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

By Shûichi HAYASHI, Katsumi YANO and Tamon MATSUURA

(Received October 7, 1963)

There have been some investigations of the monoterpene constituents of the essential oil of Hinoki (*Chamaecyparis Obtusa* (Sieb. et Zucc.) Endl.). A root oil of Hinoki has been investigated by Hirao,[1] who detected *d*-α-pinene, camphene, *d*-limonene, dipentene, camphor, borneol and α-terpinol. A leaf oil has been investigated by Uchida,[2] Kumagai[3] and Moroe;[4] they have reported the presence of α-pinene, *d*-limonene, borneol, bornyl acetate, bornyl pelargonate and α-terpinyl acetate. In the present work an attempt will be made to obtain a satisfactory confirmation for the monoterpene constituents of the essential oil by means of gas chromatography and ultraviolet and infrared absorption spectroscopies.

Results and Discussion

The essential oil obtained from leaves and twigs of Hinoki which grew in Kôchi Prefecture in Japan, after acids and phenols had been taken off, was repeatedly fractionated through a packing distillation column. The physical properties of the fractions are shown in Fig. 1. From these fractions, *d*-α-pinene, β-pinene, myrcene, *d*-limonene, β-phellandrene, *p*-cymene, 1, 8-cineole, camphor, *l*-α-terpineol, α-terpinyl acetate and bornyl acetate were identified in ways described below, while camphene, linalool and borneol were confirmed by gas chromatography. Among these constituents, β-pinene, myrcene, β-phellandrene, 1, 8-cineole, and *p*-cymene were found out for the first time in the essential oil of Hinoki.

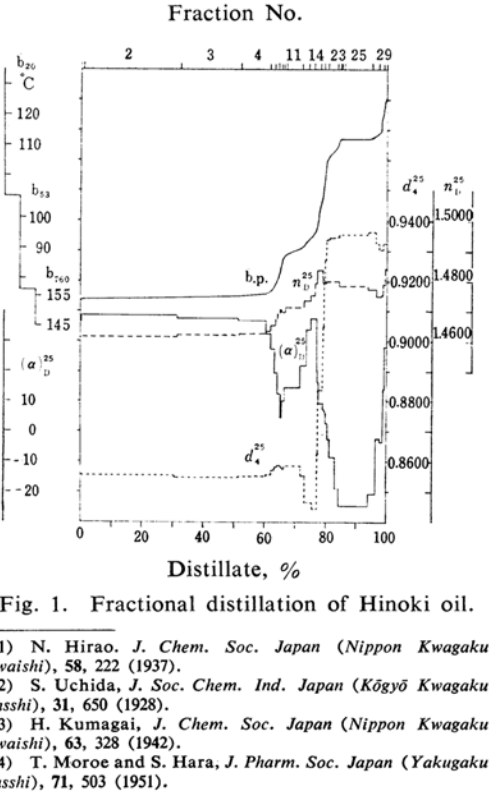

Fig. 1. Fractional distillation of Hinoki oil.

***d*-α-Pinene.**—Each infrared spectrum of fractions 2 to 4 coincides with that of α-pinene,[5] and each gas chromatogram of these fractions shows the main peak corresponding to α-pinene. From fraction 2, *d*-α-pinene hydrochloride[6], (m. p. 131.5~132.0°C) was prepared.

Camphene.—A gas chromatogram of fraction 3 exhibits a small peak corresponding to camphene, besides a main α-pinene peak.

β-Pinene.—A gas chromatogram of fraction 11 shows a strong peak associated with β-pinene, together with other peaks associated with α-pinene, myrcene, limonene, β-phellandrene and

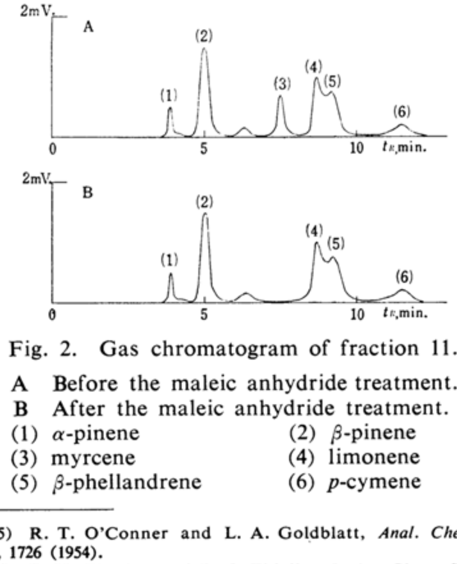

Fig. 2. Gas chromatogram of fraction 11.

