(1.00), 286 (0.83); +NaOAc, 384, 320, 285 sh; +NaOAc +H_3BO_3, 330 sh (0.77), 305 (1.00), 285 (1.00).

8-Demethylthymusin (3) (*5,6,8,4'-tetrahydroxy-7-methoxyflavone*). UV λ_{max}^{MeOH} nm: 335 sh (0.69), 304 (1.00); +NaOMe, 469 (dec.), 378 (dec.), 330 (inc.), 247 sh; +$AlCl_3$, 468 (0.17), 400i (0.52), 372 (0.93), 320 (1.00); +$AlCl_3$ + HCl, 417 sh, (0.57), 366 (0.89), 311 (1.00); +NaOAc, 385 (dec.), 316 (inc.); +NaOAc + H_3BO_3, 430 sh (0.12), 304 (1.00).

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5,7-DIHYDROXY-3,8,3',4'-TETRAMETHOXYFLAVONE FROM *PARASTREPHIA QUADRANGULARIS*

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Key Word Index—*Parastrephia quadrangularis*; Compositae; Astereae; 5,7-dihydroxy-3,8,3',4'-tetramethoxyflavone.

Abstract—A new flavone has been isolated from *Parastrephia quadrangularis* and identified as 5,7-dihydroxy-3,8,3',4'-tetramethoxyflavone.

Five species of *Parastrephia* (Compositae, tribe Astereae) are distributed in northern Chile. Only one species *P. lepidophylla*, of Bolivian origin, has been chemically examined [1]. In this communication we report the isolation of a new flavone, characterized as 5,7-dihydroxy-3,8,3',4'-tetramethoxyflavone (**1**) as well as the identification of scopoletin, umbelliferone and *p*-coumaroyloxytremetone (**2**) from *P. quadrangularis* (Meyen) Cabrera.

Compound **1** had a molecular weight of 374 corresponding to a flavone with four methoxyl and two hydroxyl groups. The UV data indicated the presence of two hydroxyl groups at the 5 and 7 positions of the A ring and also suggested that C-8 but not C-6 was substituted by methoxy group. Thus, the shift of the short wave band in the sodium acetate spectrum compared to the methanol spectrum was 26 nm, which together with the shift of the long wave band in the $AlCl_3$–HCl spectrum (+74 nm) suggested a 5,7-dihydroxyflavone [2]. The ^1H NMR spectrum showed the typical signals for a 3',4'-substituted B ring (see Experimental): a signal for four methoxyl groups at δ3.85 and one-proton singlet at δ6.27. The

substitution pattern present in the A ring was corroborated by the intensities of the $[M]^+$ (50%) and $[M-15]^+$ (100%) fragments in the mass spectrum of **1** that can be used to distinguish 5,7-dihydroxy-8-methoxyflavones from 5,7-dihydroxy-6-methoxyflavones [3].

To the best of our knowledge, this is the first report of the natural occurrence of gossypetin-3,8,3′,4′-tetramethyl ether (**1**). Its purported occurrence in *Heteroma simplicifolium* (Compositae) [4] as mentioned in a recent compilation is erroneous [5].

Scopoletin, umbelliferone and *p*-coumaroyloxytremetone (**2**) were also isolated from *P. quadrangularis*. This is the second report on the natural occurrence of **2**, which had been previously isolated from *P. lepidophylla* [1].

EXPERIMENTAL

P. quadrangularis was collected in Toconce (Calama) in April 1979. Voucher specimens were deposited in the Herbarium of the University of Concepcion and in this Centre.

Extraction and separation. The dried and ground aerial parts of *P. quadrangularis* (600 g) were Sohxlet extracted with EtOH and the extract was separated into soluble (A) and insoluble (B, 120 g) fractions after treatment with EtOH–H_2O (3:2). Fraction A, after treatment with $Pb(OAc)_2$ [6], was separated into C_6H_6 (1.9 g), $CHCl_3$ (1.5 g), EtOAc (5.9 g) and *n*-BuOH (22 g) fractions. The $CHCl_3$ fraction was chromatographed over silica gel (30 g) and elution with C_6H_6–Et_2O (1:1) afforded scopoletin (32 mg) and umbelliferone (41 mg). Fraction B was separated into a soluble (C, 36 g) and insoluble (D, 84 g) fractions after treatment with Et_2O–petrol (1:2). Silica gel CC of fraction D (20 g) gave, after elution with C_6H_6 containing increasing amounts of EtOAc, *p*-coumaroyloxytremetone (**2**, 662 mg) and **1** (74 mg).

5,7-Dihydroxy-3,8,3′,4′-tetramethoxyflavone (**1**). Mp 231° (EtOAc–Et_2O, 1:3). UV λ_{max}^{MeOH} nm: 254, 273 and 335; + NaOMe: 281, 312, 385; + $AlCl_3$: 260, 281, 355, 409; + $AlCl_3$ + HCl: 259, 281, 353, 409; + NaOAc: 280, 312, 384; + NaOAc + H_3BO_3: 252, 274, 320. ^1H NMR (60 MHz, DMSO-d_6): δ3.85 (12H, *m*, OMe), 6.27 (1H, *s*, H-6), 7.13 (1H, *d*, $J = 9$ Hz, H-5′), 7.62–7.83 (2H, *m*, H-2′, H-6′) 12.3 (1H, *s*, OH), 3.34 (*br*, OH); EIMS (70 eV, direct inlet) *m/z* (rel. int.): 374 $[M]^+$ (50), 359 $[M-Me]^+$ (100), 331 $[M-43]^+$ (8), 167 $[A_1+H]^+$ (3), 165 $[B_2]^+$ (6).

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