Presenegenin Glycosides from *Securidaca welwitschii*

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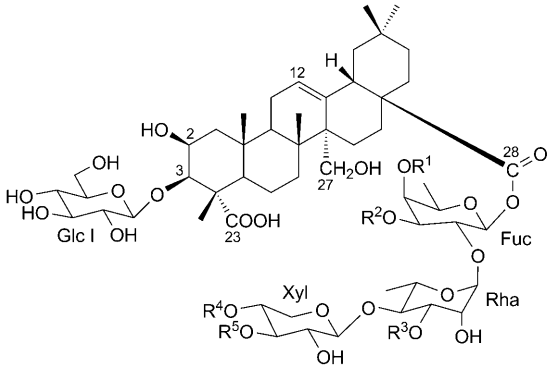
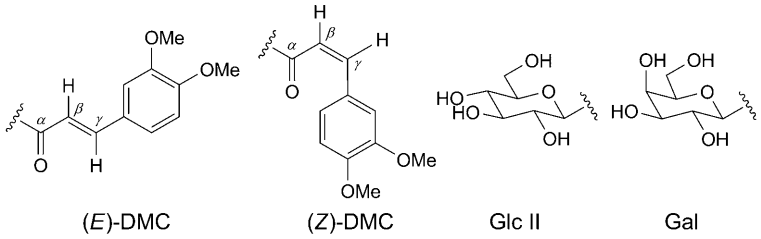
The five new presenegenin glycosides **1**–**5** were isolated from *Securidaca welwitschii*, together with one known sucrose diester. Compounds **1**–**4** were obtained as pairs of inseparable (*E*)/(*Z*)-isomers of a 3,4-dimethoxycinnamoyl derivative, *i.e.*, **1**/**2** and **3**/**4**. Their structures were elucidated mainly by 2D-NMR techniques and mass spectrometry as 3-*O*-(*β*-D-glucopyranosyl)presenegenin 28-{*O*-*β*-D-xylopyranosyl-(1→4)-*O*-*α*-L-rhamnopyranosyl-(1→2)-*O*-[*β*-D-glucopyranosyl-(1→3)]-4-*O*-[(*E*)-3,4-dimethoxycinnamoyl]-*β*-D-fucopyranosyl} ester (**1**) and its (*Z*)-isomer **2**, 3-*O*-(*β*-D-glucopyranosyl)presenegenin 28-{*O*-*β*-D-galactopyranosyl-(1→4)-*O*-*β*-D-xylopyranosyl-(1→4)-*O*-3-*O*-acetyl-*α*-L-rhamnopyranosyl-(1→2)-*O*-[*β*-D-glucopyranosyl-(1→3)]-4-*O*-[(*E*)-3,4-dimethoxycinnamoyl]-*β*-D-fucopyranosyl} ester (**3**) and its (*Z*)-isomer **4**, and 3-*O*-(*β*-D-glucopyranosyl)presenegenin 28-[*O*-*β*-D-galactopyranosyl-(1→3)-*O*-*β*-D-xylopyranosyl-(1→4)-*O*-*α*-L-rhamnopyranosyl-(1→2)-*β*-D-fucopyranosyl] ester (**5**) (presenegenin = (2*β*,3*β*,4*α*)-2,3,27-trihydroxyolean-12-ene-23,28-dioic acid).

Introduction. – The plants of the Polygalaceae family are known to contain saponins [1]. Most of them are acylated by methoxycinnamic acids, and possess a common structural sequence consisting of 3-*O*-(*β*-D-glucopyranosyl)presenegenin 28-[*O*-*β*-D-xylopyranosyl-(1→4)-*O*-*α*-L-rhamnopyranosyl-(1→2)-*β*-D-fucopyranosyl] ester, which represents a chemotaxonomic marker [2] (presenegenin = (2*β*,3*β*,4*α*)-2,3,27-trihydroxyolean-12-ene-23,28-dioic acid). This prompted us to study the genus *Securidaca* in the framework of our study of the saponin constituents of the Polygalaceae family. In a previous contribution, we reported on the isolation and characterization of trimethoxycinnamoyl saponins from *S. longepedunculata* [3]. We have now extended our investigations to another species *S. welwitschii* OLIV. It is a liana (until 25 m high) widely distributed in Guinea, Cameroon, Democratic Republic of Congo, Angola, and Uganda [4]. This plant was reported to contain methyl salicylate and one major saponin deriving from presenegenin. Its sugar part was constitued by glucose, galactose, xylose, arabinose, fucose, and rhamnose [4]. Its use in traditional medicine is rare excepted for eyes affections [4]. In this article, we describe the isolation from the stem barks and the structural elucidation of five new triterpene saponins with presenegenin as aglycon, and one known sucrose diester previously isolated from *S. longepedunculata* [5].

