Sesquiterpenoids in the Leaf Oil of Camphor Trees. II. Sesquiterpenoids of Safrole Trees[1] and Sesquiterpene Trees[1]

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Sesquiterpenoids in the leaf oil of *Cinnamomum Camphora Sieb.* (the eucamphor tree[1]) have already been reported by the present author in the previous paper.[2] The major components of the leaf oil of safrole trees and sesquiterpene trees, which are subgroups of the commonly-called camphor tree, were found to be safrole[3] (about 80%) and nerolidol[4] (about 50%) respectively. Though the major components and monoterpenoids in the leaf oil of these camphor trees have been determined,[4,5] a more precise investigation of the sesquiterpenoids of these oils will be presented in this paper.

The essential oil was obtained by steam-distillation from the leaves of camphor trees growing in Matsuyama, Japan; the trees sprouted from the seeds of mother trees which had been transplanted from Formosa to Wakayama Prefecture, Japan, by Dr. Naonori Hirota.

β-Caryophyllene, β-bisabolene, humulene, farnesene, and nerolidol were isolated and identified in the leaf oil of the safrole tree, while α-ylangene, humulene, β-elemene, β-caryophyllene, β-selinene, β-caryophyllene oxide, α-cyperone, and nerolidol were isolated from the sesquiterpene tree. It is the first time that β-caryophyllene oxide and α-cyperone have been found in camphor oil.

The sesquiterpene fraction, which amounted to about 3.2% in the leaf oil of the safrole tree, was estimated to be approximately 45% β-caryophyllene, 6% farnesene, 5% humulene, 3% β-bisabolene, 15% β-selinene, and 6% nerolidol, while the sesquiterpene fraction, which amounted to about 70% in the leaf oil of the sesquiterpene tree, was estimated to be approximately 55% nerolidol, 1.8% α-ylangene, 2.5% β-elemene,

1) N. Hirota, *Mem. Ehime Univ.*, Vol. II, No. **3**, 105 (1956); E. Gildemeister and F. Hoffman, "Die Ätherischen Öle," B. 5, Akademie-Verlag, Berlin (1959), p. 49.
2) M. Hiroi, This Bulletin, **40**, 1003 (1967).
3) N. Hirota, *Mem. Ehime Univ.*, Sect. II (Science), Vol. I, No. 3, 91 (1952).
4) N. Hirota and M. Hiroi, *Koryo*, **70**, 23 (1963).
5) N. Hirota and M. Hiroi, *Mem. Ehime Univ.*, to be published.

6.5% β-caryophyllene, 5.5% humulene, 9.0% β-selinene, 5.5% caryophyllene oxide, small amounts of α-cyperone, and 9% unidentified higher boiling substances. These conclusions were reached on the basis of fractional distillation and gas chromatography.

Experimental

For gas chromatography, a Shimadzu G. C. -2B apparatus, equipped with a thermal conductivity detector using a copper spiral packed with Celite and coated with P. E. G. 6000, was used in this experiment.

Leaves (350 kg) of the safrole tree with small twigs were submitted to steam distillation to give an oil in about a 1% yield. Safrole and monoterpenoids were removed by a combination of fractional distillation and crystallization. The residual oil was then adsorbed on a silica gel column, and eluted with *n*-hexane and then ethyl acetate successively. Both the eluates were fractionated by distillation under reduced pressure.

β - Caryophyllene, Humulene, β - Bisabolene, Farnesene and β-Selinene from Safrole Trees. The fraction, 107—116°C/10 mmHg (13.1 g) of the *n*-hexane eluate was rechromatographed on alumina (Activity I), using *n*-hexane as a solvent. The four fractions, Fr. 1 (2.3 g), n_D^{20} 1.500, $[\alpha]_D^{18}$ −8.4°; Fr. 2 (0.3 g), n_D^{20} 1.5033; Fr. 3 (0.19 g), n_D^{20} 1.4921; Fr. 4 (0.11 g), n_D^{20} 1.4889, were obtained in almost pure states. The infrared spectra of these fractions were identical with those of β-caryophyllene,[6a] humulene,[6b] β-bisabolene,[6c] and farnesene[6d] respectively. The retention time of the gas chromatography of each fraction was identical with that of the authentic sample. The last peak of the gas chromatography of the hexane eluate was supposed to be the peak of β-selinene on the basis of a comparison of retention time with that of an authentic sample of *d*-β-selinene.

