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BENZYLATED PHENANTHRENES FROM *EULOPHIA NUDA**

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Key Word Index—*Eulophia nuda*; Orchidaceae; benzylated phenanthrenes; bibenzyls.

Abstract—From the tubers of *Eulophia nuda*, further phenanthrene derivatives have been isolated: 9, 10-dihydro-1-(4′-hydroxybenzyl)-4,7-dimethoxyphenanthrene-2,8-diol, 1-(4′-hydroxybenzyl)-4,8-dimethoxyphenanthrene-2,7-diol. In addition, 3,4′-dihydroxy-3′,5,5′-trimethoxybibenzyl and bis(4-hydroxybenzyl) ether were obtained. The structures were assigned by spectroscopic methods. The structure of the penultimate compound mentioned above was also confirmed by synthesis.

INTRODUCTION

In the previous paper, the isolation from the terrestial orchid *Eulophia nuda* Lindl. of six phenanthrene derivatives was reported and the structures **1–6** assigned [1]. Further examination of the acetone extract of the tubers yielded four additional compounds.§ Two are 4-hydroxybenzyl derivatives of the phenanthrene system previously reported [1], namely: 9,10-dihydro-1-(4′-hydroxybenzyl)-4,7-dimethoxyphenanthrene-2,8-diol (**7**), 1-(4′-hydroxybenzyl)-4,8-dimethoxyphenanthrene-2,7-diol (**9**). The other two compounds were shown to be 3,4′-dihydroxy-3′,5,5′-trimethoxybibenzyl (**11**) and bis(4-hydroxybenzyl) ether (**15**).

RESULTS AND DISCUSSION

The structures of compounds (**7–17**) were determined largely by interpretation of 400 MHz ^{1}H NMR spectral data, making use especially of decoupling and nuclear Overhauser effect (NOE) enhancement results. The hydroxyphenanthrenes were characterized as their acetate derivatives, which in general, were more easily purified, and gave better NMR spectra. The NMR and mass spectra of compounds **7** and **9** indicated the presence of the *p*-hydroxybenzyl group and defined its position in each structure. The mass spectrum of each compound showed a significant loss of 94 a.m.u. from the molecular ion due to loss of phenol (C_6H_6O) through H-transfer from the adjacent phenolic hydroxyl group; the ion $[C_7H_7O]^+$ (*m/z* 107) was also prominent. In the NMR spectra, the protons of the benzyl ring (H-2′, H-6′ and H-3′, H-5′) formed a characteristic AA′BB′ pattern, with the signal from H-2′, H-6′ showing benzylic coupling and NOE enhancement from the benzylic $-CH_2-$ group. Further evidence was provided by the acetate derivatives.

The dihydrophenanthrene **7**, $C_{23}H_{22}O_5$, showed the molecular ion peak in the mass spectrum at *m/z* 378. NOE experiments established the substitution pattern of the system. Irradiation of the C-4-OMe (δ 3.80) gave enhancement of the H-3 signal (δ6.61) (18%) and of the H-5 signal (δ 7.68, *d*, $J_{5,6}=8.8$ Hz) (2%). Irradiation of the C-7-OMe (δ 3.84) enhanced only the signal of H-6 (δ 6.76, *d*, $J_{6,5}=8.8$ Hz) (14%). Irradiation of the benzylic $-CH_2-$ group (δ4.00) enhanced the signal from H-2′, H-6′ (δ7.01) (8%) and the signal from $(H\text{-}10)_2$ (δ 2.60) (4%). H-9 resonated as a narrow multiplet at δ 2.62 and H-3′, H-5′ as a multiplet at δ 6.69. Because of the observed coupling pattern and the NOE results, hydroxyl groups are located as shown in **7**. This indicates that **7** is derived from **1**. Additional data on the acetate derivative **8** was also obtained.

