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X-RAY STRUCTURE OF PSIADIARABIN, A FLAVONE FROM *PSIADIA ARABICA*

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Key Word Index—*Psiadia arabica*; Compositae; 5,3′-dihydroxy-6,7,2′,4′,5′-pentamethoxyflavone; X-ray; NMR.

Abstract—The chloroform extract of the aerial parts of *Psiadia arabica* yielded upon solvent partitioning and chromatography a new flavone with a tetraoxygenated ring B. Spectral and X-ray crystallographic data identified the compound, psiadiarabin, as 5,3′-dihydroxy-6,7,2′,4′,5′-pentamethoxyflavone.

INTRODUCTION

As a part of our on-going phytochemical investigation of plants indigenous to Saudi Arabia, a flavone now named psiadiarabin, was isolated from the aerial parts of *Psiadia arabica* Jaub. et Spach. (Compositae). The present note reports its characterization as 1 from its spectral and X-ray crystallographic data.

The molecular ion at *m/z* 404 in mass spectra, and elemental analyses were in accordance with $C_{20}H_{20}O_9$, corresponding to a flavone with two OH and five OMe groups as confirmed by ^{13}C and ^{1}H NMR (see Experimental). Other spectral data were typical of a flavone unsubstituted at C-3, with a chelated OH at C-5, and two OMe on C-6 and C-7 [1, 2]. However, the determination of the position of the remaining three OMe and one OH group on ring B proved to be a formidable task. Attempts to solve this problem by making use of the ^{13}C NMR signals [3] of the four oxygenated carbons of ring B at δ 149.1, 143.7, 141.5 and 139.8 were inconclusive. The structure was finally solved by X-ray crystallography. The solid-state conformation of 1 is given in Fig. 1 where small circles represent hydrogen atoms and the broken line indicates an intramolecular O-H. . .O hydrogen bond.

It should be noted that psiadiarabin (1) represents the third example of a flavone with a tetraoxygenated ring B obtained from a higher plant. The two other compounds, namely, agehoustin A and agehoustin B were isolated from *Ageratum houstonianum* [4, 5] and found to be 5,6,7,8,2′,3′,4′,5′-octamethoxyflavone and 5,6,7,2′,3′,4′,5′-heptamethoxyflavone, respectively. In addition, a flavone obtained from the farinose frond exudate of *Notholaena aschenborniana* was reported to be 5,4′,6′-trihydroxy-6,7,2′,3′-tetramethoxyflavone [6]. However, its structure was recently revised to 5,2′,4′-trihydroxy-3,7,8,5′-tetramethoxyflavone [7]. Also the structure of brickellin from *Brickellia veronicaefolia*, originally reported to be 5,6′-dihydroxy-6,7,2′,3′,4′-pentamethoxyflavone [8], had to be revised to 5,2′-dihydroxy-3,6,7,4′,5′-pentamethoxyflavone [8, 9].

EXPERIMENTAL

The plant material was collected in Abha, Saudi Arabia in the summer of 1979. It was identified locally by Prof. A. M. Mijahid, and a voucher specimen was deposited at the herbarium of the College of Pharmacy, King Saud University. Mps uncorr; IR, KBr; UV, MeOH; ^{1}H NMR, 90 MHz, $CDCl_3$, TMS as int. standard; ^{13}C NMR, 15.03 MHz and assignments were made by comparison with related compounds [2, 10].

Isolation of psiadiarabin (1). The powdered aerial parts (650 g) were extracted with $CHCl_3$ in a Soxhlet extractor. The extract (84 g) was partitioned between 10% aq. MeOH (400 ml) and *n*-hexane (200 ml × 4). The combined hexane phases were washed with 50 ml of the methanolic phase, and evapn of the combined methanolic layers provided a gummy residue (60 g). Chromatography of 20 g of this residue on silica gel (600 g) using $CHCl_3$–MeOH (19:1) as solvent provided 1 (120 mg) as yellow needles or prisms, mp 228°, optically inactive; IR ν_{max}^{KBr} cm^{-1}: 3210 and 3120 (OH) and 1650 (CO); UV λ_{max}^{MeOH} (nm): 273, 325; NaOAc 273, 325; NaOAc + H_3BO_3 272, 325; $AlCl_3$ 282, 305,

