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A COUMARIN FROM AERIAL PARTS OF *GEIJERA PANICULATA*

ACHILLE NOUGA BISSOUÉ, FRÉDÉRIC MUYARD, FRANÇOISE BÉVALOT, THOMAS G. HARTLEY,* FRANÇOIS TILLEQUIN,† JACQUELINE VAQUETTE and PETER G. WATERMAN‡§

Laboratoire de Pharmacognosie, Faculté de Médécine et de Pharmacie, Place Saint-Jacques, 25030 Besançon, France; * Australian National Herbarium, GPO Box 1600, Canberra, ACT 2601, Australia; † Département de Pharmacognosie, U.A. au. C.N.R.S. 1310, Université René Descartes, 4 avenue de l'Observatoire, 75006 Paris, France; ‡ Phytochemistry Research Laboratories, Department of Pharmaceutical Sciences, University of Strathclyde, Glasgow G1 1XW, U.K.

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Key Word Index—*Geijera paniculata*; Rutaceae; eriostoic acid; eriostemoic acid; coumarin; 5-methoxy-8-(3-methylbut-2-enyloxy)-2′,2′-dimethylpyrano-[3,2-*g*]-benzopyran-2-one; 8-*O*-(3-methylbut-2-enyl)xanthoxyletin.

Abstract—The bark and leaves of *Geijera paniculata* have yielded two common acidic constituents, eriostoic and eriostemoic acids, and a novel coumarin, whose structure was established on the basis of spectral data, as 5-methoxy-8-(3-methylbut-2-enyloxy)-2′,2′-dimethylpyrano-[3,2-*g*]-benzopyran-2-one (trivial name, 8-*O*-(3-methylbut-2-enyl)xanthoxyletin. © 1997 Elsevier Science Ltd

INTRODUCTION

Geijera Schotte is a genus of small trees found in Australia, New Guinea and New Caledonia [1]. *Geijera paniculata* (F. Muell.) Druce occurs only in Queensland and has not previously been investigated. Investigations of three other species [2, 3], *G. parviflora* Lindley, from Australia, *G. salicifolia* Schott., from Australia, and *G. balansae* Schintz et Guill., from New Caledonia, have revealed a range of anthranilic acid-derived alkaloids and coumarins that are typical of the Rutaceae. In this paper, we report the results of an investigation of *G. paniculata* and the isolation and identification of a novel pyranocoumarin.

RESULTS AND DISCUSSION

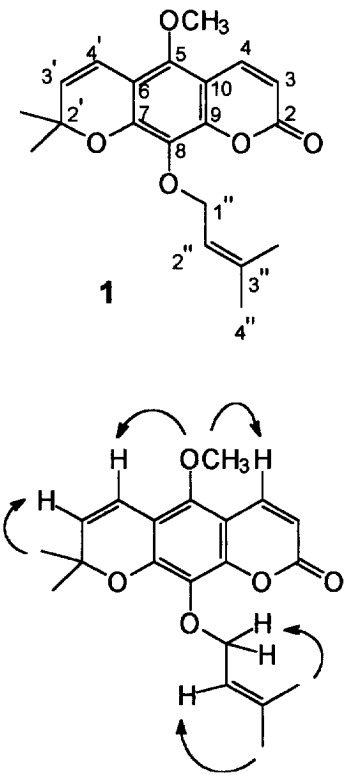
Column chromatography of the petrol (bp 40–60°) extract of the aerial parts of *G. paniculata* over silica gel, followed by preparative TLC, yielded eriostemoic acid [4, 5] and the new compound **1**. Similar treatment of the chloroform extract yielded eriostoic acid [5].

The new compound (**1**) was obtained as a white amorphous solid (content 0.0016% of the dried plant material). The UV spectrum displays characteristic absorptions of a 5,7,8-trioxygenated coumarin [6], which was substantiated by the ^{13}C NMR spectrum [7]. The HRCl mass spectrum, with a $[M]^+$ at *m/z* 343 $[M+H]^+$, suggested the empirical formula $C_{20}H_{22}O_5$. Analysis of the ^1H NMR spectrum indicated the presence of H-3 and H-4 of a coumarin, an aromatic methoxyl group and two deshielded vinylic methyl singlets which, together with an AB-system, could be attributed to a 3-methylbut-2-enyloxy side-chain. The latter was confirmed by an important ion at *m/z* 275 $[M-C_5H_8]^+$ in the Cl mass spectrum. The remaining signals in the ^1H NMR spectrum were for two methyls attached to a quaternary carbon and an AB-system, which were typical of a fused dimethylpyran unit.

