Phytochemistry, 1980, Vol. 19, pp. 2761–2762. © Pergamon Press Ltd. Printed in England 0031 9422/80/1201 2761 $02.00/0

IRREGULAR MONOTERPENE ALCOHOLS FROM *ARTEMISIA HERBA-ALBA*

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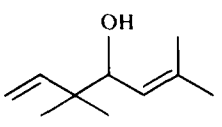
(*Received* 28 *March* 1980)

Key Word Index—*Artemisia herba-alba*; Compositae; irregular monoterpene alcohols; (+)-artemisia alcohol; santolina alcohol; yomogi alcohol; lyratol.

Artemisia herba-alba grows abundantly in the Negev Desert and in Sinai. Since it has been shown that the sesquiterpene lactones in the plant from the Negev [1] differ from those present in plants from Sinai [2], it may be assumed that there are several chemotypes of this species. Recently the antibacterial activity of the essential oil from the Negev variety was reported [3]. The present work is concerned with the isolation and characterization of four non-head-to-tail monoterpene alcohols from this oil.

About 30% of the oil is composed of four relatively non-polar compounds. These were isolated and purified by repeated column chromatography and were identified as the non-head-to-tail monoterpenes: artemisia alcohol **1** (5%), santolina alcohol **2** (10%), yomogi alcohol **3** (6%) and lyratol **4** (12%). All these irregular monoterpene alcohols are rare in nature especially the santolina alcohol and lyratol which have previously been isolated only from one plant source each, *Ormenis multicaulis* and *Cyathocline lyrata* respectively [4–6].

The artemisia alcohol isolated previously from nature always showed a negative optical rotation $[\alpha]_D = -30°$ [7–10]. It is therefore of special interest to note that the artemisia alcohol isolated from the *Artemisia herba-alba* oil showed a positive optical rotation $[\alpha]_D^{20} = +17°, +19°, +20°$, determined on three different batches. This shows that our samples contain considerable quantities of the as yet un-reported positive enantiomer. We are now investigating whether all *Artemisia herba-alba* varieties contain (+)-artemisia alcohol in their essential oil.



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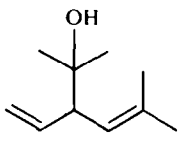

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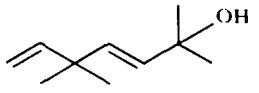

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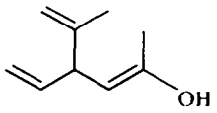

4

EXPERIMENTAL

IR spectra were recorded in liquid films. Optical rotations were determined on a Perkin Elmer 141 M Polarimeter; NMR spectra were determined in $CDCl_3$ at 60 MHz and at 100 MHz. Analytical TLC was carried out on Si gel G (Merck) plates and developed by spraying with a soln containing 5 ml phosphomolybdic acid 5% in MeOH, anisaldehyde (2.1 ml), HOAc (45 ml), conc H_2SO_4 (22.5 ml), MeOH (430 ml). The plates were heated to 100° after spraying. Si gel 60 (Merck) was used for column chromatography. Petrol refers to the fraction bp 30–40°.

Artemisia herba-alba Asso. was collected near Sde-Boker (Negev Desert) Israel. Plant material was collected and identified by Dr. Avinoam Danin, Department of Botany, The Hebrew University, Jerusalem, Israel. A voucher specimen (AHA-1) is available for inspection at the Dept. of Natural Products (Dr. R. Segal), School of Pharmacy, The Hebrew University, Jerusalem, Israel. The dried crushed flowers, leaves and small stems (150 g) were steam distilled to give a yellow oil (1.5 g); d_{20} 0.909; n_D^{25} 1.4628; $[\alpha]_D^{20}$ + 10° (1.1 MeOH).

Repeated column chromatography over Si gel using first CH_2Cl_2, then petrol Et_2O (16:1) afforded the pure monoterpene alcohols eluted in the following order: Artemisia alcohol: $[\alpha]_D^{20}$ +20° (*c* 0.49; MeOH). The compound was identified by comparison of its MS, IR, and NMR spectra (60 MHz and 100 MHz) with those of an authentic sample. The R_f values on TLC, petrol–Et_2O, 4:1 were also identical: R_f 0.7. Santolina alcohol: $[\alpha]_D^{20}$ +11° (*c* 0.39; MeOH), lit. [4] $[\alpha]_D^{20}$ +13.5°, MS *m/e* (rel. int.) 139 (M-15, 1), 96 (57), 81 (64), 62 (10), 59 (100), 43 (31). TLC, petrol Et_2O 4:1 R_f 0.6 identified by the IR and NMR spectra [4]. Yomogi alcohol: Identified by IR and NMR spectra [11], and by the MS fragmentation pattern which was identical with that described [12]. TLC, petrol–E_2O, 4:1, R_f 0.52. Lyratol: $[\alpha]_D^{20}$ +51° (*c* 0.45, hexane), lit. [5] $[\alpha]_D$ +62.3°, TLC, petrol Et_2O, 4:1, R_f 0.44. Identified by IR and NMR spectra [5,6] as well as by the MS fragmentation pattern [10].

Acknowledgements—We thank Professor C. Dale Poulter from the University of Utah for donating a sample of artemisia alcohol. We thank Professor James D. White and Prof. R. Grandi for sending us a copy of the NMR spectrum of artemisia alcohol.

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