *m/z* 1645 ($[M - H]^-$), indicating a molecular mass of 1646, leading to the determination of their

molecular formulas as $C_{77}H_{114}O_{38}$, with 42 mass units more than **1/2**. Other significant ion peaks appeared at the same *m/z* values as in **1/2**. Further investigation of 1D and 2D NMR spectroscopic data resulted in the determination of the structures of **3/4** as 3-*O*-(*β*-D-glucopyranosyl)preatroxigenin 28-{*O*-*β*-D-xylopyranosyl-(1 → 4)-*O*-*α*-L-rhamnopyranosyl-(1 → 2)-*O*-[*O*-6-*O*-acetyl-*β*-D-glucopyranosyl-(1 → 3)-*β*-D-glucopyranosyl-(1 → 3)]-4-*O*-(*trans*-4-methoxycinnamoyl)-*β*-D-fucopyranosyl} ester (**3**), and its *cis*-isomer **4**, two new natural compounds [1][5–10].

The ^{1}H- and ^{13}C-NMR spectra of **3/4** allowed us to identify preatroxigenin as aglycone (*Table 1*) and six monosaccharide units by the six anomeric protons at *δ* 6.30 (br. *s*), 5.97 (*d*, *J* = 8.0 Hz), 5.07 (*d*, *J* = 7.0 Hz), 5.02 (*d*, *J* = 7.2 Hz), 4.89 (*d*, *J* = 7.0 Hz), and 4.77 (*d*, *J* = 7.0 Hz), giving correlations in the HSQC spectrum with *δ* 100.2, 93.8, 103.7, 105.0, 103.6, and 106.0, respectively.

Comparison of the NMR spectra of **1/2** and **3/4** showed that the ^{1}H- and ^{13}C-NMR data of **3/4** due to the aglycone part and the sugar moieties at C(3) and C(28) (*Tables 1–3*) were almost superimposable to those of **1/2**. The only difference was the presence of one acetyl group giving rise to the signals at *δ*(C) 20.4 and 171.8 in **3/4**. The location of the acetyl group at C(6) of T-Glc was determined by the TOCSY and COSY plots, starting from the anomeric ^{1}H-NMR signal of T-Glc at *δ* 5.07 (*d*, *J* = 7.0 Hz). The downfield shifts observed in the HSQC spectrum for the T-Glc H–C(6)/C(6) resonances at *δ*(H) 4.57, 4.78/*δ*(C) 63.4 showed the primary-alcohol function OH–C(6) of T-Glc to be acetylated. Furthermore, the fragment-ion peak at *m/z* 1441 ([*M* – H – 162 – 42]$^-$), was consistent with the elimination of one hexosyl and one acetyl moiety.

The negative-ion FAB-MS of **5/6** showed a quasi-molecular-ion peak at *m/z* 1777 ([*M* – H]$^-$), indicating a molecular mass of 1778, compatible with a molecular formula $C_{82}H_{122}O_{42}$. The molecular mass was 132 mass units higher than that of **3/4**, which indicated the presence of one additional pentosyl unit. The assignments of all the ^{1}H- and ^{13}C-NMR signals of **5/6** were successfully carried out with 2D NMR experiments (*Tables 1–3*). Thus, the structures of **5/6** were determined as 3-*O*-(*β*-D-glucopyranosyl)preatroxigenin 28-{*O*-*β*-D-xylopyranosyl-(1 → 4)-*O*-[*β*-D-apiofuranosyl-(1 → 3)]-*O*-*α*-L-rhamnopyranosyl-(1 → 2)-*O*-[*O*-6-*O*-acetyl-*β*-D-glucopyranosyl-(1 → 3)-*β*-D-glucopyranosyl-(1 → 3)]-[4-*O*-(*trans*-4-methoxycinnamoyl)-*β*-D-fucopyranosyl} ester (**5**) and its cis-isomer **6**, two new natural compounds [1] [5–10].