Results and Discussion. – A concentrated BuOH-soluble fraction of the 70% aqueous MeOH extract of the stem barks of *S. welwitschii* was subjected to successive chromatographic methods (vacuum-liquid chromatography and medium-pressure liquid chromatography with normal and reversed-phase (*RP-18*) silica gel). Five triterpene saponins **1**–**5** were isolated, with **1**–**4** as two pairs of inseparable (*E*)/(*Z*)-isomers of a 3,4-dimethoxycinnamoyl derivative, *i.e.*, **1**/**2** and **3**/**4**, along with the known sucrose ester 3-*O*-[(*E*)-3,4,5-trimethoxycinnamoyl]-*β*-D-fructofuranosyl 6-*O*-[(*E*)-3,4,5-trimethoxycinnamoyl]-*α*-D-glucopyranoside [5]. Their structures were elucidated mainly by 600 MHz 2D-NMR (^{1}H,^{1}H-COSY, TOCSY, NOESY, HSQC, HMBC), and mass spectrometry.



	R^1	R^2	R^3	R^4	R^5
1	(*E*)-DMC	Glc II	H	H	H
2	(*Z*)-DMC	Glc II	H	H	H
3	(*E*)-DMC	Glc II	Ac	Gal	H
4	(*Z*)-DMC	Glc II	Ac	Gal	H
5	H	H	H	H	Gal



(*E*)-DMC (*Z*)-DMC Glc II Gal

For compounds **1**–**5**, the ^{1}H- and ^{13}C-NMR signals of the prosapogenin assigned from the 2D-NMR spectra were in good agreement with those of tenuifoline (= 3-*O*-(*β*-D-glucopyranosyl)presenegenin) commonly encountered in the Polygalaceae (*Table 1*) [6–8]. The differences between them were located at the oligosaccharidic chain linked to C(28) of the aglycon, which possessed a characteristic shielded signal of an ester function at *δ*(C) 176.4–176.8. The monosaccharides obtained by acid hydrolysis of each compound were identified by comparison on TLC with authentic samples as glucose, fucose (= 6-deoxygalactose), xylose, and rhamnose (= 6-deoxy-mannose) (in the case of **1**/**2**), and glucose, galactose, fucose, xylose, and rhamnose (in

Table 1. *^1H- and ^{13}C-NMR Data* (C_5D_5N, 600 MHz) *of the Aglycone Part of* **1**–**5**[a]). δ in ppm, J in Hz.

	1/2		**3/4**		**5**	
	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)
CH_2(1)	44.1	1.34, 2.20	44.0	1.3, 2.20	44.0	1.29, 2.17
CH(2)	71.3	4.74	70.1	4.58–4.62 (*m*)	70.2	4.54–4.58 (*m*)
CH(3)	86.7	4.59 (*d*, J = 2.5)	86.4	4.57 (*d*, J = 2.5)	87.3	4.43 (*d*, J = 3.0)
C(4)	53.1		53.0		53.5	
CH(5)	52.1	2.21	52.1	2.19	52.0	2.40
CH_2(6)	21.0	1.72, 1.85	20.6	1.74, 1.80	21.2	1.74, 1.82
CH_2(7)	33.4	[b])	33.5	0.96, 1.16	33.5	[b])
C(8)	40.7		41.0		41.1	
CH(9)	48.9	2.23	48.9	2.22	49.0	2.33
C(10)	36.5		36.5		36.0	
CH_2(11)	23.0	[b])	23.0	[b])	23.0	[b]), 2.04
CH(12)	127.1	5.72 (*t*-like)	127.2	5.72 (*t*-like)	127.4	5.80 (*t*-like)
C(13)	139.9		139.9		139.8	
C(14)	47.9		47.9		48.0	
CH_2(15)	24.2	1.86, 2.04	24.2	1.83, 2.03	24.4	1.77, 1.82
CH_2(16)	24.0	1.84, 2.02	24.4	1.84, 2.06	24.2	[b]), 2.01
C(17)	46.9		46.9		46.9	
CH(18)	41.4	3.11 (*dd*, J = 12.9, 3.0)	41.9	3.11 (*dd*, J = 13.7, 3.0)	41.9	3.12 (*dd*, J = 13.7, 3.0)
CH_2(19)	45.1	1.22, 1.64	45.3	1.24, 1.64	44.8	1.23, 1.66
C(20)	30.3		30.3		30.9	
CH_2(21)	33.5	[b])	33.4	[b])	33.6	[b])
CH_2(22)	31.8	1.70, 1.84	31.9	1.66, 1.85	31.8	1.66, 1.76
C(23)	183.4		184.7		186.0	
Me(24)	14.6	1.84 (*s*)	14.6	1.82 (*s*)	14.2	1.84 (*s*)
Me(25)	17.0	1.40 (*s*)	17.1	1.41 (*s*)	16.7	1.41 (*s*)
Me(26)	18.5	1.00 (*s*)	18.5	1.02 (*s*)	18.4	1.01 (*s*)
CH_2(27)	64.0	3.76, 4.08 (*d*, J = 12.0)	64.0	3.76, 4.06	63.9	3.74 (*d*, J = 12.4), 4.14
C(28)	176.4		176.8		176.4	
Me(29)	32.6	0.71 (*s*)	32.6	0.72 (*s*)	32.6	0.75 (*s*)
Me(30)	23.3	0.74 (*s*)	23.3	0.74 (*s*)	23.3	0.71 (*s*)

