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METHYL- AND METHYLTHIO-PHENANTHRENES FROM *MICRANDROPSIS SCLEROXYLON**

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Key Word Index—*Micrandropsis scleroxylon*; Euphorbiaceae; micrandrol-A; micrandrol-B; micrandrol-C; 2,6-dihydroxy-1,7-dimethylphenanthrene; 9,10-dihydro-2,6-dihydroxy-1,7-dimethylphenanthrene; 2,8-dihydroxy-7-methyl-1-methylthiophenanthrene.

Abstract—The trunk wood of *Micrandropsis scleroxylon* W. Rodr. (Euphorbiaceae) contains besides sitosterol, stigmasterol and ferulic acid, three novel compounds: 2,6-dihydroxy-1,7-dimethylphenanthrene (micrandrol-A), 9,10-dihydro-2,6-dihydroxy-1,7-dimethylphenanthrene (micrandrol-B) and 2,8-dihydroxy-7-methyl-1-methylthiophenanthrene (micrandrol-C), tentatively classified as diterpenoids.

Micrandropsis scleroxylon W. Rodr.[1] (= *Micrandra scleroxylon* W. Rodr.[2]), popularly known as acapurí, is an arboreous species of the Euphorbiaceae which occurs in relative abundance in the upland forest near Manaus, Amazonas State. The EtOH extract of its trunk wood was fractionated into five crystalline products: a *ca* 2:1 mixture of sitosterol and stigmasterol, ethyl ferulate, which probably originated by esterification or transesterification of natural ferulic acid during the extraction process, and three compounds named micrandrol-A ($C_{16}H_{14}O_2$), micrandrol-B ($C_{16}H_{16}O_2$) and micrandrol-C ($C_{16}H_{14}O_2S$).

Since the UV spectra of the micrandrols-A and -C showed these compounds to be phenanthrene derivatives, micrandrol-B was immediately suspected to be a 9,10-dihydrophenanthrene. Indeed, the micrandrols-A and -B can be interconverted by catalytic hydrogenation (A → B) and DDQ oxidation (B → A). Both compounds give diacetates and *bis*-diethylphosphates. Micrandrol-B *bis*-diethylphosphate was hydrogenated to a 9,10-dihydrodimethylphenanthrene whose DDQ oxidation gave a compound, identified by comparison of m.p., UV and PMR spectra, with pimanthrene. Micrandrol-A is thus a dihydroxy-1,7-dimethyl-phenanthrene.

The location of the hydroxyls was established by PMR spectrometry in $(CD_3)_2SO$. The aromatic spectral region shows signals due to three pairs of protons: one forming an AB system characterized by chemical shifts (τ 2·41 and 2·43) and coupling constant (*J* 9·0 Hz) which are compatible with protons at C-9 and 10;[3] one maintaining an *ortho* relation (τ 1·78 and 2·76, doublets, *J* 9·0 Hz); and one a *para* relation (τ 2·09 and 2·45, singlets). As

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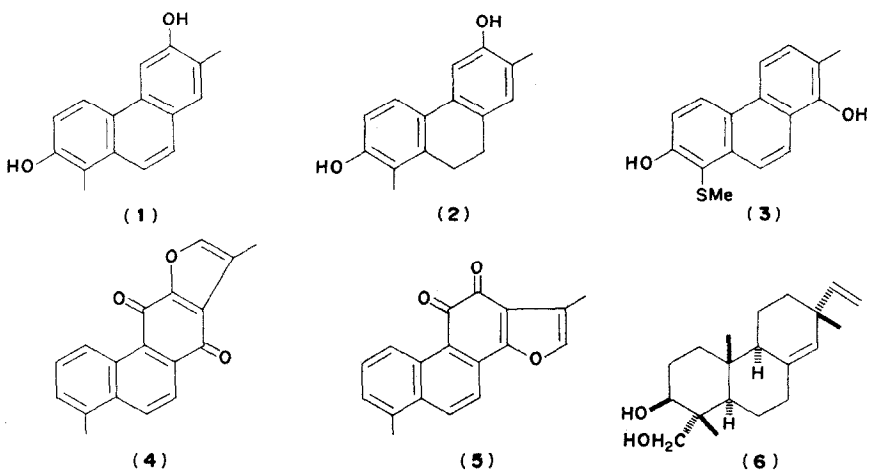
[1] RODRIGUES, W. A. (1973) *Acta Amazonica* **3**, in print.

[2] RODRIGUES, W. A. (1971) *Acta Amazonica* **1**, 3.

