

18. *The Identity of Dacrene and Sciadopitene with Phyllocladene.*

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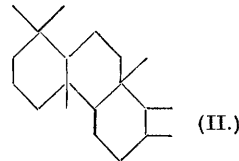
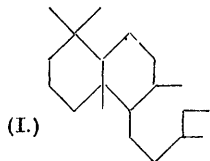
IN 1910 Baker and Smith ("Pines of Australia," p. 419) described the isolation of the first crystalline diterpene, phyllocladene, from the leaf-oil of *Phyllocladus rhomboidalis* (Celery Top Pine). From its stability towards oxidising agents and bromine in acetic acid solution it appeared to be saturated, but without further evidence a formula was proposed on the assumption that it was derived from two molecules of pinene.

In the following pages a crystalline diterpene is described, which has been isolated from the leaf-oils of *Phyllocladus alpinus* and *Araucaria excelsa*. This substance is found to be identical with the diterpenes phyllocladene (*loc. cit.*), dacrene (Goudie, *J. Soc. Chem. Ind.*, 1923, **42**, 357T; Aitken, *ibid.*, 1928, **47**, 223T; Blackie, *ibid.*, 1929, **48**, 357T; 1930, **49**, 26T), sciadopitene (Nishida and Uoda, *Bull. Agric. Chem. Soc. Japan*, 1935, **11**, 95), and an unnamed diterpene from the leaf-oil of *Dacrydium cupressinum* (Dr. J. R. Hosking, private communication). The identity of these compounds has been established by mixed melting point determinations of the diterpenes themselves and also by a comparison of the physical constants of their derivatives. The names dacrene and sciadopitene should therefore be removed from the literature. These observations are of botanical interest, showing the wide occurrence of phyllocladene in different genera.

Phyllocladene is readily and completely isomerised by alcoholic sulphuric acid to *isophyllocladene* (*cf.* Nishida and Uoda, *loc. cit.*). This ready isomerisation would indicate that the *iso*-hydrocarbon might be a natural product. No such compound, however, could be found described in the literature, but the physical constants of one of the four diterpenes isolated by Kawamura (*Bull. Imp. Forestry Exp. Sta. Tokyo*, 1931, No. 31, 93) from the leaf-oil of *Sciadopitis verticillata* suggest that this is the optical antipode of *isophyllocladene*. Its m. p. is 111—112°,  $[\alpha]_D^{25} - 24.5^\circ$  (chloroform), the monohydrochloride has m. p. 105—107° (decomp.) and the dihydro-derivative m. p. 71—72°: the corresponding constants of *isophyllocladene* and derivatives are 110.5—112°,  $[\alpha]_D^{25} + 23.4^\circ$  (chloroform), 105—107° (decomp.), 73—74°, respectively.

Hydrogenation of phyllocladene in the presence of palladised charcoal gives  $\alpha$ -dihydro-phyllocladene and from the mother-liquors a second isomer,  $\beta$ -dihydrophyllocladene, has been isolated in small yield. These are identical with the two dihydrophyllocladenes obtained by C. W. Brandt (private communication) by hydrogenation in the presence of platinum oxide. The two dihydro-compounds are probably stereoisomers.

Biogenetic relationships suggest that phyllocladene may be related to the oxygenated diterpene compounds of carbon skeleton (I), isolated from the wood of *Dacrydium colensoi* and *D. biforme* by Hosking and Brandt (*Ber.*, 1934, **67**, 1173; 1935, **68**, 37, 286, 1311; Hosking, *ibid.*, 1936, **69**, 780). Phyllocladene is tetracyclic and probably contains the phenanthrene structure (II), together with an additional 3- or 4-membered ring.



## EXPERIMENTAL.

*Phyllocladene*.—The crude diterpenes from the essential oils of *Phyllocladus alpinus* and *Araucaria excelsa* (forthcoming publication) crystallised from ethyl and methyl alcohol in glistening plates, m. p. 96°, raised to 98° on recrystallisation;  $[\alpha]_D^{25} + 15.8^\circ$  (chloroform). The m. p.'s of both hydrocarbons were not depressed by admixture, nor by admixture with an authentic specimen of phyllocladene kindly provided by Dr. F. Lions. No m. p. depression occurred by admixture with dacrene (private communication from the late Professor Inglis), sciadopitene (kindly forwarded by Prof. K. Nishida), and with the diterpene isolated from *D. cupressinum* (Hosking, *loc. cit.*) [Found: C, 88.1; H, 11.7; *M*, 268 (ebullioscopic in dioxan); M.R. 84.1 (from constants of a solution in cedrene). Calc. for  $C_{20}H_{32}$ : C, 88.2; H, 11.8%;

*M*, 272.  $C_{20}H_{32}I$  requires M.R. 85.29]. The diterpene gives a faint but definite yellow coloration with tetranitromethane. With concentrated sulphuric acid it gives a yellow coloration, which turns brown with a yellowish-green fluorescence on the addition of acetic anhydride.

