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XANTHONES AND PHENYLCOUMARINS FROM *KIELMEYERA PUMILA*

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Key Word Index—*Kielmeyera pumila*; Guttiferae; pyranoxanthones; phenylcoumarins; isomammeigin.

Abstract—The fruit of *Kielmeyera pumila* have been shown to contain friedelin, α-amyrin, shikimic acid, mammeigin and an isomer of mammeigin, isomammeigin, the structure of which was shown to be 5-hydroxy-6-isovaleryl-2,2-dimethyl-10-phenyl-2H,8H-benzo-[1,2-*b*:3,4-*b*'] dipyran-8-one.

INTRODUCTION

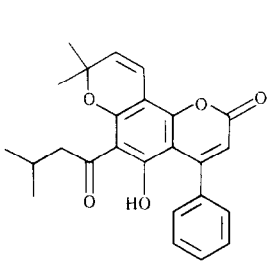
In continuation of our studies on extracts of the Guttiferae family we have examined the stems and fruit of *Kielmeyera pumila* Pohl, collected in the region of Ouro Preto, State of Minas Gerais, from a specimen identified by the botanist José Badini (Herb. Prof. José Badini, Universidade Federal de Ouro Preto, Minas Gerais, Brazil).

Several species of this genus has been shown to contain xanthones [1]. Investigation of the stems of the *K. pumila* has yielded, besides sitosterol, two previously known xanthones (osajaxanthone [2] and 6-deoxyjacareubin [3]) and two known phenylcoumarins, the 1,2-dihydro-5-hydroxy-2-(1-hydroxy-1-methylethyl)-4-(3-methylbutyryl)-6-phenyl-furo [2,3-*h*] [1] benzopyran-8-one [4] and mammeigin (**1**) [5].

The fruit of the same plant yielded friedelin, α-amyrin, shikimic acid, mammeigin and an isomer of mammeigin to which we have given the trivial name isomammeigin (**2**).

RESULTS AND DISCUSSION

Isomammeigin (**2**) showed IR bands at 3400 (chelated hydroxyl), 1745 (α-pyrone) and 700 cm^{-1} (monosubstituted benzene nucleus). Its NMR spectrum shows signals at δ 5.98 (*s*) for a C-3 ethylenic proton and at 7.28 (*m*) for five aromatic protons. The absence of a H-4 signal at δ 7.5–8.3 [6], is reminiscent of some 4-phenylcoumarins [7]. The sharp singlet at δ 0.96 for six protons and the two doublets of one proton each at δ 5.37 ($J = 10$ Hz) and 6.60 ($J = 10$ Hz) respectively establish the presence of a 2,2-dimethyl-Δ^3-pyran ring. The high intensity mass spectral peak of **2** at $[M-15]^+$ (base peak) also supported this conclusion. The signals at δ 1.07 (6 H, *d*, $J = 7$ Hz), 2.29 (1H, *m*) and 3.18 (2H, *d*, $J = 7$ Hz) are assigned to a 3-methyl-1-oxobutyl (isovaleryl) chain and further evidence for this acyl group is provided by the mass spectrum with M^+ at *m/z* 404 and a fragmentation pattern like mammeigin [8]. The hydroxyl resonance of isomammeigin (**2**) at δ 12.27 confirms the presence of the hydroxyl function chelated to the acyl group. The angular fusion of the chromene ring is indicated by the comparatively high field signals for the pyran ring protons caused by the shielding influence of the neighbouring phenyl ring. A similar feature is noted in several natural and synthetic 4-phenylcoumarins [9, 10]. Furthermore, the brown colour produced by isomammeigin (2) in the presence of ethanolic iron (III) chloride and the NMR shifts showed by the isovaleryl protons are in accordance with an 8-acyl coumarin [7, 11]. Based on the these data, we propose the structure of 5-hydroxy-6-isovaleryl-2,2-dimethyl-10-phenyl-2H,8H-benzo-[1,2-*b*:3,4-*b*'] dipyran-8-one (**2**) for isomammeigin. Confirmation for the proposed structure has been obtained by X-ray crystallography [12].