The ^{1}H-NMR spectrum of **5/6** showed seven anomeric-proton signals at *δ* 6.22 (br. *s*), 6.00 (*d*, *J* = 8.0 Hz), 5.98 (br. *s*), 5.11 (*d*, *J* = 7.0 Hz), 5.07 (*d*, *J* = 7.0 Hz), 5.02 (*d*, *J* = 7.1 Hz), and 4.90 (*d*, *J* = 7.0 Hz), which were correlated (HSQC) with *δ* 100.5, 94.2, 110.6, 104.6, 103.9, 105.4, and 103.6, respectively. Comparison of the NMR spectra of **5/6** with those of **3/4** as well as the acid and alkaline hydrolysis revealed that **5/6** had identical monosaccharides to those of **3/4**, in addition to an apiofuranosyl moiety (Api), which was easily identified by its C(3) as being a quaternary C-atom and C(4) and C(5) as being two CH_2 groups. They possessed the same prosapogenin and quite the same sequence of sugars at C(28) of the aglycone of **3/4** (*Tables 1–3*) with only one difference. The Rha of **5/6** was 1,3,4-substituted (C(3) at *δ* 80.5, C(4) at *δ* 78.1) instead of the 1,4 substitution (C(3) at *δ* 71.3, C(4) at *δ* 83.9) observed in **3/4** (*Tables 2* and *3*). The linkage of Api at C(3) of Rha was deduced by the NOESY cross-peak between *δ*(H) 5.98 (br.*s*) (Api H–C(1)) and *δ*(H) 4.44 (Rha H–C(3)).

The negative-ion FAB-MS of **7/8** showed a quasi-molecular-ion peak at *m/z* 1705 ([*M* – H]$^-$), indicating a molecular mass of 1706, leading to the determination of their molecular formulas as $C_{79}H_{118}O_{40}$, with 72 mass units less than **5/6**, which suggested the presence of one pentosyl unit in **7/8** instead of an acetylated hexosyl unit in **5/6**. On the basis of the 2D NMR spectral data and hydrolysis, the structures of **7/8** were established as 3-*O*-(*β*-D-glucopyranosyl)preatroxigenin 28-{*O*-*β*-D-xylopyranosyl-(1 → 4)-*O*-[*β*-D-apiofuranosyl-(1 → 3)]-*O*-*α*-L-rhamnopyranosyl-(1 → 2)-*O*-[*O*-*β*-D-xylopyr-

anosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 3)]-4-*O*-(*trans*-4-methoxycinnamoyl)-β-D-fucopyranosyl} ester (**7**) and its *cis*-isomer **8**, two new natural compounds[1] [5 – 10].

The ^{1}H- and ^{13}C-NMR spectra of **7**/**8** indicated that they were also bisdesmosidic glycosides. Extensive NMR study showed that **7**/**8** had the same prosapogenin as **5**/**6**. Comparison of the NMR spectra of **7**/**8** and **5**/**6** established that the only difference was the nature of the monosaccharide unit at C(3) of Glc II. From their ^{1}H- and ^{13}C-NMR data (*Tables 2* and *3*) compounds **7**/**8** were shown to possess a terminal xylopyranosyl (Xyl II) unit instead of an acetylated Glc at this position in compounds **5**/**6**. The linkage of Xyl II at C(3) of Glc II was deduced from the HMBC between δ(H) 4.12 (Glc II H–C(3)) and δ(C)104.6 (Xyl II C–(1)). These results were also in accordance with the difference in molecular mass (72 mass units) between **7**/**8** and **5**/**6**.

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). Semi-prep. and anal. HPLC: *Gilson* pumps *M 305* and *306*; autoinjector *Gilson 234*, UV/VIS-*151-Gilson* detector; *Merk-Hitachi D-7500* integrator; column *Dionex Vydac RP-18* (5 μm) 300 Å 10 × 250 mm; eluent: isocratic, 28% MeCN/H_2O with 0.06% CF_3COOH; detection wavelength 210 nm. TLC and HPTLC: silica gel *60 F_{254}* (*Merck*); solvent systems: 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*); for the acids, Et_2O/toluene 1 : 1 sat. with AcOH 10% (*D*); spray reagents: for saponins, *Komarowsky* reagent, a 5 : 1 mixture of 4-hydroxybenzaldehyde (2% in MeOH) and 50% aq. H_2SO_4; for sugars, diphenylamine/phosphoric acid reagent; for the cinnamic acids, detection by UV light. IR Spectra (KBr disc): *Perkin-Elmer-281* IR spectrophotometer; in cm^{-}. 1D- and 2D NMR spectra: see [1]. Fast-atom bombardment (FAB) MS: negative mode; *Jeol SX 102*.