Compound **9**, $C_{23}H_{20}O_5$, proved to be a hydroxybenzylphenanthrene with the same oxygenation pattern as **3**. Working with the acetate derivative **10**, irradiation of the C-4-OMe (δ4.13) gave enhancement of the H-3 signal (δ6.95) (20%) and of the H-5 signal (δ 9.44, *dd*, $J_{5,6}=9.3$ Hz, $J_{5,9}=0.8$ Hz) (4%). Irradiation of the C-8-OMe (δ 3.95) enhanced the signal of H-9 (δ 8.09, *dd*, $J_{9,10}=9.3$ Hz, $J_{9,5}=0.8$ Hz) (6%). Irradiation of the benzylic $-CH_2-$group (δ 4.37) enhanced the signal from H-2′, H-6′ (δ 7.12) (14%) and the signal from H-10 (δ 7.85) (27%). H-6 resonated as a doublet at δ 7.33 ($J_{6,5}=9.3$ Hz) and H-3′, H-5′ as a multiplet at δ 6.94. This indicates that the phenolic natural product had the structure **9**.

The phenolic bibenzyl **11** was best handled as the diacetate **12**. The mass spectrum showed sequential loss of two molecules of ketene from the molecular ion (*m/z* 388) to give peaks at *m/z* 346 and 304; the base peak was at *m/z* 167 corresponding to the ion $[C_9H_{11}O_3]^+$ from benzylic cleavage involving ring B. The ion from ring A, $[C_8H_9O_2]^+$, was less intense at *m/z* 137. In the NMR spectrum, the two protons attached to ring B resonated as a singlet at δ 6.44 (because of the symmetry) and the three

*Part 2 in a series. For part 1 see ref. [1].

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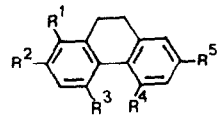
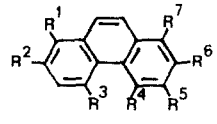
§The crude extract exhibited anti-inflammatory activity in the carrageenin induced pedal edema test (Dr Duangta Kanjanaphothi and Dr Ampai Panthong, Department of Pharmacology, Chiangmai University, private communication).



1 R^1,R^5 = OH ; R^2,R^4 = OMe ; R^3 = H

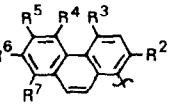
2 R^2,R^5 = OH ; R^3 = OMe ; R^1,R^4 = H

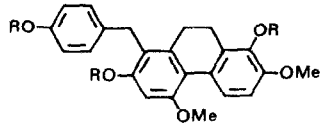


3 R^2,R^6 = OH ; R^1,R^4 = OMe ; R^3,R^5,R^7 = H

4 R^2,R^5 = OH ; R^1,R^4,R^6 = OMe ; R^3,R^7 = H

5 R^2,R^5 = OH ; R^4,R^6 = OMe ; R^1,R^3,R^7 = H

6 R^1 =  R^2,R^6 = OH ; R^3,R^7 = OMe ; R^4,R^5 = H



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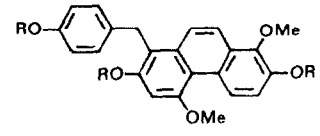
8 R = Ac



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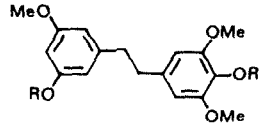
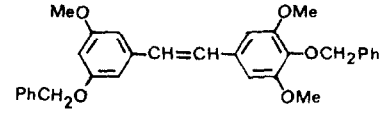
10 R = Ac



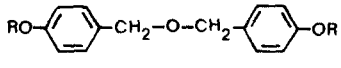
11 R = H

12 R = Ac



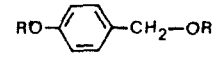
13 and 14

E – and Z – isomers



15 R = H

16 R = Ac



17 R = Ac

protons attached to ring A showed only evidence of *meta*-couplings which supported the arrangement shown in **11**.

The structure of **11** was confirmed by synthesis. Condensation of 4-hydroxy-3,5-dimethoxybenzaldehyde with the ylide of 3-benzyloxy-5-methoxybenzyltriphenylphosphonium bromide gave a mixture of *E*- and *Z*-stilbene isomers (**13** and **14**). Exposure of the mixture to hydrogen and Pd/C led to hydrogenolysis of the benzyl ethers and saturation of the double bond in each isomer to give the bibenzyl **11**.