[a]) Assignments were confirmed by COSY, TOCSY, NOESY, HSQC, and HMBC experiments; overlapped ^{1}H-NMR signals are reported without designated multiplicity. [b]) Not determined.

the case of **3/4** and **5**). The absolute configurations of the sugars were determined by GC analysis to be D for glucose, galactose, fucose, and xylose, and L for rhamnose (see *Exper. Part*). In the 1D- and 2D-NMR spectra of each compound, the relatively large ^3J(1,2) values of the anomeric proton signals of glucose, galactose, fucose, and xylose in their pyranose form (7.3–8.5 Hz), indicated a β-orientation [9] (*Table 2*). The large ^1J(H(1),C(1)) values of the rhamnose (165–168 Hz) confirmed that the anomeric proton was equatorial (α-pyranoid anomeric form).

Compounds **1/2** exhibited in the HR-ESI-MS (positive-ion mode) a *pseudo*-molecular-ion peak at m/z 1479.6413 ($[M+Na]^+$), consistent with a molecular formula $C_{70}H_{104}NaO_{32}$. The FAB-MS (negative-ion mode) showed a *quasi*-molecular-ion peak at m/z 1455 ($[M-H]^-$), which indicated the molecular mass of 1456. Other fragment-

Table 2. *^{1}H- and ^{13}C-NMR Data* (C_5D_5N, 600 MHz) *of the Sugar Moieties of* **1**–**5**[a]). δ in ppm, J in Hz.

