Phytochemistry, 1974, Vol. 13, pp. 1207 to 1208. Pergamon Press. Printed in England.

SESQUITERPENES FROM *ARTEMISIA PRINCEPS*

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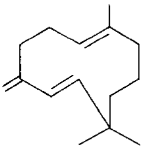
(*Received* 2 *August* 1973)

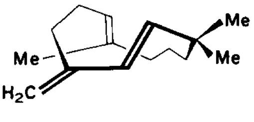
Key Word Index—*Artemisia princeps*; Compositae; mugwort; essential oil; γ-humulene; sesquiterpenes.

Abstract—Copaene, cyperene, caryophyllene, β-farnesene, α-himachalene, γ-humulene and farnesyl acetate were isolated from the root of *Artemisia princeps*. As a result of isomerization studies on γ-humulene, the main constituent, a preferred conformation was proposed.

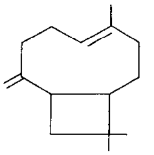
THE POLYACETYLENES of the roots[1] and the volatile constituents of the leaves[2] of *Artemisia princeps* Pamp. have been the subjects of previous studies. The presence of ylangene, caryophyllene, β-elemene, humulene, β-, γ- and δ-cadinene, α-curcumene, calamenene, calacorene and β-selinene have been confirmed.[2] Using a combination of column chromatography and preparative GLC, the root oil of *A. princeps* has now been found to contain γ-humulene (54 %), β-farnesene (13 %), caryophyllene (7 %), α-himachalene (6 %), cyperene (2 %), copaene (1 %) and farnesyl acetate (trace, from the polyacetylene fraction).[1] Freshly isolated and purified γ-humulene (**1**) was then passed in a stream of helium, through a column of diatomaceous earth heated to 180°. At that temperature γ-humulene (**1**) was almost completely rearranged to a series of hydrocarbons from which caryophyllene (**3**) and α-himachalene (**4**) were isolated as the main products of isomerization. On standing, a 10 % soln of pure γ-humulene in CCl_4 was found to rearrange principally to the same products. This isomerization shows a *trans* annular interaction between the two double bonds in the *cyclo*-undecane ring and that γ-humulene has the conformation to make either cyclobutane or cyclohexane rings with relative ease. The NMR signals at δCCl_4 1·37 (3H, *d*, J = 1·5 Hz, $\underline{CH_3}$-C=CH) indicate that a methyl group on double bond is situated over the π-electron of endocyclic double bond. From this evidence and from building molecular models, we propose the preferred conformation (**2**) for γ-humulene.



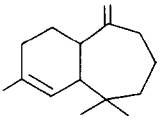
(**1**)



(**2**)



(**3**)



(**4**)

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[1] YANO, K., TAKAHASHI, S. and FURUKAWA, T. (1972) *Phytochemistry*, **11**, 2577.

It is interesting that γ-humulene has been isolated in this root oil accompanied by caryophyllene and α-himachalene and also humulene in leaf oil[2] is accompanied by caryophyllene, because it is considered to be the biogenetic intermediate for the formation of caryophyllene, himachalene and related sesquiterpenes.[3]

EXPERIMENTAL

The extract, which was described in the previous paper[1] was chromatographed on deactivated Al_2O_3 column. *n*-Hexane eluted sesquiterpene hydrocarbons (52% of the extract). GLC separation of the sesquiterpene hydrocarbons were obtained on a 3m × 4mm I.D. glass column packed with 25% polyethylene glycol 6000 adsorbed on 60–80 mesh shimalite using helium gas flow of 30 ml/min at 180°. All compounds were isolated preparatively using above conditions and their identity was characterized by IR and NMR. IR spectra were run either as liquid films or as solutions in CCl_4. NMR spectra were determined on 10% soln in CCl_4 or C_6D_6 on a 90 MHz spectrometer using TMS as an internal standard.

Characterization of γ-humulene (**1**). **1** isolated as indicated above was found to have $M^+ = 204{\cdot}186$ ($C_{15}H_{24} = 204{\cdot}188$), $[\alpha]_D^{25}$ 0°, λ_{max}^{EtOH} 245 nm (ε 12400). Hydrogenation over Adams catalyst in HOAc absorbed six equivalents of H_2. IR* 1670, 1380, 1360, 968 and 877 cm^{-1} and NMR* δCCl_4 0·93 [6H, *s*, $(C\underline{H}_3)_2C<$], δCCl_4 1·37 (3H, *d*, *J* 1·5 Hz, $C\underline{H}_3$–C=CH) overlapped with methylene signals of 1·39, but both groups in C_6D_6 soln separated to the signals at δC_6D_6 1·37 (3 H, *d*, *J* 1·5 Hz, $C\underline{H}_3$–C=CH) and methylene signals at δC_6D_6 1·28, $>C{=}C\underline{H}_2$ group at δCCl_4 4·73 (1 H, *d*, *J* 2·5 Hz) and 4·77 (1 H, *d*, *J* 2·5 Hz), δCCl_4 5·18 (1 H, *t-m*, broad, *J* 7 Hz, $C\underline{H}$=C–CH_3), AB type signals of CH=CH at δCCl_4 5·45 (1 H_A, *d*, *J* 16 Hz) and 5·73 (1 H_B, *d*, *J* 16 Hz).

Isomerization of γ-humulene (**1**). **1** was 79% isomerized by passing it in a stream of He through a heated column containing diatomaceous earth. Main products of isomerization were caryophyllene (13%) and α-himachalene (37%). After recording the NMR spectrum of a 10% soln of pure γ-humulene in CCl_4 the soln was allowed to stand at room temp. for 1 month after which time it was found that γ-humulene isomerized. Analysis of the NMR solution showed that 46% γ-humulene had isomerized to caryophyllene (4%) and α-himachalene (22%).

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[2] TSUBAKI, N., NISHIMURA, K. and HIROSE, Y. (1966) *Bull. Chem. Soc. Japan* **39**, 312.

[3] SMEDMAN, L. A., ZAVARIN, E. and TERANISHI, R. (1969) *Phytochemistry* **8**, 1457.

* The authors are grateful to Dr. E. Zavarin, Forest Products Laboratory, University of California, Richmond, California for a copy of the IR and NMR of an authentic sample of γ-humulene.