THREE NEW DIELS-ALDER TYPE ADDUCTS FROM THE ROOTS OF SOROCEA BONPLANDII BAILLON

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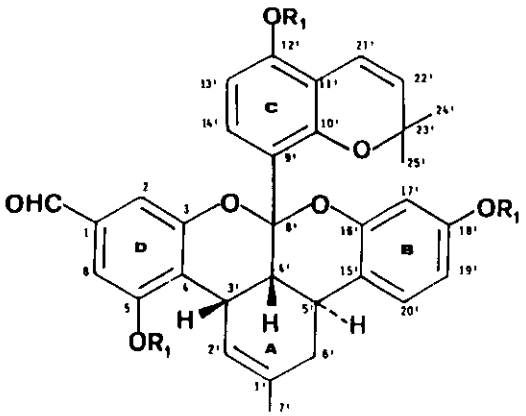
Abstract - Three new ketalized Diels-Alder type adducts named soroceal (1), sorocein A (2), sorocein B (3), were isolated from the methanolic extract of the roots of Sorocea bonplandii. The structures were assigned on the basis of chemical and spectroscopic evidences.

Sorocea bonplandii Baillon is a large tree belonging to the Moraceae family. Non-published results from our laboratories have recently demonstrated that the crude methanolic extract of the roots of this plant presents an interesting in vitro pharmacological profile. As a matter of fact the extract antagonizes in reversible manner responses elicited by different neurotransmitters in smooth muscle preparations. [1]

In order to isolate and identify the compounds responsible for the activity the methanolic extract of the roots of Sorocea bonplandii was examined. By chromatographic separation (see Experimental) the extract gave three new Diels-Alder type adducts named soroceal (1), sorocein A (2), and sorocein B (3), together with the known betulinic acid, [2] morusin, [3] and mulberrofuran K. [4]

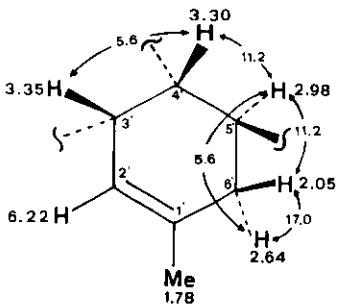
Soroceal (1), $[\alpha]_D$ + 365° (c=0.05, MeOH), showed a molecular ion at m/z 524 in the EI mass spectrum, and 32 resonances in the ^{13}C nmr spectrum. The presence of three phenolic hydroxy groups in the molecule was evidenced by the formation of a trimethyl derivative by treatment with dimethyl sulfate, (1a, M^+ at m/z 566). The band at 1680 cm^{-1} in the ir spectrum of 1 ($\nu_{C=O}$), and the signals at δ 9.84 and 192.1 ppm in the ^1H and ^{13}C nmr spectra, respectively, were attributed to an aldehydic function. In the aromatic region of the ^1H nmr spectrum the resonances for a 1,2,4-trisubstituted benzene ring, two ortho and two meta coupled aromatic protons, and a pyran ring were present. ^1H Nmr sequential decoupling experiments carried out on the spectrum of 1a assigned the complex system of signals in the range of δ 1.5 to 3.5 to those of a trisubstituted methylcyclohexene ring (see fig. 1). This moiety is a feature of the natural Diels-Alder type adducts isolated from Moraceae.[5] However, the typical resonance at ca. 208 ppm due to the carbonyl carbon of the benzoyl moiety observed in natural Diels-Alder adducts was absent in the ^{13}C nmr spectrum of soroceal, and a singlet appeared at 102.1 ppm. A structure derived through a intramolecular ketalization of the carbonyl group, such as mulberrofuran K , fitted for the above data. The substitution pattern of the aromatic rings and their positions on the methylcyclohexene were suggested by nmr data of the methyl derivative (1a) and of the acetyl derivative (1b) (M^+ at m/z 650). The substituents of C ring were assigned as in 1 by the acetylation shifts of the signals attributed to H-21' and H-22' (pyran ring, Δδ -0.22 and +0.17, respectively, in acetone-d_6) [6] and the absence of any signal for ortho disubstituted methoxyl group (ca. 60 ppm) in the ^{13}C nmr spectrum of 1a. [7] The second hydroxyl group of 1 was located at C-5 on the basis of the upfield shift of H-2' (Δδ, -0.40, in acetone-d_6) as a consequence of the acetylation, as observed in other ketalized Diels-Alder type adducts. [8] Finally the chemical shift and coupling constant values of the aromatic protons allowed us to assign the third hydroxyl group to C-18' and the aldehydic function to C-1. The relative configurations, between H-3 ' and