A Before the maleic anhydride treatment.
B After the maleic anhydride treatment.

(1) α-pinene	(2) β-pinene
(3) myrcene	(4) limonene
(5) β-phellandrene	(6) *p*-cymene

---

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

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

[3] H. Kumagai, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **63**, 328 (1942).

[4] T. Moroe and S. Hara, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **71**, 503 (1951).

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

[6] F. H. Thurber and R. C. Thielke, *J. Am. Chem. Soc.*, **53**, 1030 (1931).

p-cymene, as may be seen in Fig. 2-A. From this fraction a thioglycollic acid adduct of β-pinene was prepared; it was identified by preparing its *S*-benzylthiuronium salt.[7]

Myrcene.—The ultraviolet absorption spectrum of fraction 11 has two absorption maxima: λ_{max}^{EtOH} 224 mμ (ε 4380) corresponding to myrcene,[5] and 230 mμ corresponding to β-phellandrene.[8] When fraction 11 was treated with maleic anhydride in ether[9] at room temperature, both the absorption maximum and the peak of gas chromatogram associated with myrcene disappeared (cf. Fig. 2-B).

Limonene and Dipentene.—The gas chromatogram of fraction 14 shows three peaks associated with limonene, β-phellandrene and *p*-cymene, together with some weak peaks (cf. Fig. 3). On the bromination of this fraction, dipentene tetrabromide[10] (m. p. 123~124°C) and *d*-limonene tetrabromide[10] (m. p. 101~102°C) were obtained.

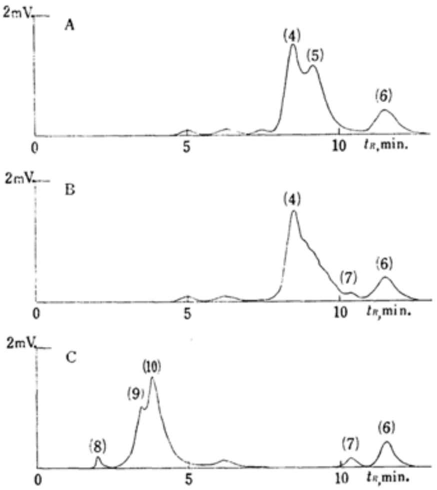

Fig. 3. Gas chromatogram of fraction 14.
A Before the maleic anhydride treatment.
B After the maleic anhydride treatment.
C After hydrogenation.
(4) limonene or dipentene
(5) β-phellandrene
(6) *p*-cymene
(7) 1,8-cineole
(8) hexahydromyrcene
(9) *cis*-*p*-menthane
(10) *trans*-*p*-menthane

β-Phellandrene.—The ultraviolet spectrum of fraction 14 shows an absorption band (λ_{max}^{EtOH} 230 mμ, ε 3590) corresponding to β-phellandrene.[8] When maleic anhydride reacted upon fraction 14, the absorption band and the peak of gas chromatogram associated with β-phellandrene disappeared (cf. Fig. 3-B). From fraction 14, β-phellandrene-β-nitrosite[11] (m. p. 96~97°C) was obtained.

***p*-Cymene.**—The ultraviolet spectrum of fraction 14 has another weak absorption band (λ_{max}^{EtOH} 273.5 mμ) characteristic of *p*-cymene,[5] in addition to the band of β-phellandrene. When fraction 14 was hydrogenated with a nickel catalyst, β-phellandrene and limonene vanished, but the peak associated with *p*-cymene in a gas chromatogram of the hydrogenation product remained, as is shown in Fig. 3-C.

1, 8-Cineole.—The peak of 1, 8-cineole was not observed in the gas chromatogram of any fraction. The peak, however, could be observed after the removal of β-phellandrene from fraction 14 by maleic anhydride-treatment or by hydrogenation, as Figs. 3-B and 3-C show.

