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PERAKENSOL: A PHENANTHRENOID ISOLATED FROM *ALSEODAPHNE PERAKENSIS*

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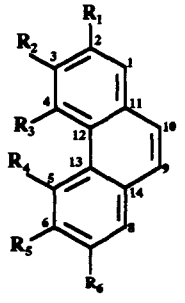
ABSTRACT.—A new non-alkaloidal minor constituent, perakensol [**1**], has been isolated from *Alseodaphne perakensis*.

In our investigation on alkaloidal constituents of *Alseodaphne perakensis* (Gamb.) Kosterm. (Lauraceae) (1) we isolated perakensol (7-hydroxy-2,3,6-trimethoxyphenanthrene) [**1**] as a minor constituent coextracted with the basic fraction. This compound [R_f 0.70–0.75; Si gel, $CHCl_3$-MeOH (9:1); mp 188–190°] has never been isolated from plants even though its isolation from thermal NaOH degradation products of *N,O*-dimethylflavinantine has been reported (2).

The eims of the title compound showed a base peak $[M]^+$ at *m/z* 284 which was consistent with the molecular formula $C_{17}H_{16}O_4$ and was also confirmed by microanalytical data. The uv spectrum gave a bathochromic shift upon addition of NaOH, supporting the presence of an OH group, and the ^{1}H-nmr spectrum showed three MeO groups at δ 4.06, 4.04, and 3.96 and six aromatic protons at δ 7.70 (H-4 and H-5), 7.14 (H-1), 7.18 (H-8), 7.44 (H-9), and 7.46 (H-10). Further spectral support for the structure was obtained from BBD ^{13}C-nmr and DEPT experiments (Table 1). The assignments for **1** and **2** (Table 1) were based on comparison with literature data for **3** (3) and **4** (4) (Table 1) and calculations for the substituent effect (5,6).



1 $R_1=R_2=R_5=OMe$, $R_6=OH$, $R_3=R_4=H$
2 $R_1=R_2=R_5=R_6=OMe$, $R_3=R_4=H$
3 $R_1=R_3=OMe$, $R_2=R_4=OH$, $R_5=R_6=H$
4 $R_1=R_2=R_3=R_4=R_5=R_6=H$

TABLE 1. ^{13}C-nmr Chemical Shifts of Phenanthrenes **1–4**.

Carbon	Compound			
	1	**2**	**3**[a]	**4**[b]
C-1	10.10	108.37	106	128.5
C-2	14.70	149.23	146	126.5
C-3	14.30	148.75	138	126.5
C-4	10.60	102.94	140	122.6
C-5	10.50	102.94	154	122.6
C-6	14.50	148.75	115	126.5
C-7	14.50	149.23	127	126.5
C-8	11.10	108.37	120	128.5
C-9	12.01	124.30	126	126.9
C-1	12.01	124.30	126	126.9
C-1	12.5	126.47	127	132.0
C-1	12.01	124.34	117	130.3
C-1	12.00	124.34	117	130.3
C-1	12.00	126.47	134	132.0
2-OMe	56.70	55.90[c]	56	—
3-OMe	56.70	56.10[c]		—
4-OMe		—	62	—
6-OMe	56.50	56.10[d]		—
7-OMe		55.90[d]		—

[a]Data in this column are from Mujumder *et al.* (3)

[b]Data in this column are from Theuns *et al.* (4).

[c,d]These assignments are ambiguous and may be reversed.

The structure was further unambiguously confirmed by methylating this compound to give *O*-methylperakensol [**2**] upon treatment with Me_2SO_4. The ^{1}H-nmr of the product was in agreement with the reported values (7).

Even though it was possible that perakensol may have been the result of degradation of sebiferine, the major alkaloid isolated from the plant, our attempt to verify this was unsuccessful. Treatment of the latter with all the conditions employed in the extraction and isolation procedures did not result in detection of the expected product. Inspection of the non-basic fraction proved that perakensol indeed existed and therefore suggested that it was not an artifact. It is also interesting to note that in a different experiment **1** was extracted with $CHCl_3$ from both the alkaline and acidic aqueous solutions.

Isolations of phenanthrenoids from plants have been previously reported. Nudol (2,7-dihydroxy-3,4-dimethoxyphenanthrene) has been isolated from orchids *Eulophia nuda*, *Eria carinata*, and *Eria stricta* (8), and bulbophyllanthrin was isolated from *Bulbophyllum leopardium* (3). The isolation of *O*-methyl-α-thebaol has also been reported (4) from *Papaver bracteatum*, and the antifungal compound isolated from *Dioscorea batatas* was identified as 2,5,7-trimethoxy-3-phenanthrenol (9).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's were determined on a Kofler hot-stage and are uncorrected. Ir spectra were recorded on a Beckmann spectrophotometer and uv spectra on an Hitachi model 200-20 instrument. Eims spectra were obtained on an AE1-MS 12 Instrument via a VG-display data acquisition system. ^{1}H- and ^{13}C-nmr spectra were recorded for $CDCl_3$ solutions on a Bruker AM 500 spectrometer at 500 and 125.7 MHz, respectively, or ^{1}H-nmr spectra on a Bruker WP 80 (80 MHz). Resonances are referenced to TMS. The adsorbents used for tlc/chromatotron and cc were Merck Kieselgel 60 PF_{254} and Merck Kieselgel 60 (230 mesh), respectively.

