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NEW SUCROSE DERIVATIVES FROM THE BARK OF
SECURIDACA LONGIPEDUNCULATA

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ABSTRACT.—Two new bitter principles were isolated from the bark of *Securidaca longipedunculata* (Polygalaceae) and identified as β-D-(3,4-disinapoyl)fructofuranosyl-α-D-(6-sinapoyl)glucopyranoside and β-D-(3-sinapoyl)fructofuranosyl-α-D-(6-sinapoyl)glucopyranoside. The structures were elucidated by a combination of ¹H nmr (1D, 2D COSY, 2D HOHAHA), ¹³C-nmr, and fabms spectra.

The bark of *Securidaca longipedunculata* Fresen (Polygalaceae) is a Senegalese crude drug used for its anti-inflammatory and antibacterial effects (1,2). From the MeOH extract of the bark of this plant we isolated two new conjugated sucrose derivatives **1** and **2** and the known compounds sinapoic acid, caffeic acid, 4,5-dicaffeoyl D-quinic acid, and 3,4,5-tricaffeoyl D-quinic acid (3–5). This is the first report of quinic acid derivatives in a plant of this family.

A considerable number of monosaccharides and oligosaccharides conju-
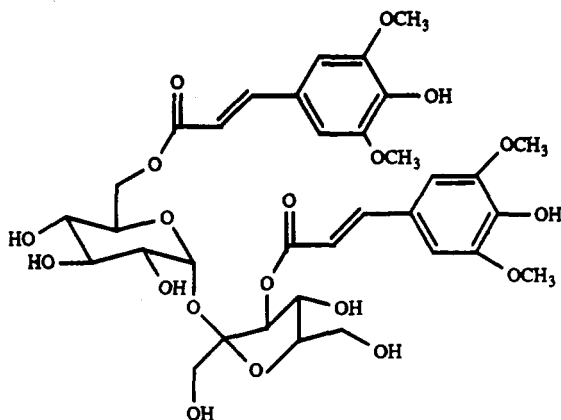
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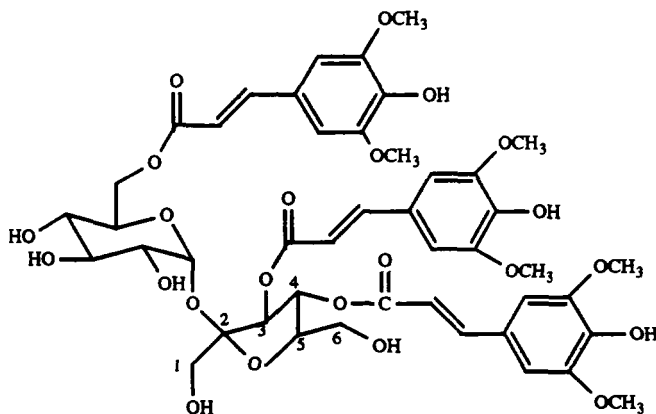
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gated with hydroxycinnamoyl groups have been found to occur in many species of higher plants (6), some of which are noted for their pharmacological and biological activities (7). The occurrence of conjugated substances containing sucrose as the core sugar, however, is limited to several groups of plants: for example, the Polygonaceae (8), Polygalaceae (9), and Brassicaceae (10). The MeOH extract of the bark of *S. longipedunculata* gave compounds **1** and **2** by a separation involving Sephadex LH-20 chromatography and reversed-phase hplc.

The molecular formulae, $C_{34}H_{42}O_{19}$ for **1** and $C_{45}H_{52}O_{23}$ for **2**, were determined by DEPT ^{13}C-nmr, ^{13}C-nmr, and fabms analysis in the negative ion mode. The fabms spectrum of **2** showed a quasimolecular ion at *m/z* 959

$[M - H]^-$. The successive elimination of three sinapoyl moieties was indicated by fragment ions at *m/z* 753 $[M - 206]^-$, *m/z* 547 $[M - (206 \times 2)]^-$, and *m/z* 341 $[M - (206 \times 3)]^-$. The peaks appearing at *m/z* 591 $[M - (206 + 162)]^-$ and 569 $[M - (206 + 178)]^-$ were due to the loss of one hexose unit with a sinapoyl moiety. In the ^{1}H-nmr spectrum the resonances for two sugar units were apparent. The assignments of sugar protons were based on decoupling experiments and on the 2D homonuclear (COSY, HOHAHA) spectra of **2** (Table 1). The 2D-COSY experiment allowed the sequential assignment of most of the resonances for each sugar ring. Nevertheless, not all proton resonances could be successfully assigned with confidence, because of the overlapping of some signals

TABLE 1. ^{1}H-nmr Data of **1** and **2** in CD_3OD.[a]