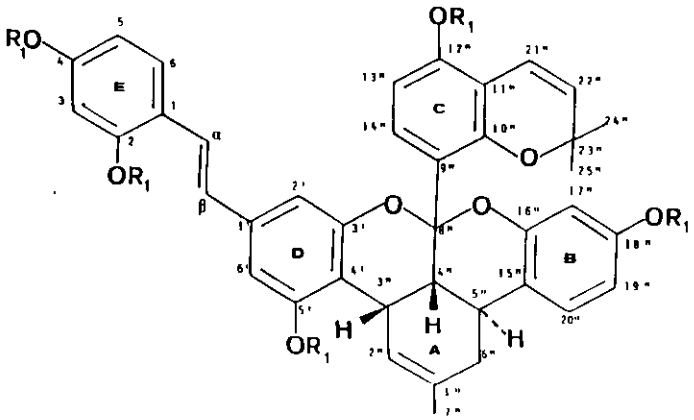
1 : R_1 = H

1a : R_1 = Me

1b : R_1 = COMe



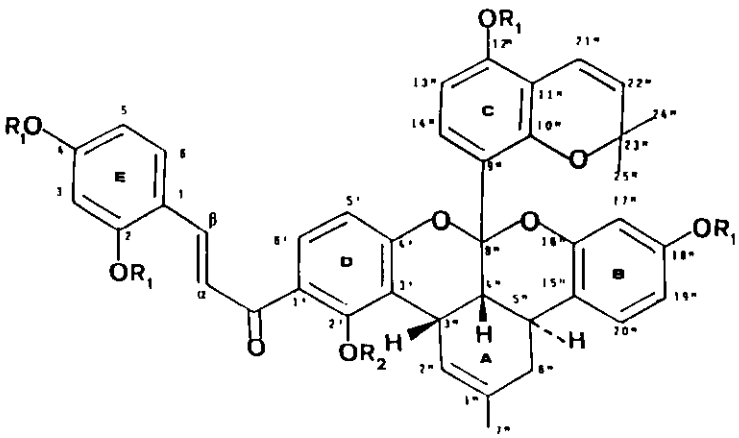
1a



2 : R_1 = H

2a : R_1 = Me

2b : R_1 = COMe



3 : R_1 = R_2 = H

3a : R_1 = Me , R_2 = H

3b : R_1 = R_2 = COMe

Table 1. ^{1}H And ^{13}C nmr chemical shift assignments of 1 and its derivatives.

	1 (acetone-d_6)	1a ($CDCl_3$)
C-1	137.6	136.2
C-2	111.1	113.9
C-3	157.8[a]	159.6[a]
C-4	118.5	118.5
C-5	158.3[a]	159.2[a]
C-6	108.3	102.3[b]
C-7	192.1	191.6
C-1'	134.5	134.0
C-2'	121.7	120.9
C-3'	37.6[b]	36.5[c]
C-4'	35.2[b]	34.3[c]
C-5'	28.4	27.2
C-6'	36.5	35.8
C-7'	23.9	23.9
C-8'	102.1	101.4
C-9'	119.7	120.6
C-10'	155.0[a]	155.7[a]
C-11'	111.1	111.5
C-12'	154.7[a]	155.9[a]
C-13'	107.6	101.9[b]
C-14'	129.4	129.0[d]
C-15'	117.3	117.6
C-16'	153.2[a]	152.0[a]
C-17'	103.8	101.5[b]
C-18'	152.7[a]	n.o.
C-19'	109.8	108.4
C-20'	127.9	126.9
C-21'	117.9	116.9
C-22'	128.9	128.0[d]
C-23'	76.7	82.2
C-24',25'	27.5,27.7	27.5
OMe	-	55.3,55.4,55.5

