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Phenylcoumarins from *Kielmeyera elata*

R. da S. Gramacho[a], Tanus J. Nagem[b,*], Tânia Toledo de Oliveira[a], Maria Eliana L. R. de Queiroz[c], Antonio A. Neves[c], Nagib Saddi[d]

[a]*Departamento de Bioquimica e Biologia Molecular, Universidade Federal de Viçosa, Viçosa, MG, 36570-000, Brazil*
[b]*Departamento de Quimica ICEB, Universidade Federal de Ouro Preto, Ouro Preto, MG, 35400-000, Brazil*
[c]*Departamento de Quimica, Universidade Federal de Viçosa, Viçosa, MG, 36570-000, Brazil*
[d]*Herbario Central, Universidade Federal de Mato Grosso, Cuiabá, Brazil*

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Abstract

Friedelin, the 4-phenylcoumarins mammeisin, 4-phenyl-5-hydroxy-6-(3-methyl-1-oxobutyl)-2′-(1-hydroxy-1-methylethyl)-3′,4′-dihydro(5′,4′:7,8) furancoumarin, and mammeigin have been purified from the stem of *Kielmeyera elata*. These compounds have previously been reported for the same species. In addition, a new derivative of mammeigin has been isolated and identified as 4-phenyl-5-hydroxy-6-(3-hydroxymethyl-1-oxo-butyl)-2′,2′-dimethyl(6′,5′:7,8)pyrancoumarin.

Keywords: *Kielmeyera elata*; Guttiferae; phenylcoumarins; hydroxymammeigin

1. Introduction

This paper is a study of *Kielmeyera elata*, Saddi, as part of a broader study of the Guttiferae family. The plant has been collected and identified by Dr. Nagib Saddi, (Central Herbarium, Universidade Federal do Mato Grosso, Cuiabá, Brazil), in Ilhéus, Bahia[1], Brazil.

Several species of this genus have been shown to contain xanthones and coumarins (Peres, 1997; Nagem & Silva, 1988; Moreira, Jesus & David, 1996; Moreira, Guedes & Chavez, 1997; Santos, Araujo & David, 1996; Santos, Guedes & Chavez, 1997). This study has revealed the presence of friedelin and of three known 4-phenylcoumarins: mammeisin (Crombie, Games & McCormick, 1966; Carpenter, McGarry & Scheinmann, 1971; Bandaranayake, Selliah, & Sultanbawa, 1975), 4-phenyl-5-hydroxy-6-(3-methyl-1-oxo-butyl)-2′]-1-hydroxy-1-methylethyl)-3′,4′-dihydro(5′,4′:7,8) furancoumarin (Bandaranayake, Selliah, & Sultanbawa, 1975; Crombie, Games & Haskins, 1972; Silva, 1986) and mammeigin (**1**) (Nagem & Silva, 1988; Finnegan & Mueller, 1965; Crombie, Games & McCormick, 1967) as well as a new coumarin derivative of mammeigin which was given the trivial name of hydroxymammeigin (**2**).

2. Results and discussion

The IR spectrum of hydroxymammeigin (**2**) showed bands at 3440 cm^{-1} (chelated hydroxyl), 1740 cm^{-1} (α-pyrone) and 700 cm^{-1} (monosubstituted benzene nucleus). Its NMR spectrum revealed a signal at δ 5.98 (s) for one hydrogen on C–3 and signals at δ 7.38 and 7.29 (m) due to the aromatic hydrogens. The absence of a signal at δ 7.5–8.3 is due to the presence of a phenyl group at the C-4 position (Santos, Guedes & Chavez, 1997). A singlet at δ 1.57 integrated for six hydrogens and the presence of two doublets of one hydrogen each at δ 8.62 (J = 10.1 Hz) and at δ 6.88 (J = 10.1 Hz) established the presence of a 2,3-dimethyl-Δ^3-pyran ring.

* Corresponding author.

[1] Herbarium material: Santos, T.S. n° 4583.

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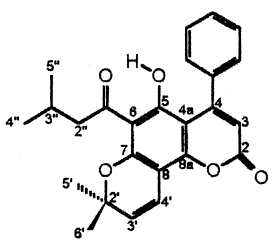

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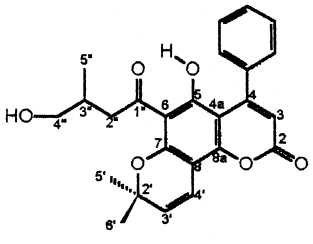

2

The presence of the $[M–15]^+$ base peak in the mass spectrum has also strengthened this conclusion. The signals at δ 3.20 (1 H. dd J = 16.4 and 6.6 Hz). δ 3.05 (1H, dd, J = 16.4 and 6.6 Hz), δ 3.57 (1H, dd, J = 10.6 and 5.3 Hz), δ 3 50 (1H, dd. J = 10.4 and 5.3 Hz) and δ 0.98 (3H d, J = 6.8 Hz) revealed the presence of a 3-hydroxymethyl-1-oxobutyl group, which has been confirmed by mass spectrum high-intensity peak $[M–18]^+$ resultant of water loss. The signal at δ 14.55 (1H, s) has been ascribed to a hydroxyl group chelated to an acyl group. The angular fusion of the chromene ring has been determined by comparison with mammeigin since both compounds have given signals corresponding to the six hydrogens in the dimethylchromene group at δ 1.57. Additionally, mammeigin and hydroxymammeigin have a green color with methanolic $FeCl_3$ solution and a similar chemical shift occurred due to the acyl group present at the C–6 position in the coumarin skeleton. From these data. we propose that compound (**2**) 4-phenyl-5-hydroxy-6–(3-hydroxymethyl-1-oxo-butyl)-2′,2′-dimethyl (6′,5′:7,8)pyrancoumarin, which, to our knowledge, has never been reported before.

