Panarine from MeOH–H_2O gave the dihydrate: $C_{20}H_{22}N_2O_2 \cdot 2H_2O$ which crystallized in the orthorhombic system, space group $P2_12_12_1$ with $z = 4$ molecules in a unit cell of dimensions *a*: 9.125(5), *b*: 13.414(8), *c*: 14.953(7)Å.

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ALKALOIDS FROM *PSEUDUVARIA INDOCHINENSIS*

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Key Word Index—*Pseuduvaria indochinensis*; Annonaceae; protoberberine; dehydroscoulerine; liriodenine; atherospermidine; oxoanolobine.

Abstract—Phytochemical investigation of the stem bark of *Pseuduvaria indochinensis* has led to the isolation and identification of a novel quaternary protoberberine alkaloid, dehydroscoulerine, together with three known oxoaporphine alkaloids, liriodenine, atherospermidine and oxoanolobine.

INTRODUCTION

Pseuduvaria indochinensis Merr. (Annonaceae) is a rainforest tree, and the only species of the genus in China [1]. No previous chemical investigation has been reported on this species. The present study has resulted in the isolation of a novel quaternary protoberberine alkaloid, dehydroscoulerine (**1**), and three known oxoaporphine alkaloids, liriodenine (**2**), atherospermidine (**3**) and oxoanolobine (**4**).

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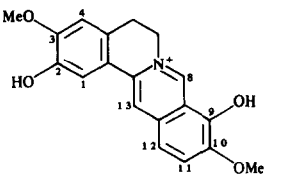
RESULTS AND DISCUSSION

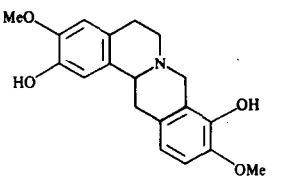
Compound **1** was obtained from the water-soluble part of the extractives and crystallized from methanol as orange-red needles, mp 275–276° (dec). FABMS showed $[M]^+$ at *m/z* 324. UV λ_{max} 229, 279, 350 nm, suggested a quaternary protoberberine type alkaloid [2]. Upon addition of base, the UV spectrum underwent a significant bathochromic shift, which indicated the presence of phenolic groups. This was further supported by IR absorption bands between 3600 to 3200 cm^{-1}. The ^1H NMR (DMSO-d_6) revealed the presence of six aromatic protons that can be assigned to H-4 (δ6.98), H-1

(δ7.50), H-11, 12 (δ7.72), H-13 (δ8.15) and H-8 (δ9.42). The existence of two methoxyl groups indicated by the signals at δ3.87 and 4.01 leaves little doubt that the other substituents are two hydroxy groups. The position of two methoxyl substituents was established by means of NOE experiments. When the signal at δ3.87 was irradiated, an intensity increase of 18% of the proton signal at δ6.98 was observed. Upon saturation of the signal at δ4.01, an intensity increase of 9% was found for the signal at δ7.72. Thus a 2-OH, 3-OMe, 9-OH, 10-OMe substitution pattern was confirmed. The spectroscopic data of the tetrahydro-derivative of **1** was found to be identical to that of scoulerine [3]. Thus **1** is 2,9-dihydroxy-3,10-dimethoxy-5, 6-dihydro-dibenzo[*a*, *g*]quinolizinium and the trivial name, dehydroscoulerine, is proposed. To date, only a few protoberberine type alkaloids have been recorded from the Annonaceae mainly in the genus *Enantia* [4].

On the basis of UV, IR, MS and ^{1}H NMR spectral data and melting points, compounds **2**, **3** and **4** were found to be identical to liriodenine [5], atherspermidine [6] and oxoanolobine [7], respectively.



1



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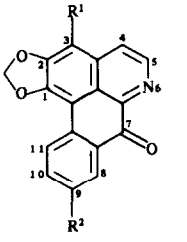

2 $R^1 = R^2 = H$
3 R^1 = OMe, R^2 = H
4 R^1 = H, R^2 = OH

EXPERIMENTAL

Mps: uncorr. UV spectra were run in MeOH and IR spectra in KBr discs. ^{1}H NMR spectra were run at 90 MHz with TMS as int. standard. MS: unless otherwise stated, direct inlet, 70 eV.

Plant material. The stem bark of *Pseuduvaria indochinensis* was collected at Xishuangbanna in Yuennan Province, China, and authenticated by Prof. Y. H. Li. A voucher specimen has been deposited in the Herbarium of Kunming Institute of Botany, Science Academy of China.

Extraction and isolation. The ground stem bark (2.5 kg) was extracted by percolation with 95% EtOH at room temp. to obtain a thick syrup (204 g). The syrup was extracted with a soln of 5% acetic acid (6 × 200 ml). The acidic extract was made alkaline to pH 10 with NH_4OH solution and extracted with CH_2Cl_2 (5 × 500 ml). The CH_2Cl_2 extract was dried over Na_2SO_4 and concd to yield a syrup (9.8 g). The syrup was chromatographed over silica gel column eluted with CH_2Cl_2–MeOH in different ratios. Fractions (16–20) yielded yellow needles (**2**, 172 mg). The aqueous solution, after removal of tertiary alkaloids, was acidified to pH 5 with glacial acetic acid. The acidic solution was treated with ammonium reinickate in the usual way to obtain crude quaternary alkaloids (0.8 g). CC over silica gel containing 0.5% Na_2CO_3, using $CHCl_3$–MeOH–$(C_2H_5)_2NH$ (20:2:1) as eluting solvent mixture, furnished orange-red needles (**1**, 19 mg). The acidic water-insoluble residue (186 g) was extracted with cyclohexane, methylene chloride, EtOAc and MeOH, respectively. The methylene chloride extract was subjected to a silica gel column separation. Treatment of fractions (48–51) through rotatory TLC yielded orange needles (**3**, 16 mg). Chrom. separation of the ethyl acetate extractive gave an orange powder (**4**, 18 mg).

Dehydroscoulerine (**1**). Mp 275–276° (dec.); FABMS 324 $[M]^+$; IR ν_{max} cm^{-1}: 3600–3200 (ν-OH), 1605, 1505, 1010; UV λ_{max} nm (log ε): 229 (4.22), 2.79 (4.27), 350 (4.21), $\lambda_{max}^{MeOH+1\%NaOH}$ 248 (4.18), 283 (4.38), 379 (4.31); ^{1}H NMR (DMSO-d_6): δ3.87 (3H, *s*, C_3-OMe), δ4.01 (3H, *s*, C_{10}-Me), δ6.98 (1H, *s*, H-4), δ7.50 (1H, *s*, H-1), δ7.72 (2H, *s*, H-11, 12), δ8.51 (1H, *s*, H-13), δ9.42 (1H, *s*, H-8). Hydrogenation of (**1**) with KBH_4 in hot methanol, followed by crystallization in MeOH gave yellowish needles, which was found to be identical to scoulerine (**5**).

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