Camphor, Linalool, Borneol and *l*-α-Terpineol.—The chromatogram of fraction 23 exhibits four peaks associated with linalool, camphor, borneol and α-terpineol (cf. Fig. 4).

The peak associated with camphor disappeared almost completely upon treatment with a 2, 4-dinitrophenyl hydrazine solution, thereby comfirming the existence of camphor.

l-α-Terpineol was identified by preparing *l*-α-terpinyl phenylurethane (m. p. 109~110°C[12]) from fraction 23.

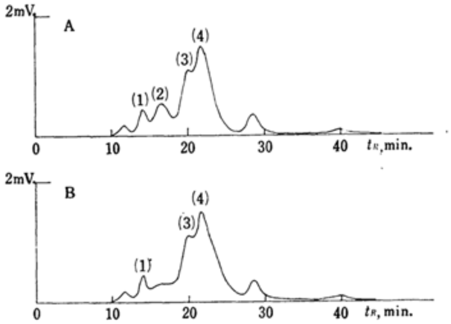

Fig. 4. Gas chromatogram of fraction 23.
A Before the 2,4-dinitrophenylhydrazine treatment.
B After the 2,4-dinitrophenylhydrazine treatment.
(1) linalool (2) camphor
(3) borneol (4) α-terpineol

Bornyl Acetate and α-Terpinyl Acetate.—The gas chromatogram of fraction 29 shows three peaks associated with α-terpineol, bornyl

---

[7] M. D. Sutherland and J. W. Wells, *J. Org. Chem.*, **21**, 1272 (1956).

[8] A. K. Macbeth, G. E. Smith and T. F. West, *J. Chem. Soc.*. **1938**, 119.

[9] G. A. Rudakov and M. M. Shestaeva, *Zhr. Priklad. Khom.*, **28**, 1199 (1955).

[10] O. Wallach, *Liebigs Ann.*, **225**, 304, 318 (1884).

[11] T. K. Gaponenkov, *J. Gen. Chem. U. S. S. R.*, **5**, 1485 (1935).

[12] O. Wallach, *Liebigs Ann.*, **230**, 268 (1885); **275**, 104 (1893).

acetate and α-terpinyl acetate (cf. Fig. 5). This fraction was then saponified. In a gas chromatogram of the saponification product, the two peaks associated with bornyl acetate and with α-terpinyl acetate both disappeared completely, while a new peak of borneol was found; furthermore, a peak of α-terpineol grew up, as may be seen in Fig. 5-B. On the other hand, from the aqueous layer of the saponification product, acetic acid was detected by paper chromatography as its hydroxamic acid.[13]

The Constitution of the Monoterpene Fractions.—The contents of the above components were calculated in the total monoterpene fractions from the results of fractionation and gas chromatography, as Table I shows. The essential oil of Hinoki was composed of 47.5% monoter penes, 43.2% sesquiterpenes, 7.1% residue and 2.2% acids and phenols.

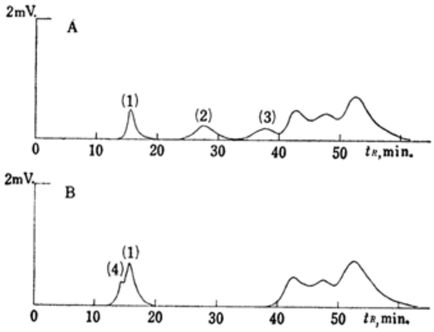

Fig. 5. Gas chromatogram of fraction 29.
A Before saponification.
B After saponification.
(1) α-terpineol (2) bornyl acetate
(3) α-terpinyl acetate (4) borneol

TABLE I. THE CONSTITUTION OF THE MONOTERPENE FRACTION OF HINOKI OIL

Compound	Content, %
d-α-Pinene	66.3
Camphene	0.2
β-Pinene	0.8
Myrcene	0.6
d-Limonene (dipentene)	1.3
β-Phellandrene	1.5
p-Cymene	1.9
1,8-Cineole	trace
Camphor	0.6
Linalool	0.4
Borneol	0.6
l-α-Terpineol	10.1
Bornyl acetate	2.3
α-Terpinyl acetate	0.8
Others	12.4

