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# PURPURASOLOL, A HIGHLY OXYGENATED COUMARIN FROM *PTEROCAULON PURPURASCENS*

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**Key Word Index**—*Pterocaulon purpurascens*; Compositae; 5,6,7,8-tetraoxygenated coumarin; purpurasolol; fraxetin.

**Abstract**—A new 5,6,7,8-tetraoxygenated coumarin, purpurasolol, has been isolated from *Pterocaulon purpurascens* and its structure was determined by spectroscopic analysis. Fraxetin was also isolated for the first time from this plant.

## INTRODUCTION

The aerial parts of *Pterocaulon purpurascens* have many applications in Argentine folk medicine [1–4]. In our previous reports we described the isolation and identification of flavonoids [5], the caffeoylquinic acid content [6] and two highly oxygenated coumarins, i.e. purpurenol [7] and purpurasol [8]. Now we describe the isolation and structural determination of purpurasolol (**1**), a new related coumarin, from the same source. The known coumarin, fraxetin, was also isolated for the first time from the same extract.

## RESULTS AND DISCUSSION

The new coumarin (**1**), related to purpurenol (**2**) and purpurasol (**3**), was isolated from the methylene chloride extract of *Pterocaulon purpurascens*. The structure of **1** was elucidated on the basis of its spectral data and was given the trivial name purpurasolol. The UV spectrum (Experimental) was consistent with a coumarin oxygenated at C-7 [9] and showed the same pattern of the tetraoxygenated coumarin **2**. On adding sodium methoxide there was a bathochromic shift, an additional band appearing at 415 nm with lower intensity, showing that it was a phenolic coumarin [10]. This new UV spectrum seems to be characteristic for 5-hydroxy-8-substituted coumarins [11].

The 500 MHz $^1$H NMR spectrum of **1** showed a pair of doublets at $\delta$ 6.22 and 7.99 (1H each, $J = 9.6$ Hz) assigned to the vinylic protons H-3 and H-4, respectively. The deshielded nature of H-4 suggested that there was an oxygen function at the C-5 position [12]. As there were no other signals between this pair of doublets in the aromatic region, compound **1** was clearly established as a 5,6,7,8-tetrasubstituted coumarin derivative. The singlet signal at $\delta$ 3.91 (3H) was attributed to an aromatic methoxyl group. The remaining doublets of doublets at $\delta$ 3.94 ($J = 9.4$ and 2.0 Hz), 4.14 ($J = 11.3$ and 9.4 Hz) and 4.62 ($J = 11.3$ and 2.0 Hz) (1H each) were consistent with a methine and methylene protons in a 1,4-dioxane ring ($O{-}CH_2{-}CH{-}O$). The singlet signals at $\delta$ 1.45 and 1.37 (3H each) and 2.60 (1H, *br s*) indicated the presence of a *gem*-dimethyl and an aliphatic hydroxyl group. These results were in good agreement with the assigned values for the closely related compounds **2** and **3**, whose structures were established by X-ray diffraction and advanced NMR pulse sequences (DIFNOE, HETCOR, COLOC, and low power heteronuclear decoupling), respectively [7, 8, 13].

The assigned structure of **1** was also supported by the EI mass spectrum, which showed the molecular ion $[M]^+$ ($C_{15}H_{16}O_7$) at $m/z$ 308. The intense fragment ion at $m/z$ 250 $[M^+ - C_3H_6O]^+$ indicated the elimination of 58 mass units, undergoing facile loss of 15 mass units to give the ion at $m/z$ 235 $[M^+ - C_3H_6O{-}Me]^+$, thus revealing that the aromatic methoxyl group must

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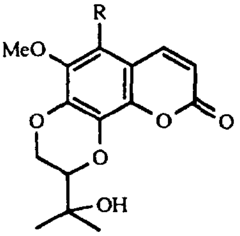
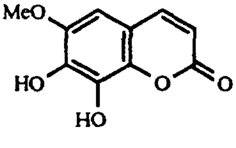


**1**: R = OH
**2**: R = OMe
**3**: R = H



**4**

be linked to C-6 [14]. This fragmentation pattern was consistent with those reported for the previously isolated coumarins **2** and **3**.

The $^{13}C$ NMR signals of **1** (Experimental) were assigned by DEPT, coupled and decoupled experiments and by comparison with those of the related tetraoxygenated coumarin **2**. The presence of only one methoxyl signal at $\delta$ 61.55 ($q$) and the C-5 signal at $\delta$ 131.04, shifted upfield by *ca* 8 ppm respective to **2** (C-5 at $\delta$ 139.7 in **2**), revealed that the hydroxyl group must be unequivocally located on C-5.

The known coumarin, fraxetin (**4**) [15], was also isolated and identified by its UV, mass and $^1H$ NMR spectra and by chromatographic comparison with an authentic sample. Further experiments with purpurenol revealed that it had an $[\alpha]_D$ value of +75° ($c$ = 1.01; $CHCl_3$).

## EXPERIMENTAL

*General.* Mps: uncorr. The $^1H$ and $^{13}C$ NMR were recorded at 500 and 125 MHz, respectively, in $CDCl_3$, using TMS as int. standard. EIMS: 70 eV, direct insert. UV spectra were recorded in MeOH, followed by addition of NaOMe and recording 1 and 5 min later.

