perature for 3.5 h. The reaction mixture was neutralized and cooled overnight at 5 °C to allow precipitation of product. The product was collected by vacuum filtration and then lyophilized to yield 0.330 g (1.1 mmol, 41%) of ethenoguanosine (**18**). The spectroscopic data of **18** were consistent with the literature values.[30]

Reaction of Guanosine (14) with Glycidaldehyde (1). Guanosine (1.942 g, 6.9 mmol) was placed in H_2O (200 mL), and the solution was basified to pH 10 with warming to aid dissolution. Glycidaldehyde (**1**) 0.57 g (7.9 mmol) was added, and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was neutralized and cooled to allow precipitation of white crystals. This material was suspended in water and lyophilized to give 1.364 g (4.0 mmol) of 5,9-dihydro-7-(hydroxymethyl)-9-oxo-3-β-D-ribofuranosyl-3*H*-imidazo[1,2-*a*]purine (**17**) as white crystals in 59% yield: mp >300 °C dec; UV (0.1 N HCl) λ_{max} 300 nm (ϵ 7.7 × 10^3), 276 (9.9 × 10^3), 226 (2.54 × 10^4), (pH 7 buffer) 285 (9.9 × 10^3), 228 (2.63 × 10^4), (0.1N NaOH) 310 (7.4 × 10^3), 285 (6.6 × 10^3), 238 (2.85 × 10^4); mass spectrum, *m/z* (relative intensity) 207 (2.6), 189 (75.9, "base" + 2 H − OH), 188 (36.5), 133 (7.1); ^{1}H NMR (Me_2SO-d_6) δ 3.53–3.65 (m, 2 H), 3.91 (m, 1 H), 4.12 (m, 1 H), 4.45 (m, 1 H), 4.84 (d, 2 H, *J* = 6.0 Hz), 4.98 (t, 1 H, *J* = 6.0 Hz), 5.05 (t, 1 H, *J* = 5.3 Hz), 5.16 (d, 1 H, *J* = 4.7 Hz), 5.42 (d, 1 H, *J* = 6.0 Hz), 5.81 (d, 1 H, *J* = 5.9 Hz), 7.23 (s, 1 H), 8.14 (s, 1 H), 12.36 (s, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 55.0, 61.2, 70.2, 73.6, 85.1, 86.8, 113.7, 115.9, 124.6, 137.3, 146.7, 150.2, 153.6.

Anal. Calcd for $C_{13}H_{15}N_5O_6 \cdot H_2O$: C, 43.95; H, 4.82; N, 19.71. Found: C, 44.37; H, 4.48; N, 20.20.

Reaction of Adenosine (19) with Glycidaldehyde (1) at pH 5. Adenosine (**19**) (0.280 g, 1.0 mmol) was allowed to react with glycidaldehyde (**1**) (0.122 g, 1.7 mmol) for 36 h at pH 5. Separation yielded 0.090 g (0.3 mmol, 30%) of 3-β-D-ribofuranosyl-7-(hydroxymethyl)-3*H*-imidazo[2,1-*i*]purine (**20**) as blunt transparent crystals: mp 214–216 °C; UV (H_2O) λ_{max} 231 nm (ϵ 2.9 × 10^4), 268 (6.7 × 10^3), 279 (6.4 × 10^3), 300 (3.0 × 10^3); mass spectrum, *m/z* (relative intensity) 321 (M^+, 4.2), 189 ("base" + H, 100.0), 188 ("base", 22.9), 172 ("base" + H − OH, 91.8), 135 (50.7), 133 (14.7); ^{1}H NMR (Me_2SO-d_6) δ 3.67 (m 2 H), 4.00 (m, 1 H), 4.22 (t, 1 H, *J* = 4.4 Hz), 4.61 (t, 1 H, *J* = 4.9 Hz), 4.91 (s, 2 H), 5.1–5.5 (brs, 4 H), 6.08 (d, 1 H, *J* = 5.4 Hz), 7.48 (s, 1 H), 8.59 (s, 1 H), 9.15 (s, 1 H).

Anal. Calcd for $C_{13}H_{15}N_5O_5$: C, 48.60; H, 4.71; N, 21.80. Found: C, 48.70; H, 4.83; N, 21.69.