Experimental

The sample was the essential oil* (n_D^{25} 1.4832, d_4^{25} 0.8877, $[\alpha]_D^{25}$ +22.76, ester value 0.5) obtained from leaves and twigs of Hinoki by steam distillation. The oil (13.9 kg.) was shaken with a 3% aqueous solution of sodium carbonate and then a 3% aqueous solution of sodium hydroxide to take off acids and phenols. The neutral oil thus obtained (13.6 kg.) was washed with water, dried over anhydrous sodium sulfate, and repeatedly fractionated through a packing distillation column under reduced pressure.

***d*-α-Pinene.**—Dry hydrogen chloride gas was reacted upon fraction 3 under cooling at −10 to −15°C. The crystals thus obtained, after being recrystallized from methyl alcohol, showed a melting point of 131.5～132.0°C, which agrees with that of *d*-α-pinene hydrochloride.[6]

β-Pinene.—From one milliliter of fraction 11, a thioglycollic acid adduct of β-pinene was prepared and converted into *S*-benzyl thiuronium salt according to the procedure of Sutherland and Wells.[7] The white crystalline solid, after being recrystallized from an acetone-methanol (2 : 1) mixture, showed a melting point of 155～157°C, which did not depress when the solid was admixed with an authentic sample (m. p. 156～157°C).

***d*-Limonene and Dipentene.**—Bromine was added to a portion of fraction 14 under ice-cooling, using ether as a solvent. The crystalline mass obtained was fractionally recrystallized from ethyl acetate to give dipentene tetrabromide (m. p. 123～124°C) and limonene tetrabromide (m. p. 101～102°C). Each tetrabromide was identified by admixing it with an authentic sample.

β-Phellandrene.—Four grams of fraction 14 were treated with acetic acid and a saturated aqueous solution of sodium nitrite. The white crystals obtained, after being recrystallized from ethanol, showed a melting point of 96～97°C, which did not depress on admixture with β-phellandrene-β-nitrosite (m. p. 96～97°C).

1, 8-Cineole.—Eight hundred milligrams of fraction 14 were hydrogenated in an autoclave using nickel catalyst and ethanol (initial pressue of hydrogen, 112 kg./cm²; reaction temperature, 155°C; reaction period, 2 hr.). The gas chromatogram of the hydrogenation product was then examined (Fig. 4).

***l*-α-Terpineol.**—Phenylisocyanate was added to 0.5 g. of fraction 25. The phenylurethane obtained showed a melting point of 109～110°C, which agrees with that of the phenylurethane of *l*-α-terpineol.

Gas Chromatography.—A Shimadzu GC-2 apparatus equipped with a thermal conductivity detector and a copper spiral packing column (inside diameter, 4 mm.; length, 3 m.) was used. For hydrocarbon analysis, Shimalite (24～48 mesh) coated with polyethylene glycol (20%) was used at 80°C as a stationary phase; for an oxygen-containing compound analysis, quartz powder (150～200 mesh) coated with Thermol-1 (5%) was used at 140°C.

---

[13] K. Inoue and M. Noda, *J. Agr. Chem. Soc. Japan* (*Nôgei Kagaku Kwaishi*), **23**, 294 (1950); **24**, 291 (1951).

* Supplied by the Soda Kôryo Co., Ltd., Tokyo, Japan.

Helium was flowed as a carrier gas at the rate of 60 ml./min.

Summary

d-α-Pinene, β-pinene, myrcene, *d*-limonene, dipentene, β-phellandrene, *p*-cymene, 1, 8-cineole, camphor, *l*-α-terpineol, α-terpinyl acetate and bornyl acetate have been identified, and camphene, linalool and borneol have been gas-chromatographically confirmed. Of these compounds, β-pinene, myrcene, β-phellandrene, 1, 8-cineole and *p*-cymene have been found for the first time in this work. The main constituents of the monoterpene fraction are *d*-α-pinene and *l*-α-terpineol; the former amounts to 66.3%, and the latter to 10.1%, the remaining constituents being within a few %.

Department of Chemistry
Faculty of Science
Hiroshima University
Higashi-sendamachi
Hiroshima