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PRENYLATED FLAVANONES FROM *SOROCEA ILICIFOLIA*

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Key Word Index—*Sorocea ilicifolia*; Moraceae; roots; prenylated flavanones.

Abstract—Chloroform extraction of the roots of *Sorocea ilicifolia* gave three new prenylated flavanones, soroceins F, E and G. In the extract, some Diels–Alder type adducts, already found in the Moraceae, were also present.

INTRODUCTION

During our research for biologically active Brazilian plants, our interest has been focused on the Moraceae from which several new compounds have been isolated [1–6]. This work concerns the results obtained by the examination of the antimicrobial active extract of the roots of *Sorocea ilicifolia* [7], a small tree known in Brazil by the common name of Soroca [8]. Examination of the chloroform extract led us to isolate, besides the known compounds kuwanol E, chalcomoracin, mulberrofuran F [9], sorocein A, sorocein B [5], sorocein C and sorocein D [6], three new natural compounds, named soroceins F (**1**), E (**2**) and G (**3**).

RESULTS AND DISCUSSION

Compound **1**, molecular formula $C_{30}H_{34}O_7$, assigned on the basis of EI-mass spectrometry and ^{13}C NMR data, was isolated as an amorphous powder. In the ^1H NMR spectrum the resonances attributable to three prenyl chains, an *ortho* coupled system, an aromatic singlet, and a chelated hydroxyl group were present (Table 1). The UV spectrum (see Experimental) and ^1H and ^{13}C NMR data (Table 2) were in agreement with a flavanone derivative with an unusual substitution of the C ring. The absence in the ^1H NMR spectrum of the characteristic signals attributable to H-2 and H-3, and the presence in the ^{13}C NMR spectrum of two signals at δ92.3 and 102.3, suggested a modified flavanone skeleton like sorocein D (**4**). A mass spectral fragment at *m/z* 221 $[A_1]^+$ was in agreement with the presence of a prenyl chain in the A ring; the two protons of the *ortho* coupled system and the third prenyl chain were thus located on the B ring.

HMBC experiments allowed us to confirm unambiguously the assignment of the three prenyl chains at C-3′, C-6 and C-2 (Fig. 1). Full proof of the skeleton of **1** was obtained by a combination of HMBC, INEPT, homonuclear COSY and ^1H–^{13}C HETCOR experiments.

Compound **2** showed a molecular ion at *m/z* 504. In the ^1H NMR spectrum of **2** (Table 1) a pattern of signals similar to that of sorocein F were present, except for the presence of the resonances due to a 2,2-dimethylchromene ring [signals at δ1.37 (3H, *s*), 1.62 (3H, *s*), 5.43 (1H, *d*), 6.45 (1H, *d*)] instead of a prenyl chain. The location of the 2,2-dimethylchromene ring was made by taking account of the mass fragmentation at *m/z* 219 $[B_1]^+$. The ^{13}C NMR data (Table 2) and mass fragmentation closely resembled those of sorocein D (**4**), already found in *Sorocea bonplandii* [6]. The different chemical shift of the aromatic singlet in **2** and **4** (δ5.78 and 5.94, respectively) was in agreement with an angular 2,2-dimethylchromene ring in **2**. On the basis of these data, structure **2** was thus assigned to sorocein E.

Spectroscopic data indicated the same skeletal type of soroceins F and E for **3**, $[M]^+$ at *m/z* 506. In the ^1H NMR spectrum the signals of three prenyl chains, a chelated hydroxyl group and an ABX system were present (Table 1). In the EI-mass spectrum the fragment ion observed at *m/z* 289 $[C_1]^+$ suggested an A ring fully substituted with two prenyl chains. The third prenyl chain was located, as in **1** and **2** at C-2 (δ91.3, see Table 2). On the basis of the above data, we assign structure **3** to sorocein G.

EXPERIMENTAL

NMR spectra of soroceins E, F, G: 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR. HMBC, INEPT, homonuclear COSY and ^1H–^{13}C HETCOR experiments for sorocein F: 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR.

Plant material. Roots of *S. ilicifolia* were collected in Engegnho Tapacura' (S. Lorenzo da Mata, Pernambuco, Brazil) in 1989 and identified by Alda Chiappeta. A voucher specimen (5623) is deposited at the Herbarium of Instituto de Antibioticos (Recife, Brazil).

