to −30 °C by means of a dichloroethane–dry ice slush. *trans*-1,3,5,7-Tetranitroso-1,3,5,7-tetraazadecalin was added to this solution over 10 min. The dichloroethane–dry ice bath was replaced with an ice–water bath. After being stirred at 0 °C for 30 min, the mixture was stirred at 50 °C for 10 min. The solution was then poured onto 30 g of ice. After the ice had melted, the product was collected by vacuum filtration and was washed well with water. After drying, the crude product weighed 0.66 g. It was purified by dissolving in warm DMF (60 °C) and by adding water until turbid. After cooling to 0 °C, the crystals were collected. The puridied product weighed 0.41–0.45 g and melted at 252–254 °C: ^{1}H NMR (Me_2SO-d_6) δ 4.10 (m, 2 H, $H_{4,8}$a), 4.50 (m, 2 H, $H_{4,8}$e), 4.89 (m, 2 H, $H_{9,10}$), 5.42 (*AB*, J_{AB} = 15 Hz, 2 H, $H_{2,6}$a), 6.81 (*AB*, J_{AB} = 15 Hz, 2 H, $H_{2,6}$e).

Anal. Calcd for $C_6H_{10}N_8O_8$: C, 22.36; H, 3.13; N, 34.78. Found: C, 22.62; H, 3.21; N, 34.62.

***meso*-(*R**,*S**)-1,1′,3,3′-Tetranitro-4,4′-biimidazolidine (4).** By diluting the mother liquors from the recrystallization of **2** with water, an impure material could be isolated. This material was purified by preparative TLC (silica gel G_1/THF–hexane) to give pure **4**: mp 198–199 °C; ^{1}H NMR (Me_2SO-d_6) δ 4.10 (m, 2 H, $H_{5,5'}$), 4.43 (m, 2 H, $H_{5,5'}$), 5.26 (m, 2 H, $H_{4,4'}$), 5.45 (*AB*, J_{AB} = 8.6 Hz, 2 H, $H_{2,2'}$), 5.68 (*AB*, J_{AB} = 8.6 Hz, 2 H, $H_{2,2'}$).

Anal. Calcd for $C_6H_{10}N_8O_8$: C, 27.36; H, 3.13; N, 34.78. Found: C, 27.52; H, 3.22; N, 34.82.

Acknowledgment. I thank Dr. C. K. Lowe-Ma for determining the densities of **1** and **3** by X-ray crystallography. Financial support for this research was provided by Naval Weapons Center Independent Research Funds and by Naval Sea Systems Command Explosive R&D Program, Task No. 61153N-SRO2402.

Registry No. (±)-**1**, 92937-59-2; **2**, 92902-06-2; (±)-**3**, 92902-01-7; *meso*-**4**, 92902-07-3; (±)-**8**, 92901-97-8; (±)-**8** (tetraacetamide deriv), 92901-98-9; *meso*-**9**, 92902-03-9; *meso*-**9** (tetraacetamide deriv), 92902-04-0; **10**, 2319-57-5; **12**, 92901-95-6; (±)-**13**, 92901-96-7; (±)-**14**, 92902-08-4; (±)-**15**, 92902-09-5; (±)-**17**, 92901-99-0; (±)-**18**, 92902-00-6; *meso*-**19**, 92998-69-1; *meso*-**20**, 92902-02-8; **21**, 92902-10-8; *meso*-**22**, 92902-11-9; **24**, 92902-05-1; **31**, 5754-91-6; diethyl 2,3-cyclohexylidene-L-tartrate, 61045-33-8; diethyl tartrate, 87-91-2; cyclohexanone, 108-94-1; 2,3-*O*-cyclohexylidene-L-threitol, 60989-82-4; benzenesulfonyl chloride, 98-09-9; *meso*-erythritol, 149-32-6.

