

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-H₂O, 3:1:1) and then in 15% HOAc; NMR spectra of the TMS ethers were recorded for the CCl₄ 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 CHCl₃. The 22 g of crude syrup thus obtained was chromatographed over silica gel (200 g in CHCl₃). Elution with CHCl₃ (1500 ml) followed by increasing amounts of acetone afforded the new flavone. *Color test* Purple (UV) to green-yellow (UV/NH₃); *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} (AlCl₃): 402, 360, 300 sh, 284, 262 sh; λ_{\max} (AlCl₃-HCl): 397, 352, 300 sh, 284, 260 sh; λ_{\max} (NaOAc): 410, 325, 280 nm; λ_{\max} (NaOAc-H₃BO₃) 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} synthesis⁴ 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°, $[\alpha]_D^{20} +50.6^\circ$, composition C₁₅H₂₀O₃ (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.

¹ H. MINATO, S. NOSAKA and I. HORIBE, *Proc. Chem. Soc.* 120 (1964); *ibid. J. Chem. Soc.* 5503 (1964).

² K. TORI, K. AONO, I. HORIBE and H. MINATO, *Annual Meeting of the Chemical Society of Japan* (1967).

³ E. T. DIAZ, *Bol. Inst. Quím. Univ. Nacl. Auton. Mex.* 20, 84 (1968).

⁴ H. MINATO and I. HORIBE, *Chem. Commun.* 358 (1967), *J. Chem. Soc. C*, 2131 (1968).

⁵ R. HERNÁNDEZ, A. SANDOVAL, A. SETZER and J. ROMO, *Bol. Inst. Quím. Univ. Nacl. Auton. Mex.* 20, 81 (1968).

signal to noise ratio): singlet at 1.07 ppm (angular methyl), triplet at 2.15 ppm with $J = 0.35$ Hz ($\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 -$), doublet at 6.23 ppm with $J = 2.75$ Hz, and doublet at 5.53 ppm with $J = 2.45$ Hz (exomethylene group; *cis*- γ -lactone).⁶

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⁶ Z. SAMEK, *Tetrahedron Letters* 671 (1970).

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STIGMASTEROL, FRIEDOOLEANAN-3 β -OL AND BACCHARIS OXIDE FROM *BACCHARIS SALICIFOLIA*

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Key Word Index—*Baccharis salicifolia*; Compositae; stigmasterol; friedooleanan-3 β -ol; baccharis oxide.

Plant. *Baccharis salicifolia* 'jarilla', Compositae. *Occurrence.* Slopes of Silla hill, N.L. *Uses.* Medicinal. *Previous work.* On sister species.¹⁻³

Present work. The whole plant (voucher No. 7216) dried and powderized, (4.5 kg) was soxhlet extracted with ETOH. The extract was evaporated and the residue taken with CHCl_3 . This solution was percolated through a silica gel column. On elution with solvents of increasing polarity the following compounds were obtained. *Stigmasterol*, $\text{C}_{29}\text{H}_{48}\text{O}$, (M^+ 412), m.p. 167–169° [α]₅₈₉²⁵ –47.9°, *acetate* m.p. 140–142° [α]₅₈₉ –52.0° m.m.p. superimposable IR, NMR, MS spectra co-TLC with authentic stigmasterol and its acetate. *Friedooleanan-3 β -ol*, $\text{C}_{30}\text{H}_{52}\text{O}$, (M^+ 428) m.p. 277° [α]₅₈₉ +16.6°; [α]₅₇₈ +17.6°; [α]₅₄₆ +19.4°; [α]₄₃₆ +24.9°, *acetate* $\text{C}_{32}\text{H}_{54}\text{O}_2$ (M^+ 470), m.p. 292–294° [α]₅₈₉ +33.1°; [α]₅₇₈ +34°; [α]₅₄₆ +40.4°; [α]₄₃₆ +66.4°. *Friedooleanan-3-one* (friedelin) $\text{C}_{30}\text{H}_{50}\text{O}$ (M^+ 426), m.p. 256–258° [α]₅₈₉ –16.3° [α]₅₇₈ –18.0°; [α]₅₄₆ –22.3°; [α]₄₃₆ –60.7°. M.m.p. for the three compounds, superimposable IR, NMR and MS spectra co-TLC. *Baccharis oxide*. $\text{C}_{30}\text{H}_{50}\text{O}$ (M^+ 426), m.p. 147–148°; [α]₅₈₉ +42.2°; [α]₅₇₆ +46.3° [α]₅₄₆ +50°; [α]₄₃₆ +87.8°; [α]₃₆₅ +135°; [α]₃₁₆ +209°, m.m.p. and IR, NMR and MS spectra superimposable.

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¹ T. ANTHONSEN, T. BRUIN, E. HEMMER, D. HOLME, A. LAMVIC, E. SUNDE and N. A. SORESEN, *Acta Chem. Scand.* **24**, 2479 (1970).

² S. MORRIS KUPCHAN and E. BAUERSCHMIDT, *Phytochem.* **10**, 664 (1971).

³ H. WAGNER, M. A. YENGER and W. HERZ, *Phytochem.* **11**, 444 (1972).