	1 (acetone-d_6)	1a ($CDCl_3$)	1b ($CDCl_3$)
H-2,H-6	6.96,7.02, 2d,J=1.5	6.96,7.14,b s	7.21,7.39, 2d,J=1.5
H-2'	6.46,b s	6.22,b s	5.89,d,J=5.1
H-3'	3.40,m	3.35,m	3.37,b t,J=5.1
H-4'	3.40,m	3.30,dd, J=11.2,5.6	3.23,dd, J=12.2,5.1
H-5'	2.8-3.0	2.98,ddd, J=11.2,11.2,5.6	3.00,ddd, J=12.2,11.0,5.8
H-6'	2.0-2.1	2.05,dd, J=17.0,11.2	2.01,dd, J=17.2,11.0
	2.73,dd, J=17.1,5.4	2.64,dd, J=17.0,5.6	2.69,dd, J=17.2,5.8
Me-7'	1.77,s	1.78,s	1.78,s
H-13'	6.27,d,J=8.6	6.24,d,J=8.6	6.50,d,J=8.7
H-14'	6.96,d,J=8.6	7.05,d,J=8.6	7.07,d,J=8.7
H-17'	6.37,d,J=2.5	6.54,d,J=2.5	6.68,d,J=2.4
H-19'	6.51,dd, J=8.4,2.5	6.57,dd, J=8.4,2.5	6.75,dd, J=8.4,2.4
H-20'	7.14,d,J=8.4	7.13,d,J=8.4	7.21,d,J=8.4
H-21'	6.68,d,J=10.0	6.63,d,J=10.0	6.32,d,J=10.0
H-22'	5.67,d,J=10.0	5.56,d,J=10.0	5.66,d,J=10.0
H-24', 25'	1.34,s	1.32,1.34,s	1.32,s
CHO	9.84,s	9.85,s	9.89,s
OCOMe	-	-	2.28,2.29,2.32,s
OMe	-	3.75,3.76,3.83,s	-

Abbreviations: s=singlet; d=doublet; t=triplet; m=multiplet; b=broad
[a-d]interchangeable. n.o.=not observed.

H-4' to be cis and between H-4' and H-5' to be trans, were determined on the basis of the coupling constant values of H-3', H-4' and H-5' (Table 1). Sorocein A (2), $[\alpha]_D$ +477° (c=0.05, MeOH) showed 39 resonances in the ^{13}C nmr spectrum, and a pseudo-molecular ion at m/z 631 $(M+H)^+$ in the FABms spectrum. It gave a pentamethyl derivative, (2a) (M^+ at m/z 700), and a pentaacetyl derivative, (2b) (M^+ at m/z 840). The ^1H and ^{13}C nmr data of 2 indicated also for this compound the structure of a ketalized Diels-Alder type adduct. The presence of a substituted 2,4,3',5'-tetraoxygenated stilbene moiety was suggested by the absorptions at 338sh, 328, 304, and 224 nm and their intensities (log ε 4.26, 4.16, 4.14, and 4.30) in the uv spectrum, and was confirmed by the doublets at δ 7.33 and 6.89 (J=16.5 Hz) and the appropriate signals for the aromatic protons in the ^1H nmr spectrum (Table 2). [9] The comparison of the ^1H nmr spectra of 2 and its derivatives with those of 1 and its derivatives evidenced the presence of the same A, B, and C rings (Tables 2 and 1, respectively) as well as the same relative configuration between H-3", H-4", and H-5". The acetylation shifts observed on H-21", H-22" and H-2" were in agreement with the structure (2) assigned to sorocein A.

Sorocein B (3), $[\alpha]_D$ +962° (c=0.05, MeOH) showed a pseudo-molecular ion at m/z 659 $(M+H)^+$ in the FABms spectrum. It gave a tetramethyl derivative (3a) (M^+ at m/z 714), still containing a chelated phenolic hydroxyl group, and a pentaacetyl derivative (3b) (M^+ at m/z 868). Again the comparison of nmr spectra of 3 and its derivatives with those of 2 and its derivatives suggested that 3 has the same A, B, C, and E rings, and the same relative configurations between H-3", H-4", and H-5" as 2. The presence of a chalcone moiety was suggested by uv data, and was confirmed by the doublets at δ 8.27 and 7.83 (J=15.0 Hz) in the ^1H nmr spectrum and the singlet at 193.6 ppm in the ^{13}C nmr spectrum. The substitution of D ring was indicated by the doublets at δ 8.02 and 6.57 (J=9.0 Hz) and the singlet at δ 14.58 in the ^1H nmr spectrum.

