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A NEW FLAVONOID FROM *AMBROSIA DUMOSA*

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Key Word Index—*Ambrosia dumosa*; Compositae; 8,3′-dimethoxy-5,7,4′-trihydroxyflavone.

In 1964, all species of the genus *Franseria* were transferred into *Ambrosia*.[1] In order to determine whether this generic revision was justified, we are presently conducting a broad biochemical systematic investigation of these taxa.

During the course of the present study, we encountered in *Ambrosia* (*Franseria*) *dumosa* (Gray) Payne, 8,3′-dimethoxy-5,7,4′-trihydroxyflavone; although previously synthesized,[2] this is the first report of this compound as a natural product.

The NMR spectrum of the trimethylsilyl ether indicated that the new compound was a flavone dimethyl ether: a six-proton singlet at 3·97* for two methoxyl groups; aromatic proton signals at 7·55 ($J = 9$, 2·5) and 7·5 ($J = 2·5$) for H-6′ and H-2′; a doublet at 6·97 ($J = 9$) for H-5′ and two one-proton singlets at 6·5 and 6·3 for H-3 and H-6†, respectively. In benzene-d_6[3] the signal for one of the methoxyls at 3·97 shifted upfield to 3·45 (+0·52 ppm), indicating that this methoxyl group was either at the 3′, 4′ or 7 position; however, the presence of a free 4′-hydroxyl was evident from the purple to green–yellow color test[4] with UV alone and with NH_3. The small upfield shift to 3·78 (+0·19 ppm) of the second methoxyl group indicated that it must be at position 8. The presence of three hydroxyl groups in the new natural product was evident from the three trimethylsilyl ether signals observed when the spectrum of the ether derivative was recorded in benzene-d_6; one signal exhibited a negative shift (−0·11 ppm) as expected for a 5-O TMS group.[3]

The presence of substituted oxygen functions at the 8 and 3′ positions and hydroxyl groups at 5,7, and 4′ was verified by UV and MS spectral analyses: (1) The presence of a C_5-hydroxyl group and absence of a C_6–oxygen substituent[5] was indicated by a bathochromic shift of 55 nm for band I in the presence of $AlCl_3$–HCl. (2) In NaOMe, band I exhibited a bathochromic shift of 70 nm, with an increase in intensity, typical for a 4′-hydroxyl group. (3) A band II bathochromic shift of 16 nm in the presence of NaOAc supported the presence of a C_7 hydroxyl group. (4) MS data were in accord with the proposed structure: M^+ 330 (65%), fragment ions at: 315 (M-15, 100%), 287 (M-43, 25%), retro-Diels–Alder (RDA) fragment ions: 167 (9%), 149 (16%), 139 (24%), 134 (6%). The

* Values are given in ppm (δ-scale) relative to TMS as internal standard.

† The NMR spectrum of the trimethylsilyated 6,3′-dimethoxy-5,7,4′-trihydroxyflavone exhibited chemical shifts (in CCl_4) of 6·63 and 6·4 for the H-8 and H-3, respectively; the methoxyl groups were at 3·95 and 3·8.

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natural product was identical by co-chromatography, NMR, UV and MS with a synthetic sample.

EXPERIMENTAL

Two-dimensional chromatograms on Whatman 3MM paper were developed first in TBA (*t*-BuOH–HOAc–H_2O, 3:1:1) and then in 15% HOAc; NMR spectra of the TMS ethers were recorded for the CCl_4 and benzene-d_6 using tetramethylsilane as an internal standard. All of the UV spectra were obtained using standard procedures.[4]

Air dried and ground leaf material of *Ambrosia dumosa* Gray (collected in dunes near El Desemboque, Sonora, Mexico; Voucher No. Seaman-FS-61 is deposited in the University of Texas at Austin Herbarium) was extracted with $CHCl_3$. The 22 g of crude syrup thus obtained was chromatographed over silica gel (200 g in $CHCl_3$). Elution with $CHCl_3$ (1500 ml) followed by increasing amounts of acetone afforded the new flavone. *Color test* Purple (UV) to green-yellow (UV/NH_3); R_f (TBA) 0·83, R_f (HOAc) 0·06; UV: λ_{max} (MeOH): 342, 274, 253 sh; λ_{max} (NaOMe): 412, 340 sh, 282, 273 sh; λ_{max} ($AlCl_3$): 402, 360, 300 sh, 284, 262 sh; λ_{max} ($AlCl_3$–HCl): 397, 352, 300 sh, 284, 260 sh; λ_{max} (NaOAc): 410, 325, 280 nm; λ_{max} (NaOAc–H_3BO_3) 340, 276, 254 sh nm.

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CARABRONE FROM *ARNICA FOLIOSA**

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Key Word Index—*Arnica foliosa*; Compositae; sesquiterpene lactone; carabrone.

Plant. Arnica foliosa Nutt. *Source.* Experimental Garden of the Institute of Organic Chemistry and Biochemistry, Průhonice near Prague grown from seeds obtained from the Botanical Garden of the University of Uppsala (Sweden) (Specimen No. 88/26; deposited in the Herbarium of our Institute of Průhonice). *Previous work.* Isolation of carabrone from the fruits of *Carpesium abrotanoides* L. and its structure;[1] stereostructure,[2,3] synthesis[4] and isolation of carabrone from *Helenium quadridentatum.*[5]

Compound isolated. The light petroleum extract of dry ground leaves after evaporation of the solvent afforded carabrone, m.p. 90–91°, $[\alpha]_D^{20}$ +50·6°, composition $C_{15}H_{20}O_3$ (M 248. Found: C, 72·7; H, 8·25. Calc.: C, 72·6; H, 8·12) which was identified directly on the basis of its PMR spectrum (100 MHz) and on comparison of its IR and PMR spectra and m.m.p. with an authentic sample. For further identification of carabrone in natural material by PMR spectra the following proton signals are analytically significant (good

* Part CCXVII in the series "On Terpenes". For Part CCXVI see *Coll. Czech. Chem. Commun.* in press.

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