Position	Compound	
	2	**1**
H-1	3.98	3.68
H-3	5.88 (d, *J* = 8 Hz)	5.53 (d, *J* = 8 Hz)
H-4	5.74 (dd, *J* = 8, 7 Hz)	4.52 (dd, *J* = 8, 7 Hz)
H-5	4.22	4.30
H_a-6	4.01	4.01
H_b-6	3.95	3.90
H-1'	5.60 (d, *J* = 4 Hz)	5.53 (d, *J* = 4 Hz)
H-2'	3.55 (dd, *J* = 4, 9.5 Hz)	3.52 (dd, *J* = 4, 9.5 Hz)
H-3'	3.75 (dd, *J* = 9.5, 9.5 Hz)	3.70 (dd, *J* = 9.5, 9.5 Hz)
H-4'	3.34	3.34
H-5'	4.45 (dd, *J* = 9.5, 12 Hz)	4.50 (dd, *J* = 9.5, 12 Hz)
H_a-6'	4.79 (d, *J* = 12 Hz)	4.79 (d, *J* = 12 Hz)
H_b-6'	4.21	4.28
H-7″	7.59 (d, *J* = 15.8 Hz)	7.71 (d, *J* = 15.8)
H-8″	6.48 (d, *J* = 15.8 Hz)	6.50 (d, *J* = 15.8 Hz)
H-2″	6.94 (s)	6.98 (s)
H-6″	6.94 (s)	6.98 (s)
H-7‴	7.73 (d, *J* = 15.8 Hz)	7.62 (d, *J* = 15.8 Hz)
H-8‴	6.52 (d, *J* = 15.8 Hz)	6.48 (d, *J* = 15.8 Hz)
H-2‴	6.84 (s)	6.90 (s)
H-6‴	6.84 (s)	6.90 (s)
H-7⁗	7.50 (d, *J* = 15.8 Hz)	
H-8⁗	6.30 (d, *J* = 15.8 Hz)	
H-2⁗	6.79 (s)	
H-6⁗	6.79 (s)	
OMe	3.90 (×2)	3.90 (×2)
	3.95 (×2)	3.95 (×2)
	4.00 (×2)	

[a]All assignments were made by 2D-COSY and 2D-HOHAHA experiments.

in the one-dimensional spectrum, e.g., that for proton pairs H-1 fru/H$_a$-6 fru, H-5 fru/H$_b$-6' Glu, H-1 fru/H$_b$-6 fru. Complete assignments were then achieved by combination of COSY and HOHAHA results. Indeed, the 2D HOHAHA experiment (Table 1) clearly showed correlation signals for the H-1 to H-6 spin system of both the glucose and fructose residues. Cross peaks in both experiments displayed full coupling information, which helped with the assignments and allowed identification of proton patterns.

Chemical shifts and coupling constants were in good agreement with values reported for sucrose (11). However, the signals attributed to H-3 and H-4 of fructose and H$_a$-6', H$_b$-6' of glucose were shifted downfield about 1–1.5 ppm if compared with sucrose (11), as expected for an ester bond (12). Again the ^{1}H nmr (Table 1) showed the presence of the typical proton signals of three sinapoyl moieties {δ 6.48, 6.52, 6.30 (each 1H, d, J = 15.8 Hz); δ 7.59, 7.63, 7.50 (each 1H, d, J = 15.8); δ 6.94, 6.84, 6.79 (each 2H, s)]. The ^{13}C-nmr spectral data (Table 2) confirmed the nature of the sinapoyl moieties and substitution pattern of sucrose (8,13,14). Compound **2** was therefore identified as β-D-(3,4-disinapoyl)-fructofuranosyl-α-D-(6-sinapoyl)glucopyranoside.

The fabms spectrum of **1** showed a quasi molecular ion at m/z 753 [M − H]$^−$. The successive elimination of two sinapoyl moieties was indicated by fragment ions at m/z 547 [M − 206]$^−$ and m/z 341 [M − (206 × 2)]$^−$. The fragments at m/z 385 [M − (206 + 162)]$^−$ and 369 [M − (206 + 178)]$^−$ were due to the loss of one hexose unit with a sinapoyl moiety. The ^{1}H-nmr spectrum of **1** is very similar to that of **2**; the main difference was the absence of one sinapoyl unit. Also a difference was observed in the chemical shift of H-4 (Table 1); it was shifted upfield about 1.2 ppm when compared with com-

TABLE 2. ^{13}C-nmr Data of **1** and **2** in CD$_3$OD.