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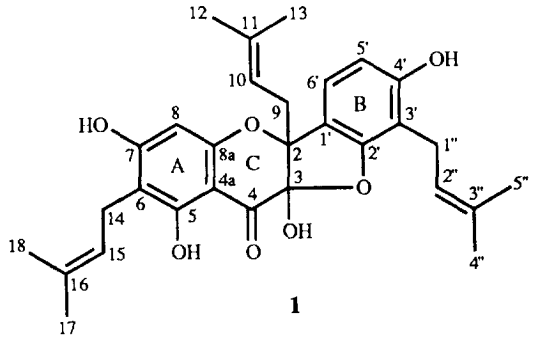

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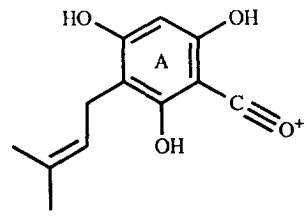
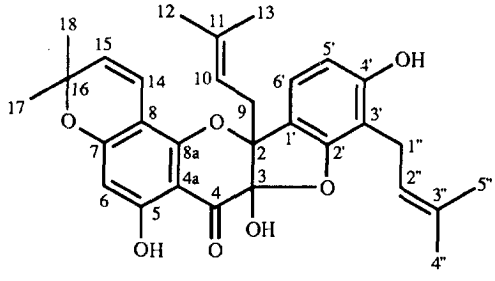


$[A_1]^+ m/z$ 221



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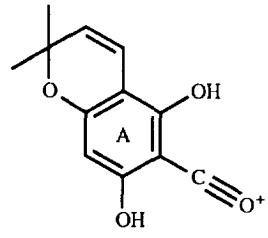
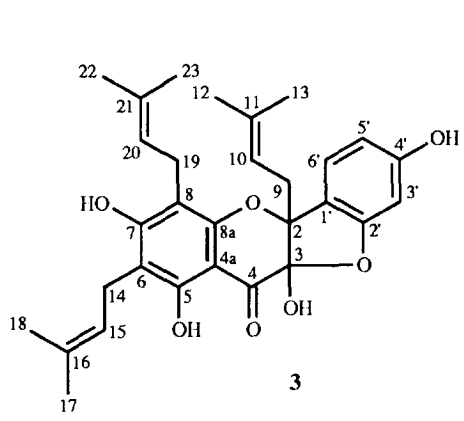


$[B_1]^+ m/z$ 219

Table 1. ^{1}H NMR spectral data of flavanones **1–4**

H	**1***	**2†**		**3***	**4†**
6	—	5.94 1H, *s*		—	—
8	5.91 1H, *s*	—		—	5.79 1H, *s*
9a	2.76 1H, *dd* (6.6, 14.7)	2.77 1H, *dd* (5.7, 14.7)		2.83 1H, *dd* (6.1, 15.4)	2.76 1H, *dd* (6.0, 15.0)
9b	3.10 1H, *dd* (8.9, 14.7)	3.10 1H, *dd* (8.9, 14.7)		3.05 1H, *dd* (8.8, 15.4)	3.07 1H, *dd* (8.8, 15.0)
10	5.22 1H, *m*	5.17 1H, *m*		5.32 1H, *br t*	5.17 1H, *m*
12	1.50 3H, *s*	1.56[a] 3H, *s*		1.57[a] 3H, *s*	1.62 3H, *s*
13	1.60 3H, *s*	1.58[a] 3H, *s*		1.68[a] 3H, *s*	1.55 3H, *s*
3′	—	—		6.36 1H, *d* (2.1)	—
5′	6.53 1H, *d* (8.0)	6.51 1H, *d* (8.1)		6.50 1H, *dd* (2.1, 8.2)	6.51 1H, *d* (8.1)
6′	7.17 1H, *d* (8.0)	7.19 1H, *d* (8.1)		7.34 1H, *d* (8.2)	7.19 1H, *d* (8.1)
14	3.22[a] 2H, *d* (8.0)	6.45 1H, *d* (10.0)		3.30 2H, *d* (6.9)	6.59 1H, *d* (10.0)
15	5.22 1H, *m*	5.43 1H, *d* (10.0)		5.13 1H, *br t*	5.50 1H, *d* (10.0)
17	1.60 3H, *s*	1.37[b] 3H, *s*		1.58[a] 3H, *s*	1.44[a] 3H, *s*
18	1.60 3H, *s*	1.44[b] 3H, *s*		1.62[a] 3H, *s*	1.40[a] 3H, *s*
1″	3.26[a] 2H, *d* (7.3)	3.34 2H, *m*	(H-19)	3.36 2H, *m*	3.34 2H, *m*
2″	5.22 1H, *m*	5.27 1H, *m*	(H-20)	5.04 1H, *br t*	5.27 1H, *m*
4″	1.70 3H, *s*	1.78[c] 3H, *s*	(H-22)	1.67[c] 3H, *s*	1.72 3H, *s*
5″	1.73 3H, *s*	1.74[c] 3H, *s*	(H-23)	1.73[c] 3H, *s*	1.76 3H, *s*
OH-5	11.98 1H, *s*	11.43 1H, *s*		11.96 1H, *s*	11.56 1H, *s*

[a–c] These signals may be interchanged within the same column.
Coupling constants (in parentheses) are given in Hz.
*Acetone-d_6.
†Chloroform-*d*.