[3] REISCH, J., BÁTHORY, M., SZENDREI, K., NOVÁK, I. and MINKER, E. (1973) *Phytochemistry* **12**, 228.

expected, signals due to only two pairs of protons appear in the aromatic spectral region of micrandrol-B. The AB-quartet is absent and replaced by a four proton singlet at high field [τ 7·32, $(CD_3)_2CO$], characteristic of the benzylic protons of 9,10-dihydrophenanthrene.[4] The *para*-related protons of micrandrol-A can be situated only on C-5 and 8, leaving C-6 for one of the hydroxyls. The *ortho*-related protons cannot be located at C-2 and 3, since one of the corresponding doublets appears at such low field (τ 1·74) that it can represent only the abnormally deshielded C-4 proton.[4]

Structure **1** for micrandrol-A was more unequivocally confirmed using micrandrol-B as substrate, and by three techniques: pyridine induced solvent shift[5] and acetylation of micrandrol-B affected more the low field (Δ resp. 0·57 and 0·27 ppm) than the high field (Δ resp. 0·15 and 0·18 ppm) proton singlets, and less the low field (Δ resp. 0·22 and 0·17 ppm) than the high field (Δ resp. 0·36 and 0·27 ppm) proton doublet. Furthermore, deuteriation eliminated the low field singlet and the high field doublet, changing its counterpart into a singlet. All this means that, with respect to the protons at the deshielded angular positions, one hydroxyl must be *ortho* and the other *meta* related, as shown in **2**. Treatment of a phenol with deuterium oxide under basic conditions is known to effect exchange of hydrogens *ortho* and *para* to phenolic hydroxy-groups.[4] Nevertheless, under these conditions, used to produce 3,5-dideuteriomicrandrol-B, only H-5 of micrandrol-A was exchanged by deuterium.



A matter which remains to be discussed concerning the PMR spectra of the micrandrols A (**1**) and B (**2**) refers to the contrasting chemical shifts of the C–CH_3 signals. In the spectrum of micrandrol-A [in $(CD_3)_2CO$] two methyl singlets appear. According to lit. data,[6] the one at lower field (τ 7·45) must be assigned to Me-1 and the other (τ 7·60) to Me-7. In the case of micrandrol-B (same solvent) no differential effect operates on either methyl and both give rise to a singlet at relatively high field (τ 7·84).

These considerations are relevant upon considering a structural proposal for micrandrol-C. The PMR spectrum of this compound in $(CD_3)_2CO$ shows not one, but two low

[4] LETCHER, R. M. and NHAMO, L. R. M. (1971) *J. Chem. Soc.* (C) 3070; (1972) *J. Chem. Soc. Perkin I* 2941.
[5] DEMARCO, P. V., FARKAS, E., DODDRELL, D., MYLARI, B. L. and WENKERT, E. (1968) *J. Am. Chem. Soc.* **90**, 5480.
[6] DURAND, P., PARELLO, J. and BUU-HOI, N. P. (1963) *Bull. Soc. Chim. (France)*, 2438.

field doublets. Though thus again H-4 and H-5 are free of substitution, the coupling constants (*J* 9·0 Hz) reveal that now both are vicinal to unsubstituted positions. One of these doublets appears at significantly lower field (τ 1·52) than the other (τ 1·77), a difference which can be rationalized assuming that the corresponding protons are respectively *meta* and *para* related to hydroxyls. The alternative in which the proton resonating at higher field is both *meta* and *para* related to the hydroxyls can be dismissed. Although micrandrol-C gives, indeed, a diacetate and a dimethyl ether, its UV spectrum is not altered upon addition of H_3BO_3 + NaOAc and thus a catechol system is not present.

The presence of a hydroxyl at C-8 was confirmed by comparing the PMR spectra of the dimethyl ether and the diacetate of micrandrol-C. A considerably stronger paramagnetic shift (Δ 0·51 ppm) of the signal due to the proton on the *peri* position (C-9) occurs, than in the analogous case of micrandrol-A derivatives (Δ 0·21 ppm).

