Sesquiterpenoids in the Leaf Oil of the Camphor Tree. I. Sesquiterpenoids of *Cinnamomum Camphora Sieb.* (Japanese Camphor Tree[1])

Mitsuru Hiroi

Department of Chemistry, Faculty of Literature and Science, Ehime University, Matsuyama

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Sesquiterpenoids of camphor oil (trunk and root oil) have been investigated by several workers, and the following compounds have been reported as constituents[2]: β-caryophyllene, α-humulene, α-ylangene, α- and γ-santalene, β-elemene, α- and γ-guaiene, δ-cadinene, calamenene, calacorene, elemol, guaiol, α-cadinol, juniper camphor, 1, 6-dimethyl-4-isopropyl-7, 8-dihydronaphthalene, α-eudesmol, myristicin, and γ-patchoulene.

Hirota has classified the commonly-called camphor tree into five subgroups from the point of view of the major components, (parenthesized below) in the leaf oil: eucamphor tree (camphor), linalool tree (linalool), safrole tree (safrole), cineole tree (cineole), and sesquiterpene tree (sesquiterpenoids).[1] It has been also reported that the substances contained in the leaf oil differ distinctly from those in the trunk and the root oil.[3]

Few thorough studies on sesquiterpenoids in leaf oil have been made, though the following substances have been reported: β-caryophyllene, humulene and camphazulene in the Hon-Sho (eucamphor tree),[4] β-caryophyllene in the Ho-Sho (linalool tree),[5] and nerolidol and humulene in the sesquiterpene tree.[6] The present work deals with a more precise investigation of sesquiterpenoids.

The essential oil was obtained from leaves and twigs of Japanese camphor trees (*C. C. Sieb.*) growing in Matsuyama, Ehime Prefecture, Japan.

The higher-boiling fraction of the oil was separated by a combination of fractional distillation and silica-gel chromatography.

The identity of humulene, β-caryophyllene, α-ylangene, β-elemene, β-selinene, and nerolidol was confirmed by a comparison of their infrared spectra, NMR spectra, and other physico-chemical properties with those reported or those of an authentic sample. Of these, β-selinene was found in camphor oil for the first time.

The sesquiterpene fraction amounted to about 10% of the liquid leaf oil and was estimated to contain approximately 35% β-caryophyllene, 14% β-selinene, 18% humulene, 8% β-elemene, 3% α-ylangene, and 1% nerolidol, on the basis of the results of both fractionation and gas chromatography.

Experimental

By steam distillation, 800 kg of the leaves with small twigs (smaller than the small finger) were treated to give about a 1 % yield of oil and solid camphor. After

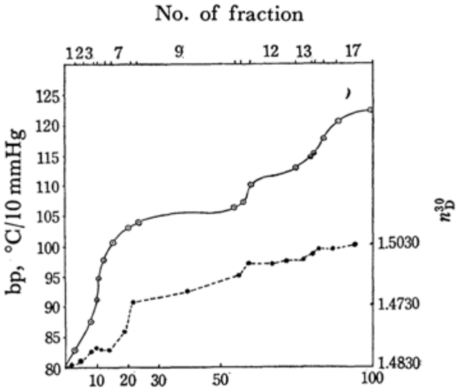

Fig. 1. Distillation of hexane-eluate.

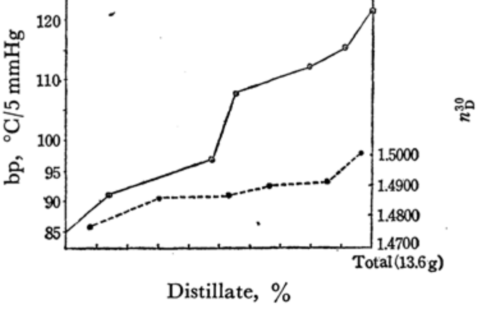

Fig. 2. Distillation of ethylacetate-eluate.

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[1] N. Hirota, *Mem. Ehime Univ.*, Vol. II, No. 3, 105 (1956); E. Gildemeister and F. Hoffman, "Die Atherischen Ole," B. 5, Akademie-Verlag Berlin (1959), S. 49.

