Pergamon

Phytochemistry, Vol. 43, No. 4, pp. 877–879, 1996
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0031-9422/96 $15.00 + 0.00

PII: S0031-9422(96)00355-X

COUMARINS FROM THE AERIAL PARTS OF *CHORILAENA QUERCIFOLIA*

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(*Received* 15 *April* 1996)

Key Word Index—*Chorilaena quercifolia*; Rutaceae; coumarins; 8,9-dihydro-8-(1-hydroxy-1-methylethyl)-6-(3-methylbut-2-enyloxy)furo-[2,3-*h*]-benzopyran-2-one; 7-(3,7-dimethyl-5-oxooct-6-enyloxy)coumarin; chemotaxonomy.

Abstract—The aerial parts of *Chorilaena quercifolia* have yielded one alkaloid, skimmianine, two common coumarins, 5,7,8-trimethoxycoumarin and marmesin, and two novel coumarins whose structures were established on the basis of spectral data, as 7-(3,7-dimethyl-5-oxooct-6-enyloxy)coumarin and 8,9-dihydro-8(1-hydroxy-1-methylethyl)-8-(3-methylbut-2-enyloxy)furo-[2,3-*h*]-benzopyran-2-one. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Chorilaena quercifolia Endl. is a shrub confined to the south west corner of Western Australia. Previous studies on the chemistry of the species have yielded the simple furoquinoline alkaloid dictamnine [1]. According to Engler's classification of the Rutaceae [2] *Chorilaena* is assigned to the subtribe Nematolepidinae of the tribe Boronieae. Little is known about the chemistry of the entirely West Australian Nematolepidinae other than the report of a pyranocoumarin and a coumarin dimer from *Nematolepis phebaloides* [3]. Recent re-evaluation of relationships between West Australia Rutaceae (J. A. Armstrong, unpublished) suggests that *Chorilaena* has morphological similarities with some taxa currently assigned to the large genus *Phebalium*, notably *P. squameum* and *P. anceps*. Previous studies carried out by Strathclyde and Besançon have revealed that *P. squameum* is a rich source of 7-geranyloxycoumarins [4, 5] while *P. anceps* yielded 7-geranyloxycoumarins and linear furocoumarins and dihydrofurocoumarins [4, 6].

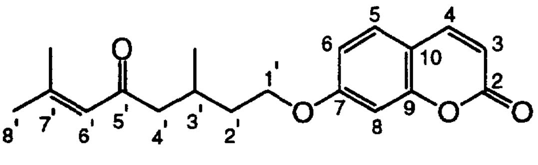
In this paper we report on the isolation of coumarins from the aerial parts of *Chorilaena quercifolia* and assess their value as taxonomic markers.

RESULTS AND DISCUSSION

Column chromatography of the petroleum ether (bp 40–60°) extract of the aerial parts over silica gel followed by preparative TLC yielded the new compound **1**. Similar treatment of the chloroform extract yielded the two known coumarins, 5,7,8-trimethoxycoumarin [7] and marmesin [8], together with a second novel coumarin (**2**) and the common alkaloid skimmianine [9].

The empirical formula of **1** was established as $C_{16}H_{22}O_4$ by HR-mass spectrometric analysis and the UV spectrum was characteristic of a 7-oxygenated coumarin [10]. In agreement with this the ^{1}H NMR spectrum exhibited signals for H-3 and H-4 of the pyran ring of a coumarin together with three aromatic signals in an ABD system for H-5, H-6 and H-8. Analysis of the remaining signals in the ^{1}H and ^{13}C NMR spectra with the aid of COSY and HETCORR were indicative of an $-O-CH_2CH_2CHMeCH_2CO-CH{=}CMe_2$ side chain and this was substantiated by an ion at m/z 153 $[C_{10}H_{17}O]^+$ in CI-mass spectrometry. The structure of compound **1** was therefore established as 7-(3,7-dimethyl-5-oxooct-6-enyloxy)coumarin.

