

Sesquiterpene Alcohols and a Phenol Ether of the Essential Oil of the Kusunoki (*Cinnamomum Camphora*, Sieb.)

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(Received December 7, 1967)

In connection with a previous report¹⁾ on sesquiterpene hydrocarbons in camphor blue oil, which is a high-boiling fraction of the essential oil of the Kusunoki, the present work will deal with the sesquiterpene alcohol fraction of the blue oil. Five alcohols, elemol (6%), guaiol (10%), α -cadinol (13%), β -eudesmol (trace), and juniper camphor (2%), and a kind of phenol ether, myristicin (trace), have been identified.

The high-boiling fraction of camphor oil has been taken up by several workers as a subject of investigation, but no oxygen-containing constituents of this fraction have been identified up to the present time*¹ except nerolidol.²⁾ In the present investigation, however, we could not detect nerolidol in spite of our great care.

Experimental

A sesquiterpene alcohol fraction, bp 120–160°C/4 mmHg, 456 g, which was separated from a camphor oil commercially supplied, was precisely fractionated through a packed-type distillation column under reduced pressure; it was divided into 19 fractions.

Myristicin. The first fraction, bp 115–116°C, $[\alpha]_D^{25} +11.31^\circ$, was eluted on a silica gel-packed column with petroleum ether; an oily substance, $n_D^{25} 1.5370$, was thus isolated, a substance which showed only one peak, at t_R 12.6 min, in gas chromatography (DEGS-Diasolid-L, 125°C). Found: C, 68.93; H, 6.60%. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29%.

*¹ Hikino *et al.* reported on the structure of the main sesquiterpene alcohols, kusunol and campherol, of camphor oil at the 11th Symposium on the Chemistry of Terpenes, Essential Oils, and Aromatics, held in October, 1967, at Matsuyama.

1) S. Hayashi, N. Hayashi, K. Yano, M. Okano and T. Matsuura, *This Bulletin*, **41**, 234 (1968).

2) M. Hiroi, *ibid.*, **40**, 1003 (1967).

The IR spectrum of this substance coincided with that of myristicin,³⁾ and bromination in chloroform produced white needles, mp 129–130°C, of dibromomyristicin dibromide.⁴⁾ The NMR spectrum of the substance, consisting of signals at 2.30 (2H, d, $J=6$ cps), 3.80 (3H, s), 5.00 (2H, m), 5.80 (2H, s), 5.80 (1H, m), and 6.25 ppm (2H, s), had a strong resemblance with that of saffrole,⁵⁾ and so the substance could easily be identified as myristicin on the basis of a comparison of the two spectra. The mass spectrum⁶⁾ also fit myristicin.

Elemol. A white crystalline mass was isolated from fraction 4, bp 122–124°C/4 mmHg, $[\alpha]_D^{25} -8.99^\circ$, by eluting it on an alumina (Grade II) column with petroleum ether. The substance showed an IR spectrum which agreed with that of elemol;⁷⁾ the gas chromatography (Thermol-1) also showed it to be elemol.

Guaiol. A white crystalline mass separated from fraction 5, bp 124–126°C/4 mmHg, $[\alpha]_D^{25} -9.31^\circ$, by keeping it in a refrigerator was recrystallized from petroleum ether; white needles, mp 92.5°C, $[\alpha]_D^{25} -30.1^\circ$ (c 1.5, ethanol), were thus obtained. The IR spectrum of the needles coincided with that of guaiol,⁸⁾ and the 3,5-dinitrobenzoate, mp 134.5–135.5°C, was established to be that of guaiol by a mixed melting point determination.

3) T. Biernacka, B. Kontnik, A. Paraczewski and J. Rajkoaski, *Dieset. Pharm.*, **15**, 419 (1963).

4) E. Guenther, "The Essential Oils," Vol. II, D. Van Nostrand Company, New York (1949), p. 531.

5) N. S. Bhacca, L. F. Johnson and J. N. Shoolery, "NMR Spectra Catalog," Vol. I, Varian Associates (1962), No. 253.

6) S. Hayashi and H. Satō, *The Hitachi Scientific Instrument News*, **8**, 365 (1965).

7) J. Pliva, M. Horak, V. Herout and F. Šorm, "Die Terpen, Sammlung der Spectren und physikalischen Konstanten," Akademie-Verlag, Berlin (1960), p. 25.

8) *Ibid.*, p. 140.

α -Cadinol and β -Eudesmol. Two spot portions, of R_f 0.33 and 0.10, were gathered in the thin-layer chromatography of fraction 9, bp 132—134°C/4 mmHg, $[\alpha]_D^{25} +16.91^\circ$, with silica gel-G coating with silver nitrate; these portions were then extracted with ether to isolate two kinds of white crystalline matter. The IR spectra of these substances agreed with those of α -cadinol (R_f 0.33)⁹⁾ and β -eudesmol (R_f 0.10)¹⁰⁾ respectively.

Juniper Camphor. A crystalline mass which appeared in fraction 14, bp 142—144°C/4 mmHg, $[\alpha]_D^{25} +1.79^\circ$, when it was left standing at room temperature was separated, and then recrystallized repeatedly from ethanol. White crystals, mp 166.7°C, were thus ob-

tained. This melting point and the IR spectrum agreed with those of juniper camphor.¹¹⁾ Furthermore, the NMR spectrum, which had three methyl singlets, at 0.96 ppm (3H, a tertiary methyl group), 1.15 ppm (3H, a tertiary methyl attached to a carbon atom carrying a hydroxyl group), and 1.18 ppm (6H, two methyl groups in a isopropylidene), and the signals of the two methylene groups adjacent to a double bond at 2.14—2.80 ppm (4H), fit the structure of juniper camphor well.

The authors are indebted to Professor Shô Ito of Tohoku University for his kind measurement of the NMR spectra and to Dr. Hiroshi Satô of the Hitachi Co., Ltd., for his measurement of the mass spectra.

9) S. Hayashi, K. Yano and T. Matsuura, *This Bulletin*, **37**, 474 (1964).

10) F. J. Mc Quillin and J. D. Parrack, *J. Chem. Soc.*, **1956**, 2973.

11) V. Herout and F. Šorm, *Collection Czechoslov. Chem. Commun.*, **19**, 990 (1954).