Sesquiterpene Constituents of the Essential Oil of Hinoki (Chamaecyparis Obtusa (Sieb. et Zucc.) Endl.)

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The sesquiterpene constituents of the essential oil of Hinoki (*Chamaecyparis Obtusa* (Sieb. et Zucc.) Endl.) have been investigated by several workers,[1-3] and two compounds, *l*-[1] or *d*-cadinene[2-3] and cadinol,[3] have been reported. Recently, β-, γ-, δ- and ε-cadinene[4] were identified as isomeric members of cadinene, and α- and δ-cadinol[5] as isomers of cadinol. The present work, along with a forthcoming investigation of the monoterpene constituents[6], was undertaken to clarify the sesquiterpene constituents.

Results

The essential oil from the leaves and twigs of the Hinoki (*Chamaecyparis Obtusa* (Sieb. et Zucc.) Endl.) growing in Kôchi Prefecture, Japan, was investigated. The residual oil, from which the monoterpene fractions were distilled off, was repeatedly fractionated through a packing distillation column to divide it into several sesquiterpene fractions. The physical properties of the fractions are illustrated in Fig. 1.

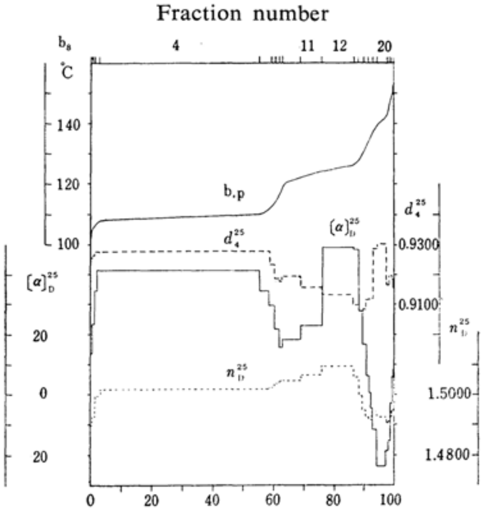

Fig. 1. Fractional distillation of sesquiterpene oil.

In the present work, *d*-longifolene and calamenene were newly identified, and cadinene and cadinol, which had formerly been reported, were confirmed to be *d*-γ-cadinene and *l*-α-cadinol respectively. On the basis of the results of both fractionation and gas chromatography, it was assumed that the sesquiterpene fractions of Hinoki oil consisted of approximately 72% *d*-longifolene, 19% *d*-γ-cadinene, 1% calamenene and 8% *l*-α-cadinol. The sesquiterpene fraction amounted to 43.2% of the total essential oil.

***d*-Longifolene.**—Fraction 4 gave a gas chromatogram which mainly showed one peak (retention time; 15.5 min.), and an infrared spectrum (1763, 1661, 1474, 1454, 1376, 1364,

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[1] R. Kondô, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **29**, 1297 (1909).

[2] S. Uchida, *J. Soc. Chem. Ind. Japan* (*Kōgyō Kwagaku Zasshi*), **28**, 1440 (1925); **31**, 650 (1928).

[3] N. Hirao, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **58**, 222 (1937).

[4] V. Herout and V. Sýkora, *Tetrahedron*, **4**, 246 (1958).

[5] O. Motl, V. Sýkora, V. Herout and F. Šorm, *Collection Czechoslov. Chem. Commun.*, **23**, 1297 (1958).

[6] To be published in this Bulletin.

1207, 1175, 873 cm^{-1}) which coincided entirely with that of longifolene.[7]

From this fraction longifolene hydrochloride (m. p. 59~60°C[8]) was prepared. Also, a nuclear magnetic resonance spectrum (τ; 9.116, 9.072, 9.049, 8.475, 8.000, 7.500, 5.630, 5.375) of this fraction agreed with that of longifolene.[9] Accordingly, it is confirmed that longifolene is a main component of fraction 4.

***d-γ*-Cadinene.** — From fraction 12 cadinene dihydrochloride (m. p. 116~117°C[10]) was prepared. However, a gas chromatogram of this fraction contained some weak peaks, together with the main peak (retention time; 30.4 min.), and so this fraction was eluted through a silica gel column, using petroleum ether to divide it into some fractions. The main fraction from the chromatography showed an infrared absorption spectrum (1649, 1454, 1389, 1369, 883, 835 cm^{-1}) which agreed with that of γ-cadinene.[11]

Calamenene.—Another small fraction from the above elution chromatography of fraction 12 gave a gas chromatogram which showed only one peak (retention time; 40.2 min.) and an infrared absorption spectrum (1642, 1613, 1550, 1500, 1464, 1385, 1369, 881, 815 cm^{-1}) which agreed with that of calamenene.[12] The ultraviolet absorption spectrum of this small fraction is shown in Fig. 2, for the ultraviolet spectrum of calamenene seems not to be found in the literature.

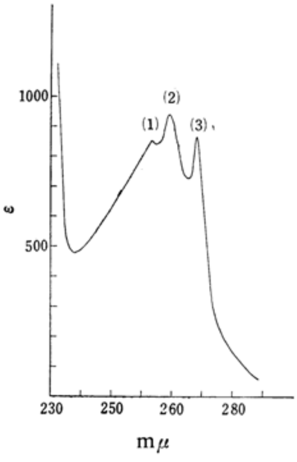

Fig. 2. The ultraviolet absorption spectrum of calamenene.