The UV spectrum of compound **2** ($C_{19}H_{22}O_5$, HR-mass spectrometry) exhibited characteristic absorptions associated with a 6,7-dioxygenated coumarin [10]. Analysis of the ^{1}H NMR spectrum indicated a single aromatic proton signal at δ 6.95. Two deshielded vinylic methyl singlets together with an AB_2 system could be attributed to a 3-methylbut-2-enyloxy side chain, which was confirmed by an important ion at m/z 233 $[M - C_5H_8]^+$ in the CI-mass spectrum. The remaining signals were for two methyls attached to an oxygenated quaternary carbon and an ABX system



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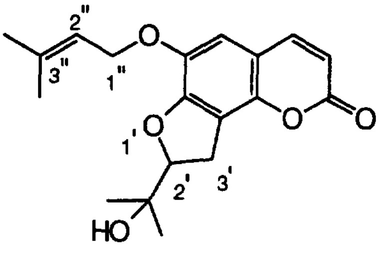

2

which were typical of a hydroxyisopropyldihydrofuran ring system. The ^{13}C NMR spectrum confirmed that oxygenation occurred at C-6 and C-7 rather than C-7 and C-8 and gave signals compatible with the components identified from the ^{1}H NMR spectrum.

Finally the placement of the single aromatic proton at C-5 on the aromatic ring of the coumarin nucleus was unambiguously confirmed from a strong crosspeak between H-5 and H-4 in the NOESY spectrum, so requiring a furo[2,3-*h*]coumarin skeleton. The structure of **2** was therefore established as 8,9-dihydro-8-(1-hydroxy-1-methylethyl)-6-(3-methylbut-2-enyloxy)furo[2,3-*h*]benzopyran-2-one.

This study confirms that like most members of the Boronieae *C. quercifolia* is able to produce a range of coumarins. The presence of **1** fits well with the proposed association of *C. quercifolia* with *Phebalium squameum* and *P. anceps*. The latter are both characterized by production of a series of 7-geranyloxycoumarins. In *P. squameum* these have, like **1**, the C-5′ of the side chain oxidised to a carbonyl, but this is not the case in *P. anceps* [4]. Important biosynthetic steps in the formation of **2** include C-8 prenylation and subsequent cyclization. The first of these two steps occurs widely in *Phebalium* species but is not currently known from either *P. anceps* or *P. squameum* [4] while formation of angular furo-[2,3-*h*]-coumarins has only been recorded once, in *P. stenophyllum* [4]. On the other hand prenylation at C-6 followed by cyclization to give the common furo-[2,3-*g*]-coumarin nucleus (as in marmesin) is seen in both *C. quercifolia* and *P. anceps*.

EXPERIMENTAL

Extractions were carried out using a Soxhlet apparatus. UV: Shimadzu UV I 60A in MeOH; MS: Nermag R-10-10-H in CI mode (NH_3); NMR: Bruker AC300 (300 MHz) in $CDCl_3$, COSY, HETCORR and NOESY experiments were performed using the standard Bruker microprograms.

Plant material. Aerial parts were collected in open karri (*Eucalyptus diversicolor*) forest; Gully Road, about 3 km east of Walpole (*ca* 400 km south-east of Perth) in Western Australia. A voucher (PERTH 02294192) has been deposited at the Herbarium of Western Australia.

Extraction. Dried powdered aerial parts (500 g) were extracted with petrol (bp 40–60°), then $CHCl_3$ and finally MeOH. The concd petrol extract (2.2 g) was submitted to CC using silica gel 60 Merck (particle size 0.063–0.200 mm) packed in petrol (bp 40–60°). Elution was performed with petrol containing increasing amounts of $CHCl_3$, and then with $CHCl_3$. Prep. TLC on silica gel 60 F_{254} (solvent: *n*-hexane–EtOAc, 7:3) of the frs obtained from $CHCl_3$ yielded **1** (3 mg). The $CHCl_3$ extract (1.1 g) was subjected to silica gel CC eluting with *n*-hexane containing increasing amounts of $CHCl_3$. Frs obtained from *n*-hexane–$CHCl_3$ (1:1) were purified by successive CC and prep. TLC (solvent: *n*-hexane–EtOAc (1:1)) to give 5,7,8-trimethoxycoumarin (3 mg), marmesin (2 mg), skimmianine (6 mg) and **2** (4 mg).

