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3,7-DIHYDROXY-8-METHOXYFLAVONE FROM *ZUCCAGNIA PUNCTATA*

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Abstract—A phytochemical examination of the leaves of *Zuccagnia punctata* resulted in the isolation and identification of 3,7-dihydroxyflavone and 3,7-dihydroxy-8-methoxyflavone. The latter is a new natural product.

INTRODUCTION

Zuccagnia punctata Cav. is a monotypic species of the Leguminosae. This is known under the common name of '*jarilla macho*' and is a shrub occurring in western Argentina from Jujuy Province to Mendoza and in Chile. We previously reported the isolation of two chalcones, 2',4'-dihydroxychalcone and 2',4'-dihydroxy-3'-methoxychalcone, and two flavanones, 7-hydroxyflavanone and 7-hydroxy-8-methoxyflavanone from this plant [1]. In that report the plant was erroneously referred to as *Larrea nitida* (Zygophyllaceae) [2]. The trivial names 'larrein' and 'isolarrein', originally suggested for the methylated chalcone and flavanone, must therefore be discarded. The present paper describes the isolation of two additional flavonoids from the leaf resin of *Zuccagnia punctata*.

RESULTS AND DISCUSSION

Leaves of *Zuccagnia punctata* collected near Villavicencio (Mendoza) were extracted with methanol and the methanolic extract obtained was partitioned between *n*-hexane, carbon tetrachloride and chloroform. Subsequent separation of the chloroform-soluble compounds was achieved by silica gel CC (see Experimental) affording 3,7-dihydroxyflavone and 3,7-dihydroxy-8-methoxyflavone. Of these 3,7-dihydroxy-8-methoxyflavone is a new natural product while 3,7-dihydroxyflavone has been reported earlier from *Platymiscium praecox* [3]. 3,7-Dihydroxyflavone was identified by UV, MS and ^{1}H NMR of the parent compound and of its diacetate. The structural assignments of the new compound are discussed below.

The MS of 3,7-dihydroxy-8-methoxyflavone exhibited a molecular ion peak at *m/z* 284 (100%) for $C_{16}H_{12}O_5$ in accord with a flavone containing two hydroxyl and one methoxyl groups, a result confirmed by the MS of the dimethoxy and trimethoxy derivatives which exhibited $[M]^{+\cdot}$ at *m/z* 298 (100%) and *m/z* 312 (68.7%) respectively. Two strong peaks at *m/z* 105 $[B_2]^+$ [4] and 77 $[B_2 - 28]^+$ [4] were characteristic for an unsubstituted B-ring. It was also indicated by ^{1}H NMR which showed two multiplets at δ7.5 and 8.2 integrating for 3H and 2H respectively.

3,7-Dihydroxy-8-methoxyflavone exhibited a yellow-green fluorescent colour under UV which did not change after fuming with ammonia, thus indicating a flavone with a free 3-hydroxyl group and 5-hydroxyl group either lacking or substituted [5]. The presence of band III at 356 nm in the sodium methoxide spectrum [6] and a 17 nm bathochromic shift in band II in the sodium acetate spectrum indicated an unsubstituted 7-hydroxyl group. The second hydroxyl was assigned to the C-3 position from its UV and ^{1}H NMR spectra. The $AlCl_3$–HCl spectrum exhibiting a shift of 58 nm. The ^{1}H NMR spectrum showed a pair of *ortho*-coupled protons at δ7.2 (*d*, *J* = 9 Hz) and 7.6 (*d*, *J* = 9 Hz) which were assigned to H-6 and H-5 respectively; which suggested a 7,8-substitution pattern for ring A, an additional signal at δ3.9 (3H, *s*, OMe) was assigned to a methoxy function at C-8. Furthermore the ^{1}H NMR spectrum presented a broad band at δ9.5 (2H, OH-3, 7) shifted by addition of D_2O. Further evidence for this structure was obtained by methylation, acetylation and spectrometric analysis of the derivatives thus obtained.

The isolation of 3,7-dihydroxyflavone and 3,7-dihydroxy-8-methoxyflavone is of biogenetic interest [7] because the corresponding chalcones and flavanones, 2',4'-dihydroxychalcone; 2',4'-dihydroxy-3'-methoxychalcone and 7-hydroxyflavanone; 7-hydroxy-8-methoxyflavanone, have been isolated from this source [1, 2]. 2',4'-Dihydroxychalcone and 2',4'-dihydroxy-3'-methoxychalcone have been reported recently to occur jointly in the leaf resin of *Acacia neovernicosa*, too [8].

EXPERIMENTAL

Mps are uncorrected Chemical shifts of the ^{1}H NMR spectra are given in δ values with TMS as int. standard. MS on a Varian Mat 112-S: 70 eV and the ion source temp was 150°

Plant material was collected in October 1982 near Villavicencio in Mendoza state and was identified by Ing. A Ambrosetti (IADIZA-Mza). A voucher specimen is deposited in the Dr Ruiz Leal Herbarium Merl No 35525.