Plant Material. The cortex of roots of *Atroxima congolana* were collected from Zaire. A voucher specimen under the reference H. Breyne No. 1865 is deposited in the Herbarium of the National Botanical Garden of Brussels, Belgium.

Extraction and Isolation. Dried powdered cortex of roots (2 kg) were macerated with 80% EtOH and further submitted to boiling for 3 h. The EtOH soln. was filtrated and evaporated. The residue was dissolved in MeOH (1500 ml). After filtration, the MeOH soln. was concentrated and purified by precipitation with Et_2O (3 × 1500 ml). The resulting residue was washed with Et_2O, dried, and solubilized in H_2O (1200 ml) and submitted to dialysis for 4 days and then lyophilized. After decolorization with charcoal and filtration, the residue was dissolved in MeOH and purified again by precipitation with Et_2O, yielding a crude saponin mixture (124.6 g). Of this mixture, 4 g was submitted to CC (*Sephadex LH-20*) and then to successive MPLC (silica gel 60 (15 – 40 μm); $CHCl_3$/MeOH/H_2O 32 : 17 : 3 and 65 : 35 : 10, lower phase), followed by semi-prep. HPLC (isocratic, 28% MeCN/H_2O with 0.06% CF_3COOH during 30 min; flow rate 4.5 ml/min): **1**/**2** (13 mg), **3**/**4** (12 mg), **5**/**6** (10 mg), and **7**/**8** (10 mg).

*(2β,3β,4α,22β)-3-(β-*D*-Glucopyranosyloxy)-2,22,27-trihydroxyolean-12-ene-23,28-dioic Acid 28-{*O*-β-*D*-Xylopyranosyl-(1 → 4)-*O*-α-*L*-rhamnopyranosyl-(1 → 2)-*O*-[*O*-β-*D*-glucopyranosyl-(1 → 3)-β-*D*-glucopyranosyl-(1 → 3)]-4-*O*-[(2*E*)-3-(4-methoxyphenyl)-1-oxoprop-2-enyl]-β-*D*-fucopyranosyl} Ester (=Atroximasaponin A_1;* **1**) *and its (2*Z*)-Isomer Atroximasaponin A_2* (**2**). White amorphous powder: TLC: R_f 0.33. IR (KBr): 3405, 2926, 1740, 1723, 1636, 1605, 1515. ^{1}H- and ^{13}C-NMR ((D_5)pyridine): *Tables 1 – 3*. FAB-MS (neg.): 1603 ($[M - H]^-$), 1441 ($[M - H - 162]^-$), 1279 ($[M - H - 2 \times 162]^-$), 695 ($[M - H - 2 \times 162 - 132 - 2 \times 146 - 160]^-$), 533 ($[M - H - 2 \times 162 - 132 - 2 \times 146 - 160 - 162]^-$).

*(2β,3β,4α,22β)-3-(β-*D*-Glucopyranosyloxy)-2,22,27-trihydroxyolean-12-ene-23,28-dioic Acid 28-{*O*-β-*D*-Xylopyranosyl-(1 → 4)-*O*-α-*L*-rhamnopyranosyl-(1 → 2)-*O*-[*O*-6-*O*-acetyl-β-*D*-glucopyranosyl-(1 → 3)-β-*D*-glucopyranosyl-(1 → 3)]-4-*O*-[(*2E*)-3-(4-methoxyphenyl)-1-oxoprop-2-enyl]-β-*D*-fucopyranosyl} Ester (=Atroximasaponin B_1;* **3**) *and Its (2*Z*)-Isomer Atroximasaponin B_2* (**4**). White amorphous powder: TLC: R_f 0.38. IR (KBr) 3406, 2927, 1740, 1723, 1717, 1635, 1574, 1514. ^{1}H- and ^{13}C-NMR ((D_5)pyridine): *Tables 1 – 3*. FAB-MS (neg.): 1645 ($[M - H]^-$), 1441 ($[M - H - 162 - 42]^-$), 1279 ($[M - H - 162 - 42 - 162]^-$), 695 ($[M - H - 162 - 42 - 162 - 132 - 2 \times 146 - 160]^-$) and 533 ($[M - H - 162 - 42 - 162 - 132 - 2 \times 146 - 160 - 162]^-$).