7-(3,7-dimethyl-5-oxooct-6-enyloxy)coumarin (**1**). Oil. UV: λ_{max} nm: 207, 221 (sh), 292 (sh), 317. CI-MS *m/z* (rel. int.): 332 $[M+NH_4]^+$ (26), 315 $[M+H]^+$ (100), 153 (8). HR-MS. Found M^+ 314.1509; $C_{19}H_{22}O_4$ requires 314.1518. ^{1}H NMR: δ 7.63 (1H, *d*, $J = 9.5$ Hz, H-4), 7.35 (1H, *d*, $J = 8.5$ Hz, H-5), 6.82 (1H, *dd*, $J = 8.5$, 2.4 Hz, H-6), 6.78 (1H, *d*, $J = 2.4$ Hz, H-8), 6.24 (1H, *d*, $J = 9.5$ Hz, H-3), 6.08 (1H, *q*, $J = 1.2$ Hz, H-6′), 4.07 (2H, *t*, $J = 6.5$ Hz, H-1′), 2.52 (1H, *m*, H-4′), 2.38 (1H, *m*, H-4′), 2.31 (1H, *m*, H-3′), 2.12 (3H, *d*, $J = 1.2$ Hz, 7′-Me), 1.88 (3H, *s*, H-8), 1.88 (1H, *m*, H-2′), 1.78 (1H, *m*, H-2′), 1.05 (3H, *d*, $J = 7.5$ Hz, 3′-Me). ^{13}C NMR: δ 200.4 (C-5′), 162.1 (C-2), 161.3 (C-7), 159.9, 155.5 (C-9, C-7′), 143.4 (C-4), 128.7 (C-5), 124.0 (C-6′), 113.0 (C-3, C-6), 112.4 (C-10), 101.4 (C-8), 66.7 (C-1′), 51.4 (C-4′), 35.7 (C-2′), 27.7 (C-8′), 26.7 (C-3′), 20.7 (7′-Me), 20.0 (3′-Me).

8,9-Dihydro-8-(1-hydroxy-1-methylethyl)-6-(3-methylbut-2-enyloxy)furo-[2,3-h]-benzopyran-2-one (**2**). Oil. UV: λ_{max} nm: 205, 223 (sh), 248, 258 (sh), 292 (sh), 328. CI-MS *m/z* (rel. int.): 348 $[M+NH_4]^+$ (25), 331 $[M+H]^+$ (100), 263 (41), 245 (16), 197 (7). HR-MS: Found M^+ 330.1458; $C_{19}H_{22}O_5$ requires 330.1467. ^{1}H NMR: δ 7.57 (1H, *d*, $J = 9.5$ Hz, H-4), 6.96 (1H, *s*, H-5), 6.21 (1H, *d*, $J = 9.5$ Hz, H-3), 5.56 (1H, *t*, $J = 7.2$ Hz, H-2″), 4.75 (2H, *d*, $J = 7.2$ Hz, H-1″), 4.75 (1H, *br.t*, $J = 8.8$ Hz, H-2′), 3.26 (1H, *ddd*, $J = 17.0$, 8.4, 1.2 Hz, H-3′), 3.21 (1H, *dd*, $J = 17.0$, 9.1, 1.0 Hz, H-3′), 1.74 (3H, *s*, 3″-Me), 1.70 (3H, *s*, 3″-Me), 1.39, 1.24 (2×3H, $2 \times s$, isopropanol $2 \times$ Me). ^{13}C NMR: δ 160.9 (C-2), 150.4 (C-7), 149.6 (C-9), 147.2 (C-6), 143.9 (C-4, C-3″), 124.2 (C-8), 120.1 (C-2″), 117.1 (C-5), 114.4 (C-10), 112.5 (C-3), 91.4 (C-2′), 71.7 (C(OH)Me_2), 69.5 (C-1″), 29.7 (C-3′), 26.1, 24.2 (C(OH)Me_2), 25.9, 18.1 (3″-Me_2).

Acknowledgement—The authors wish to thank Mrs Amy Régnier for her practical help in the isolation of the new compounds.

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