

6-METHOXY-7,8-METHYLENEDIOXYCOUMARIN FROM *MELOCHIA TOMENTOSA**

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Key Word Index—*Melochia tomentosa*; Sterculiaceae; 6-methoxy-7,8-methylenedioxy coumarin.

Plant. *Melochia tomentosa* (Sterculiaceae). **Occurrence.** The plant is a shrub 1.5 m high, abundant close to the coast in Curaçao, and common at sea level and on the nearby mountains in Coro, Venezuela. The plant is also found in Florida, Texas, the Bahamas, throughout Mexico, and extending as far south as Brazil [1]. **Uses.** A decoction of leaves or roots is recommended for the relief of throat inflammation in Curaçao [1]. During a diphtheria epidemic, a decoction of roots of this plant combined with other plants was used [2]. **Previous work.** Roots. Melochinone, a quinolinone alkaloid has been reported earlier [3]. An extract from roots of this plant was found to be oncogenic [4].

Present work. Roots. In an effort to isolate active principles, a CH_2Cl_2 extract of the roots was chromatographed on Si gel. Besides several crystalline compounds, a small amount of the title coumarin was obtained. The coumarin, mp 217° $M^+ = 220.0385$ (Calc. for $\text{C}_{11}\text{H}_8\text{O}_5 = 220.0372$) showed by PMR a OMe group at δ 3.96, and a methylenedioxy group at δ 6.20, an aromatic proton at δ 6.62 and characteristic doublets for coumarin H-3 and H-4 protons at δ 7.60 and 6.30 ($J = 10$ Hz). These data suggested its structure to be a methoxymethylenedioxy coumarin. Herz *et al.* [5] reported 6-methoxy-7,8-methylenedioxy coumarin as having a mp similar to our compound. This structure was confirmed by direct comparison (mp, mmp, NMR) with an authentic sample supplied by Professor Herz.

This communication constitutes the first report of the occurrence of this coumarin in the family Sterculiaceae.

EXPERIMENTAL

The PMR spectrum was measured in CDCl_3 at 100 MHz with TMS as internal standard.

Dried and ground roots of *M. tomentosa* (1.6 kg) were continuously extracted with boiling petrol (5 l, 2 days), boiling C_6H_6 (5 l, 2 days) and these extracts set aside for further studies. The residue was then combined with $\text{Ba}(\text{OH})_2$ (50 g) suspended in 50% aq. EtOH (1200 ml). The material was then air dried and continuously extracted with CH_2Cl_2 (5 l, 2 days). Removal of solvent provided a yellow powder (4.5 g) which was chromatographed on Si gel (300 g). The column was eluted with petrol (38–45°), petrol– C_6H_6 (3:1), petrol– C_6H_6 (1:1), petrol– C_6H_6 (1:3), C_6H_6 , C_6H_6 – CHCl_3 (3:1), C_6H_6 – CHCl_3 (1:1), C_6H_6 – CHCl_3 (1:3), CHCl_3 , CHCl_3 –EtOAc (3:1), CHCl_3 –EtOAc (1:1), CHCl_3 –EtOAc (1:3), EtOAc and EtOH.

6-Methoxy-7,8-methylenedioxy coumarin was found in the C_6H_6 – CHCl_3 (1:1) fraction and crystallized from MeOH as needles, mp 217° , $\text{C}_{11}\text{H}_8\text{O}_5$, $M^+ 220$ (100%) m/e 205 (15%), 192 (27%), 177 (13%), 149 (12%), 147 (20%), 121 (12%) and 79 (25%). PMR signals at 6.20 s (2H, $-\text{O}-\text{CH}_2-\text{O}-$), 3.96 s (3H, $-\text{OMe}$), 6.62 s (1H, H-5) and 7.60 d and 6.30 d (2H, AB, J 10 Hz, H-3 and H-4). The authentic sample gave identical signals in CDCl_3 , although in DMSO as reported in Ref. [5], the aromatic hydrogen was shifted downfield.

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|| *M. tomentosa* roots were collected at Curaçao by Mr. W. P. Maal, Klein St., Joris, Curaçao.

¶ Although ayapin (6,7-methylenedioxy coumarin) hydrolysed to the open chain form on treatment with aq. 10% NaOH, the title coumarin was unaffected. Apparently $\text{Ba}(\text{OH})_2$ treatment also left the title coumarin unaffected.