The Use of Carbon–Carbon Connectivity in the Structure Determination of Marmelerin, a Novel Benzofuran Sesquiterpene from *Croton sonderianus*

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The essential oil of *Croton sonderianus* Muell. Arg. (Euphorbiaceae) contains α- and β-pinene, camphene, myrcene, limonene, γ-terpinene, camphor, terpinen-4-ol, copaene, β-elemene, α-gurjunene, cyperene, β-caryophyllene, thujopsene, *trans*-β-farnesene, γ- and δ-cadinene, γ-muurolene, palustrol, guayazulene, and a new benzofuran sesquiterpene named marmelerin (**1**), dihydro-1,2,5,8-tetramethyl-6*H*-indeno[5,4-*b*]furan, whose structure was established by means of a two-dimensional ^{13}C INADEQUATE experiment.

Croton sonderianus Muell. Arg. is a shrub widespread in the Brazilian Northeast and known in the region as "marmeleiro preto". The bark is used in folk medicine for treatment of gastric diseases. Hexane or benzene extracts of its heartwood and roots have shown antifungal and antibacterial activity against *Saccharomyces cerevisiae*, *Helminthosporium* sp., *Trichophyton mentagrophytes*, *Polyporus sanguineus*, *Bacillus subtilis*, *Staphylococcus aureus*, and *Mycobacterium smegmatis*. From the benzene extract of the heartwood was isolated a new clerodane diterpene possessing a spirolactone ring system and named sonderianin whose structure and stereochemistry were determined by X-ray crystallography,[1] a known coumarin, and two new cleisthantane diterpenes.[2]

The leaves produce an essential oil which was analyzed by open tubular glass capillary chromatography coupled to a mass spectral–computer system allowing the identification of α- and β-pinene, camphene, myrcene, limonene, γ-terpinene, camphor, terpinen-4-ol, copaene, β-elemene, α-gurjunene, cyperene, β-caryophyllene, thujopsene, *trans*-β-farnesene, γ- and δ-cadinene, γ-muurolene, and palustrol.[3,4] Herein we are reporting the isolation of guayazulene and a novel benzofuran sesquiterpene from the residue of the fractionally distilled essential oil as well as from the nonpolar fraction of the hexanic extract of roots of the shrub.

Results and Discussion

Fractional distillation of the essential oil gave a residual fraction (bp 260–265 °C (15 mmHg)) which after column chromatography over silica gel produced two pure liquid

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0022-3263/84/1949-5154$01.50/0

Table I

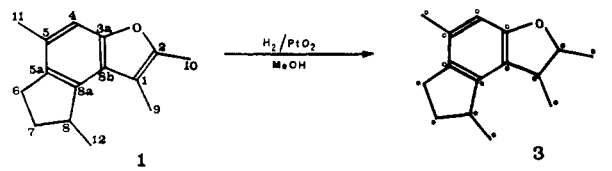
carbon	marmelerin (5) ^{13}C NMR, δ (SFORD)	connectivities	marmelerin (5) ^{1}H NMR, δ (m, H, J in Hz)	dihydromarmelerin (7) ^{13}C NMR, δ (SFORD)	dihydromarmelerin (7) ^{1}H NMR, δ (m, H, J in Hz)
3a	154.2 (s)	8b & 4		158.7 (s)	
2	149.6 (s)	10 & 1, not observed		82.9 (d)	4.70 (m, 1 H)
8a	140.2 (s)	5a, 8b & 8		144.4 (s)	
5a	135.7 (s)	8a, 5 & 6		134.8 (s)	
5	128.8 (s)	5a, 4 & 11		133.0 (s)	
8b	123.7 (s)	3a, 8a & 1		126.8 (s)	
4	109.1 (d)	3a & 5	6.90 (s, 1 H)	108.5 (d)	6.50 (s, 1 H)
1	109.0 (s)	8b & 9		39.2 (d)	
8	38.0 (d)	8a, 7 & 12	3.60 (m, 1 H, 7.0)	38.8 (d)	3.10–3.40, (m, 2 H)
7	33.8 (t)	8 & 6	1.70–1.90 (m, 2 H)	35.1 (t)	1.50–2.30 (m, 2 H)
6	28.7 (t)	5a & 7	2.50–2.90 (m, 2 H)	28.8 (t)	2.60–2.90 (m, 2 H)
12	22.2 (q)	8	1.20 (d, 3 H, 7.0)	21.1 (q)	1.15 (d, 3 H, 7.0)
11	19.7 (q)	5	2.20 (s, 3 H)	19.3 (q)	2.15 (s, 3 H)
10	11.6 (q)	2	2.30 (s, 6 H)	15.4 (q)	1.45 (d, 3 H, 8.0)
9	9.6 (q)	1		15.1 (q)	1.30 (d, 3 H, 8.0)