	1/2		**3/4**		**5**	
	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)
3-*O*-Sugar:						
Glc I						
H–C(1)	104.3	5.01 (*d*, *J* = 7.6)	104.8	4.97 (*d*, *J* = 7.6)	104.8	4.95 (*d*, *J* = 7.8)
H–C(2)	74.9	3.88	74.9	3.87	75.0	3.87
H–C(3)	77.2	4.20 (*t*, *J* = 8.8)	77.2	4.17	76.9	4.17
H–C(4)	71.0	3.99 (*d*, *J* = 8.3)	71.1	3.98	70.9	3.97
H–C(5)	77.7	3.85	77.6	3.83	77.3	3.83
CH_2(6)	62.0	4.11, 4.31 (br. *d*, *J* = 10.5)	62.0	4.11, 4.31 (br. *d*, *J* = 10.5)	61.9	4.10, 4.28 (br. *d*, *J* = 10.7)
28-*O*-Sugars:						
Fuc						
H–C(1)	94.1	6.04 (*d*, *J* = 8.5)	94.2	6.02 (*d*, *J* = 8.3)	94.5	5.87 (*d*, *J* = 8.3)
H–C(2)	72.1	4.77 (*t*, *J* = 8.8)	71.2	4.73	71.6	4.73
H–C(3)	83.3	4.55 (*dd*, *J* = 8.9, 3.5)	83.1	4.43	76.9	4.19
H–C(4)	74.0	6.05 (*d*, *J* = 3.5)	73.6	5.91 (*d*, *J* = 3.5)	72.7	3.95
H–C(5)	70.5	4.21	71.0	4.21	72.0	3.90
Me(6)	16.5	1.23 (*d*, *J* = 6.1)	16.8	1.30 (*d*, *J* = 6.4)	16.8	1.37 (*d*, *J* = 6.4)
Rha						
H–C(1)	101.0	6.44 (*d*, *J* = 1.2)	101.1	6.32 (*d*, *J* = 1.1)	101.0	6.58 (*d*, *J* = 1.2)
H–C(2)	71.3	4.72 (br. *s*)	71.2	4.72 (br. *s*)	71.0	4.69 (br. *s*)
H–C(3)	72.0	4.52 (*dd*, *J* = 8.6, 4.3)	75.7	5.46 (*dd*, *J* = 8.7, 4.0)	72.1	4.50 (*dd*, *J* = 8.6, 3.9)
H–C(4)	84.4	4.17	84.8	4.12	86.1	4.14
H–C(5)	68.0	4.42	68.0	4.37	67.2	4.37
Me(6)	18.2	1.68 (*d*, *J* = 6.1)	18.1	1.66 (*d*, *J* = 6.1)	17.9	1.57 (*d*, *J* = 6.0)
3-AcO			171.5, 20.6	2.00 (*s*)		
Xyl						
H–C(1)	106.9	4.85 (*d*, *J* = 7.4)	106.5	4.78 (*d*, *J* = 7.4)	106.2	4.79 (*d*, *J* = 7.4)
H–C(2)	75.5	4.00 (*t*, *J* = 8.8)	75.5	3.97	75.5	3.92
H–C(3)	77.8	3.99 (*t*, *J* = 8.3)	77.2	4.10	86.2	3.84
H–C(4)	70.1	4.13	77.1	4.27	68.2	4.10
CH_2(5)	66.8	3.38 (*t*, *J* = 10.5), 4.09	64.6	3.37 (*t*, *J* = 11.4), 4.28	65.7	3.41 (*t*, *J* = 11.0), 4.34
Glc II						
H–C(1)	105.2	5.06 (*d*, *J* = 7.8)	104.0	4.74 (*d*, *J* = 7.3)		
H–C(2)	74.9	3.88	74.6	3.90		
H–C(3)	77.7	4.10	77.2	4.15		
H–C(4)	71.0	3.88	71.0	4.03		
H–C(5)	77.9	3.91	77.4	3.85		
CH_2(6)	62.5	4.16, 4.44 (br. *d*, *J* = 10.5)	62.1	4.18, 4.38		
Gal						
H–C(1)			103.9	4.86 (*d*, *J* = 7.4)	102.6	4.78 (*d*, *J* = 7.4)
H–C(2)			71.0	4.37	69.5	4.41
H–C(3)			75.5	3.96	74.0	3.96
H–C(4)			69.9	4.26	69.2	4.30
H–C(5)			77.0	4.03	76.9	3.86
CH_2(6)			61.7	4.13, 4.20	61.6	4.13, 4.21 (br. *d*, *J* = 11.2)

[a]) Assignments were confirmed by COSY, TOCSY, NOESY, HSQC, and HMBC experiments; overlapped ^{1}H-NMR signals are reported without designated multiplicity.

ion peaks were observed at *m/z* 1265 ($[M-H-190]^-$) and 825 ($[M-H-190-162-146-132]^-$), which revealed the successive loss of one 3,4-dimethoxycinnamoyl group, one hexosyl, one deoxyhexosyl, and one pentosyl moiety. The ^{1}H-NMR spectrum data of **1**/**2** exhibited five anomeric H-atoms at δ(H) 6.44 (*d*, $J=1.2$ Hz), 6.04 (*d*, $J=8.5$ Hz), 5.06 (*d*, $J=7.8$ Hz), 5.01 (*d*, $J=7.6$ Hz), and 4.85 (*d*, $J=7.4$ Hz), which correlated, in the HSQC spectrum, to five anomeric C-atoms at δ(C) 101.0, 94.1, 105.2, 104.3, and 106.9, respectively. Moreover, Me *d*s at δ(H) 1.23 ($J=6.1$ Hz) and 1.68 ($J=6.1$ Hz), supported the presence of two 6-deoxyhexose sugar units. The ring H-atoms of the monosaccharide residues were assigned starting from the readily identifiable anomeric H-atom by means of the ^{1}H,^{1}H-COSY, TOCSY, HSQC, and HMBC experiments (*Table 2*). Units of two β-glucopyranosyl (Glc I and Glc II), one β-fucopyranosyl (Fuc), one β-xylopyranosyl (Xyl), and one α-rhamnopyranosyl (Rha) were identified. The attachment of a glucopyranosyl residue to C(3) of the aglycone was determined by the HMBC between Glc I H–C(1) (δ(H) 5.01 (*d*, $J=7.6$ Hz)) and C(3) (δ(C) 86.7) and the NOESY correlation between H–C(3) (δ(H) 4.59 (*d*, $J=2.5$ Hz)) and Glc I H–C(1). After subtraction of the signals of this glucopyranosyl moiety, signals of four sugars moieties of an oligosaccharidic chain linked to the aglycone by an ester linkage remained, establishing the structures of **1**/**2** as 3,28-bidesmosides. The fucopyranosyl unit linked to the C(28) of the aglycon showed NMR signals of a 1,2,3,4-tetrasubstitution. The downfield shifts observed in the HSQC spectrum for the Fuc H–C(4) and C(4) resonances at δ(H) 6.05 (*d*, $J=3.5$ Hz) and δ(C) 74.0, respectively, established that the secondary-alcohol function OH–C(4) of Fuc was acylated. The ^{1}H,^{1}H-COSY experiment of **1**/**2** allowed us to identify the (*E*)- and (*Z*)-olefinic H-atoms of a 3,4-dimethoxycinnamoyl moiety, which appeared as two *d*s at δ(H) 6.48 ($J=15.9$ Hz) and 7.83 ($J=15.9$ Hz) for the (*E*)-olefinic H-atoms, and at δ(H) 5.82 ($J=13.2$ Hz) and 6.84 ($J=13.2$ Hz) for the (*Z*)-olefinic H-atoms, respectively (*Table 3*). The full assignments of the C- and H-atoms of the 3,4-