Position	DEPT	Compound	
		1	2
C-1	CH$_2$	65.60	65.49
C-2	C	104.98	105.54
C-3	CH	79.62	77.46
C-4	CH	75.18	76.75
C-5	CH	84.43	82.96
C-6	CH$_2$	63.79	63.87
C-1'	CH	92.81	93.13
C-2'	CH	73.23	72.99
C-3'	CH	74.38	75.15
C-4'	CH	72.05	72.22
C-5'	CH	72.59	73.20
C-6'	CH$_2$	65.88	65.93
C-1″	C	126.67^c	126.83^c
C-2″	CH	107.21^a	107.54^a
C-3″	C	147.22^d	147.97^d
C-4″	C	139.47	139.40
C-5″	C	149.53^d	149.56^d
C-6″	CH	107.21^a	107.86^a
C-7″	CH	147.92^d	148.32^d
C-8″	CH	115.95^b	116.24^b
C-9″	C	169.11	169.23
C-1‴	C	126.27^c	126.85^c
C-2‴	CH	107.37^a	107.54^a
C-3‴	C	147.22	147.97^d
C-4‴	C	139.70	139.40
C-5‴	C	149.53^d	149.49^d
C-6‴	CH	107.37^a	107.36^a
C-7‴	CH	147.92^d	148.32^d
C-8‴	CH	115.58^b	116.24^b
C-9‴	C	168.29	169.23
C-1⁗	C		126.62^c
C-2⁗	CH		107.54^a
C-3⁗	C		147.03^d
C-4⁗	C		138.90
C-5⁗	C		149.56^d
C-6⁗	CH		107.86^a
C-7⁗	CH		148.32
C-8⁗	CH		116.66^b
C-9⁗	C		168.02
OMe	Me	57.01	57.01

$^{a–d}$Values bearing same superscript are interchangeable.

pound **2**, thus suggesting that **1** was not esterified at position 4. The ^{1}H-nmr and ^{13}C-nmr chemical shifts of H-3, H$_a$-6', H$_b$-6' and C-3, C-6' (see Tables 1 and 2) were indicative of the 3,6' esterification in this compound. Therefore compound **1** was assigned as β-D-(3-sinapoyl)fructofuranosyl-α-D-(6-sinapoyl)glucopyranoside.

The known compounds isolated were identified on the basis of literature data (3–5).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—For nmr, Bruker WH-250 Spectroscopin or Bruker AMX-500 spectrometers equipped with a Bruker X-32 computer using the UXNMR software package were used. Two-dimensional homonuclear proton chemical shift correlation (COSY) experiments were measured by employing the conventional pulse sequence. The COSY spectrum was obtained using a data set (t1 × t2) of 1024 × 1024 points for a spectral width of 1165 Hz (relaxation delay 1 sec). The data matrix was processed using an unshifted sine bell window function, following transformation to give a magnitude spectrum with symmetrization (digital resolution in both F2 and F1 dimensions 1.13 Hz/pt). The 2D HOHAHA experiment was performed in the phase-sensitive mode (TPPI) using an MLEV-17 sequence for mixing (15). The spectral width (t 2) was 1002 Hz; 512 experiments of 40 scans each (relaxation delay 1.5 sec, mixing time 100 msec) were acquired in both dimensions before transformation. The resulting digital resolution in F2 was 0.48 Hz/pt. Optical rotations were measured on a Perkin-Elmer 141 polarimeter using a sodium lamp operating at 589 nm. Fabms was recorded in a glycerol matrix in the negative ion mode on a VG ZAB instrument (Xe atoms of energy of 2–6 kV).

PLANT MATERIAL.—The bark of *S. longipedunculata* was collected in Dakar and identified by Prof. E. Bassene. A voucher sample is deposited at the Herbarium of the Faculté Mixte de Medicine et Pharmacie, Laboratorie de Pharmacognosie, Université de Dakar, Senegal.

EXTRACTION AND ISOLATION.—The dried bark (400 g) was successively extracted with petroleum ether and $CHCl_3$ and then with $CHCl_3$-MeOH (9:1) to give 12 g of residue. Part of the residue (4 g) was chromatographed on a Sephadex LH-20 column (100 × 5 cm). Fractions of 10 ml were eluted with MeOH. Fractions 24–26 (300 mg) and 27–29 (137 mg) were submitted to hplc on a C18 μ-Bondapak column (30 cm × 7.8 mm, flow rate 3.5 ml/min) using MeOH-H_2O (50:50) as eluent. Fractions 27–29 gave pure **1** (13.3 mg) and **2** (7.6 mg), whereas fractions 24–26 afforded **1** (6.2 mg), **2** (6 mg), sinapoic acid (8 mg), and caffeic acid (12 mg). Fractions 46–50 contained pure dicaffeoyl D-quinic acid (30 mg) and frac-

tions 52–55 tricaffeoyl D-quinic acid (20 mg). Compound **1**: hplc retention time 14.0 min; $[\alpha]^{25}D$ −42.89 (c = 1, MeOH); fabms see text; ^1H and ^{13}C nmr (CD_3OD) see Tables 1 and 2. Compound **2**: hplc retention time 25.6 min; $[\alpha]^{25}D$ −45.92 (c = 1, MeOH); fabms see text; ^1H and ^{13}C nmr (CD_3OD) see Tables 1 and 2.

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