Reaction of Adenosine (19) with 2,3-Epoxybutanal (2) at pH 5. Adenosine (**19**) (0.282 g, 1.1 mmol) was stirred for 48 h with 0.094 g (1.1 mmol) of 2,3-epoxybutanal (**2**). Separation yielded 0.022 g (0.07 mmol, 6% yield, 7% conversion based on unreacted adenosine) of **21** as fluffy white crystals: mp 219–221 °C; UV (H_2O) λ_{max} 231 nm (ϵ 3.00 × 10^4), 268 (5.9 × 10^3), 279 (5.9 × 10^3), 300 (sh, 3.1 × 10^3); mass spectrum, *m/z* (relative intensity) 203 ("base" + H, 14.2), 188 ("base" + H − CH_3, 25.0), 159 ("base" − C_2H_4O, 100.0); ^{1}H NMR (Me_2SO-d_6) δ 1.64 (d, 3 H, *J* = 6.4 Hz), 3.68 (m, 2 H), 4.00 (d, 1 H, *J* = 3.4 Hz), 4.19 (m, 1 H), 4.60 (m, 1 H), 5.24–5.05 (m, 3 H), 5.51 (m, 2 H), 6.07 (d, 1 H, *J* = 5.9 Hz), 7.44 (s, 1 H), 8.57 (s, 1 H), 9.19 (s, 1 H).

Anal. Calcd for $C_{14}H_{17}N_5O_5 \cdot H_2O$: C, 47.59; H, 5.42; N, 19.82. Found: C, 48.02; H, 5.43; N, 19.25.

Preparation of 9-Ethyl-1,N^6-ethenoadenine-10-carboxaldehyde (23). This compound was prepared as described previously[22] and was obtained in 38% yield as white crystals: mp 223–225 °C; UV (95% ethanol) λ_{max} 230 nm (ϵ 2.06 × 10^4), 328 (1.51 × 10^4), 339 (1.50 × 10^4); mass spectrum, *m/z* (relative intensity) 216 (M^+ + 1, 12.2), 215 (M^+, 100.0), 187 (M^+ − CO, 34.4), 186 (M^+ − C_2H_5, 34.4); ^{1}H NMR ($CDCl_3$) δ 1.62 (t, 3 H), 4.44 (q, 2 H), 8.13 (s, 1 H), 8.37 (s, 1 H), 10.02 (s, 1 H), 10.08 (s, 1 H).

Reduction of 9-Ethyl-1,N^6-ethenoadenine-10-carboxaldehyde (23). To a solution of 0.042 g (1.1 mmol) of $NaBH_4$ in 20 mL of cold ethanol was added 0.052 g (0.24 mmol) of 9-ethyl-1,N^6-ethenoadenine-10-carboxaldehyde (**23**). The reaction was stirred for $^1/_2$ h at room temperature and then the solvent removed in vacuo. Separation on silica gel preparative layer plates with 13% MeOH/$CHCl_3$ yielded 0.023 g (0.11 mmol, 46%) of 3-ethyl-7-(hydroxymethyl)-3*H*-imidazo[2,1-*i*]purine (**22**) as off-white crystals: mp 195 °C dec; UV (H_2O) λ_{max} 233 nm (ϵ 2.7 × 10^4), 269 (6.5 × 10^3), 279 (9.2 × 10^3), 300 (3.9 × 10^3); mass spectrum *m/z* (relative intensity) 218 (M^+ + 1, 6.7), 217 (M^+, 50.4), 200 (M^+ − OH, 100.0), 172 (39.4); ^{1}H NMR (Me_2SO-d_6) δ 1.48 (t, 3 H, *J* = 7.3 Hz), 4.35 (q, 2 H, *J* = 7.3 Hz), 4.91 (m, 2 H), 5.34 (m, 1 H), 7.44 (s, 1 H), 8.33 (s, 1 H), 9.11 (s, 1 H).

Anal. Calcd for $C_{10}H_{11}N_5O \cdot H_2O$: C, 51.05; H, 5.57; N, 29.77. Found: C, 51.22; H, 5.70; N, 29.13.