substances. The first substance was deep blue in color and was easily identified as guayazulene by comparison of its spectral data (MS, IR, and ^{1}H NMR) with those reported in the literature.[5-7] The second was colorless and formed readily upon treatment with an ethanolic solution of picric acid a picrate of mp 95–98 °C. The substance, named marmelerin (1), $[\alpha]^{23}_{D}$, –63.0° (*c* 1.0, $CHCl_3$), gave a positive Erlich test for a furan[8] and showed a characteristic UV spectrum, λ_{max}^{MeOH} 222, 255, 279, 289 nm (log ε 4.32, 4.18, 3.51, 3.42), for benzofuranoid compounds similar to dihydropyrocurzerenone.[9] The molecular ion at *m/z* 214 as well as analysis of the ^{13}C NMR spectrum, 15 peaks in the PND spectrum, suggested $C_{15}H_{18}O$ for the molecular formula. With residual coupling (SFORD), the ^{13}C spectrum showed seven sp^3 (four methyls, two methylenes, and one methine) and eight sp^2 (seven nonprotonated and one CH) carbons (Table I). The ^{1}H NMR spectrum showed a sharp singlet at δ 6.90 (1 H, H-4) very similar to the expected position of a proton located at the ortho position to the oxygen in a benzofuran system related to pyrocurzerenone (4).[9] The same spectrum presented a multiplet centered at δ 3.60 (1 H, *J* = 7.0 Hz, H-8), one singlet at δ 2.30 (6 H, H-3 and H-10), and another singlet at δ 2.20 (3 H, H-11) followed by a doublet at δ 1.20 (3 H, *J* = 7.0 Hz, H-12). Double resonance experiments showed coupling between the protons located at δ 3.60 and δ 1.20 (Table I). The absence of any absorption below δ 7.00 eliminated the possibility of protons located at α positions in a furan system, suggesting a tetrasubstituted furan ring.

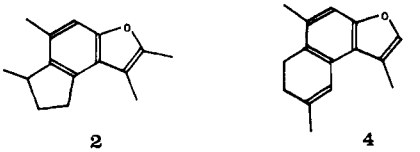
The ^{13}C NMR spectrum of marmelerin displayed a protonated aromatic carbon absorption at δ 109.1, consistent with an unsubstituted aromatic carbon ortho to an oxygen substituent. This signal appeared as a double quartet (*J* = 159, 5.8 Hz) in the fully coupled ^{13}C spectrum, suggesting the existence of a methyl group attached to the other ortho position. Selective decoupling by low-field single-frequency irradiation at the frequency of absorption of H-4 caused the appearance of C-4 as a single quartet while irradiation at the methyl hydrogens' absorption frequency caused the appearance of a C-4 as a doublet. This establishes the relative position of the aromatic methyl to the protonated carbon of the benzofuran system.

The remaining two positions must be occupied by the five-membered carbocyclic ring with its substituent methyl accounting for all the carbons, hydrogens, and double-bond equivalents.

Hydrogenation of marmelerin for 56 h over PtO_2 in MeOH yielded a dihydroderivative (3), M^+ = 216, with UV absorptions in agreement with a dihydrobenzofuran. The