Initially it was believed that compound **15** was 4-hydroxybenzyl alcohol because the ^{1}H NMR spectrum

showed a singlet at δ 4.40 which could be assigned to the benzylic $-CH_2-$ protons. However, the acetate derivative **16** differed in its spectral properties from those of the acetate derivative (**17**) of *p*-hydroxybenzyl alcohol. The mass spectrum indeed showed the molecular ion at *m/z* 230 and the base peak at *m/z* 107. Consideration of this information led to symmetrical structure **15** being assigned. Acetylation with acetic anhydride under stronger, acid conditions did give the diacetate **17** in good yield through ether cleavage. The product **15** is clearly derived from *p*-hydroxybenzyl alcohol which is involved in the formation of the benzylphenanthrene derivatives.

In conclusion, it is interesting to note that, although the occurrence of phenanthrenes, 9,10-dihydrophenanthrenes and bibenzyls has been widely reported [2–22], the natural occurring *p*-hydroxybenzylated dihydrophenanthrene derivatives are particularly rare [23]. To the best of our knowledge, our results represent the second report on the isolation of the *p*-hydroxybenzylated dihydrophenanthrene.

EXPERIMENTAL

Mps: uncorr. UV: EtOH. ^{1}H NMR: 400 MHz, Me_2CO-d_6, unless otherwise stated. NOE were measured in the FT difference mode by the method of ref. [24]. Analyses were carried out by Australian Microanalytical Service, Melbourne. Mass spectra were determined on an AEI MS 902 spectrometer. CC and prep. TLC were performed using Merck silica gel 60 PF_{254}. Chromatographic solvents were distilled at their boiling point ranges. Tubers of *Eulophia nuda* were collected near Kanchanaburi and Uthaithani, Thailand.

Extraction. Oven-dried (40–60°) pulverized tubers of *Eulophia nuda* Lindl. (3.6 kg) were successively extracted with Me_2CO (11 l) in a Soxhlet for 20 hr and then with MeOH (7.5 l) for a further 15 hr. Removal of solvents from each fraction gave 372 and 337 g, respectively.

Water (500 ml) was added to the Me_2CO fraction and the mixture extracted with Et_2O (5 × 300 ml). Further partition of the aq. layer with *n*-BuOH yielded 275.5 g of fraction A. The Et_2O extract was fractionated into neutral and acidic fractions by 10% aq. NaOH (2 l). The aq. alkaline extract was acidified with cold 6 M HCl (500 ml). The liberated solid was taken into Et_2O and the extract washed with 10% $NaHCO_3$ and Na_2CO_3. Et_2O was removed to dryness to give 28.5 g of acidic fraction B (phenolic constituents). The neutral fraction C yielded 117 g of residue. The $NaHCO_3$ and Na_2CO_3 fractions were further acidified with 6 M HCl, extracted with EtOAc and the solvent removed to give 5.1 and 5.2 g of fraction D and E, respectively.

Isolation of phenolic constituents. Fraction B (28.5 g) was subjected to coarse separation by flash CC over silica gel, gradient eluting with 20% EtOAc–*n*-hexane–100% EtOAc, followed by 5 and 10% MeOH–EtOAc, respectively and finally with MeOH.

Elution with 40–50% EtOAc–*n*-hexane gave a red gum which was further purified by prep. TLC, eluting with 5% MeOH–CH_2Cl_2 (double developed). Five compounds (**1–5**) were isolated from three bands as shown in our previous publication [1]. The lowest R_f value band (168 mg) gave bis(4-hydroxybenzyl) ether (**15**) (90 mg) after addition of CH_2Cl_2.