Table 3. *^{1}H- and ^{13}C-NMR Data* (C_5D_5N, 600 MHz) *of the 3,4-Dimethoxycinnamoyl Moieties of* **1**–**4**[a]). δ in ppm, J in Hz.

	1		**2**		**3**		**4**	
	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)
C(α)	168.0		167.4		167.0		[b])	
H–C(β)	115.5	6.48 (*d*, $J=15.9$)	116.1	5.82 (*d*, $J=13.2$)	115.2	6.43 (*d*, $J=15.9$)	116.1	5.85 (*d*, $J=13.0$)
H–C(γ)	146.4	7.83 (*d*, $J=15.9$)	144.7	6.84 (*d*, $J=13.2$)	145.2	7.81 (*d*, $J=15.9$)	144.0	6.82 (*d*, $J=13.0$)
C(1)	127.7		128.0		127.4		127.9	
H–C(2)	110.6	6.98 (*s*)	114.4	7.83 (*s*)	110.6	6.98 (*s*)	114.5	7.79 (*s*)
C(3)	148.9		149.7		149.0		149.8	
C(4)	152.0		150.5		151.0		151.0	
H–C(5)	111.8	6.94 (*d*, $J=8.1$)	111.5	6.90 (*d*, $J=8.1$)	111.8	6.93 (*d*, $J=8.1$)	111.5	6.90 (*d*, $J=8.1$)
H–C(6)	123.0	6.99 (*d*, $J=8.1$)	125.7	7.45 (*d*, $J=8.1$)	123.1	7.01 (*d*, $J=8.1$)	125.5	7.46 (*d*, $J=8.1$)
MeO–C(3)	55.7	3.82 (*s*)	55.7	3.78 (*s*)	55.5	3.82 (*s*)	55.5	3.76 (*s*)
MeO–C(4)	55.7	3.78 (*s*)	55.7	3.71 (*s*)	55.5	3.76 (*s*)	55.5	3.71 (*s*)

[a]) Assignments were confirmed by COSY, TOCSY, NOESY, HSQC, and HMBC experiments. [b]) Not determined.

dimethoxycinnamoyl units obtained by further 2D-NMR investigations were in good agreement with those described in [10][11]. These data indicated that **1**/**2** is a mixture of (*E*)- and (*Z*)-3,4-dimethoxycinnamoyl-substituted presenegenin glycosides. In the NOESY plot, correlations between Fuc H–C(2) at δ(H) 4.77 (*t*, *J* = 8.8 Hz) and Rha H–C(1) at δ(H) 6.44 (*d*, *J* = 1.2 Hz), and between Fuc H–C(3) at δ(H) 4.55 (*dd*, *J* = 8.9, 3.5 Hz) and Glc II H–C(1) at δ(H) 5.06 (*d*, *J* = 7.8 Hz), revealed a (1 → 2) linkage between Fuc and Rha, and a (1 → 3) linkage between Fuc and Glc II. A HMBC cross-peak between Rha H–C(4) at δ(H) 4.17 and Xyl C(1) at δ(C) 106.9, and a NOESY correlation between Rha H–C(4) at δ(H) 4.17 and Xyl H–C(1) at δ(H) 4.85 (*d*, *J* = 7.4 Hz), indicate a (1 → 4) linkage between Rha and Xyl. On the basis of the above results, the structures of **1**/**2** were elucidated as 3-*O*-(β-D-glucopyranosyl)presenegenin 28-{*O*-β-D-xylopyranosyl-(1 → 4)-*O*-α-L-rhamnopyranosyl-(1 → 2)-*O*-[β-D-glucopyranosyl-(1 → 3)]-4-*O*-[(*E*)-3,4-dimethoxycinnamoyl]-β-D-fucopyranosyl} ester (**1**) and its (*Z*)-isomer **2**. This structure is a derivative of the chemotaxonomic marker characterized in the Polygalaceae family as 3-*O*-(β-D-glucopyranosyl)presenegenin 28-[*O*-β-D-xylopyranosyl-(1 → 4)-*O*-α-L-rhamnopyranosyl-(1 → 2)-β-D-fucopyranosyl] ester [2].