1 3



2 4

^{13}C NMR spectrum shows only the six expected sp^2 carbons (five singlets and one doublet in the SFORD spectrum) and nine sp^3 carbons (two additional doublets in the SFORD spectrum at δ 39.2 and δ 82.9 for the two sp^3 carbons of the dihydrobenzofuran). A remarkable deshielding effect is seen on the two methyl resonances (attached to C-1 and C-2) which appear at δ 15.1 and δ 15.4 (Table I). The ^{1}H NMR of the dihydro derivative displayed two new multiplets at δ 4.70 (1 H, H-2) and δ 3.25 (2 H, H-1 and H-8) and the furan methyls now appeared as doublets at δ 1.30 (3 H, *J* = 8 Hz, H-9) and δ 1.45 (3 H, *J* = 8 Hz, H-10). The aromatic proton, δ 6.50 (1 H, H-4), now absorbs at a more shielded position. Similar resonance shift behavior was also observed for the dihydrobenzofuran analogue prepared from ε-caesalpin.[10]

From this analysis it was possible to propose two structures for marmelerin, (1 and 2), where the position of C-12 could not be directly inferred from the spectral data. Structure 1 was supported as the isomer which follows the isoprene rule, making possible a biogenetic route for 1 through a normal head-to-tail linkage of the isoprene units depicted on structure 3.

Structure 1 was confirmed by a two-dimensional "INADEQUATE" experiment for ^{13}C NMR analysis of marmelerin where carbon–carbon connectivities were de-

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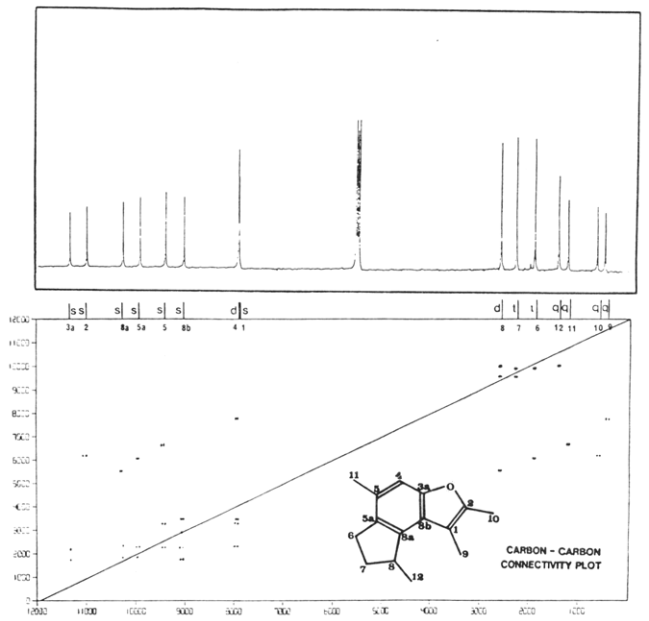

Figure 1.

termined by the technique described by Bax, Freeman, and Frenkiel[11] as modified by Mareci and Freeman[12] in which the signal arising from spin-coupled pairs of ^{13}C nuclei (in natural abundance) are separated according to their double quantum frequencies. A connectivity plot was obtained which is shown in Figure 1. This plot is a contour plot of the NMR data in which the peaks are viewed from above. The doublets arising from the spin-coupled nuclei appear as two pairs of spots on the same horizontal level at the chemical shift frequencies of the coupled nuclei. All of the signals are symmetrically located about a diagonal line through the plot, which aids in distinguishing them from noise or other artifacts. In a few cases, only one peak of the doublet was strong enough to detect, but this resulted in no loss of information in view of the symmetry property described above.

Multiplicities of each of the 15 ^{13}C peaks were determined by the APT technique.[13] Spin–lattice relaxation times for the carbon atoms without a directly bonded proton were measured and found to fall in the range from 20 to 30 s. Since this would have required an excessively long delay between pulses in the connectivity experiment, a few miligrams of chromium acetyl acetonate were added to the solution of 250 mg of marmelerin in 1 mL of $CDCl_3$.

Connectivities determined by inspection of Figure 1 are listed in Table I.

The connectivities, multiplicities, and chemical shifts not only allow an unequivocal choice between structures **1** and **2** but also completely specify the structure of marmelerin as **1**. The unobserved connectivity C-2 to C-1 cannot represent the position of the heteroatom, since the chemical shift of C-1 is incompatible with an sp^2 carbon bonded directly to oxygen, while the chemical shifts of C-3a and C-2 are both compatible with the benzofuranoid portion of the structure.

