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A COUMARIN FROM *PEREZIA COERULESCENS*

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Key Word Index—*Perezia coerulescens*; Compositae; roots; 3,4,8-trimethoxy-5-formyl coumarin; structural determination.

Abstract—The roots of *Perezia coerulescens* contain ψ-taraxasteryl acetate, β-amyrin acetate, 8-hydroxyperefiorin, pereflorin B and a new compound identified as 3,4,8-trimethoxy-5-formyl coumarin.

Perezia coerulescens Wedd., from the Andes region, is the second species of the South American section *Perezia* [1] of the genus *Perezia* that has been studied. As in the case of *P. multiflora* [2, 3], no quinones were found, in contrast to their presence [4–6] in the North American section *Acourtia* [7] of the genus.

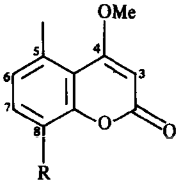
The hexane extracts of *P. coerulescens* gave the triterpenes ψ-taraxasteryl acetate and β-amyrin acetate [8], while from the chloroform extracts we now describe the isolation and characterization of three coumarins. Two were identified as compounds **2** and **7** from spectral data, their structures subsequently being confirmed by direct comparison with authentic samples of 8-hydroxypereflorin (**2**) [6] and pereflorin B (**7**) [3].

The third compound provided spectral data that indicated its structure to be **6**. The ^{1}H NMR spectrum was very informative since it showed the presence of three methoxyl singlets at δ4.30, 4.01 and 3.98, an aldehyde proton at 10.67 and two *ortho* protons on an aromatic ring as an AB system at 7.84 and 7.07 with $J = 8.6$ Hz. Their distribution on a coumarin skeleton as in **6** is consistent with the chemical shifts of the aromatic protons when calculated from **5** [3] by replacing the group effect [9] of a methyl substituent for an aldehyde. The MS, IR and UV data given in the Experimental further support the structure.

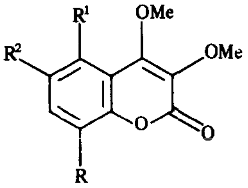
The isolation of **2**, **6** and **7** from *P. coerulescens* combined with the presence of **1**, **3**–**5** and **7** in *P. multiflora* [2, 3] indicates a close relationship between species in the South American section of the genus.

EXPERIMENTAL

Perezia coerulescens Wedd. was collected at Chicla, Perú near km 117 Central Highway (Lima–Huancayo), 3750 m above sea level in December 1980 and January 1981. Voucher samples have been deposited at Instituto de Botánica, Universidad Nacional Mayor de San Marcos, Lima, Perú where Prof. J. López Guillén identified the material Hexane extracts of the ground roots (400 g) gave ψ-taraxasteryl acetate and β-amyrin acetate [8]. Further chloroform extracts were evapd to dryness and the residue exhaustively extracted with hot C_6H_6. The conc. C_6H_6 extract was chromatographed over silica gel (100 g) yielding 4 mg **7** (C_6H_6–$CHCl_3$, 4 : 1), 2 mg **6** (C_6H_6–$CHCl_3$, 3 · 7) and 25 mg **2** (C_6H_6–$CHCl_3$, 1 . 9) Spectral data and direct comparison with authentic samples established the identities of **2** and **7** [3, 6].



	R
1	H
2	OH
3	OMe



4 R = H; R^1 = Me; R^2 = H
5 R = OMe; R^1 = Me, R^2 = H
6 R = OMe; R^1 = CHO; R^2 = H
7 R = OMe; R^1 = CHO; R^2 = OH

Compound **6**. Pale yellow needles ($CHCl_3$–C_6H_{14}), mp 185–187°; IR: Nicolet MX-1-FT, KBr; 1725 (broad, coumarin and aldehyde) 1669, 1586, 1576 cm^{-1} (aromatics); UV: $\lambda_{max}^{95\%\,EtOH}$ 225, 260, 301 nm (ε = 28 200, 14 100, 16 300); ^{1}H NMR: Varian XL-100-12 FT 16 K, $CDCl_3$ int. TMS; δ 10.67 (aldehyde), 7.84 (*d*, $J = 8.6$ Hz, H-6), 7.07 (*d*, $J = 8.6$ Hz, H-7), 4.30 4.01 and 3 98 (3s, OMe); MS: 70 eV; $[M]^+$ *m/z* 264 (100%).