*(2β,3β,4α,22β)-3-*O*-(β-*D*-Glucopyranosyloxy)-2,22,27-trihydroxyolean-12-ene-23,28-dioic Acid 28-{*O*-β-*D*-Xylopyranosyl-(1 → 4)-*O*-[β-*D*-apiofuranosyl-(1 → 3)]-*O*-α-*L*-rhamnopyranosyl-(1 → 2)-*O*-[*O*-6-*O*-acetyl-β-*D*-*

*glucopyranosyl-(1 → 3)-β-*D*-glucopyranosyl-(1 → 3)]-4-*O*-[(2*E*)-3-(4-methoxyphenyl)-1-oxoprop-2-enyl]-β-*D*-fucopyranosyl} Ester (= Atroximasaponin C_1;* **5**) *and Its (2*Z*)-Isomer Atroximasaponin C_2* (**6**). White amorphous powder: TLC: R_f 0.27. IR (KBr): 3404, 2927, 1740, 1723, 1717, 1636, 1606, 1514. ^{1}H- and ^{13}C-NMR ((D_5)pyridine): *Tables 1–3*. FAB-MS (neg.): 1777 ($[M-H]^-$), 695 ($[M-H-2\times162-42-2\times132-2\times146-160]^-$), 533 ($[M-H-2\times162-42-2\times132-2\times146-160-162]^-$).

*(2β,3β,4α,22β)-3-*O*-(β-*D*-Glucopyranosyloxy)-2,22,27-trihydroxolean-12-ene-23,28-dioic Acid 28-*O*-β-*D*-Xylopyranosyl-(1 → 4)-*O*-[β-*D*-apiofuranosyl-(1 → 3)]-*O*-α-*L*-rhamnopyranosyl-(1 → 2)-*O*-[*O*-β-*D*-xylopyranosyl-(1 → 3)-β-*D*-glucopyranosyl-(1 → 3)]-4-*O*-[(2*E*)-3-(4-methoxyphenyl)-1-oxoprop-2-enyl]-β-*D*-fucopyranosyl} Ester (= Atroximasaponin D_1;* **7**), *and Its (2*Z*)-Isomer Atroximasaponin D_2* (**8**). White amorphous powder: TLC: R_f 0.22. IR (KBr): 3405, 2928, 1736, 1723, 1717, 1634, 1605, 1515. ^{1}H- and ^{13}C-NMR ((D_5)pyridine): *Tables 1–3.* FAB-MS (neg.): 1705 ($[M-H]^-$), 1573 ($[M-H-132]^-$), 695 ($[M-H-132-162-2\times132-2\times146-160]^-$) and 533 ($[M-H-132-162-2\times132-2\times146-160-162]^-$).

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 (*C*) by comparison with standard sugars.

Alkaline Hydrolysis. The saponin (5 mg) was refluxed with 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.

Mild Alkaline Hydrolysis. The saponin was hydrolyzed with 1% aq. KOH soln. at r. t. After 1 h, the mixture was neutralized with dil. HCl soln. and extracted with Et_2O. The Et_2O layer gave *trans*- and *cis*-4-methoxycinnamic acids (= (2*E*)-and (2*Z*)-3-(4-methoxyphenyl)prop-2-enoic acids), which were identified by TLC. The aq. layer was extracted with H_2O/sat. BuOH: deacylated saponin.

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