As marmelerin is the first natural sesquiterpene containing a tetrasubstituted furan, and thus is the first example of a new structural class of sesquiterpenes, we were concerned that it had not been generated as a result of the heating during distillation. That it is, indeed, a natural constituent of the plant was shown by its isolation from the hexane extract of the roots by simple silica chromatography. Evaluation of the biological activity of marmelerin as an antimicrobial showed that it is lacking in activity. Work on identification of those substances present in the extracts with antimicrobial activity continues.

Experimental Section

^1H NMR spectra were recorded on a Varian EM-390 spectrometer operating in a CW mode, using $CDCl_3$ solution and Me_4Si as internal standard. The ^{13}C NMR experiments were recorded on a JEOL JNM-FX60 (15.03 MHz) or on a Varian XL-300 (75.0 MHz) spectrometer, which were operated in FT mode, using $CDCl_3$ solutions. Chemical shifts are expressed in parts per million (ppm) relative to Me_4Si as internal standard. Proton noise decoupled (PND) and fully coupled (GATED decoupled: decoupler off during acquisition time) were obtained with the FX60 by centering the decoupler frequency 500 Hz below Me_4Si with a noise bandwidth of 1.0 KHz, a pulse angle of 45°, a pulse repetition of 6.0 s, a sweep width of 4000 Hz, and 8K data points. Single-frequency off-resonance decoupled (SFORD) spectra were obtained with the proton decoupler set at 1000 Hz downfield from the signal for Me_4Si. Low-power selective proton decoupling was accomplished with a decoupler power of 26 dB. The two-dimensional ^{13}C INADEQUATE experiment was performed with the XL-300 spectrometer at 75 MHz, using 250 mg of marmelerin in 1.0 mL of $CDCl_3$. A few milligrams of chromium acetyl acetonate was added to the solution to bring the T_1 values for the non-protonated carbons from 20–30 s down into the range of 1–2 s. The solution was placed in a 10-mm sample tube and prevented from vortexing upon rotation by a Teflon-brand plug. The length of the liquid column was a good match to the 2-cm length of the receiver coil. The ^{13}C spectral width was 12 kHz (160 ppm) with an aquisition time of 0.085 s (2048 data points). Data was accumulated for 320 repetitions of the pulse sequence, with a 3-s recovery delay between sequences. After weighting with an exponential function (5-Hz line broadening), the weighted FID was Fourier transformed. A total of 128 separate spectra were obtained in this way with an incremental increase in the delay between the 90° pulse which created the double quantum coherence and the 135° pulse which reconverted it to observable magnetization. The evolution of the double quantum frequency appeared as a modulation of the two pairs of ^{13}C doublets arising from bonded ^{13}C nuclei and could be observed by Fourier transformation of the 128-point interferogram formed by each data point in the spectrum. The resulting two-dimensional array was plotted as a contour plot (looking down from above) with the ^{13}C chemical shift as the x axis and the double quantum frequency the y axis. The spectral width in the double quantum dimension was 12 kHz. For both ^{13}C and ^1H NMR spectra, the descriptions are s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Infrared spectra were taken on a Perkin-Elmer 281B infrared spectrometer. Mass spectra were recorded by using a Finnigan 3200 GC/MS mass spectrometer coupled to an INCOS data system. CD spectra were obtained on a JASCO J-40 automatic recording spectropolarimeter using methanol solutions. UV spectra were recorded on a Beckman spectrometer Acta III with methanol solutions. Specific rotation was obtained on a Perkin-Elmer 141 polarimeter using chloroform solutions.

Silica gel column chromatography employed MN silica gel 60 (70–270 mesh) or MN silica gel G/UV_{254} for thin-layer chromatography. TLC analysis was performed by utilizing MN precoated plates and detection of compounds was achieved by spraying with a prepared solution of EtOH/*p*-anisaldehyde/AcOH (90:5:1) to which 5% by volume of concentrated H_2SO_4 had been added immediately before use. All solvents used for chromatography purposes were A.R. grade or distilled before use. The melting point of the picrate was determined in a Fisher digital melting point analyzer Model 355 and was not corrected.

