

Ageratum houstonianum and *A. conyzoides*

Similar investigation of *A. houstonianum* (3.5 kg) gave friedelin (0.015 g), m.p. 264–265° in the light petroleum–benzene (4:1) fractions, friedelan-3 β -ol (0.06 g), m.p. 279–281°, $[\alpha]_D + 10.0^\circ$, in the light petroleum–benzene (1:1) fractions, and a mixture of stigmasterol and β -sitosterol (0.10 g), in the light petroleum–benzene (1:4) fractions. Further extraction of the plant material with EtOH yielded KCl (5 g).

A. conyzoides (4 kg) gave friedelin (0.01 g), the sterol mixture (0.20 g), and KCl (30 g).

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T-MUUROL-OL-HAUPTBESTANDTEIL VON *ARNICA LONGIFOLIA*

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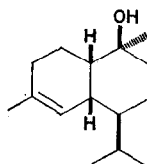
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Pflanze. *Arnica longifolia* Eat.

Frühere Arbeiten. Fettsäuren im ätherischen Öl der Blütenkörbchen.¹

Rhizome und Wurzeln: T-Muurolol kristallisiert nach längerem Stehen des Öles bei –20° aus. Schmp. 78–79°, $(\alpha)_D^{23} - 106.8^\circ$ (CHCl₃), Elementaranalyse, Massen-, NMR- und i.r.-Spektrum; p-Nitrobenzoat Schmp. 104–105°, Dinitrobenzoat Schmp. 163–164°; Bildung der Dihydrochloride (–)-Muurolendihydrochlorid und (–)-Cadinendihydrochlorid² (Schmp., Mischschmp., spez. Drehung, i.r.) sowie Dehydratisierung mit Thionylchlorid zu (–)- α -Muurolen (i.r. und Bildung der Hydrochloride).



Nach der GC-Analyse ist dieser Sesquiterpenalkohol mit 40–50% Hauptbestandteil des ätherischen Öles. Es ist dies das dritte bekannte Vorkommen von T-Muurolol in Pflanzen. Erstmals wurde dieser Alkohol vor zwei Jahren aus dem Holz von *Taiwania cryptomerioides*³ (Taxodiaceae) und *Cedrela toona*⁴ (Meliaceae) isoliert.

¹ H. KATING, W. RINN und G. WILLUHN, *Planta Med.* **18**, 130 (1970).

² L. WESTFELT, *Acta Chem. Scand.* **20**, 2893 (1966).

³ Y. S. CHENG, Y. H. KUO und Y. T. LIN, *Chem. Commun.* 565 (1967).

⁴ B. A. NAGASAMPAGI, L. YANKOV und SUKH DEV, *Tetrahedron Letters* 1913 (1968).

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6-METHOXY-7,8-METHYLENEDIOXYCOUMARIN FROM *ARTEMISIA CARRUTHII**

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EXAMINATION of *Artemisia carruthii* Wood resulted in the isolation of 6-methoxy-7,8-methylenedioxy coumarin, recently found in *Artemisia dracunculoides* Pursh.¹ Although sesquiterpene lactones were present in the extractives from the plant, no crystalline material of this class has been obtained.†

The coumarin, C₁₁H₈O₅, had m.p. 224–225°, and gave u.v. and i.r. spectra that identified it as a coumarin. Its NMR spectrum was in full accord with this conclusion and, in addition, showed the presence of the methoxy and methylenedioxy groupings. Besides a three-proton singlet at δ 3.28 and a two-proton singlet at δ 6.25, the only other signals were a one-proton singlet (H-5) at δ 7.06 and the characteristic signals for the H-3 and H-4 protons of the coumarin ring. These were seen as doublets at δ 6.30 and 7.95, ($J = 10$ Hz).

The composition and melting point of the coumarin suggested its identity with the newly described 6-methoxy-7,8-methylenedioxy coumarin,¹ and this was confirmed by a direct comparison of the compounds, which proved to be identical (mix m.p., i.r., TLC).‡

EXPERIMENTAL

Dried and ground *Artemisia carruthii* Wood,§ was extracted with CHCl₃ and the extract evaporated. The residue was partitioned between hexane (5 l.) and methanol-water (3:1, 800 ml), and the hexane layer discarded. Extraction of the alcoholic solution with CHCl₃ gave 73 g of a dark brown syrup. This was chromatographed on silica gel (900 g), eluting with CHCl₃, CHCl₃-EtOAc, EtOAc-acetone and finally acetone (1 l. fractions).

From the CHCl₃ extracts was isolated a colorless, crystalline compound which was recrystallized from pyridine, m.p. 224–225°. (Anal. Calc. for C₁₁H₈O₅: C, 60.00; H, 3.67; found, C, 60.25; H, 3.98.) The mass spectrum showed the molecular ion at m/e 220 (base peak), with prominent peaks at 205 (M-15), 192 (M-28)

* Contribution No. 2730 from the Department of Chemistry, U.C.L.A.

† As shown by the appearance of the characteristic i.r. band at about 1770 cm⁻¹.

‡ We are grateful to Professor Herz for a specimen of the coumarin, isolated from *A. dracunculoides*.

§ We are indebted to Mr. R. J. Barr, El Paso, Texas, U.S.A., for collection and authentication of the plant material used in this study.

¹ W. HERZ, S. V. BHAT and P. S. SANTHANAM, *Phytochem.* **9**, 891 (1970).