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A 4-ARYLCOUMARIN FROM *COUTAREA HEXANDRA*

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Key Word Index—*Coutarea hexandra*; Rubiaceae; neoflavonoids; new 4-arylcoumarin.

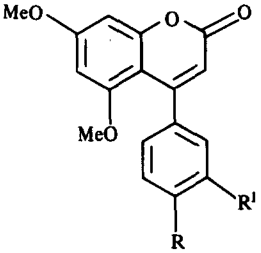
Abstract—The structure of a new 4-arylcoumarin, isolated from *Coutarea hexandra*, has been established as 5,7-dimethoxy-3′,4′-methylenedioxy-4-phenylcoumarin and confirmed by partial synthesis from 3′,4′-dihydroxy-5,7-dimethoxy-4-phenylcoumarin.

INTRODUCTION

Four new 4-arylcoumarins, **1**, **2**, **3** and **4**, have been recently isolated from *Coutarea hexandra*, Rubiaceae [1]. Careful purification of **1** afforded a new 4-arylcoumarin, to which the structure **5** was attributed. Methylenation of the coumarin **4** yielded a product identical in all respects with **5**.

RESULTS AND DISCUSSION

The new product, $C_{18}H_{14}O_6$ (**5**), was obtained during the purification of compound **1** [1]. Spectral data were consistent with those of the previously isolated 5,7-dimethoxy-4-phenylcoumarins [1]. A methylenedioxy substituent was evidenced by the ^{1}H NMR spectrum and by a positive Labat test [2], and was placed at the C-3′ and C-4′ positions on biogenetic considerations. Partial synthesis from the natural product **4** confirmed the structure **5** for the new compound and also the oxygenation pattern of the B ring of compound **4** itself, which was in doubt following the isolation of 5,2,5′-trihydroxy-7-methoxy-4-phenylcoumarin from the methanol extract of stem bark of the same plant [3]. The use of CsF instead of KF [Pechy, P., private communication] notably improved the yield of the methylenedioxy compound.



	R	R¹
1	OMe	H
2	OH	H
3	OMe	OH
4	OH	OH
5	O—CH₂—O	

EXPERIMENTAL

Isolation. Extraction and fractionation of the stem extract of *Coutarea hexandra* (Jacq) Schum are reported in our previous work [1]. Prep. TLC—with C_6H_6–EtOAc (9:1) × 2 checking with UV light—of impure fractions of compound **1** gave the new coumarin in semimicro amounts.

General. Mps are uncorr. Silica gel (Merck) plates were used for TLC and prep. TLC.

5,7-dimethoxy-3′,4′-methylenedioxy-4-phenylcoumarin (**5**). $C_{18}H_{14}O_6$ (calc. 326.0790; found 326.0794), mp 194–195° (sub., EtOH); UV λ_{max}^{MeOH} nm (log ε): 248 (4.07), 327 (4.42); ^{1}H NMR ($CDCl_3$, 60 MHz): δ 6.85–6.75 (3H, *m*, H-2′, H-5′, H-6′), 6.46 (1H, *d*, J = 2.5 Hz, H-8), 6.19 (1H, *d*, J = 2.5 Hz, H-6), 5.95 (2H, *s*, OCH_2O), 5.93 (1H, *s*, H-3), 3.83 (3H, *s*, 7-OMe), 3.47 (3H, *s*, 5-OMe); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710, 1613, 1595, 1505, 1157, 1110, 1052, 1039, 938, 904, 858, 810; EIMS (70 eV) *m/z* (rel. int.): 326 $[M]^+$ (81), 298 $[M - CO]^+$ (100), 289 $[M - MeCO]^+$ (13), 255 $[M - 43 - CO]^+$ (4).

Methylenation. 3′,4′-Dihydroxy-5,7-dimethoxy-4-phenylcoumarin (**4**, 110 mg) and anhydrous CsF (400 mg) were shaken and cooled in dry DMF (2 ml). The mixture was added with CH_2Br_2 (0.2 ml) and maintained at 115° for 15 hr under stirring. The cooled mixture was poured into $CHCl_3$ and washed with small vols of H_2O. The organic soln was evaporated *in vacuo* and the residue passed on silica gel with hexane–EtOAc (4:1), to give crude 5,7-dimethoxy-3′,4′-methylenedioxy-4-phenylcoumarin (**5**, 60 mg), mp and mmp 193–195° (EtOH).

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