Only the nature of the substituents at C-1 and C-7 of micrandrol-C remain to be defined, and it is at this point that correlations between chemical shift values and position of methyl groups in phenanthrenes become relevant. The PMR spectrum of micrandrol-C shows singlets due to two methyl groups at τ 7·67 and 7·70, upfield in relation to the signals which were seen above to be typical of C-1 methyl protons. One C–Me group was for this reason assumed to be located at C-7. The compound contains sulphur (positive Lassaigne test, M + 2/M peak intensity in MS 4·4/100) and the additional methyl must thus be present in form of a S–Me group. Only C-1 can be considered for this group. Oxidation of di-*O*-methyl and of di-*O*-acetylmicrandrol-C yielded, according to the quantity of H_2O_2 used, respectively a sulphoxide and a sulphone, as ascertained by IR and MS, as well as by downfield shift of the SMe proton signal to τ 6·90 (SOMe) and 6·74 (SO_2Me). Significantly, as a consequence of these oxidations, the signals corresponding to the protons at C-4 suffer larger shifts in the expected direction (Δ resp. −0·39 and −0·47 ppm) than the signals corresponding to the protons at other positions (H-3, Δ resp. −0·07 and 0·00 ppm; H-5, Δ resp. −0·24 and −0·32 ppm; H-6, resp. −0·10 and −0·08 ppm), a fact which reveals conjugation of H-4 and the SOMe and SO_2Me groups and confirms the location of the SMe substituent in micrandrol-C as shown in **3**.

All known natural nitrogen-free phenanthrenes[3,4,7,8] and 9,10-dihydrophenanthrenes[4,8–10] bear only hydroxy, methoxy or methylenedioxy substituents, and at such positions that their biosynthetic derivation either by the shikimate or the shikimate–acetate routes seem to be reasonable. It is improbable that the micrandrols also belong to these classes, since the nature and position of the substituents of their ring system suggest a mevalonate origin. Partially aromatic diterpenoids, such as isotanshinone-I (**4**) and tanshinone-I (**5**)[11] are known, and it is conceivable that compounds such as, e.g. sandaracopimaradiene-3β,18-diol (**6**)[12] may function as precursors in the biosynthesis of diterpenoid phenanthrenes. Although the importance of sulphur in the biosynthesis of terpenoids has long been appreciated,[13] the diterpene sulphoxides podolactones C and D (from *Podo-*

[7] Reisch, J., Báthory, M., Novák, I. and Szendrei, K. (1970) *Herba Hung.* **9**, 43; (1971) *Chem. Abstr.* **75**, 85214.
[8] Letcher, R. M., Nhamo, L. R. M. and Gumiro, I. T. (1972) *J. Chem. Soc. Perkin I* 206.
[9] Hardegger, E., Schellenbaum, M. and Corrodi, H. (1963) *Helv. Chim. Acta* **46**, 1171; Hardegger, E., Biland, H. R. and Corrodi, H. (1963) *Helv. Chim. Acta* **46**, 1354.
[10] Fisch, M. H., Flick, B. H. and Arditti, J. (1973) *Phytochemistry* **12**, 437.
[11] Kakisawa, H., Hayashi, T. and Yamazaki, T. (1969) *Tetrahedron Letters* 301.
[12] Laidlaw, R. A. and Morgan, J. W. W. (1963) *J. Chem. Soc.* 644.
[13] Agranoff, B. W., Eggerer, H., Henning, U. and Lynen, F. (1960) *J. Biol. Chem.* **235**, 326; Williams, R. J. H., Britton, G. and Goodwin, T. W. (1967) *Biochem. J.* **105**, 99.

carpus neriifolius D. Don *ex* Lamb.)[14] and the triterpene thioether neothiobinupharidine [from *Nuphar luteum* (L.) SM.][15] are still unique among natural products. The biosynthesis of a methylthiobenzene derivative was shown to involve dehydromatricaria ester.[16] Thus, alternatively, poly-ynes can be considered as potential precursors of the micrandrols.

EXPERIMENTAL

Isolation of the constituents of Micrandropsis scleroxylon. The trunk wood was reduced to powder (9·3 kg) and extracted with EtOH. The soln was filtered and the solvent evaporated under vacuum. The residue (263 g) was extracted with boiling petrol. The insol. (253 g) was extracted with $CHCl_3$. The $CHCl_3$ soln was concn to 1/3 of its vol. and cooled to room temp. The ppt which appeared was separated by filtration, and the residual soln evaporated under vacuum. The residue (65 g) was chromatographed on a silica column. $CHCl_3$ eluted initially, in order, two fractions A (2·5 g) and B (2·6 g). A was purified by preparative TLC (SiO_2, $CHCl_3$) giving ethyl ferulate (730 mg). B was recrystallized from $CHCl_3$ giving **3** (400 mg). The mother liquor was evaporated and the residue chromatographed on silica. One of the $CHCl_3$ fractions was separated by preparative TLC (SiO_2, $CHCl_3$–Me_2CO, 8:2) into a mixture of sitosterol and stigmasterol (320 mg) and ethyl ferulate (8 mg). Subsequent exhaustive percolation of the column with $CHCl_3$ produced, in order, mixtures of the aforementioned compounds, **2** + traces of **3**, **2** + **1** and **1**. The ppt (11 g) was chromatographed on a silica column. $CHCl_3$–Me_2CO (4:1) eluted, in order, two crystalline fractions C (350 mg) and D (7 g). C was purified successively by preparative TLC (SiO_2, $CHCl_3$–Me_2CO, 4:1) and recrystallization from $CHCl_3$ to give **2** (100 mg). D was purified by crystallizations from 40% aq. EtOH to give **1** (5 g). The petrol. soln contained additional quantities of sitosterol–stigmasterol and ethyl ferulate.