PLANT MATERIALS.—The leaves and bark were collected from the central part of peninsular Malaysia, and the voucher specimen was deposited at the Herbarium of the Universiti Pertanian Malaysia.

EXTRACTION AND FRACTIONATION.—Powdered, air-dried leaves (1.8 kg) of *A. perakensis* were extracted using MeOH as the solvent. Evaporation of the solvent gave a green gum which was taken up by acid (1 M H_2SO_4). Basification of the aqueous acid with Na_2CO_3 and extraction using $CHCl_3$ gave 18 g of an amorphous dark brown solid after evaporation of the solvent. The solid was fractionated through vacuum cc using a $CHCl_3$/MeOH solvent system to give four fractions.

Fraction A (1.4 g) consisted of a mixture of minor components (R_f 0.7–0.75) and a major component based on tlc [$CHCl_3$-MeOH (9:1)] was separated by chromatotron using $CHCl_3$-petroleum ether (9:1) to give a mixture of minor components. Further purification by tlc [EtOAc-petroleum ether (9:1)] on 0.5 mm plates followed by a second tlc afforded a yellowish amorphous solid of **1**: 144 mg, mp 188–190° [lit. (2) mp 186–188°]. Found C 69.7, H 5.6; $C_{17}H_{16}O_4 \cdot \frac{1}{2}H_2O$ requires C 69.7, H 5.8 (2). Uv λ max (EtOH) nm (log ε) 218 (3.90), 255 (4.25), 286 (3.90), 301 (3.70), 338 (2.74), 354 (2.50); λ max (EtOH + NaOH) nm (log ε) 236 (3.88), 265 (4.13), 292 (3.85), 320 (sh), 3.11), 350 (sh), (2.99), 370 (2.82); ir ν max cm^{-1} ($CHCl_3$) 3400–3500 (OH), 1620, 1520, 1490, 1475, 1440, 1260, 1220, 1200, 1160, 1110, 1010, 880, 865, 838, 775; ^{1}H nmr δ (500 MHz, $CDCl_3$) 7.70 (s, 2H, H-4 and H-5), 7.44 (d, 1H, J = 7.5 Hz, H-4 or H-5), 7.46 (d, 1H, J = 7.5 Hz, H-9 or H-10), 7.18 (s, 1H, H-8), 7.14 (s, 1H, H-1), 5.8 (low hump, OH), 4.06 (s, 3H, Ar-OMe), 4.04 (s, 3H, Ar-OMe), 3.96 (s, 3H, Ar-OMe): eims *m/z* (%) $[M+1]^+$ 285 (18), $[M]^+$ 284 (100), 269 (27), 241 (20), 226 (8.9), 212 (7.8), 198 (6.7), 181 (10), 142 (7).

METHYLATION OF PERAKENSOL [**1**].—Perakensol [**1**] (10.4 mg) was dissolved with NaOH (1.5 ml, 2.5 M) in a 50-ml three-neck round-bottomed flask. The solution was cooled while stirring in an ice-salt bath. Me_2SO_4 (0.5 ml) was added to the solution and the stirring continued. When the addition was completed, the ice-bath was removed and the temperature of the solvent was raised to room temperature. The solution was heated to gentle reflux using an oil bath for 1 h. After the reaction mixture cooled to room temperature it was diluted with H_2O to 10 ml and extracted with $CHCl_3$ (3 × 5 ml). The $CHCl_3$ solution was dried (Na_2SO_4) and evaporated to give a brown solid (8.6 mg). Purification by plc [$CHCl_3$-petroleum ether (9.6:0.4), Si gel] gave 6 mg (55%) of *O*-methylperakensol [**2**]. Recrystallization using a toluene/hexane mixture

gave colorless crystals: mp 179–181° [lit. (7) mp 180–181°]; uv λ max (EtOH) nm (log ε) 218 (3.15), 236 sh (3.51), 254 (3.94), 282 (3.57), 299 (3.35); ir ν max cm^{-1} 1610, 1600, 1500, 1460, 1430, 1250, 1150, 1100, 1025, 850, 790; ^1H nmr δ (500 MHz, $CDCl_3$) 7.78 (s, 2H, H-4 and H-5), 7.55 (s, 2H, H-9 and H-10), 7.21 (s, 2H, H-1 and H-8), 4.12 and 4.03 (s, 6H each, 2 × OMe); eims *m/z* (%) $[M+1]^+$ 299 (19), $[M]^+$ 298 (100), 283 (10), 255 (10), 240 (16), 225 (9), 224 (11), 149 (16).

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