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Registry No. 1, 765-34-4; 2, 3209-33-4; 3, 1122-47-0; 4, 65-46-3; 5, 99310-29-9; 6, 99310-30-2; 7, 99310-31-3; 8, 4401-11-0; 9, 99310-32-4; 10, 90754-37-3; 14, 118-00-3; 17, 89647-27-8; 18, 62462-38-8; 19, 58-61-7; 20, 99310-33-5; 21, 99310-34-6; 22, 99310-35-7; 23, 91898-80-5.

Exserohilone: A Novel Phytotoxin Produced by *Exserohilum holmii*

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A novel phytotoxin, exserohilone (**1**), was isolated from the culture broth of *Exserohilum holmii*, a pathogenic fungus of the weedy plant *Dactyloctenium aegyptium*. The structure of exserohilone (**1**) was elucidated by X-ray diffraction analysis of the bis(*p*-bromobenzoate) derivative **3**. 9,10-Dihydroexserohilone (**2**) was also isolated, and its structure was determined by spectral methods.

Bacterial and fungal pathogens of plants often produce disease symptoms by elaborating phytotoxins in the host.[3] There are relatively few studies on phytotoxins affecting weedy plants, but such compounds could be useful herbicides,[4] or serve as models for new herbicides.[3] *Exserohilum holmii* is a fungal pathogen on *Dactyloctenium aegyptium* (crowfoot grass) which is a serious grasseous

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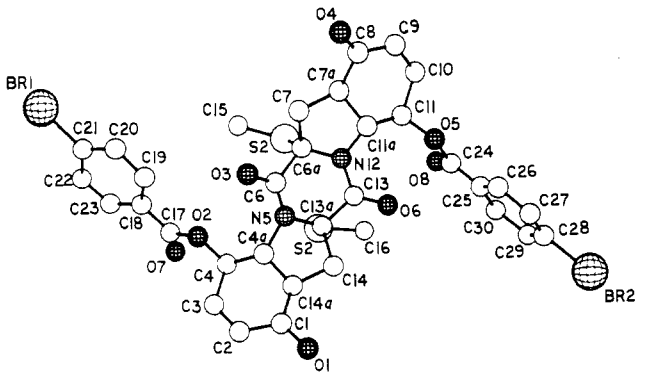
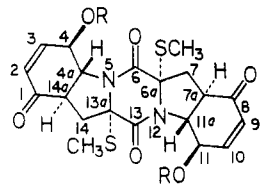


Figure 1. Computer-generated perspective drawing of the 4,11-bis(*p*-bromobenzoate) of exserochilone (3). Hydrogens are omitted for clarity, and no absolute configuration is implied.

weed in all major tropical and semitropical agricultural areas of the world. From cultures of this fungus we isolated two novel phytotoxins which are the subject of this report.

The well-split ^1H NMR of exserohilone (1) suggested that its structure consisted of rigid rings, which was also supported by its large optical rotation (−247°). The exchangable signal (D_2O) at δ 6.10 (sharp s) disappeared by either acetylation or bromobenzoylation. This extremely low-field alcohol proton was attributed to strong hydrogen bonding with a ketone moiety. ^{13}C NMR revealed the presence of hydroxycyclohexenone [δ 195.2 (s), 128.6 (d), 151.5 (d), 72.9 (d)], methyl [δ 15.1 (q)], and methylene [δ 32.1 (t)] carbons. Decoupling experiments permitted us to draw the following partial structure: OCCH=CHCH-(OH)CH(X)CH(Y)CH_2Z. Of course, both the ^{13}C and ^1H NMR spectra were misleading in that they showed one-half the number of carbons and hydrogens present in the real structure. The structure was elucidated through a single-crystal X-ray diffraction analysis of the 4,11-bis(*p*-bromobenzoate) of 1 (3).



