

CHEMICAL CONSTITUENTS OF THE AERIAL PARTS OF
ARTEMISIA DRACUNCULUS

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We have recently identified the dihydroflavonols, 3,5,4'-trihydroxy-7-methoxyflavanone and 3,5,4'-trihydroxy-7,3'-dimethoxyflavanone, as well as naringenin, in CHCl_3 extracts of the shoots of *Artemisia dracunculus* L. var. *dracunculus* (1).

Further examination of the CHCl_3 extracts have furnished another flavanone, 5,3'-dihydroxy-7,4'-dimethoxyflavanone, previously not known to occur in the Compositae. This flavanone has been found in *Prunus persica* (Rosaceae) and exudates of two species of ferns, *Notobolaene limitanaeae* var. *mexicana* and *Notobolaene fendleri* (2,3). Because few spectral data were provided in preceding communications, we describe here the ^1H nmr, as well as ^{13}C nmr, along with other unreported spectroscopic data for this minor flavonoid. The shoots were also found to contain scoparone as well as considerable amounts of capillarin, compounds which, together with phenylacetylenes, had been reported from the roots of this species (4,5).

EXPERIMENTAL

GENERAL.—The ir spectrum was recorded on an Analect FX-6160 FTIR spectrophotometer, uv spectra on a Unicam SP8-100 spectrophotometer, ^1H -nmr and ^{13}C -nmr spectra on a WH-400 (^{13}C , 100.6 MHz) Ftnmr spectrometer. Mass spectra were recorded on a Finnigan 1020 GC/MS and a KRATOS-AEI MS50 high resolution mass spectrometer at 70 eV using a heated direct sample insertion probe into the ion source, whose temperature was kept at 95° . Melting points were obtained in open-ended capillaries and are uncorrected.

PLANT MATERIAL.—Leaves and stems of *A. dracunculus* var. *dracunculus* were collected in May 1983, at Lytton, British Columbia, and freeze dried. A voucher specimen was deposited in the UBC Herbarium (R. Norton 105).

EXTRACTION AND ISOLATION.—Shoots (2.5 kg) were extracted with CHCl_3 for 72 h and the extract worked up by standard procedures (1). Initial fractions afforded 2.30 g of capillarin, identified by spectral data (6). Further fractionation provided 40 mg of white needles that were recrystallized from MeOH; mp $164\text{--}165^\circ$ [lit. $163\text{--}164^\circ$ (5)]. The crystals gave a pink color with Mg/HCl in MeOH; Rf 0.76 in $\text{CHCl}_3\text{-Me}_2\text{CO}$ (10:1) located by shortwave uv light and a red color with vanillin (7); uv (MeOH) λ max 324 (sh), 286, 230, 215 nm; ir ν max (KBr) 3418 (intramolec. bonded-OH), 1640 (C=O), 1575, 1545 (aromatic) cm^{-1} ; ^1H nmr (CDCl_3 , TMS) δ 2.79 (1H, dd, $J=17$ and 3 Hz, H-3 *cis*); 3.10 (1H, dd, $J=17$ and 13 Hz, H-3 *trans*); 3.81 (3H, s, - OCH_3); 3.94 (3H, s, - OCH_3); 5.34 (1H, dd, $J=13$ and 3 Hz, H-2); 5.70 (1H, s, OH-3'); 6.06 (1H, d, $J=2$ Hz, H-6); 6.08 (1H, d, $J=2$ Hz, H-8); 6.36 (3H, m, H-2', H-5' and H-6'); 12.02 (1H, s, OH-5). The assignments for these signals were based on spin-decoupling experiments and are in accord with the proposed structure for 5,3'-dihydroxy-7,4'-dimethoxyflavanone.