*isoPhyllocladene*.—Phyllocladene (2 g.), partly suspended in 10% alcoholic sulphuric acid (6.5 c.c.), is completely converted into *isophyllocladene* on heating at 100° for a few minutes. The product (theoretical yield), collected after pouring into water, crystallised from methyl or ethyl alcohol in needles, m. p. 108—109°, raised to 110.5—112° after further recrystallisations from acetic acid,  $[\alpha]_D^{20} + 23.4^\circ$  (chloroform), M.R. (calculated from constants of a solution in cedrene) 84.4;  $C_{20}H_{32}I$  requires M.R. 85.3. The m. p. was not depressed by a sample prepared from 30 mg. of authentic phyllocladene. The m. p.'s and rotations recorded for *isodacrene* and *isosciadopitene* are 107°,  $[\alpha]_D + 48.4^\circ$ , and 108—109°,  $[\alpha]_D^{20} 22.13$  (chloroform) respectively. The large rotation of *isodacrene* is possibly due to a factorial error. It gives a yellow coloration with tetranitromethane, and the same coloration with sulphuric acid and acetic anhydride as that with phyllocladene.

*Phyllocladene Hydrochloride*.—This was prepared by passing dry hydrogen chloride into a solution of the hydrocarbon in absolute ether at  $-15^\circ$ ; on concentration of the solvent it crystallised in plates, m. p. 105—107° (slight decomp.). Dacrene hydrochloride (Aitken, *loc. cit.*) has m. p. 108.5°, and sciadopitene hydrochloride m. p. 106° (decomp.).

$\alpha$ - and  $\beta$ -*Dihydrophyllocladene*.—Phyllocladene (100 mg.) in glacial acetic acid solution (6 c.c.) was hydrogenated in the presence of palladised charcoal. After removal of the catalyst, water was added, and the crystalline product recrystallised from alcohol, forming thin plates, m. p. 74—74.5°. From the mother-liquors another isomer was isolated, m. p. 55°. Neither of these gave a depression on admixture with the isomers prepared by C. W. Brandt (see p. 79). Both compounds are dihydro-derivatives by analysis (Brandt) and give no coloration with tetranitromethane.

*Phyllocladene Nitrosochloride*.—To phyllocladene (2 g.), mostly suspended in glacial acetic acid (2 c.c.) and amyl nitrite (1.72 g.) at  $-17^\circ$ , was added drop by drop a mixture of concentrated hydrochloric acid (1.3 c.c.) and glacial acetic acid (2 c.c.), the whole being well shaken. The green viscous oil produced solidified overnight in the ice-chest. It was collected, washed with alcohol (yield, 1.32 g.), and dissolved in the minimum amount of chloroform, acetone added, and the whole left in a freezing mixture. The nitrosochloride crystallised in colourless plates, m. p. 128° (decomp.) (Found: N, 4.2, 4.3. Calc. for  $C_{20}H_{32}ONCl$ : N, 4.2%). *Sciadopitene nitrosochloride (loc. cit.)* has m. p. 127—128° (decomp.). It gives only a slight discoloration with concentrated sulphuric acid-acetic anhydride.

*Phyllocladene Nitrosate*.—To a suspension of phyllocladene (2 g.) in glacial acetic acid (2 c.c.) and amyl nitrite (1.72 c.c.) cooled to  $-18^\circ$ , was added drop by drop, with continual shaking, a mixture of concentrated nitric acid (1.6 c.c., *d* 1.43) and glacial acetic acid (2 c.c.). The solid formed overnight in the ice-chest from the pale green oil produced was filtered off and well washed with alcohol (yield, 1.46 g.). It crystallised in colourless prisms, m. p. 129.5° (decomp.), from a solution in the minimum amount of chloroform after addition of acetone in excess and leaving in the ice-chest. *Sciadopitene nitrosate* has m. p. 126—127° (decomp.) (Found: N, 7.65, 7.9. Calc. for  $C_{20}H_{32}O_4N_2$ : N, 7.7%).

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