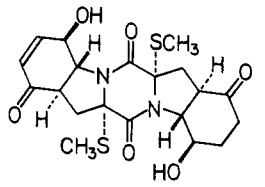
1, R = H
3, R = *p*-Br-C_6H_4CO

Compound 3 crystallized in the monoclinic space group $P2_1$ with a = 11.289 (2) Å, b = 11.224 (2) Å, c = 14.904 (2) Å, and β = 63.91 (1)° with one molecule of composition $C_{34}H_{28}Br_2N_2O_8S_2$ forming the asymmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a computer controlled four-circle diffractometer with graphite monochromated Cu K$\bar{\alpha}$ radiation (1.54178 Å) and variable speed 1° ω-scans. Of the 2430 reflections surveyed in this fashion, 2059 (85%) were judged observed ($F_o \geq 3\sigma(F_o)$) after correction for Lorentz, polarization, and background effects. A phasing model was found by locating the bromine positions in the Patterson synthesis and extending the structure with tangent formula recycling. Hydrogen atoms were located on a ΔF-synthesis or included at calculated positions. The final crystallographic discrepancy index was 0.047 for the observed reflections. Additional crystallographic details are available and are described in the paragraph entitled Supplementary Material at the end on this paper.

A computer-generated perspective drawing of the final X-ray model is given in Figure 1. Hydrogens are omitted for clarity, and the enantiomer shown is an arbitrary choice. The structure is a twofold symmetric diketopiperazine and bond distances and angles agree well with generally accepted values.

Mass spectroscopy was troublesome even when FAB or Cl was used; however finally, EIHRMS gave results consistent with the X-ray analysis as $C_{20}H_{22}N_2O_6S_2$ (M^+) at m/z 450.0919 and as $C_{19}H_{19}N_2O_6S_1$ (M^+ − SMe) at m/z 403.0963. The elucidated structure is closely related to that of spicorazine A, which is the antibiotic metabolite from *Epicoccum nigrum*.[5]

The EILRMS of 9,10-dihydroexserohilone (2) (colorless glass), gave a very similar fragmentation pattern to 1,but it was larger than 1 by 2 daltons. EIHRMS showed the molecular formula of 2 to be $C_{20}H_{24}N_2O_6S_2$ (M^+) at m/z 452.1075 and $C_{19}H_{21}N_2O_6S_1$ (M^+ − SMe) at mfz 405.1120. These MS data suggested that the structure of 2 was a saturated derivative of 1 i.e., a cyclohexenone had been reduced to a cyclohexanone. ^1H NMR supported this



2

formulation. The spectrum of 2 is more complex than that of 1, and it does not appear to be a symmetrical structure. For instance, the signals of the unsaturated side of the molecule are similar to those of 1, but the remaining signals are shifted upfield. Specifically the signals at δ 6.10 (OH), 4.70 (H-11), 3.89 (H-11a), 2.67 (Hê-7), and 2.23 (Hâ-7) are shifted to δ 5.66 (OH), 4.27 (H-11), 3.77 (H-11a), 2.51 (H-7′), and 1.96 (H-7), respectively. Decoupling experiments were completely consistent with these assignments, and 2 is most plausibly the dihydro derivative of 1 shown.

Compounds 1 and 2 show nonselectivity toward several plant species at 10^{-4}–10^{-5} M. These species include both crop and weedy plants when tests were performed by the leaf puncture bioassay method.[6] These compounds cause the production of necrotic lesions usually surrounded by a reddish brown border. Compounds 1 and 2 may possess antimicrobial or antiviral activity since structurally related compounds such as aranotine,[7] gliotoxin,[8] sporidesmin,[9] chaetocin,[10] chetomin,[11] and epicorazins[12] have comparable properties.

In addition to compounds 1 and 2, monocerin (4) was identified by spectroscopic methods as a major component of the EtOAc extract. Monocerin (4) is also a major phytotoxic compound of *Helminthosporium monoceras*.[13]

Experimental Section

^1H and ^{13}C NMR spectra were recorded with a Brucker WM-250 FT spectrometer. Chemical shifts were taken in δ units relative to Me_4Si (=0) with $CDCl_3$ as the solvent. Mass spectra

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were obtained with a VG Analytical Model VG7070HE mass spectrometer. IR spectra were recorded on a Beckman IR-20 spectrophotometer and optical rotation was observed on a Perkin-Elmer Model 241MC polarimeter.