2,6-*Dihydroxy*-1,7-*dimethylphenanthrene* (**1**). Slightly yellowish scales, m.p. 215–218° (40% aq. EtOH). [Found: C, 80·37; H, 5·83. $C_{16}H_{14}O_2$ requires: C, 80·67; H, 5·92%]. ν_{max}^{KBr} (cm^{-1}): 3571, 3448, 1610, 1481, 1258, 1136, 1064, 813. λ_{max}^{EtOH}(nm): 230, 258, 273, 288, 302 inf., 314 inf., 328 inf. (log ϵ 4·56, 4·69, 4·54, 4·26, 4·09, 3·92, 3·47); no shift upon addition of NaOAc and of H_3BO_3 + NaOAc; $\lambda_{max}^{EtOH+NaOH}$ (nm): 241, 270, 292, 312 inf. (log ϵ 4·65, 4·60, 4·61, 4·33). PMR [$(CD_3)_2SO$, 220 MHz, τ]: 0·12 (*s*, OH), 0·39 (*s*, OH), 1·78 (*d*, *J* 9·0 Hz, H-4), 2·09 (*s*, H-5), 2·41 and 2·43 (AB system, *J* 9·0 Hz, H-9 and H-10), 2·45 (*s*, H-8), 2·76 (*d*, *J* 9·0 Hz, H-3), 7·55 (*s*, CH_3-1), 7·63 (*s*, CH_3-7). PMR [$(CD_3)_2CO$, τ]: 1·44 (*s*, OH), 1·67 (*s*, OH), 1·74 (*d*, *J* 9·0 Hz, H-4), 2·02 (*s*, H-5), 2·33 and 2·35 (AB system, *J* 9·0 Hz, H-9 and H-10), 2·40 (*s*, H-8), 2·80 (*d*, *J* 9·0 Hz, H-3), 7·45 (*s*, CH_3-1), 7·60 (*s*, CH_3-7). PMR (C_5D_5N, τ): *ca* 0 (broad, two OH), 1·50 (*d*, *J* 9·0 Hz, H-4), 1·62 (*s*, H-5), 2·14 and 2·15 (AB system, *J* 9·0 Hz, H-9 and H-10), 2·27 (*s*, H-8), 2·56 (*d*, *J* 9·0 Hz, H-3), 7·18 (*s*, CH_3-1), 7·37 (*s*, CH_3-7). MS: M 238 (100%), *m/e* (%) 223 (7), 209 (10), 194 (14), 165 (11), 119 (14). *Deuteriation.* **1** (50 mg), *t*-BuOK (30 mg), D_2O (0·5 ml) DMF (0·5 ml) were heated in a sealed tube under N_2 (100–110°, 72 hr).[16] The cooled mixture was concn under vacuum. The residue was washed with H_2O and dried. PMR [$(CD_3)_2CO$]: H-5 singlet at τ 2·02 missing. All other signals as given for **1**. An identical reaction product was obtained if **1**, D_2O and Et_3N were maintained under reflux (N_2, 5 hr)[17] or if in the above procedure DMSO was used as solvent.