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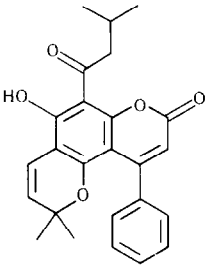

2

EXPERIMENTAL

Mps: uncorr; CC: Kieselgel (0.063–0.200 mm); TLC: Kieselgel 60 G, spots visualized with I_2 vapour and UV fluorescence; IR: only major bands quoted.

Isolation of constituents. Powdered stems of *K. pumila* (0.6 kg) were continuously extracted with hot hexane in a Soxhlet apparatus. Removal of solvent gave a residue (7.0 g) that was chromatographed on silica gel (140.0 g) using hexane, EtOAc and MeOH as eluents. Several fractions were collected and separated into three groups (A_1–A_3) by TLC. A_1 (0.2 g) was recrystallized in hexane giving mammeigin (**1**) (0.075 g). A_2 (0.05 g) was recrystallized in MeOH giving sitosterol (0.014 g). A_3 (0.775 g) was chromatographed on silica gel giving 1,2-dihydro-5-hydroxy-2-(1-hydroxy-1-methylethyl)-4-(3-methylbutyryl)-6-phenyl-furo [2, 3-*h*] [1] benzopyran-8-one [4]. The hexane-extracted powdered stems were continuously extracted with hot EtOH in a

Soxhlet apparatus. The residue (47 g) was repeatedly chromatographed on silica gel (940 g) to give osajaxanthone (0.050 g) and 6-deoxyjacareubin (0.030 g).

The fruits were dried and ground to a powder (200 g) which was thoroughly extracted with hexane in a Soxhlet apparatus. Removal of solvent gave a residue (45.0 g) that was chromatographed on silica gel (230 g) using hexane, $CHCl_3$, and MeOH as eluents. Several fractions were collected and separated into three groups (B_1–B_3) by TLC. B_1 (29.5 g) (hexane–$CHCl_3$, 1:1) was washed with hexane and the insoluble portion extracted with Me_2CO. The Me_2CO was evapd and the residue was purified by repeated TLC (silica gel, C_6H_6) to give mameigin (1.0 g) and friedelin (0.040 g). The hexane-soluble portion of B_1 furnished, after evapn, an orange oily material (22.6 g) which was chromatographed on silica gel (300.0 g) using hexane, $CHCl_3$, and MeOH to give α-amyrin (0.040 g) from the hexane–$CHCl_3$ (13:7) fraction and isomammeigin (**2**) (0.075) g) from the hexane–$CHCl_3$ (1:1) fraction.

The remaining powdered fruit was again extracted with hot EtOH by the same process as described before. The residue (47,8 *g*) gave shikimic acid (0.980 g) after extraction with $CHCl_3$–MeOH (9:1) and chromatography.

Mammeigin (**1**). Yellow needles, mp 148–150° (lit [5] 144–146°). UV λ_{max}^{EtOH} nm: 235, 288, 370 (ε 27230, 31510, 6550); $\lambda_{max}^{EtOH+NaOH}$ nm: 230 sh, 252, 312 (ε 17860, 23030, 25860); acidification reversed the shifts; $\lambda_{max}^{EtOH+NaOAc}$ nm: 240, 305 (ε 19390, 21090); $\lambda_{max}^{EtOH+NaOAC+H_3BO_3}$ nm: identical to the spectrum in EtOH; $\lambda_{max}^{EtOH+AlCl_3}$ nm: identical to the spectrum in EtOH; IR ν_{max}^{KBr} cm^{-1}: 3440 (*br*), 1745, 1645, 1615, 1380, 1125, 775, 750, 710; ^1H NMR [$(CD_3)_2CO$, 100 MHz] : δ 0.96 (6*H*, *d*, *J* = 7.0 Hz, 2 × Me-3′), 1.62 (6H, *s*, 2 × Me-8), 2.08 (1H, *m*, CH-3′), 3.02 (2H, *d*, *J* = 7.0 Hz, CH_2-2′), 5.75 (1H, *d*, *J* = 10.0 Hz, CH-9), 5.84 (1H, *s*, CH-3), 6.75 (1H, *d*, *J* = 10.0 Hz, CH-10), 7.33 (5H, *s*, C_6H_5-4), 14.73 (1H, *s*, OH-5); MS *m/z* (rel. int.): 404 $[M]^+$ (34), 389 (100), 371 (27), 347 (21), 105 (11), 77 (11), 42 (20), The compound gave an olive-green colour with ethanolic $FeCl_3$.