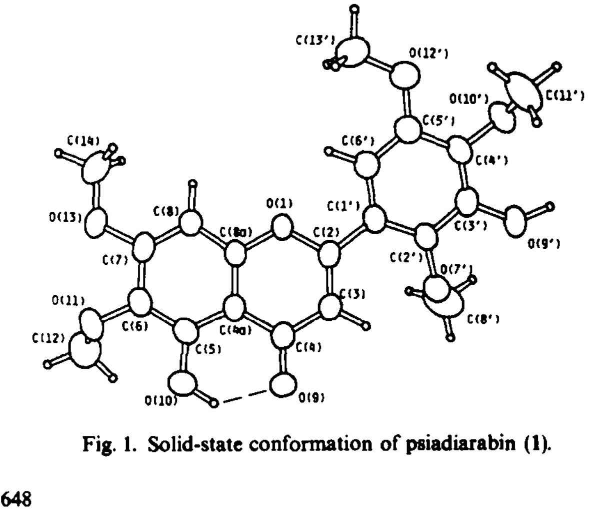

Fig. 1. Solid-state conformation of psiadiarabin (1).

356, $AlCl_3 + HCl$ 284, 305, 346 [1]; ^1H NMR ($CDCl_3$): δ6.48, 6.80 and 6.93 (3*s*, 1 H each, H-1, H-8 and H-6′), 6.57 and 13.67 (2*s*, 1 H each, D_2O exchangeable, 2 OH), 3.81, 3.88, 3.93 (double intensity) and 3.97 (*s*, 5 OMe); ^{13}C NMR ($CDCl_3$): δ183.1 (*s*, C-4), 161.9 (*s*, C-2), 159.1 (*s*, C-7), 153.6 and 153.0 (2*s*, C-5 and C-8a, indistinguishable), 90.7 (*s*, C-8), 119.6 (*s*-C-1′), 109.5 (*d*, C-3), 102.7 (*d*, C-6′), 106.2 (*s*, C-4a), 132.7 (*s*, C-6), 149.1, 143.7, 141.5 and 139.8 (4*s*, C-2′, C-3′, C-4′ and C-5′, indistinguishable), 61.1 (*q*, double intensity-2 OMe), 60.8 (*q*, OMe), and 56.4 (*q*, double intensity, 2 OMe); MS: m/z 404 $[M]^{\cdot +}$ (13 %) with the base peak at m/z 153. (Found: C, 59.49; H, 4.89. $C_{20}H_{20}O_9$ (404) requires: C, 59.39; H, 4.99 %.)

Crystal data. $C_{20}H_{20}O_9$, $M = 404.38$, monoclinic, $a = 9.828(2)$ Å, $b = 14.091(3)$ Å, $c = 16.602(3)$ Å, $\beta = 122.74(2)°$, $V = 1933.9$ Å^3, $Z = 4$, $D_{calcd} = 1.389$ g cm^{-3}, μ(Cu-Kα radiation, $\lambda = 1.5418$ Å) = 9.0 cm^{-1}. Space group $P2_1/c(C^5_{2h})$ uniquely from the systematic absences: O*k*O when $k \neq 2n$, *h*O*l* when $l \neq 2n$. Simple dimensions: 0.16 × 0.40 × 0.40 mm.

Crystallographic measurements. Preliminary unit-cell parameters and space group information were obtained from oscillation and Weissenberg photographs. Intensity data ($hk + l$) to $\theta = 67°$ were recorded on an Enraf-Nonius CAD-4 diffractometer (Cu-Kα radiation, incident-beam graphite monochromator; ω-2θ scans). From a total of 3439 independent measurements after averaging equivalent forms, those 2174 reflections with $I > 3.0\,\sigma(I)$ were retained for the structure analysis and the usual Lorentz and polarization corrections were applied. An empirical absorption correction, based on the ϕ-dependence of the intensities of 4 reflections with χ *ca* 90°, was also applied to these data. Refined unit-cell parameters were derived by least-squares treatment of the diffractometer setting angles for 25 reflections ($45° < \theta < 62°$) widely separated in reciprocal space.

Structure analysis. The crystal structure was solved routinely by direct methods. Approximate non-hydrogen atom coordinates were obtained from an *E*-map. Hydrogen atoms were all located in a difference Fourier synthesis evaluated following several cycles of full-matrix least-squares adjustment of non-hydrogen atom positional and anisotropic thermal parameters. With the inclusion of the hydrogen atoms at their calculated positions in the subsequent least-squares iterations, the refinement converged at $R = 0.054$ ($R_w = 0.081$). A view of the solid-state conformation, with the atom numbering scheme, is provided in Fig. 1. Non-hydrogen atom positional and anisotropic thermal parameters, hydrogen atom parameters, bond lengths and angles, torsion angles, and a list of observed and calculated structure amplitudes have been deposited with the Cambridge Crystallographic Data Centre. Neutral atom scattering factors used in the structure-factor calculations were taken from lit. [11]. In the least-squares iterations, $\sum w\Delta^2$ [$w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] was minimized.

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