The sign of rotatory powers of 1, 2, and 3 and the relative configurations

Table 2. ^{1}H Nmr chemical shift assignments of 2, 2a, 2b, 3, 3a, and 3b.

	2(acetone-d_6)	2a($CDCl_3$)	2b(acetone-d_6)	3(acetone-d_6)	3a($CDCl_3$)	3b(acetone-d_6)
H-3	6.44,d, J=2.3	6.45,d,J=2.3	7.17,d,J=2.3	6.40,d,J=2.3	6.46,d,J=2.3	7.08,d,J=2.3
H-5	6.38,dd,J=8.5, 2.3	6.50,dd,J=8.5, 2.3	7.06,dd,J=8.5, 2.3	6.48,dd,J=8.7, 2.3	6.52,dd,J=8.7, 2.3	7.15,dd,J=8.7, 2.3
H-6	7.38,d,J=8.5	7.48,d,J=8.5	7.81,d,J=8.5	7.71,d,J=8.7	7.55,d,J=8.7	7.79,d,J=8.7
H-α	6.89,d,J=16.5	6.89,d,J=16.5	7.15,d,J=16.5	7.83,d,J=15.0	7.62,d,J=15.0	7.38,d,J=15.0
H-β	7.33,d,J=16.5	7.33,d,J=16.5	7.29,d,J=16.5	8.27,d,J=15.0	8.08,d,J=15.0	7.58,d,J=15.0
H-2'*	6.62,s	6.86,b d	6.98[a],d,J=2.3	6.57,d,J=9.0	6.58,d,J=9.0	7.06,d,J=8.7
H-6'	6.62,s	6.5-6.6,m	6.93[a],d,J=2.3	8.02,d,J=9.0	7.75,d,J=9.0	8.01,d,J=8.7
H-2"	6.44,b d	6.23,ov.	6.00,b d,J=5.2	6.5,ov.	6.47,ov.	6.05,b d,J=4.5
H-3"	3.3-3.4	3.38,ov.	3.30,b t,J=5.2	3.37,b t,J=5.5	3.38,m	3.3-3.5
H-4"	3.3-3.4	3.33,dd,J=12.0, 5.4	3.36,dd,J=11.8, 5.0	3.42,dd,J=12.0, 5.5	3.33,dd,J=12.0, 5.4	3.3-3.5
H-5"	2.98,ddd,J=11.0, 10.0,5.0	3.00,ddd,J=12.0, 12.0,5.4	3.01,ddd,J=11.8, 11.8,5.0	2.91,ddd,J=12.0, 12.0,5.5	3.00,ddd,J=12.0, 12.0,5.0	3.00,m
H-6"	2.74,dd,J=17.0, 5.0 ov.	2.06,dd,J=17.0, 12.0 2.65,dd,J=12.0, 5.4	ov. ov.	ov. 2.72,dd,J=17.0, 5.5	2.06,dd,J=17.0, 12.0 2.65,dd,J=17.0, 5.0	ov. ov.
H-7"	1.80,b s	1.77,b s	1.79,b s	1.78,b s	1.80,b s	1.80,b s
H-13"	6.27,d,J=8.8	6.25,d,J=8.9	6.60,d,J=8.7	6.29,d,J=8.3	6.24,d,J=8.5	6.61,d,J=8.5
H-14"	7.06,d,J=8.8	7.15,d,J=8.9	7.20,d,J=8.7	6.91,d,J=8.3	7.01,d,J=8.5	7.13,d,J=8.5
H-17"	6.35,d,J=2.5	6.5-6.6	6.70,d,J=2.3	6.52,d,J=2.3	6.54,d,J=2.3	6.72,d,J=2.3
H-19"	6.49,dd,J=8.5, 2.5	6.5-6.6	6.79,dd,J=8.3, 2.3	6.54,dd,J=8.3, 2.3	6.59,dd,J=8.5, 2.3	6.81,dd,J=8.5, 2.3
H-20"	7.13,d,J=8.5	7.13,d,J=8.0	7.37,b d,J=8.7	7.16,d,J=8.3	7.16,d,J=8.5	7.38,b d,J=8.5
H-21"	6.68,d,J=8.5	6.63,d,J=10.0	6.47,d,J=10.0	6.69,d,J=10.0	6.63,d,J=10.0	6.46,d,J=10.0
H-22"	5.65,d,J=10.0	5.55,d,J=10.0	5.83,d,J=10.0	5.66,d,J=10.0	5.56,d,J=10.0	5.85,d,J=10.0
H-24",25"	1.36,s (x2)	1.31, 1.34,2s	1.32, 1.34,2s[#]	1.34,s (x2)	1.32, 1.34,2s	1.35,s (x2)
OH	-	-	-	14.58,s;9.0,bs	14.0,s	-
OMe	-	3.75,3.76,3.81 3.83,3.85	-	-	3.74,3.76,3.84 3.90	-
OCOMe	-	-	2.25,2.26,2.29(x2) 2.35	-	-	2.22,2.25,2.28 2.33