Compounds **3**/**4** exhibited in the HR-ESI-MS (positive-ion mode) a *pseudo*-molecular-ion peak at *m*/*z* 1683.7049 ($[M+Na]^+$), consistent with a molecular formula $C_{78}H_{116}NaO_{38}$. The FAB-MS (negative-ion mode) showed a *quasi*-molecular-ion peak at *m*/*z* 1659 ($[M-H]^-$), which indicated the molecular mass of 1660, (162 + 42) mass units higher than that of **1**/**2**. Other fragment-ion peaks were observed at *m*/*z* 1497 ($[M-H-162]^-$), 1103 ($[M-H-162-162-190-42]^-$), and 795 ($[M-H-162-162-190-42-162-146]^-$), due to the elimination of three hexosyl, and one deoxyhexosyl moiety, one 3,4-dimethoxycinnamoyl group, and one acetyl function. ^{1}H- and ^{13}C-NMR signals of an oligosaccharide sequence common with **1**/**2**, *i.e.*, *O*-β-D-xylopyranosyl-(1 → 4)-*O*-α-L-rhamnopyranosyl-(1 → 2)-*O*-[β-D-glucopyranosyl-(1 → 3)]-4-*O*-[(*E*)-3,4-dimethoxycinnamoyl]-β-D-fucopyranosyl and its (*Z*) isomer, were found for the oligosaccharide chain linked at C(28) of the prosapogenin tenuifolin in **3**/**4**. The difference was located at the rhamnopyranosyl moiety in which a deshielded signal at δ(H) 5.46/δ(C) 75.7 suggested a substitution at the Rha-3 position. Characteristic signals of an acetyl group at δ(H) 2.00 (*s*)/δ(C) 20.6 and 171.5 confirmed an acetylation at Rha OH–C(3). Furthermore, additional signals of a terminal galactopyranosyl unit (Gal) were assigned. An HMBC correlation between Gal H–C(1) at δ(H) 4.86 (*d*, *J* = 7.4 Hz) and Xyl C(4) at δ(C) 77.1 revealed that Gal was linked to C(4) of Xyl. This was confirmed by a NOESY cross-peak between Gal H–C(1) at δ(H) 4.86 (*d*, *J* = 7.4 Hz) and Xyl H–C(4) at δ (H) 4.27. On the basis of spectral evidence, the structures of compounds **3**/**4** were elucidated as 3-*O*-(β-D-glucopyranosyl)presenegenin 28-{*O*-β-D-galactopyranosyl-(1 → 4)-*O*-β-D-xylopyranosyl-(1 → 4)-*O*-3-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 2)-*O*-[β-D-glucopyranosyl-(1 → 3)]-4-*O*-[(*E*)-3,4-dimethoxycinnamoyl]-β-D-fucopyranosyl} ester (**3**) and its (*Z*)-isomer **4**.

Compound **5** exhibited in the HR-ESI-MS (positive-ion mode) a *pseudo*-molecular ion peak at *m*/*z* 1289.5784 ($[M+Na]^+$), consistent with a molecular formula of $C_{59}H_{94}NaO_{29}$. The FAB-MS (negative-ion mode) showed a *quasi*-molecular-ion peak at *m*/*z* 1265 ($[M-H]^-$), which indicated the molecular mass of 1266. Two other significant fragment-ion peaks were observed at *m*/*z* 971 ($[M-H-162-132]^-$) and