Acknowledgements—We are indebted to Prof. J. López Guillén for botanical identification, to Prof. H. Wagner (Münich, F.R.G.) for a ^{13}C NMR spectrum of **2**, and to Dr. F. Walls (University of México) for a mass spectrum of **6**

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ANGUSTIFOLIN, A COUMARIN FROM *RUTA ANGUSTIFOLIA*

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Key Word Index—*Ruta angustifolia*; Rutaceae; coumarins; angustifolin; scoparone; 6,7,8-trimethoxycoumarin; alkaloid; graveolin

Abstract—From the aerial parts of *Ruta angustifolia*, a new natural coumarin, angustifolin, was obtained. Two other coumarins (scoparone and 6,7,8-trimethoxycoumarin) and the alkaloid graveolin were also isolated.

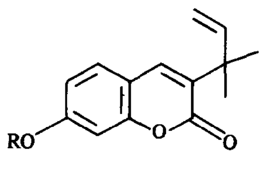
From the chloroform extract of 2.1 kg of aerial parts of *Ruta angustifolia* Pers., collected in San Agustín de Guadalix, Madrid province, Spain, a new natural coumarin, angustifolin (**1**) has been isolated. This coumarin was found in a very small amounts (about 15 mg and it could not be crystallized) together with the alkaloid graveolin (**2**) and the two coumarins scoparone (**3**) and 6,7,8-trimethoxycoumarin (**4**), from which it was separated by flash chromatography.

Angustifolin shows blue fluorescence in UV light; it absorbs at $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 325 (4.01), 297 (h, 3.83), 269 (3.64) and 258 (h, 3.66); IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3400, 1740, 1630; ^{1}H NMR (CDCl$_3$): δ7.53 (*s*, H, β-coumarin proton), aromatic protons H-5, H-8 and H-6 at 7.30 (*d*, H, J = 7 Hz), 6.94 (*d*, H, J = 2 Hz) and 6.80 (*dd*, H, J = 7, J' = 2 Hz) respectively, and 1.47 (*s*, 6H, gem-dimethyl), vinylic group signals at 6.15 (*dd*, H, J = 17.4, J' = 10.5 Hz), 5.09 (*dd*, H, J' = 10.5, J'' = 0.9) and 5.08 (*dd*, H, J = 17.4, J'' = 0.9 Hz); MS at m/z (rel. int.): 230 (3.7 %) $[\mathrm{M}]^+$, 215 (4.8 %) $[\mathrm{M}-\mathrm{CH}_3]^+$, 202 (8.8 %) $[\mathrm{M}-\mathrm{CO}]^+$ and 161 (5.1 %) $[\mathrm{M}-\mathrm{CMe}_2\ \mathrm{CH{=}CH}_2]^+$.

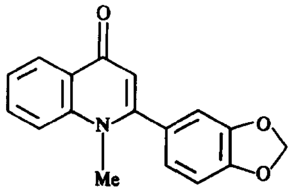
These data suggest that angustifolin must be 3-(1′,1′-dimethylallyl)-7-hydroxycoumarin (**1**), which possibly has been produced in the plant from 7-(3′,3′-dimethylallyloxy)-coumarin through a multiple rearrangement. The structure was confirmed by treatment of **1** with $\mathrm{Me_2SO_4}$–$\mathrm{K_2CO_3}$–$\mathrm{Me_2CO}$, yielding **5**, a substance obtained before from *Ruta graveolens* roots [1] and later synthesized [2]. Compound **5** was identified by its ^{1}H NMR spectrum.

EXPERIMENTAL

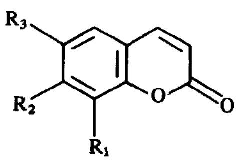
Material was collected by the authors during the plant's flowering season, in June, 1982. The plant was classified by Dr J Fernández Casas, of the Departamento de Botánica, Universidad Autónoma de Madrid, to whom the authors express their gratitude. Voucher specimens were deposited in the Herbario del Jardín Botánico de Madrid, where they are classified with n° of



1 R = H
5 R = Me



2



3 R$_1$ = H, R$_2$ = R$_3$ = OMe
4 R$_1$ = R$_2$ = R$_3$ = OMe