376. *Diterpenes. Part I. The Identity of Kaurene with Podocarprene.*

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The diterpenes kaurene, from *Agathis australis*, and podocarprene, from *Podocarpus* spp., are shown to be identical.

From the highest-boiling fraction of the essential oil of *Agathis australis* (" kauri "), Hosking (*Rec. Trav. chim.*, 1928, **47**, 578; 1930, **49**, 1036) isolated a crystalline diterpene, kaurene, $C_{20}H_{32}$, forming a monohydrochloride from which the hydrocarbon could be recovered unchanged, a dihydro-derivative by catalytic hydrogenation, and pimanthrene on dehydrogenation. Kaurene and its derivatives were all optically inactive. It has already been pointed out in a review of the diterpenes (Briggs, *Proc. Aust. New Zealand Assoc. Adv. Sci.*, 1937, **23**, 45) that the melting points of kaurene and its derivatives approximate to those of α-podocarprene from the essential oils of *Podocarpus macrophylla* (Nishida and Uota, *Bull. Agric. Chem. Soc. Japan*, 1930, **7**, 1—3) and *Sciadopitys verticillata* (Kawamura, *Bull. Imp. Forestry Exp. Sta. Tokyo*, 1931, No. 31, 93) but that further work would be necessary to make a full comparison (the reference to " isokaurene " in this review is an error). With the kind permission of the late Dr. J. R. Hosking we have continued the investigation on kaurene.

By distilling the essential oil of *Agathis australis* at a lower pressure than that used by Hosking and omitting all distillations from sodium we have obtained an optically active diterpene, the properties of which and of its derivatives leave no doubt as to its identity with α-podocarprene, which also does not depress its melting point. In the following comparison the data in brackets refer to those of α-podocarprene: hydrocarbon, m. p. 50° (50—50·5°), $[\alpha]_D^{20°}$ −75·2° (−71·9°); hydrochloride, m. p. 114—115° (115—117°), $[\alpha]_D^{20°}$ −40·0° (−27·4°); hydrocarbon recovered from the hydrochloride, m. p. 64° (65°), $[\alpha]_D^{20°}$ −25·9° (−27·1°); dihydro-derivative, m. p. 88° (86—87°), $[\alpha]_D^{20°}$ −35·7° (−29·3°); nitrosochloride, m. p. 138°, decomp. (136°, decomp.*); nitrosate, m. p. 135°, decomp. (140°, decomp.). The optical inactivity of Hosking's kaurene is, in our opinion, probably due to heat- or alkali-isomerisation. There is no need to retain separate names for the optically active and inactive forms, and we suggest retaining only the name kaurene for this hydrocarbon.

Nishida and Uota (*loc. cit.*; *J. Agric. Chem. Soc. Japan*, 1931, **7**, 157, 954) have described the original crystalline podocarprene (designated α-), m. p. 50°, and two other isomers, β-podocarprene, the high-boiling liquid diterpene from the oil, and γ-podocarprene, m. p. 197—199°, a hydrocarbon obtained by the action of alcoholic potash on the hydrochloride which both α- and β-podocarprene give with hydrogen chloride. Kawamura (*loc. cit.*), on the other hand, obtained another isomer, δ-podocarprene, m. p. 65°, naturally occurring along with α-podocarprene and identical with the product obtained by the action of alcoholic potassium acetate on the hydrochloride of α-podocarprene. α- and δ-Podocarprenes afforded the same hydrochloride and dihydro-derivative, suggesting that the difference between these isomers is in the position of the double bond.

We have confirmed Kawamura's results, and since the change from α- to δ-podocarprene is similar to that of phyllocladene to *iso*phyllocladene, we suggest naming the isomers, m. p. 50° and 65°, kaurene and *iso*kaurene respectively. Constitutional work on these compounds is in progress.

Experimental.

371 Lb. of leaves and terminal branchlets of *Agathis australis*, collected in the Waitakere Ranges near Auckland, produced on steam-distillation 258 g. (0·26%) of light yellow oil. This was distilled in a Bower and Cooke type of column (*Ind. Eng. Chem. Anal.*, 1943, **15**, 290) at 20 mm. pressure for the major part of the oil, and at 5 mm. in the final stages, the bath temperature not exceeding 215°, until the sesquiterpene fractions were mostly removed. The residual oil (54 g.) was removed with ether and distilled at 0·01 mm. in a modified Craig column (*ibid.*, 1937, **9**, 441), 20 cm. long, without condenser, with a side arm dipping into a series of receivers, the results being recorded in the following table.