2,6-*Dimethoxy*-1,7-*dimethylphenanthrene*. Obtained by treatment of **1** with Me_2SO_4–K_2CO_3–Me_2CO. Colourrogenation of **2** diacetate (50 mg) by DDQ (52 mg) in C_6H_6 (5 ml) under reflux (12 hr).[4] The crystals which ppted upon cooling were redissolved in $CHCl_3$. The soln was washed successively with aq. NaOH and H_2O, dried and evaporated. The residue was crystallized from C_6H_6 giving a product (38 mg, 78%) which proved to be identical to that obtained by procedure (a) through direct comparison (m.m.p., co-TLC, spectra). Colourless crystals, m.p. 230–231° (closed capillary) [Found: C, 74·54; H, 5·59. $C_{20}H_{18}O_4$ requires: C, 74·53; H, 5·63%]. ν_{max}^{KBr} (cm^{-1}): 1739, 1610, 1575, 1493, 1368, 1214, 1127, 1042, 924, 818. PMR ($CDCl_3$, τ): 1·55 (*d*, *J* 9·0 Hz, H-4), 1·72 (*s*, H-5), 2·11 and 2·25 (AB system, *J* 9·0 Hz, H-9 and H-10), 2·27 (*s*, H-8), 2·66 (*d*, *J* 9·0 Hz, H-3), 7·50 (*s*, CH_3-1), 7·63 (*s*, CH_3-7 and two $COCH_3$). MS: M 322 (20%), *m/e* (%) 280 (28), 238 (100), 209 (16), 194 (28), 165 (6), 43 (11).

2,6-*Dimethoxy*-1,7-*dimethylphenanthrene*. Obtained by treatment of **1** with Me_2SO_4–K_2CO_3–Me_2CO. Colourless crystals (C_6H_6), m.p. 206–207° (closed capillary). ν_{min}^{KBr} (cm^{-1}): 1618, 1499, 1468, 1255, 1220, 1163, 1099, 850, 810. PMR ($CDCl_3$, τ): 1·57 (*d*, *J* 9·0 Hz, H-4), 2·15 (*s*, H-5), 2·32 and 2·37 (AB system, *J* 9·0 Hz, H-9 and H-10), 2·43 (*s*, H-8), 2·73 (*d*, *J* 9·0 Hz, H-3), 5·97 (*s*, OCH_3), 6·04 (*s*, OCH_3), 7·42 (*s*, CH_3-1), 7·62 (*s*, CH_3-7). MS: M 266 (100%), *m/e* (%) 251 (18), 222 (15), 208 (9), 165 (8), 133 (6).

9,10-*Dihydro*-2,6-*dihydroxy*-1,7-*dimethylphenanthrene* (**2**). **1** (77 mg) and 10% Pd–C (50 mg) in AcOH (20 ml) were hydrogenated (pressure, 7 hr). Purification by preparative TLC (SiO_2, $CHCl_3$–Me_2CO, 4:1) gave a product (41 mg) which was proved to be identical with natural micrandrol-B through direct comparison (m.m.p., co-TLC, spectra). Colourless needles, m.p. 167–170° ($CHCl_3$) [Found: C, 80·07; H, 6·80. $C_{16}H_{16}O_2$ requires: C, 80·00; H, 6·72%]. ν_{max}^{KBr} (cm^{-1}): 3330, 3279, 1595, 1479, 1266, 1250, 1140, 1070, 889, 820. λ_{max}^{MeOH} (nm): 277, 296, 317 inf. (log

[14] GALBRAITH, M. N., HORN, D. H. S. and SASSE, J. M. (1971) *Chem. Commun.* 1362.
[15] BIRNBAUM, G. I. (1965) *Tetrahedron Letters* 4149.
[16] BOHLMANN, F. and LASER, J. (1966) *Chem. Ber.* **99**, 1834.
[17] KIRBY, G. W. and OGUNKOYA, L. (1965) *J. Chem. Soc.* 6914.

