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THE ABSOLUTE CONFIGURATION OF PHYLLOCLADENE, MIRENE, RIMUENE, CUPRESSENE AND KAURENE

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THE previous paper* summarizes the evidence for the constitution of the main naturally occurring diterpenes, this deals with their absolute configuration.

We agree with Ruzicka[1] and Wenkert[2,3] that biogenetically the diterpenes may be derived through a pimaradiene skeleton. Rimuene is stable to prolonged heating with glacial acetic acid, sulphuric acid (6%) in acetic acid, and 85% phosphoric acid and hence must have a stable configuration, particularly at C-13. Specifically, however, with formic acid it is converted into isophyllocladene, readily explained by the sequence, (I) - (IV). The intermediate carbonium ion (III) can yield either phyllocladene or isophyllocladene in biosyntheses (these two diterpenes co-occur in Araucaria excelsa and Phyllocladus trichomanoides)

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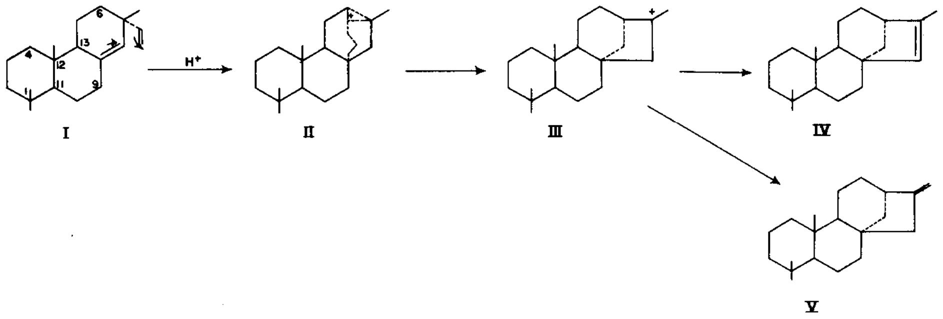
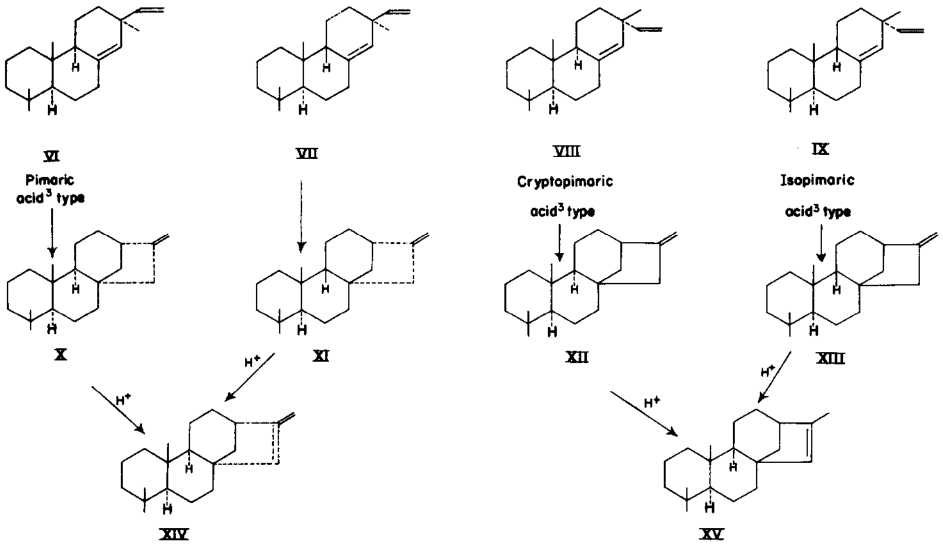
* L. H. Briggs, B. F. Cain, B. R. Davis and J. K. Wilmshurst, Tetrahedron Letters No. 8, 8 (1959).

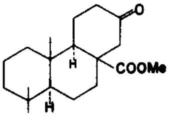
[1] L. Ruzicka, Experientia 9, 357 (1953).

[2] E. Wenkert, Chem. & Ind. 282 (1955).

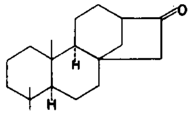
[3] E. Wenkert and J. W. Chamberlin, J. Amer. Chem. Soc. 81, 688 (1959). This paper also summarizes the present position of the stereochemistry of the pimaric acids.







XVI



XVII

but only the more stable isophyllocladene by the above treatment. It should also be noted that the new bridged ring appears on the side opposite the original vinyl group which must take up a quasi-axial conformation in the first step.

This mechanism was first proposed by one of us[4] but a similar mechanism has also been suggested by Wenkert.[2]

The formation of the tetracyclic diterpenes can then be represented by (VI) - (XV).

It should be noted that in (XI) and (XIII) ring B must be in a boat form. In the further shift of the double bond from the exocyclic to the endocyclic position the less stable boat form can pass over to the more stable all-chair form of iso-hydrocarbon. Assuming that kaurene represents the more stable all-chair form then phyllocladene and kaurene must be (X) and (XII). The rotatory dispersion of the ketoester (XVI) derived from (XII) has a positive Cotton effect in agreement with that predicted by Djerassi[5] by the octant rule[6] while the ketoester from (X) has a predicted negative Cotton effect. Phyllocladene must therefore be (XII) and kaurene (X), and isophyllocladene and isokaurene (XV) and (XIV) respectively. Further, rimuene must be (VIII) (the more stable confirmation would have the vinyl group in quasi-equatorial position) and mirene (XIII).

Approximate calculations of the sign of the Cotton effect of the rotatory dispersions of the norketones from phyllocladene (XVII), mirene and kaurene likewise are in agreement with the observed results, positive, negative and positive respectively.

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[4] J. K. Wilmshurst, Thesis, University of New Zealand (1953).

[5] C. Djerassi, M. Cais and L. A. Mitscher, forthcoming publication.

[6] W. Moffitt, A. Moscowitz, R. B. Woodward, C. Djerassi and W. Klyne, forthcoming publication. We are most grateful to Professor Djerassi for sending us their data prior to publication.

Since cupressene is stable to alcoholic sulphuric acid but may be isomerized to isophyllocladene by heating with palladium charcoal[7] it, too, will have the same configuration at C-11, C-12 and C-13 as phyllocladene.

Finally, in support of this biogenetic scheme is the fact that ferruginol, sugiol (identified with isomiropinic acid by infra-red spectrum) and isopimaric (miropinic)[8] acid, all with proved normal trans A/B ring junctions, phyllocladene, mirene and kaurene all co-occur in *Podocarpus ferrugineus*.

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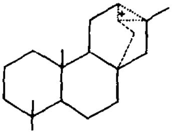
[7] L. H. Briggs and M. D. Sutherland, *J. Org. Chem.* **7**, 397 (1942).

[8] A. Brossi and O. Jeger, *Helv. Chim. Acta* **33**, 722 (1950).

ERRATA

1. L. H. BRIGGS, B. F. CAIN, B. R. DAVIS and J. K. WILMHURST: The absolute configuration of phyllocladene, mirene, rimuene, cupressene and kaurene, Tetrahedron Letters No. 8, 13-16 (1959).

Formulae II and XIV on p. 14 of the above article were published with slight errors. The correct formulae appear below.



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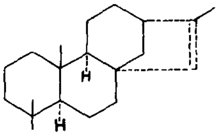

XIV