extracted overnight with $CHCl_3$ and filtered to yield a light yellow oil.

Separation and identification of the cyanolipids. Seed oil was subjected to TLC on Si gel G plates using Et_2O–hexane, 1:3 [1,2]. After spraying with 0.2% 2',7'-dichlorofluoroscein and viewing under UV light, 3 major bands were observed (R_f 0.65, 0.53 and 0.45). These bands were subsequently identified as glycerides and compounds **2** & **1** respectively, by their IR, NMR and MS, which were identical to those previously reported [1,9]. Oil samples were spotted on preparative Si gel G plates (10–20 mg per 20 × 20 cm plate), the bands scraped off and the lipid materials desorbed with $CHCl_3$. The $CHCl_3$ solution was filtered through a small column of silica gel to remove 2',7'-dichlorofluoroscein and subsequently concentrated. The samples were counted on a Packard 3350 Scintillation spectrometer using the counting solution described by Bray [10].

Transesterification of glycerides and compounds I & II. Glycerides (R_f 0.65) and **1** and **2** (R_f 0.45 and 0.53) were transesterified by refluxing with MeOH containing 2% H_2SO_4 (1 ml) for 8 hrs. The samples were then concd under vacuum and H_2O (25 ml) and ether (25 ml) added. The ethereal phase was dried, filtered, and the Et_2O removed to yield a light yellow oil. Methyl esters from both cyanolipids and glycosides were then purified by preparative TLC and radioactivity determined as described above.

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METHYLPHENANTHRENES FROM *SAGOTIA RACEMOSA**

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Key Word Index—*Sagotia racemosa*; Euphorbiaceae; 6-hydroxy-7-methoxy-1,2-dimethylphenanthrene; 6-hydroxy-7-methoxy-1,2-dimethyl-9,10-dihydrophenanthrene; micrandrol-E; micrandrol-F.

Abstract—The trunk wood of *Sagotia racemosa* Baill. (Euphorbiaceae) contains two previously unknown micrandrols E (6-hydroxy-7-methoxy-1,2-dimethylphenanthrene) and F (6-hydroxy-7-methoxy-1,2-dimethyl-9,10-dihydrophenanthrene).

The micrandrols A (**1a**), B (**2a**) and C, considered to be diterpenoids [1], were located originally in *Micrandropsis scleroxylon* W.Rodr. [2]. Two additional compounds of this series, micrandrols E (**1b**) and F (**2b**), occur in *Sagotia racemosa* Baill., a further arboreous Amazonian species of the Euphorbiaceae.

UV spectroscopy showed micrandrol-E (**1b**), $C_{17}H_{16}O_2$, to be a hydroxylated phenanthrene. Additional substitution by two methyls and one methoxyl became evident upon inspection of the ^{1}HMR spectrum and led to the formula $C_{14}H_6.OH.OMe.Me_2$. The compound is, nevertheless, not simply a monomethyl ether of **1a**, since *O*-methylmicrandrol-E (**1d**) is not identical with di-*O*-methyl **1a** (**1c**) [1]. In spite of this fact, the substitution pattern of **1a** must prevail in micrandrol-E. The ^{1}HMR spectra of both compounds in $(CD_3)_2CO$ contain, in addition to the AB signal typical of protons at C-9 and 10 of a phenanthrene nucleus, two pairs of signals, one for *ortho*- and one for *para*-related protons, both encompassing the relatively unprotected C-4 (**1a**: τ 1.74; **1b**: τ 1.71; both *d*, *J* 9.0 Hz) and C-5 (**1a**: τ 2.02, **1b**: τ 1.98; both *s*) positions. While thus the chemical shifts of H-4 and H-5 for micrandrols A and E are closely comparable, the difference for H-3 (**1a**: τ 2.80, **1b**: τ 2.63, both *d*, *J* 9.0 Hz) and H-8 (**1a**: τ 2.40, **1b**: τ 2.73 both *s*) can be rationalized by the allo-

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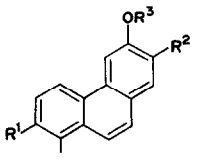
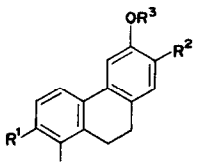
cation in micrandrol-E of a methyl instead of a hydroxyl to C-2 and of an oxy-group instead of a methyl to C-7. These data led to structure **1b** for micrandrol-E, where the relative placement of the OH and the OMe groups was based on two pieces of evidence: 1. pyridine induced solvent shift [3] affects most strongly the H-5 signal [$\tau(CDCl_3)$–$\tau(C_5H_5N)$: H-5 0.45 ppm, H-8 0.23 ppm], and