Plant Material. The whole plant was collected in Sobral, Ceara, Brazil, and identified by Prof. Afranio G. Fernandes. The voucher specimens representing the collection are deposited at the herbarium of the Departamento de Botanica, Universidade Federal do Ceara, Fortaleza-CE, 60.000, Brazil. The fresh leaves

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were steam distilled to give a blue essential oil (0.33%) which was distilled at reduced pressure (15 mmHg) to produce different fractions of clear oil and a residue (bp 260–265 °C). This residue (120 mL) was mixed with 300 g of silica gel 60 packed into a cylindrical decantation funnel and eluted with 1.5 L of hexane. The eluent was combined into 12 fractions based on TLC comparison. The column was then washed with EtOAc/MeOH (5%) to yield a brown, viscous oil. Fractions 1–4 (60 g) yielded a mixture of terpenes which was analyzed by the method of Craveiro et al.[3,14] The following terpenes were identified: α- and β-pinene, camphene, myrcene, limonene, γ-terpinene, camphor, terpinen-4-ol, copaene, β-elemene, α-gurjunene, cyperene, β-caryophyllene, thujopsene, *trans*-β-farnesene, γ- and δ-cadinene, γ-muurolene, and palustrol.

Fractions 5–9 (2.5 g) yielded a dark blue oil that was rechromatographed on a column of silica gel G (25 g) using hexane as eluent and nitrogen pressure to produce a convenient flow rate. Guayazulene (50 mg) and 240 mg of pure marmelerin (1), as a clear, colorless oil were obtained. An additional 140 mg of 1 were also obtained from the less polar fraction of the neutral part of the hexane extract of roots by elution with hexane of a similar type of silica gel column.

Marmelerin (1): colorless, mobil oil, positive Erlich test; $[\alpha]^{23}_D$ −63° (*c* 1.0, $CHCl_3$); CD (*c* 5.0, MeOH) $\Delta\epsilon_{292}$ −0.65; $\Delta\epsilon_{280}$ −0.78, $\Delta\epsilon_{270}$ −1.7, $\Delta\epsilon_{257}$ +10.1, $\Delta\epsilon_{225}$ +9.1; UV λ_{max}^{MeOH} (log ε) 289 (3.42), 278 (3.51), 255 (4.18), 222 (4.32); IR (neat, cm^{-1}) 3040–2850, 1658, 1626, 1585, 1453, 1298, 1216, 1146, 1040, 850; MS, *m/z* (relative intensity) 214 (M^+, 51), 199 (100), 184 (13), 171 (21), 153 (11), 143 (15), 141 (15), 129 (11), 128 (18), 115 (18), 105 (11), 91 (21), 77 (12).

To a solution of 50 mg of marmelerin in 1.0 mL of $CHCl_3$ were added 4 drops of a saturated solution of picric acid in ethanol that after refrigeration, filtration, and recrystallization attempts yielded 40 mg of a reddish solid material: mp 95–98 °C; ^1H NMR (90 MHz, $CHCl_3$), δ 9.75 (1 H, br s), 9.15 (2 H, s), 6.90 (1 H, s), 3.60 (1 H, m), 2.80 (2 H, m), 2.35 (3 H, s), 2.30 (3 H, s), 2.25 (3 H, s), 1.90 (1 H, m), 1.20 (3 H, d, *J* = 8.0 Hz).

Dihydromarmelerin (3). Marmelerin (50 mg) was hydrogenated over PtO_2 in MeOH during 56 h and gave the dihydro derivative **3** as a colorless, mobil oil: negative Erlich test; CD (*c*, 10% in MeOH) $\Delta\epsilon_{289}$ −0.46, $\Delta\epsilon_{237}$ −1.37, $\Delta\epsilon_{223}$ +3.40, $\Delta\epsilon_{219}$ +3.70; UV λ_{max}^{MeOH} (log ε) 286 (3.51), 235 sh (3.52), 221 sh (3.89), 211 (3.89); IR (neat, cm^{-1}) 3040–2850, 1616, 1605, 1460, 1330, 1260, 1188, 1087, 878, 850; MS, *m/z* (relative intensity) 216 (M^+, 74), 201 (79), 187 (17), 173 (29), 159 (100), 141 (19), 131 (12), 128 (26), 115 (28), 93 (15), 91 (22).