825 ([M – H – 162 – 132 – 146]$^-$), corresponding to the successive loss of one hexosyl, one pentosyl, and one deoxyhexosyl moiety, respectively. Once again, the structure of **5** was established as a derivative of the chemotaxonomic marker 3-*O*-(β-D-glucopyranosyl)presenegenin 28-[*O*-β-D-xylopyranosyl-(1 → 4)-*O*-α-L-rhamnopyranosyl-(1 → 2)-β-D-fucopyranosyl] ester, with a 1,2-disubstituted fucopyranosyl moiety [11] instead of a 1,2,3,4 substitution as in **1**/**2** and **3**/**4** (*Table 2*). The deacylated fucopyranosyl unit is linked to only one sugar which is Rha. After subtraction of the NMR signals of the Glc, Fuc, Rha, and Xyl, signals of a terminal galactopyranosyl moiety (Gal) remained. The deshielded signal of Xyl C(3) at δ(C) 86.2 suggested substitution of this position by the terminal Gal. The structure of compound **5** was thus established as 3-*O*-(β-D-glucopyranosyl)presenegenin 28-{*O*-β-D-galactopyranosyl-(1 → 3)-*O*-β-D-xylopyranosyl-(1 → 4)-*O*-α-L-rhamnopyranosyl-(1 → 2)-β-D-fucopyranosyl} ester.

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Experimental Part

General. Vacuum liquid chromatography (VLC): reversed-phase silica gel *RP-18* (75 – 200 μm; *SiliCycle Inc.*). Medium-pressure liquid chromatography (MPLC): silica gel *60* (15 – 40 μm; *Merck*), reversed-phase silica gel *RP-18* (75 – 200 μm; *SiliCycle Inc.*), *Gilson* pump *M 303*; *Büchi* glass column (460 × 15 mm and 230 × 15 mm), *Büchi* precolumn (110 × 15 mm). TLC: silica gel *60* F_{254} (*SiliCycle Inc.*); HP-TLC silica gel *60* F_{254} (*Merck*); solvent system: $CHCl_3$/MeOH/AcOH/H_2O 60 : 32 : 0.5 : 10 lower phase; spray reagent: *Komarowsky* reagent, 2% 4-hydroxybenzaldehyde in MeOH/50% H_2SO_4 soln. 5 : 1. Optical rotations: *AA-OR* automatic polarimeter. NMR Spectra: *Varian-Unity-Inova-600* (600 MHz) spectrometer or *Varian-VNMR-S-600* spectrometer. HR-ESI-MS (positive-ion mode): *Q-TOF-1-Micromass* spectrometer. FAB-MS (negative-ion mode, glycerol matrix): *JEOL-SX-102* mass spectrometer; in *m*/*z*.

Plant Material. The lianous stem barks of *S. welwitschii* OLIV. were collected in Avril 2008 in Mvuazi, Democratic Republic of Congo, by Dr. *Léopold Nsimundele* of the Botanical Garden of Kisantu. The stem barks were conformed to the sample Devred 289, deposited with the National Botanical Garden of Brussels, Belgium. A voucher specimen N° 01,28,2010 is deposited with the herbarium of the laboratory of Pharmacognosy, Burgundy University.

Extraction and Isolation. Dried stem barks of *S. welwitschii* (300 g) were powdered and heated to reflux three times in MeOH/H_2O 7 : 3 (3 × 2 l) for 1 h, yielding after evaporation 43 g of crude extract. The MeOH extract (20 g) was dissolved in H_2O (300 ml) and partitioned with H_2O-sat. BuOH (3 × 200 ml) to give, after evaporation, the BuOH fraction (5.3 g). A 1.4 g aliquot of the BuOH residue was submitted to VLC (reversed-phase silica gel, H_2O (3 × 200 ml), MeOH/H_2O 1 : 1 (5 × 200 ml), and finally MeOH (3 × 200 ml)). This VLC was done two times and the similar eluates were combined. After evaporation of the solvents, two fractions rich in saponins were obtained: *Fr. 1* (with MeOH/H_2O 1 : 1; 1.15 g) and *Fr. 2* (with MeOH; 118 mg). *Fr. 1* (400 mg) was submitted to another VLC (SiO_2, $CHCl_3$/MeOH/H_2O 85 : 15 : 2 (*a*), 40 : 10 : 1 (*b*), and 60 : 32 : 7 (*c*)). The elution with the solvent system (*a*) gave *Frs. 1.1 – 1.8*. Final purification was carried out with *Fr. 1.7* by MPLC (SiO_2, solvent system (*a*)) yielding 3-*O*-[(*E*)-3,4,5-trimethoxycinnamoyl]-β-D-fructofuranosyl 6-*O*-[(*E*)-3,4,5-trimethoxycinnamoyl]-α-D-glucopyranoside (9 mg). *Fr. 2* (118 mg) was then fractionated by MPLC (reversed-phase silica gel, MeOH/H_2O 40 → 70%): *Frs. 2.1 – 2.5*. Compounds **1**/**2** (3.4 mg) were obtained from *Fr. 2.2*, whereas compounds **3**/**4** (7 mg) and **5** (4.5 mg) were obtained from *Fr. 2.4* by MPLC (SiO_2, $CHCl_3$/MeOH//H_2O 13 : 7 : 2 lower phase).