* H-5' in compounds 3, 3a, 3b; # measured in $CDCl_3$.

Abbreviations: s=singlet; d=doublet; m=multiplet; b=broad; ov.=overlapped; [a]interchangeable.

Table 3. ^{13}C Nmr chemical shift assignments of 2, 2a, 2b, 3, and 3a.

	2*,@	2a#	2b*	3*	3a#
C-1	117.7	118.1	128.2	115.2[a]	n.o.
C-2	156.9[a]	155.5[a]	153.7[a]	160.0	160.4
C-3	103.7	98.4	117.1	103.8	98.4
C-4	157.6[a]	158.0[a]	152.6[a]	162.4	163.1
C-5	108.3	104.9[b]	120.4	108.8	102.3
C-6	127.8	126.9[c]	130.2	128.5	126.9
C-α	125.6	126.7[c]	123.1	117.7	118.5
C-β	124.4	122.2	121.0	141.5	140.0
C-1'	139.4	138.1	138.4	113.4	112.9
C-2'	106.8[b]	107.6	116.2	166.0	165.2
C-3'	154.5[a]	153.1[a]	152.2[a]	115.1[a]	114.7
C-4'	111.7	111.3	116.5	159.3[b]	159.1[a]
C-5'	154.5[a]	159.0[a]	151.5[a]	109.2	108.3
C-6'	106.5[b]	102.3	112.3	129.4	129.0[b]
C-1"	133.3	132.9	135.7	134.2	133.2
C-2"	123.1	123.2	127.6	122.0	121.5
C-3"	37.7[c]	36.6[d]	36.9[b]	37.4[c]	36.4[c]
C-4"	34.7[c]	33.8[d]	34.3[b]	34.2[c]	33.3[c]
C-5"	28.3	27.4	28.3	28.2	27.3
C-6"	36.6	35.9	36.1	36.4	35.9
C-7"	23.9	23.9	23.7	23.8	23.7
C-8"	101.8	101.2	101.6	102.7	102.1
C-9"	119.1	119.2[e]	124.6	118.2	117.7
C-10"	157.7[a]	159.0[a]	151.4[a]	157.6[b]	158.5[a]
C-11"	111.0	n.o.	118.1	111.2	111.5
C-12"	159.1[a]	160.5	151.2[a]	154.6[b]	155.7[a]
C-13"	107.5	102.3[b]	115.8[c]	107.6	105.4
C-14"	129.1	128.9[c]	128.0	131.8	131.3
C-15"	117.1	119.4[e]	123.7	117.2	117.0
C-16"	152.6[a]	152.2[a]	149.6[a]	153.0[b]	152.0[a]
C-17"	103.6	101.5	110.8	103.5	101.5
C-18"	153.3[a]	151.4[a]	148.3[a]	152.5[b]	151.3[a]
C-19"	109.6	108.1	114.9[c]	110.0	108.3
C-20"	128.3	127.2[c]	128.3	127.9	127.6
C-21"	117.9	117.0	117.6	117.1	116.9
C-22"	129.3	128.4[c]	132.5	130.5	129.3[b]
C-23"	76.5	75.9	77.5	76.7	76.0
C-24",25"	27.4,27.6	27.2,27.4	27.4,27.6	27.4,27.5	27.2,27.4
C=O	-	-	-	193.6	192.8
OMe	-	55.3,55.4,55.5	-	-	55.3,55.4,55.5
OCOMe	-	-	168.8,169.2,169.3 169.4,169.5	-	-
OCOMe	-	-	20.6,20.8,20.9,21.3	-	-

Solvents: *acetone-d_6 ; #$CDCl_3$. @Assigned by heteronuclear correlation.
[a-e] Interchangeable. n.o.=not observed.

between the three chiral centers of the methylcyclohexene ring are in agreement with the results obtained by Y. Hano et al., that reported that cis-trans adducts exhibit positive optical rotations, while all-trans adducts exhibit negative values .[10]

In addition to compounds 1, 2, and 3, kuwanol A, [11] and mulberrofurans F, G[8] and K[4] are the only examples of natural ketalized Diels-Alder type adducts reported in the literature.