[2] S. Hayashi *et al.*, Abstract of the 9th Symposium on Chemistry of Terpenes, Essential Oils and Aromatics, Kumamoto, Oct. 17, 1965.

[3] N. Hirota, *Mem. Ehime Univ.*, Sect. 2, Vol. I, No. 4, 69 (1953).

[4] S. Kitajima, *Sci. Papers, Central Research Inst., Govt. Monopoly Bur., Japan, Tokyo,* No. 80 (1948).

[5] T. Naito, *Nippon Kwagaku Kwaishi (J. Chem. Soc. Japan)*, **64**, 1125 (1943).

[6] N. Hirota and M. Hiroi, *Koryo,* **70**, 23 (1963).

the camphor had been removed by cooling at −25°C and the monoterpenoids, by fractional distillation, the residual oil was dissolved into hexane and separatec by silica-gel chromatography, the substances adsorbed being eluted with *n*-hexane and ethylacetate successively. The two eluates with *n*-hexane and ethylacetate were then divided by fractional distillation (Fig. 1 and Fig. 2).

Fractions 1—7 of Fig. 1 (8.4 g) were rechromatographed on a silicagel column (Merck, less than 0.08 mm), using *n*-hexane as a solvent.

The following three fractions were obtained in almost pure states:

(1)	n_D^{30}	1.4849	$[\alpha]_D$	−19.8	yield	0.2 g
(2)	n_D^{30}	1.4924	$[\alpha]_D$	−13	yield	0.5 g
(3)	n_D^{30}	1.4975	$[\alpha]_D$	− 7.8	yield	1.8 g

***l*-α-Ylangene, *l*-β-Elemene and *l*-β-Caryophyllene.** The infrared spectra of fractions 1, 2 and 3 agreed with those of α-ylangene,7a) β-elemene,7b) and β-caryophyllene7c) respectively.

The NMR spectra of fractions 1 and 2 showed τ= 4.83, 8.32 (3H), 9.10 (3H) and 9.21 (6H doublet), and τ=3.97—5.05 (multiplet) 8.32 (3H), 8.34 (3H), and 9.03 (3H), respectively. The melting point, 157°C, of the nitrosochloride of fraction 3 is identical with that of *l*-β-caryophyllene nitrosochloride.8)

Humulene. Fractions 8—11 of Fig. 1 (25 g), presumed to consist mainly of β-caryophyllene, were again chromatographed on silica gel with *n*-hexane. The infrared spectrum of a fraction (1.2 g) separated from β-caryophyllene agreed with that of humulene.7d) It gave a nitrosochloride (mp 176°C)9) and a nitrolpiperidide (mp 153°C).9) The major component of fraction 12 of Fig. 1 (9.3 g) was confirmed to be humulene.

***d*-β-Selinene.** Fractions 13—15 (5.4 g) were chromatographed on a silica-gel column with *n*-hexane, and two main fractions were obtained. One of them was identified as humulene, while the other (1.3 g) shows n_D^{30} 1.5031, and $[\alpha]_D^{30}$ +40.5. The infrared spectrum of this fraction was identical with that of β-selinene7e); its NMR spectrum showed τ=5.35 (4H) 8.31 (3H), and 9.3 (3H).

***d*-Nerolidol.** Fractions 4—6 of Fig. 2 (6.1 g) were separated by gas chromatography on a column of P.E.G. 6000 with helium at 180°C. Besides terpineol and geraniol, an oily substance (0.4 g) was obtained; n_D^{30} 1.4803, $[\alpha]_D^{30}$ +13. The infrared spectrum of this compound, and the retention time of gas chromatography agreed with those of an authentic sample of nerolidol.

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

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7) a) J. Pliva, M. Horak, V. Herout and F. Sorm, "Terpenespectren," Akademie-Verlag, Berlin (1960), p. 221; b), p. 24; c) p. 176; d), p. 30; e), p. 82.

8) E. Gildemeister and F. Hoffman, "Die Ätherischen Öle," B. 3a Akademie-Verlag Berlin (1960), p. 292.

9) E. Guenther, "The Essential Oils," Vol. II, D. Van Nostrand Company, New York (1949), p. 101.