

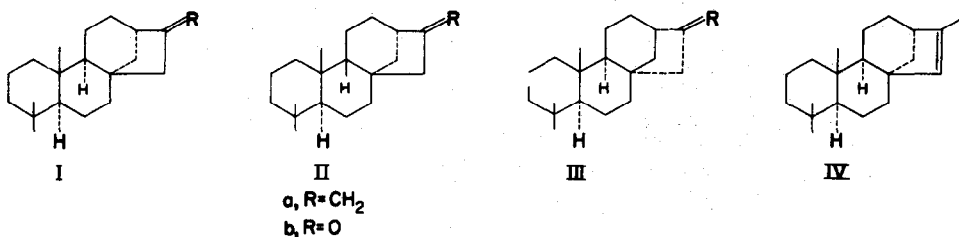
REVISED STRUCTURES FOR MIRENE AND KAURENE

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IN previous communications¹ structures (Ia), (IIa) and (IIIa) were put forward for phyllocladene, mirene and kaurene respectively. The structure and absolute configuration of phyllocladene was confirmed by relating it to



abiatic acid^{1c} and later by Grant and Hodges to manool.²

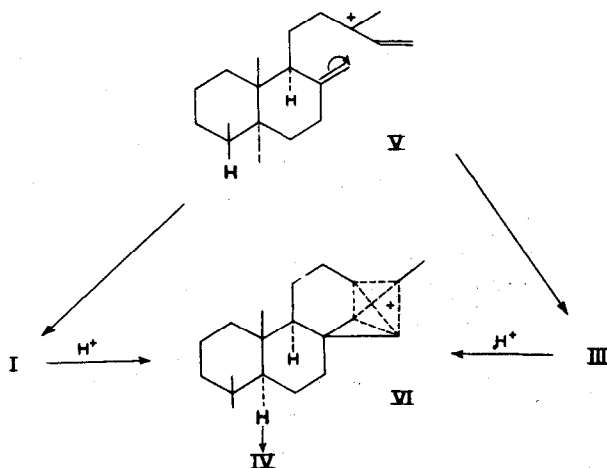
Mirene is converted by mild acids into isophyllocladene (IV). There is no simple mechanism for this transformation on the structure suggested for mirene and a model shows that it is the most strained form of isomeric

^{1a} L.H. Briggs, B.F. Cain, B.R. Davis and J.K. Wilmhurst, Tetrahedron Letters No. 8, 8 (1959); ^b Ibid. No. 8, 13 (1959); ^c L.H. Briggs, B.F. Cain and R.C. Cambie, Ibid. No. 8, 17 (1959); ^d L.H. Briggs, J. New Zealand Inst. Chem. 23, 92 (1959).

² P.K. Grant and R. Hodges, Tetrahedron 8, 261 (1960).

diterpenes of this type.

In the biosynthesis of diterpenes³ the intermediate (V) would be formed at one stage which can give rise^{1b} to isomeric diterpenes (I) and (III) differing only in the disposition of the bridged ring. We now suggest that



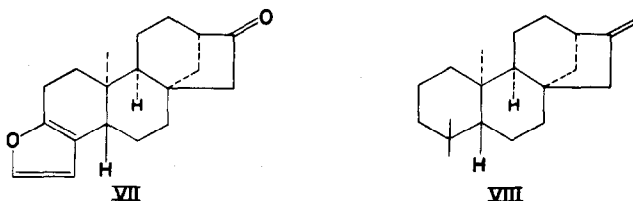
mirene be represented by (IIIa) which allows for a more satisfactory explanation for its transformation into isophyllocladene through the intermediate non-classical carbonium ion (VI).

The structure (III a) was previously given to kaurene on the basis of the positive sign of the Cotton effect of the related norketone (III b) but without reference to its rotation. Kaurene, however, occurs in dextro- and laevo-rotatory forms in the essential oils of Podocarpus ferrugineus⁴ and

³ cf. F. Lynen, B.W. Agranoff, H. Eggerer, V. Henning and E.M. Möslin, Angew. Chem. 71, 657 (1959).

⁴ L.H. Briggs, R.W. Cawley, J.A. Loe and W.I. Taylor, J. Chem. Soc. 955 (1950).

Agathis australis⁵ respectively. The laevorotatory form, $[\alpha]_D - 54^\circ$, from Agathis australis was used for the preparation of the norketone which has a rotatory dispersion curve* [R.D. in dioxan (c, 0.203): $[\alpha]_{700} - 25^\circ$; $[\alpha]_{589} - 25^\circ$; $[\alpha]_{320} + 1500^\circ$; $[\alpha]_{295} - 1000^\circ$] characterized by a Cotton effect with the same sign (positive) as and an intensity comparable with those of phyllocladene norketone (I b) and epoxynorcafestadienone (VII)⁶ (R.D. peaks at $+2240^\circ/322.5 \mu$ and $+2000^\circ/324 \mu$ respectively). By application



of the "octant rule",⁷ and as we have accumulating evidence that it can be applied in bridged ring systems, we now suggest that (-)kaurene be represented by (VIII), in which the configuration in rings B/C/D is the same as that in phyllocladene and cafestol. In cafestol and (-)kaurene, however, ring B must be present in a boat form.

It is of interest that (-)kaurene has the antipodal form of the normal diterpenoid configuration as exemplified by agathenedicarboxylic acid occurring in the same ~~time~~ and whose absolute configuration has already been determined.⁸ The (+)kaurene, however, in Podocarpus ferrugineus must

* We are grateful for Professor Djerassi for this measurement.

⁵ L.H. Briggs and R.W. Cawley, J. Chem. Soc. 1888 (1948).

⁶ C. Djerassi, M. Cais and L.A. Mitscher, J. Amer. Chem. Soc. 81, 2386 (1959); R.A. Finnegan and C. Djerassi, Ibid. 82, 4342 (1960).

⁷ C. Djerassi, Optical Rotatory Dispersion Chap. 13. McGraw-Hill, New York (1960).

⁸ W. Klyne, J. Chem. Soc. 3072 (1953).

have the enantiomorphic structure with a normal trans A/B ring junction agreeing with the absolute configuration of the other diterpenoid compounds from the same tree, i.e. ferruginol, sugiol, isopimaric acid, phyllocladene and mirene.