EXPERIMENTAL

^1H And ^{13}C nmr spectra were registered at 400 and 100 MHz, respectively, on a Bruker AM 400 (TMS as internal standard).

Plant material. Roots of S. bonplandii were collected in Florianopolis island (Santa Catarina , Brazil) and identified by Daniel Falkenberg; a voucher specimen (SB 8889) is kept at the Herbarium of Horto Botanico, Universidade Federal de Santa Catarina (Brazil).

Extraction and purification. The roots (3.8 Kg) were extracted with MeOH (3 x 4 l) at room temperature for three days (47 g of residue). Part of the residue (10 g) was chromatographed on SiO_2 using a gradient of $CHCl_3$-MeOH. The following substances were obtained: betulinic acid (50 mg) with $CHCl_3$, morusin (70 mg) with 5% MeOH, 1 (100 mg), mulberrofuran K (150 mg), 2 (900 mg), and 3 (200 mg) with 10% MeOH. Mulberrofuran K, 1, 2, and 3 were further purified using LiChroprep RP-8 (MeOH-H_2O, 8:2). The known compounds were identified by comparison of their physical and spectral data with those reported in the literature.

Soroceal, (1). $C_{32}H_{28}O_7$. Amorphous powder. EIms, m/z (%): 524 (M^+, 32), 509 (23), 414 (8), 399 (20), 252 (100), 237 (70). $[\alpha]_D$ +365° (c=0.05, MeOH). Uv (MeOH), λ_{max} nm (log ε): 280 (4.20), 223 (4.63). Ir (KBr), ν_{max} cm^{-1}: 3500-3300, 2920, 1680, 1580, 1500, 1430, 1110; ^1H And ^{13}C nmr: see Table 1.

Methylation of 1: 1a. A mixture of 1 (13 mg), dimethyl sulfate (0.2 ml), and K_2CO_3 (1 g) in anhydrous acetone (5 ml) was refluxed for 1.5 h. The usual work up gave a residue that was purified on SiO_2 (n-hexane-AcOEt, 3:1) to give pure 1a (8 mg). Amorphous powder. $[\alpha]_D$ +377° (c=0.05, MeOH). EIms, m/z

(%): 566 (M^+, 100), 555 (80), 427 (70). ^1H And ^{13}C nmr: see Table 1.

Acetylation of 1: 1b. Soroceal (10 mg), pyridine (0.2 ml) and acetic anhydride (0.2 ml) were kept at room temperature for 16 h . The reaction mixture was evaporated, and the residue was purified on SiO_2 (n-hexane-Et_2O, 1:2) to give 1b (7 mg). Amorphous powder. EIms, m/z (%): 650 (M^+, 8), 608 (5), 583 (8), 581 (8), 566 (5), 531 (5), 489 (85), 442 (12), 420 (40), 405 (100). ^1H Nmr : see Table 1.

Sorocein A, (2). $C_{39}H_{34}O_8$. Amorphous powder. FABms, $(M+H)^+$ at m/z 631. $[\alpha]_D$ +477° (c=0.05, MeOH). Uv (MeOH), λ_{max} nm (log ε): 338sh (4.15), 328 (4.16), 304 (4.14), 287 (4.16), 224 (4.30). Ir (KBr), ν_{max} cm^{-1}: 3500-3300, 2920, 1600, 1500, 1420, 1255. ^1H And ^{13}C nmr: see Tables 2 and 3, respectively.

Methylation of 2: 2a. A mixture of sorocein A (15 mg), dimethyl sulfate (0.2 ml), and K_2CO_3 (1 g) in anhydrous acetone (5 ml) was refluxed for 3 h , and treated as usual. The residue was purified on SiO_2 ($CHCl_3$-n-hexane, 8:2) to give 2a (10 mg). mp 116-121°C (from MeOH). $[\alpha]_D$ +421° (c=0.03, MeOH). EIms, m/z (%): 700 (M^+, 100), 685 (80). ^1H And ^{13}C nmr: see Tables 2 and 3, respectively.