Toxin Production and Purification. The mycelium of *E. holmii*[14] was inoculated into M-1-D culture broth[15] and then shaken at 200 rpm for 2–3 weeks at 26 °C under luminescence (25 μEinsteins M^{-2} s^{-1}). Both the culture filtrate and the fluid obtained after centrifugation of the homogenized mycelium were extracted with EtOAc, and the extract was evaporated to dryness under reduced pressure and subjected to flash chromatography[16] using (a) PhMe/EtOAc (2:1) and (b) $CHCl_3$/MeOH (70:1). On TLC (silica gel) the R_f values in $CHCl_3$/MeOH (50:1) were 0.19 for **1**, 0.15 for **2**, and 0.52 for monocerin (**4**). Both **1** and **2** could be isolated in mg quantities by reverse phase HPLC (Merck, RP-18) with CH_3CN/H_2O (63:35) as the solvent (1 mL/min). The retention time of both **1** and **2** in this HPLC system was 3.5 min, and that of **4** was 5.8 min. *E. holmii* produced a total of ca. 3.3 mg of **1**, 0.2 mg of **2**, and 75 mg of **4** in each liter of culture broth.

Exserohilone (1): colorless glass; $[\alpha]^{21}_D$ −247° (*c* 0.32, $CHCl_3$); IR (KBr) ν_{max} 3320, 2910, 1680, 1640, 1395, 1260 cm^{-1}; EILRMS, *m/z* (relative intensity) 450 (2), 405 (24), 403 (100), 375 (27), 356 (27), 355 (28), 329 (9), 328 (18), 160 (6), 133 (8), 132 (8), 110 (5), 95 (7). EIHRMS, $C_{20}H_{22}N_2O_6S_2$ (M^+; obsd *m/z* 450.0919, calcd *m/z* 450.0920) and $C_{19}H_{19}N_2O_6S_1$ (M^+ − SMe; obsd *m/z* 403.0963, calcd *m/z* 403.0964); ^1H NMR ($CDCl_3$, 250 MHz) δ 2.26 (6 H, s, SMe), 2.23 (2 H, overlapping, d, d, *J* = 12.6, 13.6 Hz, H_a-7, H_a-14), 2.67 (2 H, d, d, *J* = 4.7, 13.6 Hz, H_e-7, H_e-14), 3.49 (2 H, d, d, *J* = 4.7, 12.6 Hz, H-7a, H-14a), 3.89 (2 H, d, d, *J* = 8.7, 12.6 Hz, H-4a, H-11a), 4.70 (2 H, d, d, d, *J* = 1.9, 1.9, 8.7 Hz, H-4, H-11), 6.10 (2 H, s, OH), 6.11 (2 H, d, d, *J* = 1.9, 9.1 Hz, H-3, H-10), 6.93 (2 H, d, d, *J* = 1.9, 9.1 Hz, H-2, H-9); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 15.1 (q, SMe), 32.1 (t, C-7, C-14), 46.3 (d, C-7a, C-14a), 69.0 (d, C-4a, C-11a), 72.4 (s, C-6a, C-13a), 72.9 (d, C-4, C-11), 128.6 (d, C-2, C-9) 151.1 (d C-3, C-10), 168.0 (s, C-6, C-13), 195.2 (s, C-1, C-8).

Acetate of Exserohilone. Exserohilone **1** (1.6 mg) was acetylated in the usual manner using dry pyridine and acetic anhydride to give the acetate in a quantitative yield: EILRMS, *m/z* (relative intensity) 534 (1.9, M^+), 488 (21), 487 (30, M^+ − SMe), 459 (6), 440 (22, M^+ − 2 SMe), 439 (32), 397 (10), 379 (16), 367 (8), 160 (11), 133 (11), 132 (13), 94 (11); ^1H NMR ($CDCl_3$, 250 MHz) δ 2.129 (6 H, s, OAc), 2.132 (6 H, s, SMe), 2.11 (2 H, overlapping, d, d, *J* = 7.6, 13.6 Hz, H_a-7, H_a-14), 2.55 (2 H, d, d, *J* = 4.9, 13.6 Hz, H_e-7, H_e-14), 3.58 (2 H, d, d, d, *J* = 4.9, 7.6 Hz, 13.6, H-7a, H-14a), 4.08 (2 H, d, d, *J* = 8.6, 13.6 Hz, H-4a, H-11a), 5.89 (2 H, d, d, d, *J* = 1.8, 2.3, 8.6 Hz, H-4, H-11), 6.16 (2 H, d, *J* = 2.3, 10.0 Hz, H-3, H-10), 6.70 (2 H, d, d, *J* = 1.8, 10.0 Hz, H-2, H-9).