Fraction no.	B. p./0·01 mm.	$d_{4°}^{25°}$.	$n_D^{25°}$.	$[R_L]_D$.	$[\alpha]_D^{25°}$.	Wt., g.
I	115°	—	1·5189	—		0·8
II	120—130	—	1·5210	—		6·7
III	130	—	1·5216	—		7·8
IV	130	0·9890	1·5225	84·0°	−26·2°	12·5
V	130—140	0·9906	1·5230	83·9	−35·1	10·1
VI	130—140	0·9950	1·5229	83·5	−29·5	5·45

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* The m. p. is incorrectly recorded as 163° in the abstract (*Brit. Abs.*, 1933, *B*, 321) and in the review by one of us (L. H. B.).

Although fractions IV and VI solidified on cooling to −15° and seeding, it was subsequently found better to dissolve the fractions in warm absolute alcohol, allow them to cool slowly, and seed them with a crystal of podocarprene. The diterpene then crystallised in long radiating needles and after repeated crystallisation from the same solvent had $[\alpha]_D^{20^\circ}$ −75·1° ($l = 1$; c, 4·0 in chloroform) and m. p. 50°, undepressed by authentic podocarprene, kindly forwarded by Professor Nishida. The yield of pure material was only 3·1 g., 1·2% of the original essential oil. The liquid diterpene residues have not yet been investigated.

Kaurene Hydrochloride.—1·5 G. of fraction IV were dissolved in a mixture of glacial acetic acid (2 c.c.) and dry ether (0·5 c.c.), the solution cooled in ice, and dry hydrogen chloride passed over the liquid. The crystalline product (1·05 g.) after repeated crystallisation from ethyl acetate formed long colourless needles, m. p. 114—115°, $[\alpha]_D^{20^\circ}$ −40·0° ($l = 1$; c, 3·1 in chloroform). Pure kaurene gave the same product in higher yield.

iso*Kaurene.*—A solution of kaurene hydrochloride (500 mg.) in alcohol (10 c.c.) was boiled under reflux with potassium hydroxide (300 mg.) for 6 hours. The crystalline precipitate, formed in quantitative yield on pouring the solution into water (100 c.c.), after repeated crystallisation from absolute alcohol gave irregular colourless plates, m. p. 64°, $[\alpha]_D^{20^\circ}$ −25·9° ($l = 1$; c, 0·35 in chloroform). *iso*Kaurene formed kaurene hydrochloride, identical with this (m. p. and mixed m. p.), when treated with hydrogen chloride.

Dihydrokaurene.—Kaurene (100 mg.) in glacial acetic acid (10 c.c.) was hydrogenated at 2 atm. pressure with palladised charcoal (100 mg.). The product crystallised on concentration of the filtered solution and after further recrystallisations from the same solvent formed long colourless needles, m. p. 88°, $[\alpha]_D^{20^\circ}$ −35·7° ($l = 1$; c, 0·33 in chloroform). On the small scale employed no isomeric hydrocarbon [cf. the preparation of α- and β-dihydrophyllocladene (Briggs, *J.*, 1937, 79; Brandt, *New Zealand J. Sci. Tech.*, 1938, **20**, 8B)] could be isolated from the mother-liquors.

Kaurene Nitrosochloride.—Kaurene (200 mg.) and amyl nitrite (170 mg.) were dissolved in dry ether (0·3 c.c.), cooled to −12°, and a mixture of concentrated hydrochloric acid (0·13 c.c.) and ether (0·2 c.c.) added dropwise. After standing, the nitrosochloride was precipitated from the solution by the addition of absolute alcohol, and purified by solution in chloroform and precipitation with absolute alcohol, and then had m. p. 138° (decomp.).

Kaurene Nitrosate.—Kaurene (200 mg.) and amyl nitrite (170 mg.) were dissolved in dry ether (0·2 c.c.), cooled to −11°, and a mixture of concentrated nitric acid (0·16 c.c.) in dry ether (0·2 c.c.) added dropwise. The product was isolated and purified as for the nitrosochloride and then had m. p. 135°. The yields in both cases were low.

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