Coumarins and Alkaloids from the Stems of Metrodorea Flavida

Ana Cristina S. Baetas, Mara S.P. Arruda*, Adolfo H. Müller, and Alberto C. Arruda

Departamento de Química, CCEN, Campus Universitário, Universidade Federal do Pará, 66075-900 Belém - PA, Brazil

A new coumarin, 5,6-methylenedioxy-7,8-dimethoxycoumarin has been isolated from the stems of Metrodorea flavida, as well as known coumarins and alkaloids. The structures of the new and the known compounds were established by spectral data and by comparison with the literature data.

Keywords: Metrodorea flavida, Rutaceae, coumarins, alkaloids

Introduction

In a previous paper, we reported the characterization of a new coumarin, 8-(2,3-dihydroxy-3-methylbutyloxy)-6,7-methylenedioxycoumarin, together with known furocoumarins and a furofuran lignan, which were isolated from the leaves of Metrodorea flavida1. In continuation of our phytochemical studies on the constituents of this species, we report from the stem the isolation and structural elucidation of a new coumarin 5,6-methylenedioxy-7,8-dimethoxycoumarin (1), in addition to the known compounds: scoparone (2)2; 6,7-methylenedioxy-8-methoxycoumarin (3)3; xanthotoxin (4)4; isopimpinellin (5)4; imperatorin (6)4; braylin (7)5; γ-fagarine (8)6; kokusaginine (9)7; maculin (10)8; syringic aldehyde (11)9; ruteacarpine (12)10; sitosterol and lupeol.

All the compounds were isolated by chromatographic techniques. The structural elucidation of these compounds were based on spectrometric data, especially IR, 1H NMR and 13C NMR, involving comparison with the literature data.

Experimental

Equipment

Mps uncorr. IR were recorded in KBr discs. 1H and 13C-NMR spectra were recorded at 300 and 75 MHz, respectively, in CDCl3 on a Varian GEMINI 300 instrument and at 400 and 100 MHz, in DMSO, on a Brucker ARX 400 instrument. EIMS were obtained by direct probe insertion at 70 eV.

Plant material

Metrodorea flavida was collected in Paragominas, State of Pará, Brazil, in December 1991. A voucher specimen is deposited at the Herbarium of the CPATU-EMBRAPA, Belém, Brazil.

Extraction and isolation

After drying, stems (231 g) were ground and percolated with hexane and CH2Cl2 successively. The concd. hexane extract (3.5 g) was submitted to CC using silica gel 60 Merck (particula size 0.063-0.200 mm) packed in hexane. Elution was performed with a gradient of hexane, Me2CO and MeOH, affording 22 frs. The frs 3 and 7 after prep. TLC (silica gel and hexane-CH2Cl2-MeOH/10:10:0.1) yielded lupeol and sitosterol, respectively.

Fr. 17 was submitted to CC on silica gel eluting with gradients of hexane, CH2Cl2, Me2CO and MeOH affording 9 (3.1 mg). The CH2Cl2 extract (4.2 g) was subjected to chromatographic treatments similar to those used for the hexane
extract. Frs. 4-5 afforded a mixture (6.3 mg) of lupeol and sitosterol. Fr. 7 afforded 6 (4.8 mg). Fr. 8 was rechromatographed on silica gel using gradients of hexane, Me₂CO and MeOH yielding 4 (3.7 mg), 6 (8.1 mg), 7 (5.2 mg) and 12 (1.3 mg). Fr. 9 was subjected to CC on silica gel using hexane, Me₂CO and MeOH at different ratios of increasing polarity to give 7.0 mg of the new coumarin 1.

Results and Discussion

The new coumarin 1 was obtained from the dichloromethane extract of M. flavida and showed as a blue color on TLC under UV light 336 nm. Its ¹H NMR spectrum exhibited resonances typical of H-3 and H-4 (δ 6.20 and 7.91) of the coumarin nucleus in which C-5 was oxygenated. The presence of a methylenedioxy group was indicated from the methylene hydrogens signal at δ 6.01 (s) and two methoxy groups from the signals at δ 4.04 and 3.99 (s, 3H each one). These groups were located at the positions 5, 6, 7 and 8 suggesting one of the possible structures 1, 1a or 1b. Further information concerning the actual positions of the methoxy groups was obtained by analysis of the 1D-NOE difference spectrum. Irradiation of the signal at δ 7.91 (d, H-4) didn’t enhance the signals at δ 4.04 and 3.99 (2x OMe), which confirmed the placement of the methylenedioxy group at C-5/C-6. This result is consistent with the structure 1.

Acknowledgements

The authors are grateful to Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior (CAPES) and Financiadora de Estudos e Projetos (FINEP) for financial support.
support and to Universidade Federal de São Carlos (São Carlos - São Paulo, Brazil) for $^1$H and $^{13}$C-NMR spectra at 400 and 100 MHz, respectively.

**References**


*Received: September 9, 1998*