3. Experimental

Mps: Quimis, mod 340D23; CC: Kieselgel (0.07-0.23 mm); TLC: Kieselgel GF 254 60, spots, were visualized with phosphoromolybdic acid, seric sulphate and UV fluorescence; IR: only major bands are quoted.

Constituent isolation. 3.2 kg of stems of *Kielmeyera elata* were submitted to successive extractions with hexane, by mechanical agitation under room temperature. After the removal of the solvent 9.41 g of the extract was chromatographed with silica gel (180 g) using hexane, ethyl ether and ethanol as eluents. Several fractions were collected and separated into 11 groups (H_1–H_{11}) by TLC. H_3 group (1.06 g) was chromatographed with silica gel (40 g) using hexane, ethyl ether and ethanol as eluents and produced eight subgroups. The $H_{3.4}$ subgroup was washed with hexane, and recrystallised in hexane/chloroform, giving friedelin (0.025 g). $H_{3.5}$ and $H_{3.6}$ were repeatedly washed with hexane and purified by repeated TLC (silica gel, hexane, chloroform, methanol 60:20:20) to give mammeigin (**1**) (0.2 g). After several chromatographies of H_4 (4.27 g) using silica gel, hexane, chloroform and ethanol as eluents, 4-phenyl-5-hydroxy-6-(3-methyl-1-oxo-butyl)-2′-(1-hydroxy-1-methylethyl)-3′,4′-dihydro(5′,4′:7,8) furancomnarin was obtained. The remaining material from the extraction with hexane was repeatedly extracted with acetone, at room temperature. The extract obtained (160 g) was solubilized in chloroform yielding two phases after filtration. The chloroform solubles were concentrated to 75.38 g and chromatographed with silica gel (1500 g) using hexane, ethyl acetate, ethanol and methanol as eluents. Several fractions were obtained (A_1–A_{21}) by TLC. A_1 was washed with ethyl acetate and recrystallised in an ethyl acetate/chloroform mixture which provided friedelin (0.20 g). A_3–A_8 were repeatedly washed with petroleum ether and recrystallised in a hexane/chloroform mixture to give an additional amount of mammeigin (**1**) (5.5 g). A_{12} and A_{13} were washed with diethyl ether and recrystallised in hexane/acetone, and provided 4-phenyl-5-hydroxy-6-(3-methyl-1-oxo-butyl)-2′-(1-hydroxy-1-methylethyl)-3′,4′dihydro(5′,4′:7,8)furancoumarin. A_{14} was washed with ethyl ether and recrystallised in hexane/chloroform producing 4-phenyl-5-hydroxy-6-(3-hydroxymethyl-1-oxobutyl)-2′,2′-dimethyl(6′,5′:7,8)pyrancoumarin (**2**) (0.23 g).

Hydroxymammeigin (2). Yellow needles, mp 174–176° hexane/chloroform), UV λ_{max}^{MeOH} nm (log ε): 232 (4.53), 284 (4.60), 335 (3.94); $\lambda_{max}^{MeOH+NaOH}$ nm (log ε) 252 (4.45), 308 (4.48), 405 (3.78); acidification reversed the shifts: $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε): 232 (4.48), 286 (4.51), 336 (4.07); $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$ nm identical to the spectrum in MeOH; $\lambda_{max}^{MeOH+AlCl_3}$ nm: identical to the spectrum in MeOH; IR ν_{max}^{KBr} cm^{-1} 3440 (br), 1740, 1720, 1600, 1590, 1380, 1260, 1125, 78O, 750, 700; ^1H NMR (400 MHz, $CDCl_3$): δ 0.98 (3H, d, J = 6.8 Hz, H–5″), 1.57 (6H, s, H–5′ and H-6′), 2.35 (1H, m, H–3″), 3.05 (1H, dd, J = 16.4, 6.6 Hz, H–2a″), 3.20 (1H, dd, J = 16.4, 6.9 Hz, H–2b″), 3.50 (1H, dd, J = 10.4, 6.3 Hz, H–4a″), 3.57 (1H, dd, J = 10.6, 5.3 Hz, H-4b″) 5.62 (1H, d, J = 10.1 Hz, H–2′), 5.98 (1H, s, H–3), 6.88 (1H. d, J = 10.1 Hz, H–1′), 7.30 and 7.38 (2H, m and 3H, m, $–C_6H_5$), 14.55 (1H, s, H-5); EIMS (probe) 70ev m/z (rel. int.): 420 $[M]^+$·(**2**), 402 $[M–H_2O]^+$·(65), 387 $[M–H_2O–Me]^+$ (100), 359 $[M–Me–CO]^+$ (5), 334 (12), 331 (16), 303 (4), 165 (5), 77 (5). The compound gave an olive-green color with methanolic $FeCl_3$.

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Ba – Brasil) for locating the plant. The Voucher specimen is located in Herbarium Central–n° 4583, classified by Santos, T. S. We are indebted to Conselho Nacional de Desenvolvimento Cientifico e Tecnológico (CNPq), Fundação de Amparo a Pesquisa do Estado de Minas Gerais (FAPEMIG), Coordenação de Aperfeiçoamento Pessoal de Ensino Superior (CAPES) and Universidade Federal de Viçosa (UFV) for financial aid.

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