

Pyridin), DC in den Systemen: (a) 15%iger Essigsäure Zellulose (R_f 0,42) und (b) BEW (4:1:5) Zellulose (R_f 0,66) (c) Äa:As:W (10:2:3) Kieselgel (R_f 0,81) UV: λ_{\max} (MeOH) 259,270 sh, 355; λ_{\max} (NaOAc) 273,384; λ_{\max} (NaOAc/H₃BO₃) 263,385; λ_{\max} (NaOMe) 277,320 sh, 400; λ_{\max} (AlCl₃) 278,302 sh, 425. IR: KBr. OH-(br) 2,8–3,3 μ . Flavonol-carbonyl 6,1 μ . NMR: (CD₃)₂SO, TMS Intern.St: H-2'-H-6' δ = 7,5–7,7 (m); H-5' δ = 6,88 (d) J = 9; H-8 δ = 6,55 (s); CH-1 Glucose δ = 5,35–5,56 (br); OH-Glucose δ = 4,0–4,5; CH-Glucose δ = 2,9–3,7 (m); OCH₃ δ = 3,79 (s); OH-5 δ = 12,9 (s); OH-7 δ = 10,6 (s); OH-3',4' δ = 9,0–9,7 (m). Hydrolyse mit HCl (4%) 1 Std.: Patuletin, Schmp. 257° und Glucose als Zucker. Acetylierung mit Essigsäureanhydrid + Pyridin liefert Patuletin-3-glucosid-octaacetat: Schmp. 99°, $[\alpha]_D^{25}$ – 80,0 (c = 1,02 CHCl₃); NMR: CDCl₃ TMS Int.St. OAc-5' δ = 2,52 (s); OAc-7,3',4' δ = 2,30–2,35 (s); 4 OAc-Glucose δ = 1,90–2,12 (s). Das Glykosid stimmt im Schmp., UV-Spektrum und chromatographischen Verhalten mit dem von Thomas und Mabry¹ erstmalig aus *Hymenoxys scaposa* DC. isolierten Flavonolglykosid gleicher Struktur überein.²

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² Dieses Glucosid wurde ebenfalls aus *Lasthenia conjugens* und *L. fremontii* (Compositae) isoliert, cf. N. A. M. SALEH, B. A. BOHM und R. ORNDUFF, *Phytochem.* **10**, 611 (1971).

Phytochemistry, 1971, Vol. 10, pp. 2825 to 2826. Pergamon Press. Printed in England.

CONCERNING THE CHEMICAL CONSTITUENTS OF *MATRICARIA MATRICARIOIDES*

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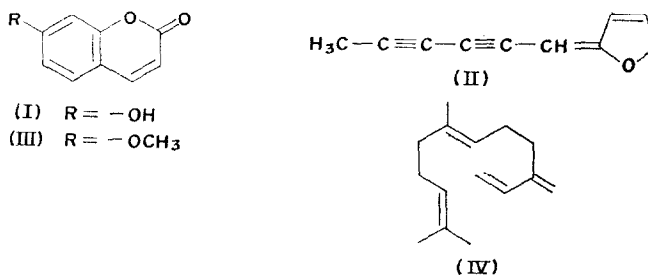
ON THE basis of comparison of its UV spectrum with that of umbelliferone(I) the main component of rayless chamomile, *Matricaria matricarioides* (Compositae), was at first labelled¹ 'perhaps coumarins?'. Without isolating it in a crystalline form, Christensen² carried out degradative work leading to a tentative formula(II) for this major component. Because of our chemical interest in Christensen's compound (II), we extracted the aerial part of

* The isolation of various constituents of pineapple weed was carried out in collaboration with this author. The structural identification reported in this communication is due to T.C.J.; see also Ref. 5.

¹ N. A. SØRENSEN, *Proc. Chem. Soc.* 98 (1961).

