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# MARSUPOL: A NOVEL ISOFLAVONOID GLYCOL FROM *PTEROCARPUS MARSUPIUM*

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**Key Word Index**—*Pterocarpus marsupium*; Leguminosae; heartwood; isoflavonoid; α-methylhydrobenzoin; marsupol.

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**Abstract**—The isolation, structure and synthesis of 4, 4′-dihydroxy-α-methylhydrobenzoin are described. This is the first report of a naturally occurring hydrobenzoin.

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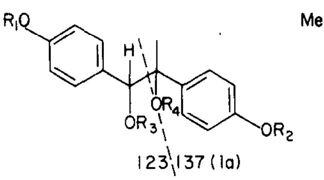
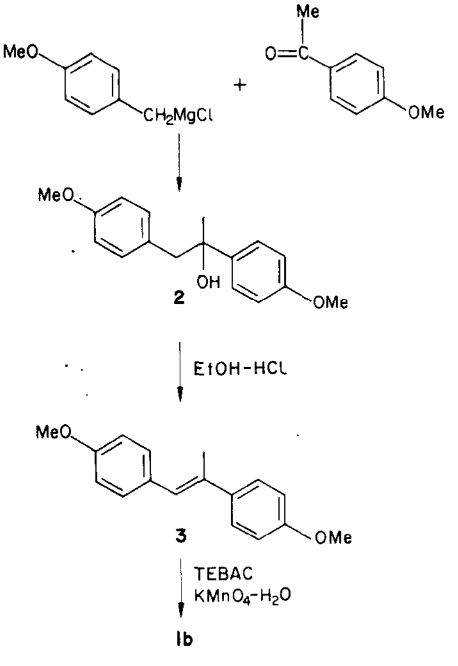
In continuation of our work [1] on the extractives of the heartwood of *Pterocarpus marsupium*, we now report the isolation of a novel isoflavonoid glycol, 4, 4′-dihydroxy-α-methylhydrobenzoin (**1a**) designated as marsupol. The ether extract of the heartwood of the title plant on CC over Si gel using chloroform–ethyl acetate (7 : 3) as eluent yielded marsupol, colourless plates, mp 156°, $[\alpha]_D - 13.6°$ (*c* 2.3, MeOH). Found: C, 69.3; H, 6.21. $C_{15}H_{16}O_4$ requires: C, 69.3; H, 6.15%. ($M^+$ 260), IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3600–3550 (*br*, OH), 2900 and 1470 ($CH_3$), 1600, 1580, 1500 and 1450 (aromatic). UV $\lambda_{max}^{MeOH}$ nm (log ε) 280 (3.40) (*p*-C-alkylated phenol) [2]. $^1H$ NMR (60 MHz $CDCl_3$/DMSO-$d_6$, TMS as int. standard): $A_2B_2$ signals [δ 8.6 (*d*, *J* = 8.5 Hz, 4H), δ 7.3 (*d*, *J* = 8.5 Hz, 4H)], δ 8.6 (*s*, 2H) and δ 4.1 (*s*, 2H) (phenolic and alcoholic hydroxyls respectively which are deuterium exchanged), δ 4.7 [*s*, 1H, –(OH)C$\underline{H}$–Ar] [3] and a broad signal centred at δ 2.6 [3H, Ar–CH(OH)–COH(C$\underline{H}_3$)–Ar] [4].

Marsupol on treatment with diazomethane gave a dimethyl ether (**1b**), mp 115°, $[\alpha]_D - 10.2°$ (*c* 1.9, MeOH). Found: C, 70.81; H, 6.92. $C_{17}H_{20}O_4$ requires C, 70.83; H, 6.94% ($M^+$ 288). NMR of **1b** showed an additional signal at δ 3.9 (two $-OCH_3$) suggesting the presence of two phenolic hydroxyl groups in marsupol. **1b** on treatment with acetic anhydride–pyridine gave a diacetate (**1c**), mp 97°, $[\alpha]_D - 10°$ (*c* 0.89, MeOH). Found: C, 67.5; H, 6.41. $C_{21}H_{24}O_6$ requires C, 67.74; H, 6.45%. $M^+$ 372. Thus the presence of two phenolic and two alcoholic hydroxyl groups in marsupol was indicated.

