

ON A FLAVONE FROM *Teucrium orientale*

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The aerial part of oriental germander (*Teucrium orientale* L., Lamiaceae) has previously afforded [1] a lipophilic flavone **1** of formula $C_{18}H_{16}O_7$, mp 194-195°C (MeOH), and mass spectrum (EI, 70 eV, m/z , I_{rel} , %): 344 (100) $[M]^+$ that was identified as fastigenin or cirsilineol (5,4'-dihydroxy-6,7,3'-trimethoxyflavone). A careful study of the spectra of **1** with performance of modern research enabled the structure of this compound to be re-examined.

UV spectra of **1** with diagnostic reagents [2] (MeOH, λ_{max} , nm): 244sh, 254sh, 276, 340 (log ϵ 4.07, 4.18); (+MeONa) 244sh, 272 (log ϵ 4.25), 298sh, 327sh, 378 (log ϵ 3.79); (+AcONa) 245sh, 256sh, 277, 341; (AcONa + H_3BO_3) 255sh, 275, 342; (+ $AlCl_3$) 263, 281sh, 297sh, 373; ($AlCl_3$ + HCl) 262, 281sh, 297sh, 363; (+ $ZrOCl_2$) 294, 371; ($ZrOCl_2$ + citric acid) 273sh, 344; agreed with IR, PMR, and mass spectra of **1** and its acetate and corresponded with spectral data of eupatorin (5,3'-dihydroxy-6,7,4'-trimethoxyflavone) [3-6] and not its positional isomers for the substituents, in particular, cirsilineol [7, 8]. The smaller bathochromic shift and reduced strength of the first band in the UV spectrum with MeONa than for cirsilineol and the lack of a color change in UV light and UV/ NH_3 [2, 4] are indicative of eupatorin. The lack of a free OH on C-6 and OH and MeO on C-8 is consistent with the wavelength and strength of the second band in the UV spectrum of **1** [9, 10] and the ratio of intensities of $[M]^+$ (100) > $[M - Me]^+$ (67) in the mass spectrum (6,7-dimethoxy group) [11].

The structure of **1** was also confirmed by PMR and ^{13}C NMR spectra.

PMR spectrum (300.08 MHz, $CDCl_3$, δ , ppm, J/Hz): 12.75 (1H, br.s, 5-OH), 7.49 (1H, d, J = 2.3, H-2'), 7.45 (1H, dd, $J_1 = 8.5$, $J_2 = 2.3$, H-6'), 6.97 (1H, d, J = 8.5, H-5'), 6.59 (1H, s, H-3), 6.56 (1H, s, H-8), 5.75 (1H, br.s, 3'-OH), 4.00 (3H, s, MeO-4'), 3.98 (3H, s, MeO-7), 3.94 (3H, s, MeO-6).

^{13}C NMR spectrum (75.46 MHz, $CDCl_3$): 182.8 (C-4) 163.9 (C-2), 158.9 (C-7), 153.4 (C-9), 153.3 (C-5), 149.7 (C-4'), 146.3 (C-3'), 132.9 (C-6), 124.8 (C-1'), 119.2 (C-6'), 112.6 (C-5'), 110.9 (C-2'), 106.4 (C-10), 104.8 (C-3), 90.7 (C-8), 61.0 (MeO), 56.4 (MeO), 56.3 (MeO).

Assignments of resonances were made on the basis of multiplicities; for singlets of MeO and CH groups in the 3- and 8-positions, NOESY spectra. Because the assignment of protons in the 2', 5', and 6'-positions were unambiguous, the cross peak observed in the NOESY spectrum between H-5' and MeO indicated that the MeO was located on C-4' and the OH, on C-3'. The assignments of resonances for H-3 and H-8 were also unambiguous according to cross peaks observed between H-2', H-6', and H-3 on the one hand and MeO-7 and H-8 on the other. Assignments of certain resonances in the ^{13}C NMR spectrum were made by consulting the literature [8, 12].

Thus, the structure eupatorin (5,3'-dihydroxy-6,7,4'-trimethoxyflavone) was determined for **1**.

Both cirsilineol [13] and eupatorin [5, 6] were isolated previously from plants of the genus *Teucrium*. Eupatorin was isolated for the first time from *T. orientale*.

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