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A NEW DIHYDROPHENANTHRENE FROM *DIOSCOREA DECIPIENS*

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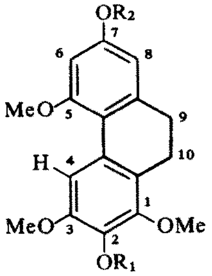
Key Word Index—*Dioscorea decipiens*; Dioscoreaceae; rhizome; 2,7-dihydroxy-1,3,5-trimethoxy-9, 10-dihydrophenanthrene.

INTRODUCTION

So far only two dihydrophenanthrene derivatives have been reported from the family Dioscoreaceae [1]. Our present work describes the isolation and structure elucidation of a new dihydrophenanthrene derivative (**1**) from the rhizomes of *Dioscorea decipiens*.

RESULTS AND DISCUSSION

Elemental composition of compound (**1**) established its molecular formula as $C_{17}H_{18}O_5$. It gave a bluish violet colour with alcoholic $FeCl_3$ and developed a deep orange coloured spot when placed in I_2 vapour. Compound **1** has 3 OMe groups and 2 phenolic groups as revealed by its molecular formula, PMR spectrum and Zeisel's estimation. Its IR spectrum showed a strong absorption at 3500 cm^{-1} (OH). It was recognized as a 9,10-dihydrophenanthrene derivative from the PMR signal characteristic of the 9,10-methylene groups [2]. It formed a diacetate (**2**) with Ac_2O–Py at room temperature. With CH_2I_2–K_2CO_3 it did not form a methylenedioxy derivative ruling out the possibility of 2 OH groups in *o*-positions. On treatment with CH_2N_2 it gave a di-Me ether (**3**); this ruled out [3, 4] the presence of an OH group at position-4 and/or 5. A lone downfield proton singlet at δ 7.9 (this proton being unexchangeable with D_2O) in both **1** and **2** was assigned to the proton at position −4 [5]. The upfield position of the PMR signal of one of the methoxyls in **1** and **2** favoured [6, 7] the placement of this methoxyl at position −5. In **1**, besides others, there were two *m*-coupled proton doublets which are shifted on acetylation, whereas the chemical shift of H-4 remained almost unaltered. This eliminated positions −1 and/or −3 for the OH and left positions −2 and −7 for the placement of 2 OH groups in the parent compound (**1**). Since there were no *o*-coupled protons observed in the aromatic proton region of PMR spectrum of **1** and **2**, the *m*-coupled protons were assigned the positions −6 and −8. These considerations leave the positions −1 and −3 as the only alternative for the remaining 2 OMe groups. This assignment was favoured by the chemical shift observed in the OMe proton resonance on the addition of C_6H_6 to a $CDCl_3$ solution of **2**, wherein, only 2 of the 3 OMe signals suffered an upfield shift (one being the 5 −OMe). Thus **1** has the structure 2,7-dihydroxy-1,3,5-trimethoxy-9,10-dihydrophenanthrene.



(1) $R_1 = R_2 = H$
(2) $R_1 = R_2 = Ac$
(3) $R_1 = R_2 = Me$

EXPERIMENTAL

Mps were recorded on a heat block apparatus and are uncorr. UV spectrum was recorded in MeOH and IR spectra as KBr discs. PMR spectra were obtained in $CDCl_3$ using TMS as int. stand. at 60 MHz.

Extraction and isolation. Dried rhizomes (1.25 kg) of *Dioscorea decipiens* were extracted with hot petrol. The combined petrol extracts were evapd to dryness to yield 1 g of brownish residue which was chromatographed over 50 g Si gel. The fractions eluted with C_6H_6 were combined and purified by prep-TLC in C_6H_6–EtOAc (9:1) to yield pure **1**.

Compound **1**. Obtained as a microcrystalline solid from CCl_4, TLC R_f 0.7 (C_6H_6–EtOAc, 9:1), mp 120–122°; (Found: C, 67.3; H, 6.2; OMe, 31.3. $C_{17}H_{18}O_5$ requires C, 67.5; H, 6.0; 3 × OMe, 30.8%); +ve ferric colour and −ve Gibbs test, UV λ_{max}: 275 nm (log ε 4.28); IR ν_{max}^{KBr} cm^{-1}: 3500(OH), PMR: δ 2.63 (4H, *s*, H-9 and H-10), 3.6 (3H, *s*, OMe −5), 3.83 and 3.86 (2 × OMe at 1 and 3), 5.9 (2H, *br*, disappears on shaking with D_2O, OH −2 and OH −7), 6.5 (1H, *d*, J = 2 Hz) and 6.7 (1H, *d*, J = 2 Hz) (H-6 and H-8) and 7.9 (1H, *s*, 4-H).

Diacetate (**2**). $C_{21}H_{22}O_7$, mp 105–107°, IR ν_{max}^{KBr} cm^{-1}: 1730 and 1250, PMR: δ 2.2 (6H, *s*, 2 × OAc), 2.66 (4H, *s*, H-9 and H-10), 3.6 (3H, *s*, OMe −5; $+C_6H_6$; 3.35), 3.75 (3H, *s*, OMe −3; $+C_6H_6$; 3.5), 3.8 (3H, *s*, OMe −1; $+C_6H_6$; 3.81), 6.7 (1H, *d*, J = 2 Hz) and 6.9 (1H, *d*, J = 2 Hz) (H-6 and H-8) and 7.95 (1H, *s*, 4-H).

Dimethyl ether (**3**). (CH_2N_2), $C_{19}H_{22}O_5$, mp 94–96°, −ve ferric colour and Gibbs test.

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