Sesquiterpene Hydrocarbons of the Essential Oil of the Kusunoki *(Cinnamomum Camphora Sieb.)*

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The investigation concerning sesquiterpene constituents of camphor oil was first undertaken by workers at Schimmel & Co., who detected bisabolene[1] and cadinene;[2] it was then continued by many workers. In this way, caryophyllene was identified by Simonsen,[3] α-santalene by Kato,[4] and α-humulene and nerolidol by Hirota,[5] while recently cadina-9, 11(12)-diene has been detected by Araki.[6] Further, Ono,[7] Komatsu[8] and Kafuku[9] have pointed out the presence of new sesquiterpene constituents characteristic of camphor oil.

The present study was made of a high-boiling fraction of camphor oil commercially obtained. Nine newly-found constituents, α-ylangene, β-elemene, β-santalene, δ-guaiene, δ-cadinene, calamenene, calacorene, 1, 6-dimethyl-4-isopropyl-7, 8-dihydronaphthalene, and γ-patchoulene, and four formerly-detected constituents, caryophyllene, α-santalene, α-humulene, cadina 9, 11(12)-diene, were identified. α-Santalene, α-ylangene, β-santalene, and δ-cadinene are the main constituents, each amounting to more than ten per cent, while cadina-9, 11(12)-diene, which was detected as a main constituent by Araki,[6] was very little in quantity. It was the first case of the detection of 1,6-dimethyl-4-isopropyl-7,8-dihydronaphthalene in a natural product. The bisabolene previously reported and the constituents whose structures were

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[1] Ber. Schimmel & Co., April, **1889**, 9.

[2] *Ibid.*, October, **1909**, 24.

[3] J. L. Simonsen and T. P. Ghose, *J. Soc. Chem. Ind.*, **39**, 296 T (1920).

[4] T. Katô, T. Mukai and T. Nozoe, 3rd Symposium on the Chemistry of Terpenes, Essential Oils and Aromatics, Tokyo, 1959.

[5] N. Hirota and M. Hiroi, *The Kôryô*, No. 70, 23 (1962).

[6] M. Araki, T. Ôhara, T. Yamada and R. Gotô, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)* **87**, 63 (1966).

[7] K. Ono, *Mem. Coll. Science Imp. Univ. Kyoto,* **8**, 1 (1925).

[8] S. Komatsu, H. Fuzimoto and S. Tanaka, *Nippon Kwagaku Kwaishi (J. Chem. Soc. Japan)*, **51**, 489 (1930).

[9] K. Kafuku, T. Ikeda and M. Kato, *ibid.*, **54**, 311 (1933).

assumed by Ono,7) Komatsu8) and Kafuku9) could not be detected.

Experimental

The high-boiling fraction (bp above 215°C, 6135 g) of camphor oil, after being treated with 3% aqueous solutions of sodium carbonate and of sodium hydroxide successively, was distilled under reduced pressure; the sesquiterpene hydrocarbon fraction (bp 85—145°C/2 mmHg) was thus obtained. By repeating the precise fractionation with a packed-type distillation column, and the adsorption chromatography on an alumina or silica gel column using *n*-hexane, the hydrocarbon fraction was separated into individual hydrocarbons; these hydrocarbons were identified as will be described below.

α-Ylangene (17.7%).[*1] Found: C, 88.39; H, 11.61%. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84%. The constituent consumed one equivalent of hydrogen in catalytic hydrogenation with platinum oxide in glacial acetic acid. The IR10) and NMR11) spectra of the original hydrocarbon coincided with those of α-ylangene; this spectrometric result was also supported by a gas chromatographic comparison with authentic α-ylangene.

β-Elemene (5.0%). The constituent ($[\alpha]^{25}_{D}$ −21.0°) showed IR12) and NMR13) spectra, and the gas chromatogram agreed with those of β-elemene.

α-Santalene (34.8%). Found: C, 87.85; H, 11.71%. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84%. This hydrocarbon ($[\alpha]^{25}_{D}$ +11.1°) had a molecular weight of 204 (mass spectrometry, Fig. 1-A), and its IR14) and NMR15) spectra agreed with those of α-santalene. Besides, a nitrosochloride of colorless needles melted at 115—115.5°C, thus corresponding to α-santalene nitrosochloride.16)

β-Santalene (12.0%). Found: C, 88.30; H, 11.70%. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84%. The molecular weight of this hydrocarbon was 204 (mass spectrometry, Fig. 1-B). Its IR14) and NMR15) spectra showed a good agreement with those of β-santalene.