Further confirmation of this structure was obtained through ^{13}C -nmr analysis. A total of seventeen carbon signals were identified in the ^1H -decoupled ^{13}C -nmr spectrum in CDCl_3 . Assignments of these signals were carried out on the basis of earlier data on flavanones (8) as well as from the single frequency off-resonance decoupled spectrum (sford). ^{13}C nmr (CDCl_3 , TMS) δ 195.9 (C-4); 168.0 (C-7); 164.2 (C-5); 162.8 (C-9); 146.8 (C-4'); 146.3 (C-3'); 130.3 (C-1'); 119.6 (C-6'); 114.6 (C-2); 108.8 (C-5'); 103.1 (C-10); 95.1 (C-6); 94.3 (C-8); 79.3 (C-2); 56.0 (-OMe); 55.6 (-OMe); 43.4 (- CH_2 -). Mass spectral analysis furnished a molecular ion at m/z 316.0935, calcd. 316.0947, corresponding to a molecular formula of $\text{C}_{17}\text{H}_{16}\text{O}_6$. Major fragments arising from the retro-Diels Alder cleavage at m/z 150, $\text{C}_9\text{H}_{10}\text{O}_2$ (87%) and m/z 167, $\text{C}_8\text{H}_7\text{O}_4$ (91%) denoted the degree of substitution in both aromatic rings. Other significant fragment ions, where shown at m/z 137, $\text{C}_8\text{H}_9\text{O}_2$, base peak, m/z 315 ($\text{M}^+ - 1$), m/z 193, $\text{C}_{10}\text{H}_9\text{O}_4$, m/z 180, $\text{C}_9\text{H}_8\text{O}_4$, m/z 135, $\text{C}_8\text{H}_7\text{O}_2$, and m/z 107, $\text{C}_7\text{H}_7\text{O}$, typical of those of flavanones (9). The optical rotation $[\alpha]_D^{25} = -36.1^\circ$ (C=0.46, CHCl_3) is characteristic of naturally occurring flavanones, the configurations of which have been assigned as 2S (10).

Later fractions afforded 20 mg of scoparone characterized by gc/ms and NBS library search. Rf=0.53 in $\text{CHCl}_3\text{-Et}_2\text{O}$ (6:1) located by uv fluorescence; uv (MeOH) λ max 342, 292, 248 (sh) 228, 204 nm. Its structure was also confirmed by direct comparison with an authentic sample available in our laboratory.

Full details of the isolation and identification are available upon request from the senior author.

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SESQUITERPENE LACTONES AND FLAVONES FROM *STEVIA PROCUMBENS*

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In continuation of our work on the chemistry of Argentinian *Stevia* species (1, 2), we have studied *Stevia procumbens* Hieron. (Compositae, Eupatorieae). Two sesquiterpene lactones were isolated, the germacradienolide eupatoriopicrin (3) and the biogenetically related guaianolide eupahakonenin B(4). Flavonoids found were eupatorin (5,3'-dihydroxy-6,7,4'-trimethoxyflavone) and artemetin [5-hydroxy-3,6,7,3',4'-pentamethoxyflavone]. Eupahakonenin B and eupatorin have been found also in *S. satuireiaefolia* (2).

EXPERIMENTAL

PLANT MATERIAL.—*S. procumbens* was collected on March 15, 1984, in Rio Vaqueros, Dept. La Caldera, Province of Salta, Argentina, and identified by A.L. Cabrera, Instituto Darwinion, San Isidor, Buenos Aires. A voucher specimen is deposited in the Museo Botánico de Córdoba.

EXTRACTION AND ISOLATION.—Dried aerial parts, wt. 0.60 kg, were extracted with CHCl_3 . The usual workup (1) afforded 21.8 g of syrupy residue. A 9-g portion was chromatographed on 220 g of Si gel packed with CHCl_3 and eluted with CHCl_3 containing increasing amounts of MeOH, 20-ml fractions being collected. Fractions 4-11 contained a mixture of two flavonoids; rechromatography of 69 mg of this material (Si gel, CHCl_3 and CHCl_3 -0.1% MeOH) yielded 5 mg of artemetin in fractions 7-11, a mixture of eupatorin and artemetin in fractions 12 and 7 mg of eupatorin from fractions 13-17. Fractions 62-71 of the original chromatogram gave 1.7 g of a mixture of two sesquiterpene lactones; fractions 72-73 afforded 0.14 g of eupatoriopicrin, mp 134-136° (C_6H_6). Rechromatography of the lactone mixture (70 g Si gel, CHCl_3 with increasing amounts of MeOH) gave 479 mg of eupahakonenin B, mp 78-79° (C_6H_6) and 20 mg of eupatoriopicrin. Eupatorin, eupatoriopicrin, and eupahakonenin B were identified by comparison (tlc, nmr, mp) with authentic samples. Artemetin was characterized by its mass spectral fragmentation (5) and identified by comparison (tlc, nmr and nmr of its acetate) with authentic samples of artemetin and artemetin acetate.

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