(1) λ_{max}^{EtOH} 263 mμ (ε 850)
(2) λ_{max}^{EtOH} 269 mμ (ε 940)
(3) λ_{max}^{EtOH} 278 mμ (ε 860)

In addition to *d*-γ-cadinene and calamenene, fraction 12 contained a component which showed an absorption band of λ_{max}^{EtOH} 246 mμ ($E_{1cm}^{1\%}$ 65.2) in its ultraviolet spectrum. This band suggests the presence of the isocadinene named by Gillam.[13] Thus, it is certain that fraction 12 consists of large quantity of *d*-γ-cadinene and small quantities of calamenene and other elements.

***l-α*-Cadinol.** — Cadinene dihydrochloride[5] (m. p. 115.0~116.5°C) and α-cadinol *p*-nitrobenzoate[5,14] (m. p. 134~135°C) were prepared from fraction 20. After being purified by elution chromatography on alumina (activity IV[15]) using petroleum ether, fraction 20 ($[\alpha]_D^{25}$ $-32.3°$, 0.1066 g./cc., ethanol) gave an infrared absorption spectrum (1656, 1450, 1380, 1370, 1119, 815 cm^{-1}) which agreed with that of α-cadinol.[5] Accordingly, it is certain that fraction 20 consists mainly of *l*-α-cadinol.

Experimental

In the present work, the residual oil (b. p. above 126°C/20 mmHg, 7.14 kg.) from which the monoterpene fractions were distilled off as described in the forthcoming work,[6] was used.

***d*-Longifolene.** — One-half gram of fraction 4 (Found: C, 88.32; H, 11.63%) was dissolved in ether and saturated with dry hydrogen chloride under cooling at $-15°C$. After the reaction mixture had stood for two hours, needle crystals (0.31 g.) were obtained; these, after being recrystallized from petroleum ether, melted at 59~60°C ($[\alpha]_D^{25}$ $+7.5°$, 0.2221 g./cc., chloroform). This melting point agrees with that of longifolene hydrochloride.[8]

***d-γ*-Cadinene.**—Seven hundred and twenty milligrams of fraction 12 was treated with dry hydrogen chloride as in the case of longifolene to give needle crystals (0.24 g.) which, after being recrystallized from ethanol, melted at 116~117°C ($[\alpha]_D^{25}$ $-36.2°$, 0.0486 g./cc. chloroform). This melting point agrees with that of cadinene dihydrochloride.[10] For further purification, 1.46 g. of fraction 12 was chromatographed on silica gel (100~200 mesh, 150 g.) which had been packed in a glass tube (inside diameter, 1.8 cm.) using petroleum ether. The eluate was divided into several fractions by testing its refractive index.

***l-α*-Cadinol.**—When one-half gram. of fraction 20 was treated with dry hydrogen chloride, needle crystals (0.04 g.) were obtained. The needles, after being recrystallized from ethanol, showed a melting

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7) G. Dupont, R. Dulou, P. Naffa and G. Ourisson, *Bull. soc. chim. France*, **1954**, 1075.

8) R. H. Moffet and D. Rogers, *Chem. & Ind.*, **1953**, 916.

9) S. Dev, *Tetrahedron*, **9**, 1 (1960).

10) G. G. Henderson and A. Robertson, *J. Chem. Soc.*, **1924**, 1992.

11) V. Sýkora and V. Herout, *Collection Czechoslov. Chem. Commun.*, **24**, 1732 (1959).

12) F. Šorm, K. Vereš and V. Herout, ibid., **18**, 106 (1953).

13) A. E. Gillam, D. G. Moss and T. F. West, *J. Chem. Soc.*, **1948'** 1306.

14) Pl. A. Plattner and R. Márkus, *Helv. Chim. Acta*, **25**, 1674 (1942).

15) H. Brockmann and H. Schodder, *Chem. Ber.*, **74**, 73 (1941).

point of 115.0~116.5°C ($[\alpha]_D^{25}$ −35.15°, 0.0382 g./cc., chloroform), which was confirmed by admixture with cadinene dihydrochloride (m. p. 116~117°C). One gram of fraction 20 was acylated with *p*-nitrobenzoyl chloride, and the crystalline mass (0.03 g.) was prepared. The mass, after being recrystallized from ethanol, showed a melting point of 134~135°C, which agrees with that of *p*-nitrobenzoate of α-cadinol.[5,14]

Gas Chromatography.—A gas chromatogram was made by a Shimadzu GC-2 apparatus equipped with a thermal conductivity cell using a copper spiral column (inside diameter, 4 mm.; length, 3 m.). For hydrocarbon analysis, Shimalite (24~48 mesh) coated with polyethylene glycol-6000 (20%) was used at 140°C, while for oxygen-containing compound analysis, quartz powder (150~200 mesh) coated with Thermol-1 (5%) was used at 170°C.

Summary

d-Longifolene and calamenene have been newly identified from the essential oil of Hinoki. Cadinene and cadinol, which had been formerly reported, have been confirmed to be *d*-γ-cadinene and *l*-α-cadinol respectively.

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