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SHORT COMMUNICATION

SESQUITERPENE LACTONES OF ARTEMISIA SPECIES—II.

ARTEMISIA TRIDENTATA NUTT. SSP. *TRIDENTATA*

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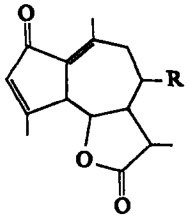
Artemisia tridenata Nutt. ssp. *tridentata* is one of the common types of "sagebrush" of the Western United States. It is a member of the subgenus (Section) Seriphidium, and one of the group of Tridentatae of this Section.[1-3]

The plant is an aromatic perennial shrub which is rich in terpenoid compounds and preliminary examination showed that it contains sesquiterpenoid lactones, a class of compounds that are widespread in the Compositae.

Extraction of the dried leaves and stems of a specimen of the plant collected in Southern California yielded a crystalline sesquiterpenoid lactone that was identified as deacetoxymatricarin (leucodin[4]) (I).



(I) R=H
(II) R=OAc

Deacetoxymatricarin, $C_{15}H_{18}O_3$, had m.p. 204–206° and showed i.r. absorption at 1780 cm^{-1} (γ-lactone), 1690 cm^{-1} (cyclopentenone) and 1630 cm^{-1} (double bond). It had the u.v. absorption maximum at 255 nm ($\log \epsilon$ 4·15) characteristic of the dienone system of (I). Its NMR spectrum showed signals for the two vinylic methyl groups ($\delta = 2{\cdot}51$ and 2·65 ppm, singlets), the methyl group on the lactone ring (1·38 ppm, doublet, $J = 7$) and the vinylic proton at C-3 (6·75 ppm, singlet). The NMR and i.r. spectra corresponded in all details with those of an authentic specimen of deacetoxymatricarin.[5]

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[1] G. W. Ward, *Contrib. Dudley Herb.* 4, 155 (1953).

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[3] H. M. Hall and F. E. Clements, *The Phylogenetic Method in Taxonomy.* Carnegie Institute, Washington, D.C. (1923).

[4] M. Holub and V. Herout, *Collection Czech. Chem. Commun.* 27, 2980 (1962).

[5] We are grateful to Professor W. Herz for providing a specimen of deacetoxymatricarin for comparison.

Deacetoxymatricarin is known to occur only in members of the tribe Anthemideae, and has so far been isolated only from *Artemisia tridentata* ssp. *tridentata* and *A. leucodes* Kitam.[4] Matricarin (II) itself occurs in *Matricaria chamomilla* L.,[6] *Achillea lanulosa*[7] and *Artemisia tilessi* Ledeb.,[8] and *Achillea lanulosa* contains a stereoisomer of deacetoxymatricarin (achillin).

Artemisia tridentata ssp. *tridentata* contains other sesquiterpenoid lactones in addition to (I) (which is the principal component); these are still under investigation.

EXPERIMENTAL

Artemisia tridentata (Nutt.) ssp. *tridentata*[9] was collected at an altitude of about 3000 ft near Valyermo, California, in October, 1965. The non-woody aerial parts (250 g) were dried and ground in a Wiley mill and extracted (cold) exhaustively with chloroform. Removal of the solvent left a green–black residue (45·3 g) which was taken up in 50 ml of ethanol, to which solution was added 100 ml of hot water. The aqueous solution was decanted from tar, clarified by filtration (with the aid of celite and norite) and extracted repeatedly with $CHCl_3$. Removal of the $CHCl_3$ left a yellow–brown syrup which was dissolved in benzene and applied to a column of neutral alumina (100 g). A benzene-insoluble syrup deposited from the solution. Development was carried out with benzene, followed by benzene–ether, ether, and finally methanol to give ten 25-ml fractions, eight 125-ml fractions and two final 500-ml fractions, the first thirteen of which were benzene eluates. Fractions 1–5 yielded residues which crystallized upon the addition of ether. Smaller amounts of the same crystalline material were obtained from fractions 6–13. No crystalline material was isolated from the benzene–ether (fractions 14–18) and ether (500 ml) eluates, but from the residue of the methanol fraction (500 ml) a crystalline solid slowly formed when the gum was covered with ethyl acetate and allowed to stand for several weeks.

The crystalline material from the benzene eluates was deacetoxymatricarin, of which 250 g of plant material gave 680 mg. The pure material had m.p. 204–206° (corr.) and its optical rotation was: $[\alpha]_D^{25} = 53{\cdot}2°$ ($CHCl_3 C = 2{\cdot}05$). (Found: C, 73·16; H, 7·28. Calc. for $C_{15}H_{18}O_3$: C, 73·15; H, 7·37%). The spectral data are described in the introduction.

In another experiment, the crude residue of the original chloroform extract of 1·3 kg of plant material was extracted seven times with ethanol–water (1:3), and each aqueous solution extracted with chloroform. The third and fourth of these yielded crystalline deacetoxymatricarin (3 g) without the need for chromatography.

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[7] E. H. WHITE and E. R. K. WINTER, *Tetrahedron Letters* No. 137 (1963).

[8] W. HERZ and K. UEDA, *J. Am. Chem. Soc.* **83**, 1139 (1961).

[9] A voucher specimen of the plant bears the herbarium designation 31966-ATA. The identification of the specimen was made by Dr. A. A. Beetle, University of Wyoming.