**1b** on oxidation with potassium periodate furnished *p*-methoxyacetophenone [2, 4-DNP: mp 217°, mmp 216°, (lit. [5] mp 220°)] and anisaldehyde [2, 4-DNP: mp 250°, mmp 248°, (lit. [5] mp 254°)] the identities of



**1a** $R_1 = R_2 = R_3 = R_4 = H$
**1b** $R_1 = R_2 = Me, \quad R_3 = R_4 = H$
**1c** $R_1 = R_2 = Me, \quad R_3 = R_4 = Ac$



which were further confirmed by superimposable IR with the respective authentic samples. Based on the above spectral characteristics and reactions structure **1a** may be assigned to marsupol.

In the mass spectrum of marsupol, the prominent ions $m/z$ 123 (100%) and $m/z$ 137 (30%), may be considered to have been formed by the symmetrical cleavage (shown by the dotted lines in structure **1a**) of the molecule. EIMS (probe) 70 eV $m/z$ (rel. int.); 260 $[M]^+$ (85), 242 $[M-H_2O]^+$ (5), 137 $[M-123]^+$ (30), 123 $[M-137]^+$ (100), 119 $[M-123-H_2O]^+$ (30), 91 $[M-123-H_2O-CO]^+$ (50). The position ($\delta$ 2.6) and the broadening of the methyl signal in the NMR spectrum of marsupol may be attributed to the deshielding [6] and the varying eclipsing [4] effects, respectively, caused by the $\beta$-OH group.

The structure of marsupol has been confirmed by the synthesis of its dimethyl ether (**1b**) as follows. The required $\alpha$-methylstilbene (**3**), mp 123° (lit. [7] mp 124°), was prepared by the Grignard reaction between $p$-methoxybenzyl magnesium chloride and $p$-methoxacetophenone; and the subsequent dehydration of the resulting alcohol (**2**), mp 60° (lit. [7] mp 62°), using ethanolic HCl. **3** on reaction with aq. potassium permanganate under phase transfer catalysis conditions [8] using triethylbenzylammonium chloride (TEBAC) as a catalyst, yielded a racemic glycol which was found to be identical with the dimethyl ether of marsupol (**1b**) (mp, and superimposable IR).

The structure of marsupol may be considered as closely related to angolensin [9], an isoflavonoid isolated from *Pterocarpus angolensis*.

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# FURTHER FUROQUINOLONE ALKALOIDS FROM *RUTA CHALEPENSIS**

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**Key Word Index**—*Ruta chalepensis*; Rutaceae; furoquinolone alkaloids; chalepin.

**Abstract**—Two new alkaloids, 9-ethyl-8-methoxy-furo[2,3]quinol-4-one and 9-ethyl-7,8-dimethoxy-furo[2,3]quinol-4-one, and the known furocoumarin chalepin were isolated from *Ruta chalepensis*.

In a recent publication[1], we described the isolation and structure elucidation of taifine (**1**), the first representative of a $N$-ethylfuroquinolone alkaloid. We wish now to report on two further members of this class, viz. isotaifine (**2**) and 8-methoxytaifine (**3**) also isolated from *Ruta chalepensis* L.

As shown by exact mass measurements, **2** has an elemental composition of $C_{14}H_{13}NO_3$ and is, therefore, an isomer of **1**. Its mass and UV spectra are very similar to those of **1**. The NMR spectrum (see Table 1) differs from that of **1**; the pattern is typical

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*Part 14 in the series "Constituents of Local Plants". For Part 13, see ref. [1].