	R¹	R²	R³	
(1a)	OH	Me	H	micrandrol-A
(1b)	Me	OMe	H	micrandrol-E
(1c)	OMe	Me	Me	
(1d)	Me	OMe	Me	

	R¹	R²	R³	
(2a)	OH	Me	H	micrandrol-B
(2b)	Me	OMe	H	micrandrol-F

2. double irradiation at τ 5.98 (OMe) produces NOE intensity enhancement of the H-8 signal. The constancy of the IR 3535 cm^{-1} OH band upon dilution confirmed the vicinal relationship of the OH/OMe groups [4], while the absence of significant pyridine-induced solvent shifts for the ^{1}HMR Me signals [3] confirmed the absence of *ortho*-OH/Me systems.

A comparative spectral analysis of micrandrol-F, $C_{14}H_8.OH.OMe_2.Me_2$, and **2a** [1], conducted as indicated above for the pair **1b**/**1a**, suggested the 9,10-dihydrophenanthrene structure **2b**, which displays the same substitution pattern as **1b**. The relative placement of the OH and the OMe groups was again based on the observation of pyridine induced solvent shifts $|\tau(CDCl_3)$–$\tau(C_5H_5N)$: H-5 0.40 ppm, H-8 0.17 ppm| and, this time, of the relative widths at half height of the H-8/H-5 signals (1.9 Hz/1.5 Hz). This signal broadening must be at least partly due to long range coupling of H-8 to the vicinal methoxyl [5], since it can be attenuated by double irradiation at τ 6.11 ($W_{1/2}$ H8/H5: 1.6 Hz/1.5 Hz).

EXPERIMENTAL

Isolation of the constituents. Sagotia racemosa was collected near Belém, Pará, and identified by the botanist J. Murça Pires. Trunk wood (4 kg) was powdered and extracted with C_6H_6. The ext. (26 g) was chromatographed on SiO_2 giving the following fractions with the indicated eluants: A (2.3 g, C_6H_6), B (1.8 g, $CHCl_3$ and $CHCl_3$-MeOH 99:1), C (15.7 g, $CHCl_3$–MeOH 97:3). A was separated by TLC (SiO_2, C_6H_6) into two fractions. Fr. 1 (32 mg) was recryst. from EtOH 80% to give **1b** (23 mg); fr. 2 (2.1 g) gave upon repeated fractionation by TLC ferulates of fatty alcohols (1.9 g) and a mixt. (22 mg). This was resolved into **1b** and **2b** (5 mg) by repeated TLC (SiO_2, C_2H_6). B was separated by TLC (SiO_2, $CHCl_3$–Me_2CO 8:2) into ferulates (1.2 g) and sitosterol (0.5 g). C gave an additional quantity of sitosterol (5.6 g).

