Farnesenes Isolated from the Volatile Oil of *Perilla frutscens f. viridis* Makino

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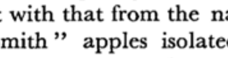
Three farnesene isomers, *cis*-α-farnesene (I), *trans*-(C_{10})- and *cis*(C_{10})- allofarnesenes (II and III), together with β-farnesene and farnesol, were isolated from the sesquiterpene fraction of the volatile oil now obtained from *Perilla frutscens f. viridis* Makino (Ao-shiso in Japanese) for the first time.

These three hydrocarbons (I, II and III) all had the same molecular formula, $C_{15}H_{24}$ (from MS data), and the same mother skeleton, farnesane (by hydrogenation).

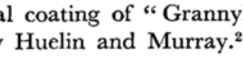
cis-α-Farnesene (I): IR; ν_{max}^{film} 1590, 3085, 985, 900, 1635, 830 cm^{-1}. NMR; δ^{CCl_4} 1.60, 165, 1.69 (12H, 3 s.), δ 2.00 (4H, unresolved d.), δ 2.78 (2H, t., J=7.0 Hz), δ 6.74 (1H, qua.), δ 4.95—5.25 (5H, complex m.). UV; λ_{max}^{EtOH} 238 mμ (ε=11300).

Cavill *et al.*1) reported the isloation and characterization of α-farnesene from Dufour's gland in the ant *Aphenogaster longiceps* (F. Sm.); they identified it with that from the natural coating of "Grannyl Smith" apples isolated by Huelin and Murray.2) They also showed that the α-farnesene from the ant and apples has a *trans*-conjugated diene. The lone proton in the R–CH=CH$_2$ system in the α-farnesene from the ant appears as a signal centered at δ 6.3 in the NMR spectrum, and its UV absorption maximum is at 232 mμ (ε=36400). On the other hand, our α-farnesene has the following values: δ 6.73; λ_{max}^{EtOH} 238 mμ (ε=11300). According to Ohloff *et al.*,3) the proton at C_7 in the isomeric β-ocimene has a signal centered at δ 6.30 in *trans*-β-ocimene (IVb) and at δ 6.73 in *cis*-β-ocimene (IVa). Moreover, they reported an UV absorption maximum at 232 mμ (ε=27600) for *trans*-β-ocimene and one at 237 mμ (ε=21000) for *cis*-β-ocimene.

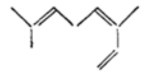
Therefore, it may be concluded that α-farnesene from the ant and from apples is *trans*-α-farnesene (V), while that from Perilla is *cis*-α-farnesene (I).



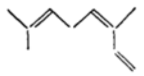
(I)



(V)



(IVa)



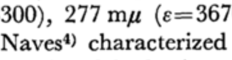
(IVb)

trans(C_{10})-Allofarnesene (II) : IR; ν_{max}^{film} 960 cm^{-1}. NMR; δ 1,60, 1.63, 1.79 (15H, 3 s.), δ 2.06, 2.11 (4H, 2 s.), δ 5.07—7.44 (5H, complex m.). UV; λ_{max}^{EtOH} 270 mμ (ε=26800), 281 mμ (ε=35700), 292 mμ (ε=26700).

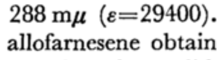
cis(C_{10})-Allofarnesene (III) : NMR; δ 1.60, 1.67, 1.75 (15H, 3 s.), δ 2.05, 2.10 (4H, 2 s.), δ 5.08—6.25 (5H, complex m.). UV; λ_{max}^{EtOH} 266 mμ (ε=28300), 277 mμ (ε=36700), 288 mμ (ε=29400).

Naves4) characterized the allofarnesene obtained from the dehydration of farnesol and nerolidol; he also identified the sesquiterpene hydrocarbon isolated from ylang-ylang oil and also "sesquicitronellene" with allofarnesene. However, the allofarnesene used for the structural analysis was a mixture of *trans*- and *cis*-isomers. The spectral data of allofarnesene reported by Naves resemble those of our *cis*(C_{10})-allofarnesene (III). O'Connor and Goldblatt5) reported the UV absorption maxima at 270 mμ (ε=31319), 278 mμ (ε=39874), and 289 mμ (ε=30542) for *trans*(C_4)-*trans*(C_6)-alloocimene, and those at 265 mμ (ε=32872), 273 mμ (ε=42,871), and 285 mμ (ε=33757) for *trans*(C_4)-*cis*(C_6)-alloocimene.

Therefore, it may be concluded that the hydrocarbon II (Kovats index 1758)[*1] is *trans*(C_8)-*trans*(C_{10})-allofarnesene and that the hydrocarbon III (Kovats index 1783) is *trans*(C_8)-*cis*(C_{10})-allofarnesene.



(II)



(III)

When passed through a Carbowax 20M column operating at a high temperature,[*2] *cis*-α-farnesene (I) isomerized quantitatively to *trans*(C_{10})-allofarnesene (II).

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1) G. W. K. Cavill, P. J. Williams and F. B. Whitfield, *Tetrahedron Letters*, **1967**, 2201.

2) F. E. Huelin and K. E. Murray, *Nature*, **210**, 1260 (1966).

3) G. Ohloff, J. Seibl and E. sz. Kovats, *Liebig Ann.*, **675**, 83 (1964).

4) Y. R. Naves, *Helv. Chim. Acta*, **49**, 1029 (1966).

5) R. T. O'connor and L. A. Goldblatt, *Anal. Chem.*, **26**, 1726 (1954).

[*1] Hitachi K-53, HB-2000, 45 m × 0.25 mm, 150°C/ 1.0 kg N_2.

[*2] Varian 90-P, 20% Carbowax 20M-Chromosorb w, 3/8 inch × 20 ft aluminium column, oven temp. 200°C, detector temp. 250°C, He carrier gas.