Elution with 50% EtOAc–*n*-hexane also afforded a red gum (1.97 g) which was chromatographed (prep. TLC, 5% MeOH–CH_2Cl_2, double developed). Four compounds of decreasing R_f value were isolated. Three were identified as 3,4′-dihydroxy-3′,5,5′-trimethoxybibenzyl (**11**) (143 mg), 9,10-dihydro-1-(4′-hydroxybenzyl)-4,7-dimethoxyphenanthrene-2,8-diol (**7**) (170 mg), 1-(4′-hydroxybenzyl)-4,8-dimethoxyphenanthrene-2,7-diol (**9**) (68 mg), respectively. Another compound is under investigation.

Elution with 50–55% EtOAc–*n*-hexane yielded a semi-solid mixture (4.9 g). More crystalline solid (2.4 g) of (**9**) was collected after addition of CH_2Cl_2. The residue (2.5 g) after prep. TLC (5% MeOH–CH_2Cl_2, double developed) gave the biphenanthrene derivative **6** as mentioned in [1]. The more polar band (365 mg) awaits examination.

9,10-*Dihydro*-1-(4′-*hydroxybenzyl*)-4,7-*dimethoxyphenanthrene*-2,8-*diol* (**7**). Colourless plates from $CHCl_3$–*n*-hexane–Me_2CO, mp 200–201°. (Found: C, 73.0; H, 6.1. $C_{23}H_{22}O_5$ requires: C, 73.0; H, 5.9%). IR ν_{max} cm^{-1}: 3540, 3340, 2920, 1600, 1515, 1420, 1375, 1280; UV λ_{max} nm (log ε): 220 (4.45), 274 (4.19), 281 (4.23), 304 (4.00), 313 (4.02); ^{1}H NMR: δ 2.60 (2H, *m*, H-10), 2.62 (2H, *m*, H-9), 3.80 (3H, *s*, C-4-OMe), 3.84 (3H, *s*, C-7-OMe), 4.00 (2H, *s*, benzylic $-CH_2-$), 6.61 (1H, *s*, H-3), 6.69 (2H, part of AA′BB′ pattern, $J_{3',2'}$ and $J_{5',6'}$ = 8.8 Hz, H-3′,5′), 6.76 (1H, *d*, $J_{6,5}$ = 8.8 Hz, H-6), 7.01 (2H, part of AA′BB′ pattern, $J_{2',3'}$ and $J_{6',5'}$ = 8.8 Hz, H-2′, 6′), 7.68 (1H, *d*, $J_{5,6}$ = 8.8 Hz, H-5); MS *m/z* (rel. int.): 378 [M]$^+$ (100), 363 (15), 284 (27). 270 (6), 269 (27), 241 (6), 107 (17), 58 (6), 43 (15).

The acetate **8** crystallized as colourless needles from CH_2Cl_2–*n*-hexane, mp 155–156°. (Found: C, 69.1; H, 6.0. $C_{29}H_{28}O_8$ requires C, 69.0; H, 5.6%). IR ν_{max} cm^{-1}: 1750 (OAc), 1600, 1500, 1440, 1365, 1280, 1220; UV λ_{max} nm (log ε): 220 (4.59), 273 (4.38), 280 (4.41), 298 (4.21), 310 (4.17); ^{1}H NMR ($CDCl_3$): δ 2.24 (3H, *s*, OAc), 2.27 (3H, *s*, OAc), 2.32 (3H, *s*, OAc), 2.51 (2H, *m*, H-10), 2.54 (2H, *m*, H-9), 3.85 (3H, *s*, C-7-OMe), 3.87 (3H, *s*, C-4-OMe), 3.93 (2H, *s*, benzylic–CH_2-), 6.67 (1H, *s*, H-3), 6.86 (1H, *d*, $J_{6,5}$ = 9 Hz, H-6), 6.94 (2H, part of AA′BB′ pattern, $J_{3',2'}$ and $J_{5',6'}$ = 8.8 Hz, H-3′, 5′), 7.06 (2H, part of AA′BB′ pattern, $J_{2',3'}$ and $J_{6',5'}$ = 8.8 Hz, H-2′, 6′); MS *m/z* (rel. int.): 504 [M]$^+$ (28), 462 (66), 420 (100), 405 (6), 378 (11), 284 (6), 269 (7), 107 (31), 69 (9), 58 (34).