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Registry No. 1, 93304-72-4; 3, 93304-73-5; α-pinene, 80-56-8; β-pinene, 127-91-3; camphene, 79-92-5; myrcene, 123-35-3; limonene, 138-86-3; γ-terpinene, 99-85-4; camphor, 76-22-2; terpinen-4-ol, 562-74-3; copaene, 3856-25-5; β-elemene, 515-13-9; α-gurjunene, 489-40-7; cyperene, 2387-78-2; β-caryophyllene, 87-44-5; thujopsene, 470-40-6; *trans*-β-farnesene, 18794-84-8; γ-cadinene, 39029-41-9; δ-cadinene, 483-76-1; γ-muurolene, 30021-74-0; palustrol, 5986-49-2.

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Two Steroidal Alkaloids from a Marine Sponge, *Plakina* sp.

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The antimicrobial metabolites of *Plakina* sp., a marine sponge that overgrows coral heads, are the steroidal alkaloids plakinamine A (**1**) and plakinamine B (**2**). The structures were elucidated by interpretation of spectral data and by comparison of the ^{13}C NMR data with those of model compounds synthesized from ergosterol.

Steroidal alkaloids are well-known metabolites of certain terrestrial plants,[1] but they have not been reported previously from marine organisms. During a search for antibiotics from marine invertebrates, we encountered a sponge of the genus *Plakina* whose crude extracts showed antimicrobial activity against *Staphylococcus aureus* and *Candida albicans*. Bioassay-directed fractionation of the crude extract led to the isolation of two steroidal alkaloids, plakinamine A (**1**) and plakinamine B (**2**) (Chart I). The structures of the two steroidal alkaloids were elucidated by interpretation of spectral data and comparison with model compounds synthesized from ergosterol.

The sponge, *Plakina* sp., was collected in shallow waters (−5 m) at Mant Island, Ponape, where it was observed to overgrow and kill corals. A methanolic extract of the freeze-dried sponge was found to possess antimicrobial activity. Solvent partition was followed by chromatography on Sephadex LH-20 (methanol) and Sephadex G-15 (water) to obtain an active fraction containing one major and one minor component. The minor metabolite, plakinamine B (**2**, 0.1% dry weight), was obtained as a hydrochloride salt by fractional crystallization from methanol. The major metabolite, plakinamine A (**1**, 0.3% dry weight), was separated from the residue by taking advantage of its solubility in aqueous acid.

The steroidal nature of plakinamine A (**1**) was suggested by the molecular formula, $C_{29}H_{46}N_2$, and by ^1H NMR signals at δ 0.59 (s, 3 H) and 0.77 (s, 3 H) and two ^{13}C NMR signals at δ 12.0 (q) that could be assigned to the C-18 and C-19 methyl groups of a steroid. A striking feature of the ^{13}C NMR spectrum was the presence of five signals at δ >100; the signals at δ 117.7 (d) and 139.2 (s) were in good agreement with literature values for C-7 and C-8 of a Δ^7 sterol[2] while the signals at δ 173.2 (s), 137.1 (s), and 129.0 (s) could be assigned to a fully substituted double bond and an imine group. The ultraviolet chromophore at 246 nm (ε 7100) implied the presence of an α,β-unsaturated imine. A major fragmentation in the mass spectrum gave peaks at *m/z* 123.1052 ($C_8H_{13}N$, base peak), 299.2645 ($C_{21}H_{33}N$), and 300.2721 ($C_{21}H_{34}N$) that could be explained

(1) The steroidal alkaloids are regularly reviewed in "The Alkaloids", Specialist Periodical Reports, Royal Society of Chemistry, London, Vols. 1–13, 1971–1983.

(2) Blunt, J. W.; Stothers, J. B. *Org. Magn. Reson.* 1977, *9*, 439.

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