ϵ 4·27, 4·07, 4·01). $\lambda_{max}^{MeOH+NaOH}$ (nm): 289, 317 (log ϵ 4·16, 4·17). Gibbs test negative. PMR ($CDCl_3$, τ): 2·62 (*d*, *J* 9·0 Hz, H-4), 2·97 (*s*, H-5), 3·10 (*s*, H-8), 3·34 (*d*, *J* 9·0 Hz, H-3), ~5·4 (broad *s*, OH), ~6·4 (broad *s*, OH), 7·24 (*s*, two CH_2), 7·77 (*s*, two $ArCH_3$). PMR [$(CD_3)_2CO$, τ]: 1·90 (*s*, OH), 2·20 (*s*, OH), 2·69 (*d*, *J* 9·0 Hz, H-4), 2·90 (*s*, H-5), 3·12 (*s*, H-8), 3·25 (*d*, *J* 9·0 Hz, H-3), 7·32 (*s*, two CH_2), 7·84 (*s*, two $ArCH_3$). PMR (C_5D_5N, τ): 1·34 (broad *s*, two OH), 2·40 (*d*, *J* 9·0 Hz, H-4), 2·40 (*s*, H-5), 2·95 (*s*, H-8), 2·98 (*d*, *J* 9·0 Hz, H-3), 7·19 (*s*, two CH_2), 7·52 (*s*, $ArCH_3$), 7·57 ($ArCH_3$). MS: M 240 (100%), *m/e* (%) 225 (20), 224 (10). *Deuteriation.* **2** (23 mg), *t*-BuOK (12 mg), D_2O (0·5 ml), DMF (0·5 ml) were treated as described above. PMR of the reaction product [$(CD_3)_2CO$, τ]: 2·14 (*s*, two OH), 2·69 (*s*, H-4), 3·12 (*s*, H-8), 7·32 (*s*, two CH_2), 7·84 (*s*, two $ArCH_3$). *Transformation into pimanthrene.* **2** *bis*-diethylphosphate was prepared (yield 50%) by the method of Kenner and Williams[18] as an oil, ν_{max}^{film} (cm^{-1}): 1587, 1473, 1258, 1036, 980, 826. PMR (CCl_4, τ): 2·40 (*s*, H-5), 2·49 (*d*, *J* 9·0 Hz, H-3), 2·79 (*d*, *J* 9·0 Hz, H-4), 3·02 (*s*, H-8), 5·70 (*q*, *J* 7·0 Hz, two OCH_2), 5·84 (*q*, *J* 7·0 Hz, two OCH_2), 7·20 (*s*, two CH_2), 7·68 (*s*, two $ArCH_3$), 8·60 (*t*, four CH_3). The product (202 mg) was reduced with Na in liq. NH_3 by the method of Kenner and Williams[18] to 9,10-*dihydropimanthrene* (24 mg, 29%). Oil, ν_{max}^{film} (cm^{-1}): 1460, 1087, 893, 823, 781, 730. PMR (CCl_4, τ): 2·48 (*ca d*, *J* 8·0 Hz, H-4, H-5), 2·9–3·1 (*m*, H-2, H-3, H-6, H-8), 7·20 (*s*, two CH_2), 7·65 (*s*, two $ArCH_3$). 9,10-*Dihydropimanthrene* (16 mg) and DDQ (26 mg) in anhd. C_6H_6 (5 ml) were kept at room temp. (12 hr) and subsequently refluxed (8 hr). The cooled reaction mixture was diluted in $CHCl_3$ and washed successively with 20% aq. NaOH and with H_2O. The solvents were evaporated and the residue purified by TLC (SiO_2, *n*-hexane–C_6H_6, 4:1) to give *pimanthrene* (10·5 mg, 66%), colourless crystals, m.p. 83–85° (EtOH) [lit.[19] 75°, 78–81°, 86°], UV[20] and PMR[21] data as given in lit. By the same procedure, **1** also yielded pimanthrene, although accompanied by impurities which could not be removed.

9,10-*Dihydro*-2,6-*diacetoxy*-1,7-*dimethylphenanthrene.* Obtained by Ac_2O–C_5H_5N acetylation either of **2** or of dihydro-**1** as colourless crystals, m.p. 135–137° (95% EtOH). ν_{max}^{KBr} (cm^{-1}): 1754, 1468, 1429, 1361, 1209, 1175, 1127, 1066, 916, 873, 819. PMR ($CDCl_3$, τ): 2·45 (*d*, *J* 9·0 Hz, H-4), 2·70 (*s*, H-5), 2·92 (*s*, H-8), 3·07 (*d*, *J* 9·0 Hz, H-3), 7·17 (*s*, two CH_2), 7·65 (*s*, two $COCH_3$), 7·80 (*s*, $ArCH_3$), 7·84 (*s*, $ArCH_3$). MS: M 324 (23%), *m/e* (%) 282 (39), 240 (100), 239 (12), 224 (8), 181 (8), 165 (8), 43 (80); M Found: 324·1370. $C_{20}H_{20}O_4$ requires: 324·1363.

9,10-*Dihydro*-2,6-*dimethoxy*-1,7-*dimethylphenanthrene.* Obtained by Me_2SO_4–K_2CO_3–Me_2CO methylatin of **2** as colourless crystals, m.p. 169–172° (95% EtOH). ν_{max}^{KBr} (cm^{-1}): 1592, 1563, 1504, 1481, 1319, 1266, 1149, 1105, 1058, 1015, 894, 850, 822. PMR ($CDCl_3$, τ): 2·47 (*d*, *J* 9·0 Hz, H-4), 2·70 (*s*, H-5), 3·05 (*s*, H-8), 3·24 (*d*, *J* 9·0 Hz, H-3), 6·14 (*s*, OCH_3), 6·17 (*s*, OCH_3), 7·25 (*s*, two CH_2), 7·79 (*s*, two $ArCH_3$).

