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AN APORPHINOID ALKALOID FROM *PSEUDUVARIA MACROPHYLLA*

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Key Word Index—*Pseuduvaria macrophylla*; Annonaceae; stem bark; aporphinoid alkaloids; *O*-methylmoschatoline; 1,2,3-trimethoxy-4,5-dioxo-6a,7-dehydroaporphine.

Abstract—Chromatographic separation of the alkaloid fraction of the methanol extract from the stem bark of *Pseuduvaria macrophylla* resulted in the isolation of a new aporphinoid alkaloid, 1,2,3-trimethoxy-4,5-dioxo-6a,7-dehydroaporphine, together with possibly the known *O*-methylmoschatoline.

INTRODUCTION

In our investigation on the constituents of *Pseuduvaria macrophylla* (Annonaceae) we report the isolation and characterization of two aporphinoid alkaloids from its stem bark extract. *P. macrophylla*, a tree *ca* 20–30 ft tall, was collected in the primary forest, near Taman Negara, Pahang, Malaysia.

RESULTS AND DISCUSSION

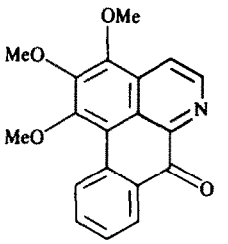
CC of the alkaloid fraction of the methanol extract of the stem bark, followed by prep. TLC and crystallization yielded orange needles (1), mp 182–184° ($C_{19}H_{15}NO_4$; $[M]^+$ *m/z* 321). Its IR spectrum showed a strong absorption at 1665 cm^{-1} which indicated the presence of conjugation of a carbonyl group with two aromatic rings. The UV spectrum with λ_{max} 233, 238, 274, 315 and 436.5 nm indicated that it possessed a 7-oxodibenzo[de,g]quinoline skeleton [1]. The ^1H NMR spectrum displayed characteristic peaks for three methoxy groups at δ4.07, 4.10 and 4.18, AB quartet aromatic protons at δ8.20, (1H, J = 5.3 Hz, H-4), 8.96 (1H, J = 5.3 Hz, H-5) and four aromatic protons at δ7.43–7.84 (2H, *m*, H-9, H-10), 8.57 (1H, *dd*, J = 7.6, 1.8 Hz, H-8) and 9.10 (1H, *dd*, J = 8.1, 1.1 Hz, H-11). In view of the fact that the spectral data were similar to those of *O*-methylmoschatoline [1], it was reasonable to conclude that compound **1** was identical with *O*-methylmoschatoline [1–3].

Compound **2** was crystallized from methanol as yellow needles, mp 198–201°. Its mass spectrum showed an $[M]^+$ at *m/z* 351, thus giving a possible molecular formula of $C_{20}H_{17}NO_5$. The IR spectrum of **2** showed the presence of two carbonyl groups at 1620 and 1665 cm^{-1} and its UV spectrum showed absorption bands at λ_{max} 241, 271, 303, 316 and 416 nm. The ^1H NMR spectrum showed one N–Me group at δ3.86 (3H), three methoxy groups at δ4.08, 4.13 and 4.18, one aromatic singlet at δ7.61 (1H, *s*, H-7) and four aromatic protons at δ7.64 (2H, *m*, H-9, H-10), 7.87 (1H, *m*, H-8) and 9.44 (1H, *m*, H-11) which were ascribed to the protons of the unsubstituted D ring of aporphine [4–6]. Its structure could be related to pontevedrine, a member of the small group of 4,5-dioxoaporphine alkaloids [7, 8]. On the basis of the above data, the structure for **2** was formulated as 1,2,3-trimethoxy-4,5-dioxo-6a,7-dehydroaporphine. It is a new alkaloid and does not appear to have been previously isolated from the Annonaceae.

EXPERIMENTAL

Mps are uncorr. MS were recorded using a GC/MS system. ^1H NMR spectra were recorded at 80 MHz with TMS as int. standard.

Extraction and fractionation. Finely ground dried stem bark (1.5 kg) of *P. macrophylla* (oliv.) Merr was extracted with boiling MeOH (6 l. × 3) for 3 hr. The MeOH extracts were evapd *in vacuo*



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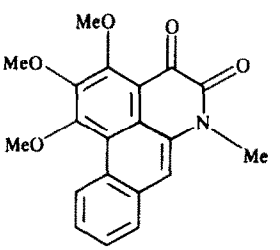

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to afford a thick syrup (117 g) which was suspended in H_2O (400 ml) and extracted with Et_2O (3 × 500 ml). The combined Et_2O extracts were concd to small vol. (500 ml) and extracted with a soln of 5% HCl (3 × 200 ml). The acidic extract was thoroughly washed with Et_2O, basified to pH 10 with conc NH_3 soln and extract with $CHCl_3$ (3 × 400 ml). The $CHCl_3$ extracts were combined, dried (Na_2SO_4) and concd to yield a crude alkaloid fraction (0.27 g). The alkaloid fraction was chromatographed over silica gel (2.5 × 28 cm) using cyclohexane–Me_2CO–MeOH (35:15:1). One hundred (10 ml) fractions were collected. Fractions (9–20) were combined, evapd to a residue (80 mg) and purified by prep. TLC using $CHCl_3$–MeOH (100:1); each plate was developed × 3. The solid residue obtained from the upper orange band was recrystallized from MeOH to yield fine needles (**1**, 8 mg) and the solid residue obtained from the lower yellow band was also recrystallized from MeOH to give needles (**2**, 3 mg).

Compound **1**. Mp 182–184°; MS *m/z* (rel. int.): 321 $[M]^+$ (50.5), 306 (40.0), 291 (34.3), 278 (49.5), 263 (100), 248 (48.6), 235 (41), 220 (78.1); IR ν_{max}^{KBr} cm^{-1}: 1665 (conjugated C=O); UV λ_{max}^{MeOH} nm (log ε): 233 (4.31), 238 (4.27), 274 (4.34), 315 (3.67), 436.5 (3.83); ^1H NMR ($CDCl_3$): δ4.07 (3H, *s*, 1-OMe), 4.10 (3H, *s*, 2-OMe), 4.18 (3H, *s*, 3-OMe), 7.43–7.84) (2H, *m*, H-9, H-10), 8.20 (1H, *d*, J = 5.3 Hz, H-4), 8.57 (1H, *dd*, J = 7.6, 1.8 Hz, H-8), 8.96 (1H, *d*, J = 5.3 Hz, H-5), 9.10 (1H, *dd*, J = 8.1, 1.1 Hz, H-11).

Compound **2**. Mp 198–201°; MS *m/z* (rel. int.): 351 $[M]^+$ (100), 336 (57.4), 308 (9.8), 294 (13.9), 278 (16.4), 265 (74.6), 250 (73.8), 235 (14.8); IR ν_{max}^{KBr} cm^{-1}: 1620, 1665 (conjugated C=O); UV λ_{max}^{MeOH} nm (log ε): 241 (4.49), 271 (4.15), 303 (3.97), 316 (4.06), 416 (3.97); ^1H NMR ($CDCl_3$): 3.86 (3H, *s*, N–Me), 4.08 (3H, *s*, 1-OMe), 4.13 (3H, *s*, 2-OMe), 4.18 (3H, *s*, 3-OMe), 7.61 (1H, *s*, H-7), 7.64 (2H, *m*, H-9, H-10), 7.87 (1H, *m*, H-8), 9.44 (1H, *m*, H-11).

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