Acetylation of 2: 2b. Sorocein A (78 mg), pyridine (0.5 ml) and acetic anhydride (0.5 ml) were kept at room temperature for 16 h . The residue after evaporation was purified on SiO_2 ($CHCl_3$) to give pure 2b (60 mg). *Amorphous powder. EIms, m/z (%):* 840 (M^+, 100), 825 (50), 798 (60), 782 (80), 756 (40), 755 (40), 739 (50), 714 (25). ^1H And ^{13}C nmr: see Tables 2 and 3, respectively.

Sorocein B, (3). $C_{40}H_{34}O_9$. Amorphous powder. FABms, $(M+H)^+$ at m/z 659. $[\alpha]_D$ + 962°(c=0.05, MeOH). Uv (MeOH), λ_{max} nm (log ε): 390 (4.21), 311 (4.17), 285 (4.17), 260 (4.17), 228sh (4.60); (MeOH+$AlCl_3$ after 15'): 455, 320sh, 275, 228sh; (MeOH+$AlCl_3$+HCl): 455, 320sh, 275, 228sh. Ir (KBr), ν_{max} cm^{-1}: 3500-3200, 2920, 1700sh, 1600,1430, 1355. ^1H And ^{13}C nmr: see Tables 2 and 3, respectively.

Methylation of 3: 3a. Sorocein B (3), was methylated as reported for sorocein A. Amorphous powder. EIms, m/z (%): 714 (M^+, 100), 699 (42), 590 (12),

563 (54), 522 (36). Uv (MeOH), λ_{max} nm: 383, 311, 285, 260, 228sh; (MeOH+$AlCl_3$ after 20'): 440, 400sh, 320sh, 275, 228sh; (MeOH+$AlCl_3$+HCl): 440, 400sh, 320sh, 275, 228sh. ^1H And ^{13}C nmr: see Tables 2 and 3, respectively.

Acetylation of 3: 3b. Sorocein B was acetylated as reported for sorocein A. The residue after evaporation of the reagents was purified on SiO_2 ($CHCl_3$) to give 3b . Amorphous powder. EIms, m/z (%): 868 (M^+, 18), 826 (100), 784 (29). ^1H Nmr: see Table 2.

ACKNOWLEDGMENTS

The authors are indebted to Mr. Enrico Rossi, who carried out the HETCOR nmr experiment on a Bruker AC 200 at the Servizio Nmr, Area Ricerca, CNR, Roma.

REFERENCES

1. J. B. Calixto, T. Bisognin, F. Delle Monache, and R. A. Yunes, XI Simposio de Planta Medicinal do Brasil, Joao Pessoa, September 1990, N. 3.32.
2. I. Heilbron, and H. M. Bumbury, "Dictionary of Carbon Compounds", Eyre and Spottiswoode, London, 1953, p. 287.
3. T. Nomura, T. Fukai, S. Yamada, and M. Katayanagi, Chem. Pharm. Bull., 1978, 26, 1394.
4. Y. Hano, H. Kohno, M. Itoh, and T. Nomura, Chem. Pharm. Bull., 1985, 33, 5294.
5. T. Nomura, "Progress in the Chemistry of Organic Natural Products", vol. 53, Springer-Verlag, Wien New York, 1988, pp 115-147.
6. A. Arnone, G. Cardillo, L. Merlini, and R. Mondelli, Tetrahedron Lett., 1967, 4201.
7. K. Panichpol, and P. G. Waterman, Phytochemistry, 1978, 17, 1363.
8. T. Fukai, Y. Hano, K. Hirakura, T. Nomura, J. Uzawa, and K. Fukushima, Heterocycles, 1984, 22, 473.
9. L. P. Christensen, J. Lam, and T. Sigsgaard, Phytochemistry, 1988, 27, 3014.
10. Y. Hano, S. Suzuki, T. Nomura, and Y. Iitaka, Heterocycles, 1988, 27, 2315.
11. Y. Hano, M. Itoh, and T. Nomura, Heterocycles, 1985, 23, 819.

Received, 25th February, 1991