2,8-*Dihydroxy*-7-*methyl*-1-*methylthiophenanthrene* (**3**). Colourless needles (C_6H_6), m.p. 151–153° (closed capillary). Lassaigne test positive for S. ν_{max}^{KBr} (cm^{-1}): 3392, 3369, 1628, 1589, 1495, 1470, 1420, 1257, 1211, 1181, 1128, 1009, 896, 820. λ_{max}^{MeOH} (nm): 230, 256, 277 inf., 294, 320 inf. (log ϵ 4·60, 4·63, 4·36, 4·30, 3·94); $\lambda_{max}^{MeOH+NaOH}$ (nm): 237, 268, 292 inf., 314 inf. (log ϵ 4·55, 4·62, 4·39, 4·21; no shift upon addition of NaOAc, NaOAc + H_3BO_3, $AlCl_3$. PMR ($CDCl_3$, τ): 1·60 (*d*, *J* 9·0 Hz, H-4), 1·78 (*d*, *J* 9·0 Hz, H-5), 2·17 and 2·37 (AB system, *J* 9·0 Hz, H-9 and H-10), 2·30 (*d*, *J* 9·0 Hz, H-6), 2·72 (*d*, *J* 9·0 Hz, H-3), 7·55 (*s*, SCH_3-1), 7·70 (*s*, CH_3-7). PMR [$(CD_3)_2CO$, τ]: 1·44 (*s*, OH), 1·52 (*d*, *J* 9·0 Hz, H-4), 1·67 (*s*, OH), 1·77 (*d*, *J* 9·0 Hz, H-5), 2·00 and 2·04 (AB system, *J* indet., H-9 and H-10), 2·29 (*d*, *J* 9·0 Hz, H-8), 2·75 (*d*, *J* 9·0 Hz, H-3), 7·67 (*s*, SCH_3-1), 7·70 (*s*, CH_3-7). MS: M + 2 272 (4·4%), M 270 (100%), *m/e* (%) 257 (1·3), 255 (23), 229 (0·7), 227 (21), 167 (1·4), 165 (25); M Found: 270·0721. $C_{16}H_{14}O_2S$ requires: 270·0715.

2,8-*Dimethoxy*-7-*methyl*-1-*methylthiophenanthrene.* Obtained by treatment of **3** with Me_2SO_4–K_2CO_3–Me_2CO (8 hr reflux) or CH_2N_2–Et_2O–MeOH (48 hr room temp.). Colourless crystals, m.p. 140–142° (EtOH). ν_{max}^{KBr} (cm^{-1}): 1637, 1582, 1488, 1451, 1270, 1250, 1214, 1148, 1067, 884, 842, 803, 772. PMR ($CDCl_3$, τ): 1·59 (*d*, *J*, 9·0 Hz, H-4, H-5), 2·30 and 2·52 (AB system, *J* indet., H-9 and H-10), 2·44 (*d*, *J* 9·0 Hz, H-6), 2·84 (*d*, *J* 9·0 Hz, H-3), 6·00 (*s*, two OCH_3), 7·64 (*s*, two CH_3).

2,8-*Dimethoxy*-7-*methyl*-1-*methylsulphinylphenanthrene.* A soln **3** dimethyl ether (69 mg) in AcOH (2 ml) and Me_2CO (0·1 ml) was treated with 30% H_2O_2 (0·02 ml) and maintained at room temp. (6 hr).[20] The mixture was evaporated and the residue submitted to preparative TLC (SiO_2, $CHCl_3$–Me_2CO, 8:2). The major fraction consisted of colourless crystals (47 mg, 62%), m.p. 215–218° (MeOH). ν_{max}^{KBr} (cm^{-1}): 1613, 1493, 1290, 1252, 1220, 1139, 1047, 1042 (very intense, SO stretching), 807. PMR ($CDCl_3$, τ): 1·20 (*d*, *J* 9·0 Hz, H-4), 1·35 (*d*, *J* 9·0 Hz, H-5), 2·24 and 2·42 (H-9 and H-10), 2·34 (*d*, *J* 9·0 Hz, H-6), 2·77 (*d*, *J* 9·0 Hz, H-3), 5·98 (*s*, two OCH_3), 6·90 (*s*, $SOCH_3$), 7·62 (*s*, CH_3). MS (*m/e*): M of trace of sulphonyl derivative 330 (< 1%), M 314 (83%), *m/e* (%) 299 (100) M-15, 284 (8), 282 (8), 269 (16), 251 (21) M–SOMe, 224 (50). M Found: 314·0969. $C_{18}H_{18}O_3S$ requires: 314·0978.