6-Hydroxy-7-methoxy-1,2-dimethylphenanthrene (**1b**), mp 194–197° (80% EtOH) (Found: C, 80.65; H, 6.27. $C_{17}H_{16}O_2$ requires C, 80.95; H, 6.35%). ν_{max}^{KBr} (cm^{-1}): 3522, 2902, 1610, 1502, 1482, 1270, 1153, 1055, 850, 820, 804. $\nu_{max}^{CH_2Cl_2}$ 0.03M (cm^{-1}): 3535 invariable upon dilution. λ_{max}^{MeOH} (nm): 248 inf., 257, 280 (log ϵ 4.44, 4.59, 4.26); $\lambda_{max}^{MeOH+NaOH}$ (nm): 248 inf., 256, 266 inf., 295 (log ϵ 4.41, 4.54, 4.39, 4.19). ^{1}HMR ($CDCl_3$, 60 MHz, τ): 1.72 (*d*, *J* 9.0 Hz, H-4), 1.92 (*s*, H-5), 2.13 (*d*, *J* 9.0 Hz, H-9), 2.40 (*d*, *J* 9.0 Hz, H-10), 2.60 (*d*, *J* 9.0 Hz, H-3), 2.80 (*s*, H-8), 4.43 (*s*, OH), 5.98 (*s*, OMe), 7.37 (*s*, Me-1), 7.50 (*s*, Me-2). ^{1}HMR (C_5D_5N, τ): 1.47 (*s*, H-5), 1.68 (*d*, *J* 9.0 Hz, H-4), 2.13 (*d*, *J* 9.0 Hz, H-9), 2.19 (*d*, *J* 9.0 Hz, H-10), 2.57 (*s*, H-8), 2.60 (*d*, *J* 9.0 Hz, H-3), 4.95 (*s*, OH), 6.10 (*s*, OMe), 7.46 (*s*, Me-1), 7.60 (*s*, Me-2). ^{1}HMR [$(CD_3)_2CO$, τ): 1.71 (*d*, *J* 9.0 Hz, H-4), 1.98 (*s*, H-5), 2.17 (*d*, *J* 9.0 Hz, H-9), 2.41 (*d*, *J* 9.0 Hz, H-10), 2.63 (*d*, *J* 9.0 Hz, H-3), 2.73 (*s*, H-8), 5.99 (*s*, OMe), 7.50 (*s*, Me-1), 7.55 (*s*, Me-2). NOE (100 MHz): Irrad. between 5.85 and 5.95 with 100 dB resulted in signal enhancements of 18% (H-8) and 0% (H-5) in $(CD_3)_2CO$. MS (*m/e*): 252 (100%) M, 237 (44), 209 (52), 194 (7), 165 (7), 166 (7).

5,6-Dimethoxy-1,2-dimethylphenanthrene (**1d**, Me_2SO_4, K_2CO_3, Me_2CO), mp 159–161° (80% MeOH) (Found: C 81.23; H, 6.79. $C_{18}H_{18}O_2$ requires: C, 81.20; H, 6.76%). ν_{max}^{KBr} 1620, 1498, 1465, 1254, 1222, 1161, 1099, 850, 818, 802. $\lambda_{max}^{CCl_4}$ (nm): 261, 282 inf. (log ϵ 4.66, 4.41). ^{1}HMR ($CDCl_3$, τ): 1.68 (*d*, *J* 9.0 Hz, H-4), 2.0 (*s*, H-5), 2.08 (*d*, *J* 9.0 Hz, H-9), 2.38 (*d*, *J* 9.0 Hz, H-10), 2.60 (*d*, *J* 9.0 Hz, H-3), 2.78 (*s*, H-8), 5.90 (*s*, OMe-6), 5.98 (*s*, OMe-7), 7.34 (*s*, Me-1), 7.47 (*s*, Me-2). MS (*m/e*): 266 (100) M, 251 (29), 222 (29), 148 (41).

6-Hydroxy-7-methoxy-1,2-dimethyl-9,10-dihydrophenanthrene (**2b**), mp 162–164° (MeOH–H_2O 7:3) (Found: C, 79.98; H, 7.00. $C_{17}H_{18}O_2$ requires: C, 80.28; H, 7.13%). ν_{max}^{KBr} (cm^{-1}): 3366, 1616, 1600, 1568, 1511, 1444, 1307, 1265, 1249, 1150, 1053, 873, 825, 802. λ_{max}^{MeOH} (nm) 218, 276, 291, 313 (log ϵ 4.67, 4.22, 4.02, 4.03); $\lambda_{max}^{MeOH+NaOH}$ (nm) 221, 254, 277, 325 (log ϵ 4.37, 4.24, 3.93, 3.73). ^{1}HMR ($CDCl_3$, τ): 2.60 (*d*, *J* 8.0 Hz, H-4), 2.70 (*s*, H-5), 2.92 (*d*, *J* 8.0 Hz, H-3), 3.28 (*s*, H-8), 4.50 (*s*, OH), 6.11 (*s*, OMe), 7.21 (*s*, $2CH_2$), 7.68 (*s*, Me-1), 7.77 (*s*, Me-2); ^{1}HMR (C_5D_5N, τ): 2.30 (*s*, H-5), 2.43 (*d*, *J* 8.0 Hz, H-4), 2.93 (*d*, *J* 8.0 Hz, H-3), 3.12 (*s*, H-8). ~4.0 (*s*, OH), 6.20 (*s*, OMe), 7.20 (*s*, $2CH_2$), 7.75 (*s*, Me-1), 7.85 (*s*, Me-2). MS (*m/e*): 254 (100%) M, 239 (58), 211 (10), 196 (14).

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