Dried leaves of *Z. punctata* (2650 g) were extracted with MeOH at room temp for 120 hr. The extract was concd to 3 l, H_2O was added (10, 20 and 30%) then partitioned between *n*-

hexane, CCl_4 and $CHCl_3$ respectively. The $CHCl_3$ was evapd and the residue (255 g) was subjected to CC on silica gel (5 × 120 cm; 800 g) developed successively with C_6H_6 and C_6H_6 containing increasing proportions of EtOAc, 500 ml fraction being collected. Frs 31–33 (9 g) were combined and purified by repeated CC on silica gel with a C_6H_6–EtOAc gradient and on Sephadex LH-20 with MeOH as solvent to yield 3,7-dihydroxyflavone. It was crystallized from MeOH, mp 256–258°. Frs 34–36 (27 g) were combined and purified as before to give 3,7-dihydroxy-8-methoxyflavone. It was crystallized from EtOH–H_2O, mp > 200° (d). MS fragments are ascribed according to ref. [4].

3,7-Dihydroxy-8-methoxyflavone. UV λ_{max}^{MeOH} nm: 227 (sh), 260, 312, 352; + NaOMe: 240 (sh), 275, 356, 408; + NaOAc: 277, 320 (sh), 338 (sh), 406; + $AlCl_3$: 248, 269, 326, 410; + $AlCl_3$–HCl: 248, 269, 326, 410 ^{1}H NMR (DMSO-d_6): 3.9 (3H, *s*, OMe-8), 7.2 (1H, *d*, *J* = 9 Hz, H-6), 7.5 (3H, *m*, H-3′, H-4′, H-5′), 7.6 (1H, *d*, *J* = 9 Hz, H-5), 8.2 (2H, *m*, H-2′, H-6′), 9.5 (2H, *m*, OH-3,7). MS *m/z* (rel. int.): 285 $[M+1]^+$ (19), 284 $[M]^+$ (100), 283 $[M-1]^+$ (29), 269 $[M-15(Me)]^+$ (22), 256 $[M-28(CO)]^+$ (5), 241 $[M-43(-Me-CO)]^+$ (31), 167 $[A_1+H]^+$, (2), 151 (7), 123 (9), 105 $[B_2]^+$ (25), 77 $[B_2-28]^+$ (18).

Methylation 80 mg of 3,7-dihydroxy-8-methoxyflavone was treated with excess ethereal CH_2N_2 soln giving a methyl ether derivative mixture. The reaction mixture was chromatographed on Sephadex LH-20 with MeOH as solvent. The early fractions (9 mg) on crystallization (MeOH) gave 3,7,8-trimethoxyflavone and the later fractions (38 mg) on crystallization (MeOH) gave 3-hydroxy-7,8-dimethoxyflavone.

3,7,8-Trimethoxyflavone. Colorless needles, mp 153–154°. MS *m/z* (rel. int.): 313 $[M+1]^+$ (14), 312 $[M]^+$ (68.7), 311 $[M-1]^+$ (100), 267 (7), 181 $[A_1+H]^+$ (8), 152 (8), 137 (11), 109 (6), 105 $[B_2]^+$ (18), 89 (8), 77 $[B_2-28]^+$ (21).

3-Hydroxy-7,8-dimethoxyflavone. Light yellow needles, mp 205–207°; ^{1}H NMR (DMSO-d_6): 3.9 (6H, *s*, OMe-7,8), 7.2 (1H, *d*, *J* = 9 Hz, H-6), 7.5 (3H, *m*, H-3′, H-4′, H-5′), 7.8 (1H, *d*, *J* = 9 Hz, H-5), 8.2 (2H, *m*, H-2′, H-6′), 9.5 (1H, *s*, D_2O exchangeable, OH-3, [9]). MS *m/z* (rel. int.): 299 $[M+1]^+$ (21), 298 $[M]^+$ (100), 297 $[M-1]^+$ (16), 283 $[M-15(Me)]^+$ (9), 255 $[M-43(-Me-CO)]^+$ (30), 165 (13), 149 (9), 137 (17), 121 (6), 105 $[B_2]^+$ (40), 77 $[B_2-28]^+$ (24).

3,7-Diacetoxy-8-methoxyflavone. 3,7-Dihydroxy-8-methoxyflavone was converted to the diacetoxy derivative by the usual procedure (Ac_2O, pyridine). ^{1}H NMR ($CDCl_3$): 8.1 (1H, *d*, *J* = 9 Hz, H-5), 7.55 (5H, *m*, H-2′ to H-6′), 7.1 (1H, *d*, *J* = 9 Hz, H-6), 4.0 (3H, *s*, OMe-8), 2.3 (6H, *s*, OCOMe-3,7)

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