2,8-*Diacetoxy*-7-*methyl*-1-*methylthiophenanthrene.* Obtained from **3** as colourless crystals (C_6H_6), m.p. 184–186° (closed capillary). ν_{max}^{KBr} (cm^{-1}): 1748, 1488, 1429, 1418, 1370, 1200, 1171, 1134, 1114, 1022, 922, 901, 859, 821. PMR ($CDCl_3$, τ): 1·54 (*d*, *J* 9·0 Hz, H-4, H-5), 1·79 and 2·29 (AB system, *J* indet., H-9 and H-10), 2·25 (*d*, *J* 9·0 Hz, H-6), 2·67 (*d*, *J* 9·0 Hz, H-3), 7·57, 7·62, 7·65, 7·67 (*s*, four CH_3). MS: M + 2 356 (1·5%), M 354 (29·2%), *m/e* (%) 314 (1·2), 312 (29·1), 272 (4·7), 270 (100·0), 255 (12), 227 (11), 165 (14), 43 (74); M Found: 354·0931. $C_{20}H_{18}O_4S$ requires: 354·0927.

[18] KENNER, G. W. and WILLIAMS, N. R. (1955) *J. Chem. Soc.* 522.
[19] GARMAN, R. M. and GRANT, P. K. (1961) *J. Chem. Soc.* 2187.
[20] HEILBRONNER, E., DÄNIKER, H. V. and PLATTNER, P. A. (1949) *Helv. Chim. Acta* **32,** 1723.
[21] CARMAN, R. M. and CRAIG, W. (1971) *Australian J. Chem.* **24,** 361.

2,8-*Diacetoxy*-7-*methyl*-1-*methylsulphonylphenanthrene*. A soln **3** diacetate (65 mg) in AcOH (1 ml) and Me_2CO (2 ml) was treated with 30% H_2O_2 (0·2 ml) and maintained under reflux (1 hr).[22] Upon cooling in ice, brown crystals appeared. These were separated by filtration, washed with H_2O and purified by TLC (SiO_2, $CHCl_3$–Me_2CO, 9:1). Colourless crystals (32 mg, 45%), m.p. 212–215° (CCl_4–Me_2CO). ν_{max}^{KBr} (cm^{-1}): 1764, 1742, 1484, 1370, 1309 ($\nu_{as}SO_2$), 1212, 1200, 1176, 1149 (ν_sSO_2), 1112, 1025, 952, 920, 901, 820, 763. λ_{max}^{MeOH} (nm): 227 inf., 244, 250, 281, 310 inf. (log ϵ 4·49, 4·63, 4·64, 4·34, 3·95). PMR ($CDCl_3$, τ): 1·07 (*d*, *J* 9·0 Hz, H-4), 1·22 (*d*, *J* 9·0 Hz, H-5), 1·87 and 2·25 (AB system, *J* indet., H-9 and H-10), 2·17 (*d*, *J* 9·0 Hz, H-6), 2·67 (*d*, *J* 9·0 Hz, H-3), 6·74 (*s*, $SO_2C\underline{H}_3$-1), 7·59 (*s*, $C\underline{H}_3$-7). MS: M + 2 388 (0·6%), M 386 (7), *m/e* (%) 346 (1·7), 344 (M-CH_2CO, 22), 304 (7), 302 (M-2 CH_2CO, 100), 265 (M-CH_2CO–SO_2Me, 2), 239 (7), 223 (M-2 CH_2CO–SO_2Me, 6), 195 (9), 43 (21).

Sitosterol–stigmasterol mixture. Colourless crystals, m.p. 152–155° (MeOH), MS: M 414/412 10:6. *Acetate*, m.p. 130–133°.

Ethyl ferulate. Colourless crystals, m.p. 35–37° [lit.[23] m.p. 38°]. Hydrolysis gave *ferulic acid*, m.p. 170–172° [lit.[23] m.p. 174°].

[22] REID, E. E. (1960) *Organic Chemistry of Bivalent Sulfur*, Vol. II, Chemical Publishing, New York.
[23] PEARL, I. A. and BEYER, D. L. (1951) *J. Org. Chem.* **16**, 216.