Acid Hydrolysis. Each compound (3 mg) was hydrolyzed with 2N aq. CF_3COOH (5 ml) for 3 h at 95°. After extraction with CH_2Cl_2 (3 × 5 ml), the aq. layer was repeatedly evaporated to dryness with MeOH until neutral, and then analyzed by TLC (SiO_2, $CHCl_3$/MeOH/H_2O 8 : 5 : 1) by comparison with authentic samples. The trimethylsilyl ethers of the thiazolidine derivatives of the sugar residues of each

compound were prepared and analyzed by GC by means of a method described previously [12]. The absolute configurations were determined by comparing the retention times with thiazolidine derivatives prepared in a similar way from standard sugars. The D configuration of glucose, galactose, fucose, and xylose and the L configuration of rhamnose were determined.

*(2β,3β,4α)-3-(β-*D*-Glucopyranosyloxy)-2,27-dihydroxyolean-12-ene-23,28-dioic Acid 28-{*O*-β-*D*-Xylopyranosyl-(1 → 4)-*O*-6-deoxy-α-*L*-mannopyranosyl-(1 → 2)-*O*-[β-*D*-glucopyranosyl-(1 → 3)]-6-deoxy-4-*O*-[(2*E*)-3-(3,4-dimethoxyphenyl)-1-oxoprop-2-en-1-yl]-β-*D*-galactopyranosyl} Ester* (**1**) *and its (2Z)-Isomer* **2**: White amorphous powder. TLC (*a*): R_f 0.28. ^{1}H- and ^{13}C-NMR (C_5D_5N, 600 MHz): *Tables 1–3*. FAB-MS (neg.): 1455 ($[M-H]^-$), 1265 ($[M-H-190]^-$), 825 ($[M-H-190-162-146-132]^-$). HR-ESI-MS (pos.): 1479.6413 ($[M+Na]^+$, $C_{70}H_{104}NaO_{32}^+$; calc. 1479.6408).

*(2β,3β,4α)-3-(β-*D*-Glucopyranosyloxy)-2,27-dihydroxyolean-12-ene-23,28-dioic Acid 28-{*O*-β-*D*-Galactopyranosyl-(1 → 4)-*O*-β-*D*-xylopyranosyl-(1 → 4)-*O*-(3-*O*-acetyl-6-deoxy-α-*L*-mannopyranosyl-(1 → 2)-*O*-[β-*D*-glucopyranosyl-(1 → 3)]-6-deoxy-4-*O*-[(2*E*)-3-(3,4-dimethoxyphenyl)-1-oxoprop-2-en-1-yl]-β-*D*-galactopyranosyl} Ester* (**3**) *and its (2Z)-Isomer* **4**: White amorphous powder. TLC (*a*): R_f 0.18. ^{1}H- and ^{13}C-NMR (C_5D_5N, 600 MHz): *Tables 1–3*. FAB-MS (neg.): 1659 ($[M-H]^-$), 1497 ($[M-H-162]^-$), 1103 ($[M-H-162-162-190-42]^-$), 795 ($[M-H-162-162-190-42-162-146]^-$). HR-ESI-MS (pos.): 1683.7049 ($[M+Na]^+$, $C_{78}H_{116}NaO_{38}^+$; calc. 1683.7042).

*(2β,3β,4α)-3-(β-*D*-Glucopyranosyloxy)-2,27-dihydroxyolean-12-ene-23,28-dioic Acid 28-[*O*-β-*D*-Galactopyranosyl-(1 → 3)-β-*D*-xylopyranosyl-(1 → 4)-6-deoxy-α-*L*-mannopyranosyl-(1 → 2)-6-deoxy-β-*D*-galactopyranosyl] Ester* (**5**): White amorphous powder. $[\alpha]_D^{25} = -14.0$ ($c = 0.1$ MeOH). TLC (*a*): R_f 0.13. ^{1}H- and ^{13}C-NMR (C_5D_5N, 600 MHz): *Tables 1–3*. FAB-MS (neg.): 1265 ($[M-H]^-$), 971 ($[M-H-162-132]^-$), 825 ($[M-H-162-132-146]^-$). HR-ESI-MS (pos.): 1289.5784 ($[M+Na]^+$, $C_{59}H_{94}NaO_{29}^+$; calc. 1289.5778).

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