Isomammeigin (**2**). Pale yellow prisms, mp 173–175° (Me_2CO). UV λ_{max}^{EtOH} nm: 265, 273, 314, 373 sh (ε 2500, 25 000, 22 600, 4600); $\lambda_{max}^{EtOH+NaOH}$ nm: 226, 261, 398 (ε 18 700, 24 400, 18 700) acidification reversed the shifts; $\lambda_{max}^{EtOH+NaOAc}$ nm: 262, 398 (ε 19 600, 17 200); $\lambda_{max}^{EtOH+NaOAc+H_3BO_3}$ nm: identical to the spectrum in EtOH; $\lambda_{max}^{EtOH+AlCl_3}$ nm: 265 sh, 273, 316 (ε 21 600, 25 000, 21 000); $\lambda_{max}^{EtOH+AlCl_3+HCl}$ nm: identical to the spectrum in EtOH + $AlCl_3$; IR ν_{max}^{KBr} cm^{-1}: 3400 (*br*), 2920, 1745, 1635, 1605, 1580, 1550, 1380, 1190, 1175, 1150, 1135, 910, 870, 790, 755, 700; ^1H NMR ($CDCl_3$, 100 MHz): δ 0.96 (6H, *s*, 2 × Me-2), 1.07 (6H, *d*, *J* = 7.0 Hz, Me-3′), 2.29 (1H, *m*, CH-3′), 3.18 (2H, *d*, *J* = 7.0 Hz, CH_2-2′), 5.37 (1H, *d*, *J* = 10.0 Hz, CH-3), 5.98 (1H, *s*, CH-9), 6.60 (1H, *d*, *J* = 10.0 Hz, CH-4), 7.28 (5H, *m*, C_6H_5-10), 12.27 (1H, *s*, OH-5); MS *m/z* (rel. int.): 404 $[M]^+$ (22), 389 (100), 371 (11), 347 (10). (Found: C 74.29; H 6.05; $C_{25}H_{24}O_5$ requires C, 74.24; H 5.98%). The compound gave a brown colour with ethanolic $FeCl_3$.

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REFERENCES

1. Sultanbawa, M. V. S. (1980) *Tetrahedron* **36**, 1465.
2. Wolfrom, M. L., Komitsky, F. and Looker, J. H. (1965) *J. Org. Chem.* **30**, 144.
3. Gottlieb, O. R., Magalhães, M. T., Pereira, M. O. da S., Mesquita, A. A. L., Corrêa, D. B. and Oliveira, G. G. (1968) *Tetrahedron* **24**, 1601.
4. Crombie, L., Gomes, D. E., Haskins, N. J. and Reed, G. F. (1972) *J. Chem. Soc. Perkin Trans 1*, **18**, 2248.
5. Finnegan, R. A. and Mueller, W. H. (1964) *Chem. Ind.* 1065.
6. Steck, W. and Mazureck, M. (1972) *Lloydia* 418.
7. Crombie, L., Games, D. E. and McCormick, A. (1967) *J. Chem. Soc. C*, 2553.
8. Murti, V. S. S., Kumar, P. S. S. and Seshadri, T. R. (1972) *Indian J. Chem.* **10**, 19.
9. Nigam, S. K. and Mitra, C. R. (1967) *Tetrahedron Letters* **28**, 2633.
10. Matsui, T., Nishimura, S., Nakayama, M., Hayashi, S. and Fukwi, K. (1977) *Bull. Chem. Soc. Jpn* **50**, 1975.
11. Crombie, L., Games, D. E. and McCormick, A. (1967) *J. Chem. Soc.* 2545.
12. Castellano, E. E., Zukerman-Schpector, J., Abreu e Silva, M de and Nagem, T. J. (1988) *Acta Crystallog.* (in press).