² P. K. CHRISTENSEN, *Norg. Tek. Vitenskaps. Ser. 2*, No. 7 p. 68. (1959).

pineapple weed,*† an annual herb that is widespread on Vancouver Island. Instead of isolating the diacetylcne (II), we obtained a crystalline coumarin, rigorously identified as 7-methoxycoumarin (III) by mixed m.p., IR, UV, NMR and mass spectral comparisons.‡



The crude extract was fractionated on silica gel column and the benzene eluted fraction, on repeated column chromatography on neutral alumina and silica gel, yielded an interesting sesquiterpene hydrocarbon§ [ν_{max} (liquid film): 1601 cm^{-1} (conjugated diene), 1645, 990 and 904 cm^{-1} (terminal vinyl and methylene), 830 cm^{-1} (trisubstituted olefinic linkage); NMR (CCl_4) τ : 3.68(q,1H), 4.69–5.05(m,6H), 7.80, 7.84, 7.98, 8.03 (8H), 8.33, 8.38(9H); overall yield: 46 mg from 8.6 kg dry plant] showing a single spot on TLC plates using different solvents. The hydrocarbon analyzed for $\text{C}_{15}\text{H}_{24}$ by high resolution mass measurement (observed 204.1880, calculated 204.1878) and displayed a characteristic UV max. at 227.5 nm (ϵ 10,873). The isolation procedure was monitored by means of this UV max. which remained virtually constant.

In a communication³ dealing with a convenient preparation of *trans*- β -farnesene, Brieger|| included the fact that he had isolated *trans*- β -farnesene from *Matricaria matricarioides* which was compared with a synthetic specimen of IV(80% GLC pure).³ However, the sesquiterpene isolated in this laboratory is not identical with the 'Brieger's farnesene' since the IR spectra of the two specimens are different.⁵ This conclusion is further supported by the observed λ_{max} of 227.5 nm in our compound due to a typical disubstituted conjugated diene chromophore.⁶ Thus, the isolation of a sesquiterpene, different from the 'Brieger's farnesene', from the same plant is of chemotaxonomic interest.¶

* Identified as *Matricaria matricarioides* (Less.) Porter by Dr. M. Bell (Biology Department, UVIC) and by Dr. C. L. Hitchcock, Curator of the Herbarium at the University of Washington, Seattle. The author (T.C.J.) wishes to thank them for this identification.

† The leaves of the plant when bruised possess an odour reminiscent of pineapple weed. The plant was collected on the Gordon Head Campus of this University in 1966.

‡ BOHLMANN *et al.* have investigated the aerial parts of *Matricaria matricarioides* growing in Berlin and have isolated spiranes. See, F. BOHLMANN, C. ARNDT, H. SCHONOWSKY and H. GLEINIG, *Chem. Ber.* **94**, 3193 (1963). Besides this Prof. Bohlmann informed T.C.J. that there was no sign of the '3200' compound.

§ This hydrocarbon is extremely thermolabile and air-sensitive and hence all operations involving removal of solvent were carried out at $35^\circ \pm 5^\circ$ *in vacuo*, the material being stored in a refrigerator in N_2 .

|| In a personal communication, Prof. Brieger informed that he had done some incidental work on terpenic components of *M. matricarioides* (unpublished). Moreover, his identification of the natural product as *trans*- β -farnesene is also based on the literature report of IV in *Matricaria* species.⁴

¶ T.C.J. appreciates the financial support from the National Research Council of Canada. He is indebted to Professor Sørensen for his valuable comments on the manuscript concerning the compound '3200'. He thanks Prof. Brieger for providing a copy of the IR spectrum of his natural farnesene.

³ G. BRIEGER, *J. Org. Chem.* **32**, 3720 (1967).

⁴ F. ŠORM, M. ZAORAL and V. HEROUT, *Coll. Czech. Chem. Commun.* **16**, 626 (1951).

⁵ J. J. KARCHESY, *M.Sc. Thesis*, University of Victoria (1970).

⁶ A. I. SCOTT, *Interpretation of the Ultraviolet Spectra of Natural Products*, Chap. 2, Pergamon Press, Oxford (1964).