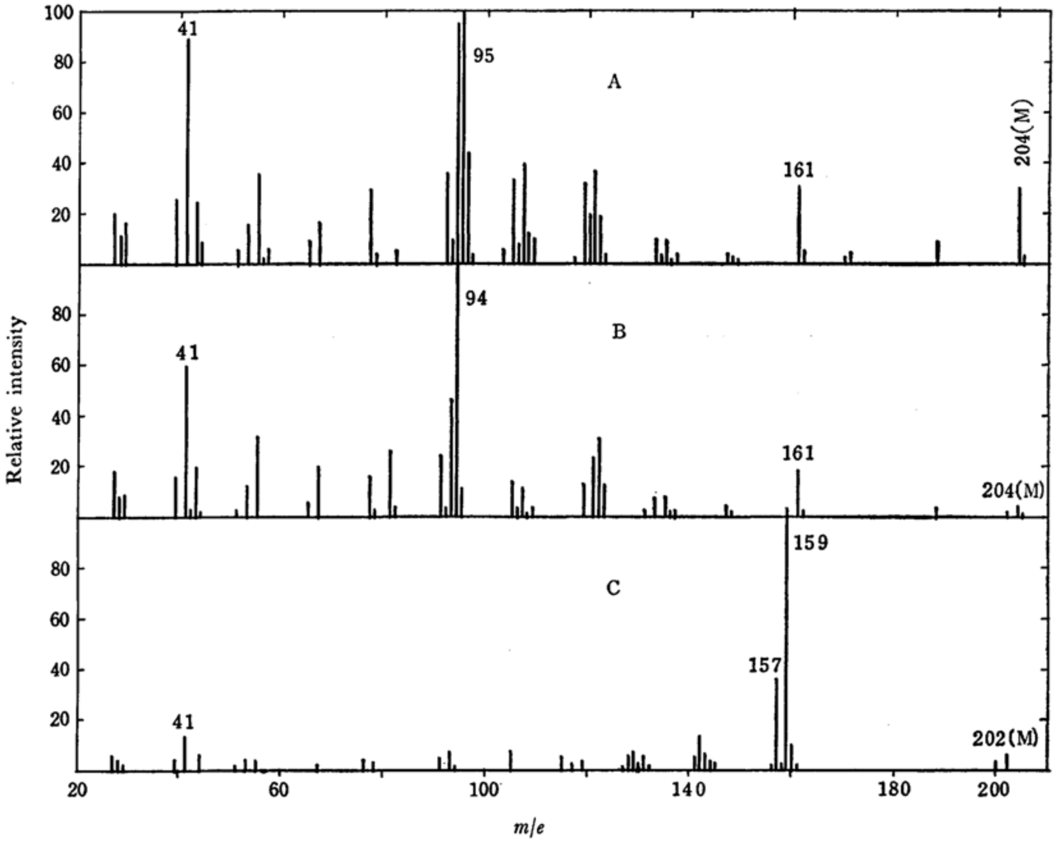

Fig. 1. Mass spectra of α-santalene (A), β-santalene (B) and calamenene (C).

[*1] The content (%) of each constituent was calculated from the relative peak area of the gas chromatogram, which was obtained by use of a Golay Apiezon-L column at 150°C, and which showed 21 peaks, including 8 unidentified ones.

10) G. L. K. Hunter, Chemist, Fruit and Vegetable Products Laboratory, Fla., private communication.

11) O. Motl, V. G. Bucharov, V. Herout and F. Šorm, *Chem. & Ind.*, **1963**, 1759.

12) C. Asselineau and J. Asselineau, *Bull. Soc. Chim. France*, **1957**, 1361.

13) M. Takahashi, K. Isoi, Y. Kimura and M. Yosikura, *J. Pharm. Soc. Japan*, **84**, 752 (1964).

14) V. Herout, V. Jarolím and J. Plíva, *Coll. Czech. Chem. Commn.*, **22**, 775 (1957).

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α-Humulene (2.5%). The constituent had the same IR spectrum as that of α-humulene,[17] and the gas chromatograms of the constituent and α-humulene were identical.

δ-Guaiene (0.2%). The constituent was dehydrogenated by heating with sulfur and produced s-guaiazulene in a good yield. The IR spectrum and the gas chromatogram of the constituent agreed with those of δ-guaiene,[18] and the NMR spectrum, which has two broad singlets at 5.36—5.62 τ (2H, exocyclic methylene) and two near-singlets at 8.37 τ (6H, two methyl groups attached to double bonds,) supported the structure of δ-guaiene well.

δ-Cadinene (11.2%). Found: C, 88.35; H, 11.58%. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84%. $[\alpha]^{25}_{D}$ +24.54°, molecular weight 204 (mass spectrometry). The IR,[19] NMR,[20] and mass spectra[21] agreed with those of δ-cadiene. This hydrocarbon produced cadinene dihydrochloride; 116—116.5°C, confirmed admixing.

Calamenene (2.5%). When the residue of the precise fractional distillation was chromatographed on a silica-gel adsorption column using petroleum ether as the solvent, calamenene, calacorene, and 1, 6-dimethyl-4-isopropyl-7, 8-dihydronaphthalene were eluted in this order. The first-eluted constituent ($[\alpha]^{25}_{D}$ $-44.0°$) had a molecular weight of 202 (mass spectrometry, Fig. 1-C). The IR[22] and NMR[23] spectra and the gas chromatogram were the same as calamenene.

Calacorene (0.4%). $[\alpha]^{25}_{D}$ +15.40°. The IR[19] and UV[19] spectra agreed with those of calacorene, and the NMR spectrum, which has a singlet at 7.74 τ (3H, a methyl group on a double bond conjugated with a benzene ring) and a doublet at 8.05 τ (3H, methyl group), fit the structure of calacorene well.

1, 6-Dimethyl-4-isopropyl-7, 8-dihydronaphthalene (0.3%). The IR and UV spectra of this constituent agreed with those of 1, 6-dimethyl-4-isopropyl-7, 8-dihydronaphthalene.[24]

Caryophyllene (3.0%), **γ-Patchoulene** (0.6%), **and Cadina-9, 11(12)-diene** (2.3%) were identified only by depending upon a gas chromatographic comparison with authentic specimens using a Golay Apiezon-L column.

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