4,11-Bis(*p*-bromobenzoate) of Exserohilone (3). Exserohilone **1** (2.0 mg) was *p*-bromobenzoylated under standard conditions to give the bis(*p*-bromobenzoate) in a quantitative yield: ^1H NMR ($CDCl_3$, 250 MHz) δ 1.93 (6 H, s, SMe), 2.06 (2 H, d, d, *J* = 13.0, 13.7 Hz, H_a-7, H_a-14), 2.47 (2 H, d, d, *J* = 4.9, 13.7 Hz, H_e-7, H_e-14), 3.63 (2 H, d, d, d, *J* = 4.9, 13.0, 13.0 Hz, H-7a, H-14a), 4.27 (2 H, d, d, *J* = 8.8, 13.0 Hz, H-4a, H-11a), 6.08 (2 H, d, d, d, *J* = 1.9, 2.0, 8.8, H-4, H-11), 6.21 (2 H, d, d, *J* = 2.0, 10.3 Hz, H-3, H-10), 6.83 (2 H, d, d, *J* = 1.9, 10.3 Hz, H-2, H-9), 7.61 (4 H, d, *J* = 8.5 Hz, Ar), 7.98 (4 H, d, *J* = 8.5 Hz, Ar).

9,10-Dihydroexserohilone (2): $[\alpha]^{21}_D$ −110° (*c* 0.33 $CHCl_3$); EILRMS, *m/z* (relative intensity) 452 (1.8, M^+), 406 (8), 405 (33, M^+ − SMe), 359 (9), 358 (33, M^+ − 2 SMe), 357 (100), 341 (5) 339 (7), 323 (6), 273 (13); EIHRMS, $C_{20}H_{24}N_2O_6S_2$ (M^+, obsd *m/z* 452.1075, calcd *m/z* 452.1077) and $C_{19}H_{21}N_2O_6S_1$ (M^+ − SMe, obsd *m/z* 405.1120, calcd *m/z* 405.1121); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.6 (2 H, m, H-10), 1.96 (1 H, m, H-7), 2.238 (3 H, s, SMe), 2.242 (3 H, s, SMe), 2.27 (1 H, d, d, *J* = 12.0, 13.7 Hz, H_a-14), 2.51 (3 H, overlapping, m, H-7′, H-9), 2.64 (1 H, d, d, *J* = 4.7, 13.7 Hz, H_e-14), 3.49 (2 H, m, H-7a, H-14a), 3.77 (1 H, d, d, *J* = 8.6, 13.9, H-11a), 3.86 (1 H, d, d, *J* = 8.6, 13.9 Hz, H-4a), 4.27 (1 H, d, d, *J* = ca. 6, 8.6 Hz, H-11), 4.69 (1 H, d, d, d, *J* = ca. 1.6, 2.0, 8.6 Hz, H-4), 5.66 (1 H, s, OH), 6.09 (1 H, d, d, *J* = 2.0, 10.1 Hz, H-3), 6.12 (1 H, s, OH), 6.92 (1 H, d, d, *J* = 1.6, 10.1 Hz, H-2).

Crystallographic Data and X-ray Structure Analysis of Bis(*p*-bromobenzoate) 3. All crystallographic calculations were done on a PRIME 850 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were as follows: REDUCE and UNIQUE, data reduction programs by M. E. Leonowicz, Cornell University, 1978; MULTAN 78, MULTAN 80, and RANTAN 80, systems of computer programs for the automatic solution of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses) written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978 and 1980; BLS78A, an anisotropic block diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, a crystallographic illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Centre, 1978; BOND, a program to calculate molecular parameters and prepared tables written by K. Hirotsu, Cornell University, 1978.

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Supplementary Material Available: Tables of fractional coordinates, thermal parameters, interatomic distances, and interatomic angles for compound **3** (5 pages). Ordering information is given on any current masthead page.

(14) *E. holmii* was kindly provided by Dr. E. S. Luttrell, University of Georgia, Athens.

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