

*Terpenoids. V. A Note on the Diterpene
Isolated from the Leaves of "Sugi"*
(*Cryptomeria Japonica* D. Don.)*

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A diterpene hydrocarbon named α -cryptomerene was first isolated by Uchida¹⁾ from the steam-distillate of "Sugi" leaves. Another diterpene, α -podocarpene²⁾, has also been found to occur in the same oil³⁾. Briggs and Cawley⁴⁾ have reported that α -podocarpene is identical with the kaurene** obtained from *Agathis australis*. Kaurene has been isomerized via its hydrochloride to isokaurene, and this isomer has recently been shown to be identical with Uchida's α -cryptomerene⁵⁾.

Upon careful re-examination of the "Sugi" diterpene fraction, the present author was able to obtain kaurene (or α -podocarpene) as the sole isolable product. The presence of isokaurene (or α -cryptomerene) could not be confirmed. This deviation from the observations of previous investigators should be ascribed to the changes in isolation procedures. In this investigation, the diterpene fraction was obtained by extracting "Sugi" leaves with acetone; the sesquiterpene alcohols were removed

by distillation in vacuo, and the less volatile residue was subjected to chromatography on an alumina column to afford kaurene.

The heating of kaurene in the presence of abietic acid resulted in the formation of isokaurene, no isomerization being observed in the absence of the acid. These findings suggest that the previous isolation of isokaurene was presumably a consequence of the isomerization of kaurene during the isolation procedures.

Experimental

Isolation.—Foliage and terminal twigs of Sugi (6 kg.), collected on Mt. Seburu, near Fukuoka city, were chopped up and extracted twice with hot acetone for 20 hr. The precipitate was filtered off, and the acetone was evaporated. The residue was extracted with petroleum ether (b. p., 40–60°C), and the neutral fraction was steam-distilled. The steam volatile oil (15 g.) was dried over sodium sulfate and distilled under reduced pressure (5 mmHg) with a Claisen flask. When the bath temperature reached to 180°C and the sesquiterpene alcohol fraction had been removed, the heating bath was removed quickly and the distillation residue (about 3 g.) was chromatographed on an alumina column (20 g.). Petroleum ether eluted kaurene (1.5 g.); m. p., 49–50°C (lit.⁴⁾ m. p. 50°C) (recrystallized from ethanol), $[\alpha]_D -78^\circ$ (c 2.09, chloroform) (lit.⁴⁾ $[\alpha]_D -75.2^\circ$). Mixed m. p. with authentic sample (m. p., 48–51.5°C), 48–51°C.

Isomerization.—A mixture of kaurene (200 mg.) and abietic acid (100 mg.) was heated at 200°C for 1 hr. Distillation under reduced pressure (10 mmHg, bath temp. 230–240°C) gave isokaurene, m. p. and mixed m. p., 62–64°C (lit.⁴⁾ m. p., 64°C) (recrystallized from ethanol) $[\alpha]_D -30^\circ$ (c 1.27, chloroform) (lit.⁴⁾ $[\alpha]_D -27.4^\circ$). The infrared spectrum was superimposable on that of an authentic sample. The distillation of kaurene under the same conditions without added abietic acid did not cause isomerization. Authentic isokaurene was obtained by heating kaurene with iodine⁶⁾.

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** The English authors have pointed out that the so-called "Kaurene" originally recorded by Hosking (*Rec. trav. Chim.*, 47, 578 (1928)) is probably impure isokaurene. (*J. Chem. Soc.*, 1950, 407)

1) S. Uchida, *J. Soc. Chem. Ind. (Kōgyō Kwagaku Zasshi)*, 19, 610 (1916); *J. Am. Chem. Soc.*, 38, 687 (1916).

2) K. Nishida and H. Uota, *J. Agr. Chem. Soc. Japan (Nippon Nōgei Kagaku Kaishi)*, 7, 157 (1931); *Bull. Agr. Chem. Soc. Japan*, 7, 1 (1931); J. Kawamura, *Bull. Imp. Forestry Exp. Sta. Tokyo (Rinyō Shiken Hōkoku)*, No. 31, 77, 93 (1931).

3) T. Nakatsuka, Y. Hirose and M. Matsuda, *J. Japan Wood Research Soc. (Mokuzai Gakkaishi)*, 3, 206 (1957).

4) L. H. Briggs and R. W. Cawley, *J. Chem. Soc.*, 1948, 1888.

5) L. H. Briggs, B. F. Cain, B. R. Davis and J. K. Wilmshurst, *Tetrahedron Letters*, 1959, No 8, 8.

6) L. H. Briggs, B. F. Cain, R. C. Cambie, B. R. Davis and P. S. Rutledge, *J. Chem. Soc.*, 1962, 1850.