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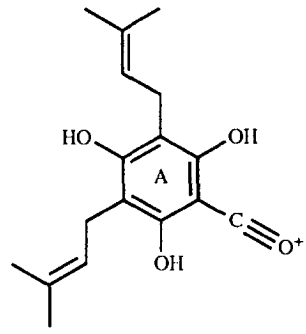


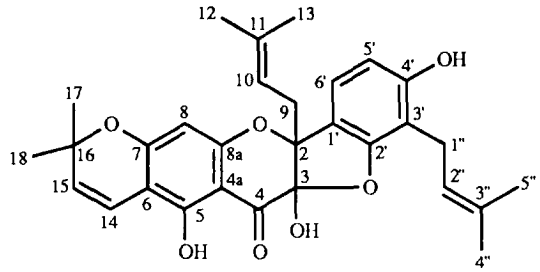
$[C_1]^+ m/z$ 289

Table 2. ^{13}C NMR spectral data of flavonones **1–4** (in acetone-d_6)

C	1	2		3	4
2	92.3	93.1		91.3	93.1
3	102.3	102.0[a]		102.8	102.0
4	188.6	189.1		188.4	189.2
4a	100.3	100.6		100.8	100.6
5	162.6	157.5		161.0[a]	158.6
6	109.1	97.4		108.9[b]	103.2
7	166.6	165.2		164.4	164.2
8	95.3	102.1[a]		108.1[b]	96.4
8a	161.6	164.2		n.o.	162.3
1′	121.1	121.0		121.2	120.9
2′	159.2	159.2		160.6[a]	159.5
3′	113.0	113.0		99.3	113.1
4′	158.4	158.6		161.0[a]	159.3
5′	109.5	109.6		109.6	109.9
6′	122.4	122.5[b]		125.8	123.0
9	32.2	32.2		32.3	32.1
10	118.8	118.5		118.8	118.7
11	136.3	137.0		135.8	136.6
Me-12	25.8	25.7[c]		25.8[c]	25.8
Me-13	17.8	17.8		17.9[d]	18.1
14	21.5	115.8		21.7	115.5
15	123.3	127.3		123.0[e]	127.4
16	131.7	79.3		132.3[f]	79.4
Me-17	25.8	28.4[d]		26.0[c]	28.4[a]
Me-18	18.1	25.8[d]		18.0[d]	28.5[a]
1″	23.2	23.2	(C-19)	22.3	23.2
2″	123.3	122.9[b]	(C-20)	123.2[e]	122.5
3″	131.4	131.8	(C-21)	132.0[f]	131.8
Me-4″	25.8	25.9[c]	(Me-22)	25.8[c]	25.9
Me-5″	18.0	18.1	(Me-23)	18.1[d]	17.9

[a–f] These signals may be interchanged within the same column.

Extraction and purification. The roots (470 g) were extracted exhaustively with MeOH. The dried residue (48 g), was extracted again with $CHCl_3$. Part of the $CHCl_3$ extract was chromatographed on silica gel using a $CHCl_3$–MeOH gradient. The compounds obtained were further purified using Lichroprep RP-8 (MeOH–H_2O, 9:1).



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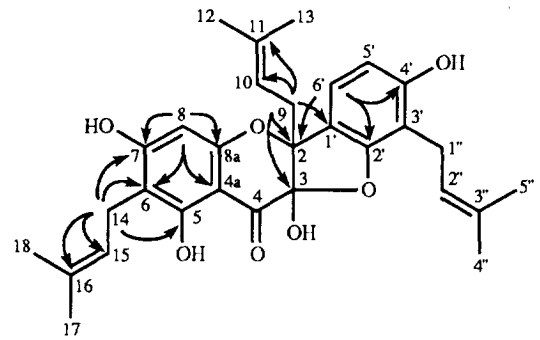

Fig. 1. Correlations in HMBC spectrum of **1**.

Biological activity. In a preliminary screening for biological activity, compounds **1–4**, tested against three yeast strains (*Candida albicans FTV*, *C. albicans OTF* and *Cryptococcus neoformans*), were inactive.

Sorocein F (**1**). Amorphous powder. $[\alpha]_D + 111$ (MeOH; *c* 0.1). EI-MS *m/z* (rel. int.): 506 $[M]^+$ (25), 437 (28), 381 (27), 285 (15), 221 (100). UV λ_{max}^{MeOH} nm (log ε): 240sh (4.24), 286sh (3.96), 307 (4.13), 360 (3.40). ^1H and ^{13}C NMR: Tables 1 and 2, respectively.

Sorocein E (**2**). Amorphous powder. $[\alpha]_D + 10$ ($CHCl_3$; *c* 0.1). EI-MS *m/z* (rel. int.): 504 $[M]^+$ (10), 436 (5), 285 (10), 230 (15), 219 (100), 203 (25). UV λ_{max}^{MeOH} nm (log ε): 230sh (4.44), 268sh (4.47), 276 (4.50), 317 (4.14), 370 (3.60). ^1H and ^{13}C NMR: Tables 1 and 2, respectively.

Sorocein G (**3**). Amorphous powder. $[\alpha]_D + 112$ (MeOH; *c* 0.1). EI-MS *m/z* (rel. int.): 506 $[M]^+$ (30), 438 (25), 381 (20), 289 (100), 233 (83), 221 (75). UV λ_{max}^{MeOH} nm (log ε): 232sh (4.39), 280sh (4.06), 286sh (4.08), 311 (4.20), 360 (3.53). ^1H and ^{13}C NMR: Tables 1 and 2, respectively.

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