*Plant material.* Aerial parts of *Pterocaulon purpurascens* were collected in Chaco, Argentina, by Prof. A. Schultz. Voucher specimens are deposited at the Botanical Museum 'Juan A. Domínguez' in Buenos Aires.

*Extraction and isolation.* Dried and powdered aerial parts of *P. purpurascens* (800 g) were successively extracted with petrol, $CH_2Cl_2$, EtOAc and MeOH in a Soxhlet apparatus. The $CH_2Cl_2$ extract (752 mg) was subjected to CC on Polyclar, eluted with a $C_6H_6$–EtOAc solvent mixt. of increasing polarity to give **1** (20 mg) and (**4**) (15 mg).

*Purpurasolol* {*2,3-dihydro-6-hydroxy-2-(1-hydroxy-1-methylethyl)-5-methoxy-9H-pyrano*[2,3-f]*-1,4-benzodioxin-9-one*} (**1**). Yellow prisms (MeOH), mp 160–162°. UV $\lambda_{max}^{MeOH}$ nm: 217, (235), 267, 327; $\lambda_{max}^{NaOMe}$: 220, (235), 280, 332, 415. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.99 (1H, *d*, $J$ = 9.6 Hz, H-4), 6.22 (1H, *d*, $J$ = 9.6 Hz, H-3), 4.62 (1H, *dd*, $J$ = 2.0, 11.3 Hz, O–CH(H)–CH–O), 4.14 (1H, *dd*, $J$ = 9.4, 11.3 Hz, O–CH(H)–CH–O), 3.94 (1H, *dd*, $J$ = 2.0, 9.4 Hz, O–$CH_2$–CH–O), 3.91 (3H, *s*, OMe), 3.0–1.7 (1H, *br s*, OH), 1.45, 1.36 (each 3H, each *s*, $Me_2$). $^{13}C$ NMR (125 MHz, $CDCl_3$); 25.08, 25.09 (each *q*, $Me_2$), 61.55 (*q*, OMe), 65.89 (*t*, $OCH_2$), 70.66 (*s*, $Me_2\underline{C}$–OH), 78.70 (*d*, CH–O), 102.24 (*s*, C-4a), 112.06 (*d*, CH-3), 138.83 (*d*, CH-4), 125.89, 131.04, 138.92, 139.67, 140.31 (all *s*, C-8, C-5, C-6, C-7, C-8a, respectively), 160.91 (*s*, C=O). EIMS (probe) 70 eV $m/z$ (rel. int.): 308 $[M]^+$ (76); 293 (4), 250 (58), 235 (38), 224 (18), 223 (18), 221 (14), 209 (22), 207 (16), 204 (12), 194 (12), 176 (12), 167 (8), 150 (16), 95 (32), 84 (34), 71 (30), 69 (34), 67 (22), 59 (72), 57 (46), 55 (40), 43 (100), 41 (38). Anal. found : C, 58.59; H, 5.12, $C_{15}H_{16}O_7$ requires C, 58.44; H, 5.23.

## REFERENCES

1. Soraru, B. and Bandoni, A. (1978) *Plantas de la Medicina Popular Argentina.* Albatros, Buenos Aires, p. 41.
2. Hieronymus, J. (1882), *Bol. Acad. Nac. Cienc. Córdoba, Argentina* **4**, 343.
3. Arenas, P. (1981) *Etnobotánica Lengua Maskoy*, p. 332. FECYC, Buenos Aires.
4. Boelke, O. (1981), *Plantas Vasculares de la Argentina, Nativas y Exóticas*, p. 265. FECYC, Buenos Aires.
5. Debenedetti, S. L., Nadinic, E. L., Gómez, M. A. and Coussio, J. D. (1987) *J. Nat. Prod.* **50**, 512.
6. Martino, V. S., Ferraro, G. E., Debenedetti, S. L. and Coussio, J. D. (1989), *Acta Farm. Bon.* **8**, 3.
7. Debenedetti, S. L., Nadinic, E. L., Coussio, J D., De Kimpe, N., Feneau-Dupont, J. and Declercq, J. P. (1991) *Phytochemistry* **30**, 2757.
8. Debenedetti, S. L., Nadinic, E. L., Gómez, M. A., Coussio, J D., De Kimpe, N. and Boeykens, M. (1992) *Phytochemistry* **31**, 3284.
9. Smith, E., Hosansky, N., Bywater, W. G. and van Tamelen, E. E. (1957) *J. Am. Chem. Soc.* **79**, 3534.
10. Murray, R. D. H., Mendez J. and Brown, S. A. (1982) *The Natural Coumarins, Occurrence, Chemistry and Biochemistry*, p. 47. John Wiley, New York.
11. Jefferies, P. R. and Worth, G. K. (1973) *Tetrahedron* **29**, 903.
12. Steck, W. and Mazurek, M. (1972) *J. Nat. Prod.* **35**, 418.
13. Boeykens, M., De Kimpe, N., Debenedetti, S. L., Nadinic, E. L., Gomez, M. A., Coussio, J D., Abyshev, A. Z. and Gindin, V. A. (1994) *Phytochemistry* **36**, 1559.
14. Aplin, R. T. and Page, C. B. (1967) *J. Chem. Soc. C* 2593.
15. Herz, W., Bhat, S. V. and Santhanam, P. S. (1970) *Phytochemistry* **9**, 891.