1-(4′-*hydroxybenzyl*)-4,8-*Dimethoxyphenanthrene*-2,7-*diol* (**9**). Colourless needles from $CHCl_3$–Et_2O, mp 249–250°. IR ν_{max} cm^{-1}: 3325 (Ar-OH), 2930, 1612, 1600, 1587, 1515, 1470, 1376, 1350, 1220, 1175; UV λ_{max} nm (log ε): 212 (4.39), 248 (4.46), 265 (4.58), 285 (4.24), 303 (3.90), 317 (3.85); ^{1}H NMR: δ 3.89 (3H, *s*, C-8-OMe), 4.05 (3H, *s*, C-4-OMe), 4.38 (2H, *s*, benzylic–CH_2-), 6.68 (2H, part of AA′BB′ pattern, $J_{3',2'}$ and $J_{5',6'}$ = 8.8 Hz, H-3′,5′), 7.00 (1H, *s*, H-3), 7.06 (2H, part of AA′BB′ pattern, $J_{2',3'}$ and $J_{6',5'}$ = 8.8 Hz, H-2′,6′), 7.19 (1H, *d*, $J_{6,5}$ = 9.4 Hz, H-6), 7.88 (1H, *d*, $J_{10,9}$ = 9.4 Hz, H-10), 7.94 (1H, *dd*, $J_{9,10}$ = 9.4 Hz, $J_{9,5}$ = 0.8 Hz, H-9), 9.24 (1H, *dd*, $J_{5,6}$ = 9.4 Hz, $J_{5,9}$ = 0.8 Hz, H-5); MS *m/z* (rel. int.): 376 [M]$^+$ (100), 282 (13), 267 (25), 107 (10), 44 (12).

The acetate **10** crystallized as colourless needles from EtOH, mp 169–170°. IR ν_{max} cm^{-1}: 1760 (OAc), 1600, 1580, 1460, 1370, 1190; UV λ_{max} nm (log ε): 214 (4.25), 254 (4.47), 279 (4.32), 299 (3.96), 313 (3.85); ^{1}H NMR ($CDCl_3$): δ 2.27 (3H, *s*, OAc), 2.32 (3H, *s*, OAc), 2.42 (3H, *s*, OAc), 3.95 (3H, *s*, C-8-OMe), 4.13 (3H, *s*, C-4-OMe), 4.37 (2H, *s*, benzylic–CH_2-), 6.94 (2H, part of AA′BB′ pattern, $J_{3',2'}$ and $J_{5',6'}$ = 8.5 Hz, H-3′, 5′), 6.95 (1H, *s*, H-3), 7.12 (2H, part of AA′BB′ pattern, $J_{2',3'}$ and $J_{6',5'}$ = 8.5 Hz, H-2′, 6′), 7.33 (1H, *d*, $J_{6,5}$ = 9.3 Hz, H-6), 7.85 (1H, *d*, $J_{10,9}$ = 9.3 Hz, H-10), 8.09 (1H, *dd*, $J_{9,10}$ = 9.3 Hz, $J_{9,5}$ = 0.8 Hz, H-9), 9.44 (1H, *dd*, $J_{5,6}$ = 9.3 Hz, $J_{5,9}$ = 0.8 Hz, H-5); MS *m/z* (rel. int.): 502.1627 [M]$^+$ (55) ($C_{29}H_{26}O_8$ requires 502.1626), 460 (50), 418 (100), 376 (10), 267 (10), 107 (15), 57 (25), 43 (70).