Nerolidol. From a fraction (120—135°C/5 mmHg) of the ethyl acetate elute, an oil (n_D^{20} 1.4803, $[\alpha]_D$ +11.4°) was obtained by preparative gas chromatography using P. E. G. 6000. This oil was proved to be identical with *d*-nerolidol by comparing the infrared spectrum and the retention time of gas chromatography with those of an authentic sample.

On the steam distillation of leaves of the sesquiterpene trees, a leaf oil was obtained in about a 0.3% yield. After the monoterpenoids had been removed from the leaf oil by fractional distillation, the residual oil was treated as in the case of oil from the safrole trees.

Nerolidol from Sesquiterpene Trees. The sesquiterpenoid fraction of the ethyl acetate eluate, 99—115°C/2 mmHg, n_D^{30} 1.4795—1.4880, was confirmed to consist mainly of nerolidol by comparing its infrared spectrum and its gas chromatogram with those of an authentic sample, though a small quantity of unidentified higher-boiling sesquiterpenoids was also present.

α-Ylangene, Humulene, β-Elemene, β-Caryophyllene and β-Selinene, from Sesquiterpene Trees. From a fraction (95°C/5.5 mmHg—88°C/3 mmHg) of the *n*-hexane eluate, the following five fractions were obtained in almost pure states by preparative gas chromatography with P. E. G. 6000; Fr. 1 (0.4 g), n_D^{20} 1.4912, $[\alpha]_D^{17}$ −18°; Fr. 2 (1.1 g), n_D^{20} 1.4998, $[\alpha]_D^{17}$ −8.5°; Fr. 3 (0.5 g), n_D^{20} 1.4945, $[\alpha]_D$ −6.3°; Fr. 4 (0.8 g) n_D^{20} 1.5038 $[\alpha]_D^{17}$ −0.3°; Fr. 5 (1.3 g) n_D^{20} 1.5041, $[\alpha]_D^{17}$ +31°. The infrared spectra of those fractions are identical with those of α-ylangene,[6e] β-caryophyllene,[6a] β-elemene,[6f] humulene,[6b] and β-selinene[6g] respectively. They were also confirmed by gas chromatography.

Caryophyllene Oxide. From a fraction (88—97°C/3 mmHg, n_D^{13} 1.5006—1.4991) of the *n*-hexane eluate, an oily fraction (n_D^{20} 1.4992, $[\alpha]_D^{15}$ −27°C, yield 1.4 g), besides, β-selinene was obtained by chromatography on an alumina column, using *n*-hexane containing 10% ethyl acetate. The infrared spectrum was identical with that of β-caryophyllene oxide,[6h]: and the R_f value of a thin-layer chromatography on silica gel with *n*-hexane containing 10% ethyl acetate was identical with that of the authentic sample of β-caryophyllene oxide prepared from β-caryophyllene.

***d*-α-Cyperone.** From a fraction (97—101°/2.5 mmHg, n_D^{13} 1.5058—1.5157), an oily fraction (n_D^{15} 1.5260, $[\alpha]_D^{15}$ +35°, IR $\nu_{C=O}$ 1665 cm^{-1}, yield 0.2 g), besides caryophyllene oxide and a very small amount of unidentified compounds, was obtained by chromatography on an alumina column with *n*-hexane containing 10% ethyl acetate. The infrared spectrum and the melting point, 210°C, of 2, 4-dinitrophenylhydrazone are identical with those[6i,7] of α-cyperone.

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6a) J. Pliva, M. Horak, V. Herout und F. Sorm, "Terpenespectren," Akademie-Verlag, Berlin (1960), p. 176; b) *ibid.*, p. 30; c) *ibid.*, p. 8; d) *ibid.*, p. 2; e) *ibid.*, p. 221; f) *ibid.*, p. 24; g) *ibid.*, p. 82; h) *ibid.*, p. 179; i) *ibid.*, p. 96.

7) E. Guenther, "The Essential Oils," Vol. 2, D. Nostrand Company, New York (1949), p. 453.