Location of the substituents was deduced unambiguously from strong cross-peaks on the NOESY spectrum (Scheme 1) between the methoxyl protons and the benzylic protons of the coumarin (H-4) and the pyran ring (H-4′), so requiring a pyrano-[3,2-*g*]-benzopyran-2-one. The structure of **1** was therefore established as 5-methoxy-8-(3-methylbut-2-enyloxy)-2′,2′-dimethylpyrano-[3,2-*g*]-benzopyran-2-one, to which we have assigned the trivial name 8-*O*-(3-methylbut-2-enyl)xanthoxyletin.

The yield of secondary metabolites from this sample of *G. paniculata* was rather disappointing. Like all other *Geijera* species investigated to date it is able to produce coumarins. A pyranocoumarin (xanthoxyletin) had hitherto been found only in the New Caledonian species, *G. balansae*, while the other two Australian species had given simple coumarins. Eriostoic and eriostemoic acids are linear and angular dipyranodihydrocinnamic acid derivatives which appear to be quite common in Australian Rutaceae of the Boronieae but have not previously been reported in

§ Author to whom correspondence should be addressed.



Scheme 1. Correlations in NOESY spectrum of compound 1.

Geijera. Geijera is not generally associated with the Boronieae. However, the most surprising feature of this sample was the apparent absence of furoquinoline and/or pyranoquinoline alkaloids, which had previously been a feature of the genus.

EXPERIMENTAL

General. Extractions were carried out using a Soxhlet apparatus. UV: in MEOH. MS: in El or Cl mode. NMR: 300 MHz in $CDCl_3$; COSY, HETCORR and NOESY experiments were performed using the standard Bruker microprograms.

Plant material. Collected at Wide Bay, Didcot, Stony Creek, Queensland, on the 24th October 1991. A voucher (Hartley 15174) is deposited at the Australian National Herbarium.

Extraction. Dried powdered aerial parts (600 g) were extracted with petrol (bp 40–60°), then $CHCl_3$ and finally MeOH. The petrol extract (1.4 g) was purified by CC (silica gel 60 Merck, particle size 0.063–0.200 mm) packed in petrol. Elution was performed with petrol containing increasing amounts of $CHCl_3$, and then $CHCl_3$. Prep. TLC on silica gel 60 F254 (*n*-hexane–EtOAc, 1:1) of the frs obtained from petrol–EtOAc (4:1) yielded **1** (10 mg). Similar treatment of the frs from petrol–EtOAc (1:1) afforded eriostemoic acid (20 mg). The $CHCl_3$ extract (1.3 g) was subjected to silica gel CC eluting with *n*-hexane containing increasing amounts of $CHCl_3$, and then $CHCl_3$ containing increasing amounts of MeOH. Frs obtained from $CHCl_3$ were purified by further CC to give eriostoic acid (200 mg). Eriostemoic acid and eriostoic acid were identified by comparison with lit. data [4, 5].

8-O-(3-*Methylbut-2-enyl*)*xanthoxyletin* (**1**). Amorphous solid. UV: λ_{max} nm ($\log\varepsilon$): 209 (4.61), 235 sh (4.57), 277 (4.49), 328 (4.21). ^{1}H NMR: δ 1.51 (6H, *s*, 2×2′-Me), 1.72, 1.75 (2×3H, 2×*s*, 3″-Me, 4″-H_3), 3.85 (3H, *s*, OMe), 4.60 (2H, *d*, J = 7.2 Hz, H_2-1″), 5.60 (1 H, *t*, J = 7.2 Hz, H-2″), 5.72 (1H, *d*, J = 10.1 Hz, H-3′), 6.22 (1H, *d*, J = 9.7 Hz, H-3), 6.58 (1H, *d*, J = 10.1 Hz, H-4′), 7.85 (1H, *d*, J = 9.7 Hz, H-4). ^{13}C NMR δ (* assignments may be reversed): 18.2, 25.8 (3″-Me, C-4″), 28.1, 29.7 (2′-Me_2), 63.8 (OMe), 70.0 (C-1″), 72.2 (C-2′), 107.2 (C-6), 111.7 (C-10), 112.5 (C-3), 116.0 (C-4′), 120.2 (C-2″), 130.5 (C-3′), 131.3 (C-8), 138.6 (C-4), 139.2 (C-3″), 147.9* (C-9), 148.7* (C-7), 150.4* (C-5), 160.5 (C-2). HRCIMS: found $[M]^+$ 342.1471; $C_{20}H_{22}O_5$ requires 342.1467.

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