3,4′-*Dihydroxy*-3′,5,5′-*trimethoxybibenzyl* (**11**). Oil. IR ν_{max} cm^{-1}: 3400, 2830, 1610, 1590, 1510, 1455, 1325, 1210; UV λ_{max} nm (log ε): 218 (4.30), 274 (3.71), 281 (3.69); ^{1}H NMR: δ 2.76 (4H, *br s*, benzylic–CH_2-), 3.66 (3H, *s*, C-5′-OMe), 3.76 (6H, *s*, C-3-OMe and C-5-OMe), 6.23 (1H, *s*, H-4), 6.30 (2H, *s*, H-2, 6),

6.45 (2H, *s*, H-2',6'), 6.56 (1H, *br s*, OH), 7.76 (1H, *br s*, OH); MS *m/z* (rel. int.): 304 $[M]^+$ (20), 167 $[C_9H_{11}O_3]^+$ (100).

The acetate **12** crystallized as colourless needles from EtOH, mp 105–106°. (Found: C, 65.1; H, 6.4. $C_{21}H_{24}O_7$ requires: C, 64.9; H, 6.2%). IR ν_{max} cm^{-1}: 1750 (OAc), 1600, 1500, 1450, 1420, 1365, 1290; UV λ_{max} nm (log ε): 211 (4.24), 2.71 (3.19), 278 (3.07); ^1H NMR ($CDCl_3$): δ 2.29 (3H, *s*, OAc), 2.35 (3H, *s*, OAc), 2.89 (4H, *s*, benzylic–CH_2–), 3.76 (3H, *s*, C-5-OMe), 3.79 (6H, *s*, C-3'-OMe and C-5'-OMe), 6.44 (2H, *s*, H-2',6'), 6.48 (1H, *t*, $J_{4,2}$ and $J_{4,6}$ = 2 Hz, H-4), 6.54 (1H, *dd*, $J_{6,2}$ = 1.5 Hz, $J_{6,4}$ = 2 Hz, H-6), 6.57 (1H, *dd*, $J_{2,4}$ = 2 Hz, $J_{2,6}$ = 1.5 Hz, H-2); MS *m/z* (rel. int.): 388 $[M]^+$ (2), 346 (35), 304 (35), 179 (2), 167 (100), 137 (12), 91 (2), 69 (5), 43 (14).

Bis(4-hydroxybenzyl) ether (**15**). Colourless plates from CH_2Cl_2, mp 95–96°. IR ν_{max} cm^{-1}: 3330, 3200, 2930, 1615, 1600, 1517, 1460, 1377, 1240; UV λ_{max} nm (log ε): 210 (3.72), 227 (4.03), 275 (3.26); ^1H NMR: δ 4.40 (4H, *s*, benzylic–CH_2–), 6.81 (4H, part of AA'BB' pattern, $J_{3,2}$, $J_{3',2'}$, $J_{5,6}$ and $J_{5',6'}$ = 8.6 Hz, H-3, 3', 5, 5'), 7.19 (4H, part of AA'BB' pattern, $J_{2,3}$, $J_{2',3'}$, $J_{6,5}$ and $J_{6',5'}$ = 8.6 Hz, H-2, 2', 6, 6'); MS *m/z* (rel. int.): 230 $[M]^+$ (1), 213 (3), 107 (100), 41 (30).

The acetate **16** crystallized as colourless needles from CH_2Cl_2–*n*-hexane, mp 113–114°. IR ν_{max} cm^{-1}: 1750, 1600, 1505, 1408, 1370. UV λ_{max}nm (log ε): 209 (4.11), 217 (4.18); ^1H NMR ($CDCl_3$): δ2.30 (6H, *s*, 2. OAc), 4.55 (4H, *s*, benzylic–CH_2–), 7.08 (4H, part of AA'BB' pattern, $J_{3,2}$, $J_{3',2'}$, $J_{5,6}$ and $J_{5',6'}$ = 8.6 Hz, H-3,3',5,5'), 7.37 (4H, part of AA'BB' pattern, $J_{2,3}$, $J_{2',3'}$, $J_{6,5}$, $J_{6',5'}$ = 8.6 Hz, H-2,2',6,6'); MS *m/z* (rel. int.): 315 $[M+H]^+$ (1), 272 (11), 107 (100), 69 (15), 43 (2).

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