196. *Diterpenes. Part IV. The Isolation of Phyllocladene from the Essential Oil of* Podocarpus spicatus *Grown in the North Island of New Zealand.*

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Phyllocladene has been isolated as the only solid diterpene from the essential oil of *Podocarpus spicatus* grown in the North Island of New Zealand, whereas that grown in the South Island yields kaurene (cf. Butler and Holloway, *J. Soc. Chem. Ind.*, 1939, **58**, 223).

From the essential oil of *Podocarpus spicatus* growing in the South Island of New Zealand Butler and Holloway (*J. Soc. Chem. Ind.*, 1939, **58**, 223) isolated a diterpene which they suggested was kaurene [cf. Part I (*J.*, 1948, 1888) for the identification of podocarpene with kaurene] without definitely claiming its identity. From the evidence submitted in Part III (preceding paper) it is clear that they isolated the lævo-isomer. Seeking a better source of kaurene [a yield of only 1·2% was obtained from the essential oil of *Agathis australis* (Part I, *loc. cit.*) whereas Butler and Holloway record a yield of 25% from the oil of *Podocarpus spicatus*], we have examined the essential oil of *P. spicatus* grown in the centre of the North Island of New Zealand. Although a thorough search, by careful fractionation followed by chromatography, was made for different diterpenes, particularly kaurene, the only diterpene isolated was phyllocladene in very small yield.

Wide variation in the percentage of constituents and also in the type of compounds present in species of plants, morphologically indistinguishable, has frequently been observed in the Australian flora but this is the first record from New Zealand.

The essential oil of *Podocarpus totara* contains rimuene and possibly a liquid diterpene, totarene (Aitken, *J. Soc. Chem. Ind.*, 1929, **48**, 344T; Beath, *ibid.*, 1933, **52**, 338T). The isolation of phyllocladene from the leaf-oil of "*P. hallii*," considered by botanists to be a variety of *P. totara* and not a separate species led one of us (Briggs, *Proc. Roy. Soc. New Zealand*, 1941, **70**, 173) to the suggestion that this fact would support the classification of *P. hallii* as a true species and not a variety. The above evidence from *P. spicatus* weakens the case for such a suggestion.

An unusual constituent, a liquid *olefin*, $[CH_2]_n$, b.p. 130—135°/0·01 mm., was isolated from the diterpene portion of the oil.

Experimental.

The leaves and terminal branchlets of *Podocarpus spicatus* (832 lbs.) collected from the Pureora Forest, Mangapehi, through the courtesy of Mr. G. R. Hammond, State Forest Service, to whom we are greatly indebted, produced, on steam distillation for 16—18 hours, 477 g. (0·13% yield) of pale yellow oil. The oil was then distilled through a column of the type described by Dostrovsky and Hughes (*Nature*, 1946, **158**, 164), the terpene fraction (279 g.) at 10 mm. and the oxygenated terpenes and sesquiterpene fraction

(89 g.) at 5 mm. The temperature of the still-pot did not exceed 140° at any stage. The residual oil was transferred to a modified Craig column (*Ind. Eng. Chem. Anal.*, 1937, **9**, 441), 20 cm. long, without condenser and with a side arm dipping into a series of receivers, and was distilled at 0·01 mm. The first yellowish-green fraction (33·8 g.), b. p. 66—97°/0·01 mm., n_D^{25} 1·5056 ~ 1·5057, consisted of sesquiterpene alcohols whilst the remaining fractions: *A*, greenish-blue (3·82 g.), b. p. 111—122°/0·01 mm., n_D^{25} 1·5059; *B*, greenish blue (3·52 g.), b. p. 122—129°/0·01 mm., n_D^{25} 1·5102; *C*, blue (8·95 g.), b. p. 129—145°/0·01 mm., n_D^{25} 1·5173; *D*, blue (2·90 g.), b. p. 130—140°/0·01 mm., n_D^{25} 1·5177; and the residue (24·5 g.) were investigated for diterpenes.

Fractions *A* and *B* were dissolved in dry light petroleum (10 c.c.), chromatographed on a 18 × 1·5 cm. column of alumina (Brockmann, grade I), and eluted with light petroleum and finally with light petroleum containing 1% methyl alcohol. Six fractions, each of *ca.* 10 c.c., were collected in each case, and the solvent was removed and the residual oils were kept dry in the refrigerator. No solid separated from any of these fractions.

A part of fraction *C* (1·89 g.) was similarly treated and gave the following fractions (all colourless):

Fraction	*C*1	*C*2	*C*3	*C*4	*C*5—*C*10
n_D^{25}	1·5100	1·5158	1·5174	1·5205	—
Weight (g.)	0·01	0·81	0·51	0·30	0·03

From *C*2 a solid separated (12 mg.) which, after recrystallisation from alcohol, had m. p. 95°, undepressed by a specimen of phyllocladene. A trial experiment showed that phyllocladene was not isomerised on chromatography as above.

Fraction *C*4 was distilled in a Craig micro-column and gave an oil, b. p. 130—135°/0·01 mm., n_D^{24} 1·5202, d_4^{19} 0·9718 (determined in a micro-pyknometer similar to that described by Clemo and McQuillen, *J.*, 1935, 1220), $[\alpha]_D^{21}$ + 39·73° (*l* = 1, *c* = 0·8 in chloroform) (Found: C, 85·9; H, 14·2. $[CH_2]_n$ requires C, 85·7; H, 14·3%). The ***hydrocarbon*** decolorised a solution of bromine in chloroform and gave a brown coloration with tetranitromethane.

From the main bulk of fraction *C* a colourless solid separated which, after recrystallisation from alcohol, had $[\alpha]_D^{20}$ + 14·99° (*l* = 1, *c* = 2·1 in chloroform) and m. p. 96°, undepressed by phyllocladene. Briggs (*J.*, 1937, 79) records $[\alpha]_D^{25}$ + 15·8° for phyllocladene. The material, after isomerisation with sulphuric acid in alcoholic solution (Briggs, *loc. cit.*) and crystallisation from methyl alcohol, had m. p. 109—110°, undepressed by a specimen of *iso*phyllocladene.

The solid separating from fraction *D* was also proved to be phyllocladene by mixed m. p. and rotation, $[\alpha]_D^{20}$ + 15·62° (*l* = 1, *c* = 0·3 in chloroform).

The residue was only partly soluble in hot alcohol from which solution there separated on storage 2 g. of crystalline material which was proved to be phyllocladene by mixed m. p.

The analysis is by Mr. Seelye of this department.

We are indebted to the Chemical Society, the Royal Society of New Zealand, and the Australian and New Zealand Association for the Advancement of Science for grants.

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