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THE STRUCTURE AND STEREOCHEMISTRY OF RIMUENE

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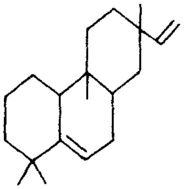
The diterpene hydrocarbon rimuene first isolated by McDowall and Findlay (1) from the essential oil of Dacrydium cupressinum (rimu) has been the subject of a number of structural investigations (2,3,4,5,6). The proposed structure (3,4) has been shown by recent synthetic work (7) to be incorrect.

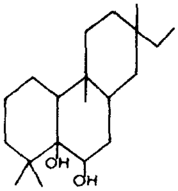
Earlier investigations had established that rimuene has the usual perhydrophenanthrene skeleton with a genimal dimethyl group at C(4), vinyl and methyl groups at C(13) and a trisubstituted double bond. Initial investigations were therefore directed at locating the position of the trisubstituted double bond.

Rimuene (I), m.p. 55 - 56°, $C_{20}H_{32}$, on hydrogenation under mild conditions, gave dihydrorimuene, m.p. 26°, $C_{20}H_{34}$, which under more vigorous conditions was readily reduced to rimuane, m.p. 86 - 87°, $C_{20}H_{36}$. The ease of this reaction was in marked contrast to the less facile reduction of the C(7) - C(8) double bond in, for example, isopimaric acid (8). Hydroxylation of dihydrorimuene with osmic acid yielded a diol (II), m.p. 134 - 5°, $C_{20}H_{36}O_2$, which gave a monoacetate, m.p. 143° - 144°, $C_{22}H_{38}O_3$. Cleavage of this diol with periodate followed by reduction of the product with lithium aluminium hydride gave a second diol, $C_{20}H_{38}O_2$, (b.p. 150° @ 0.005 mm) which was dehydrogenated with selenium in the usual manner. No trace of naphthalenic absorption could be detected in the U.V. spectrum of the hydrocarbons produced from this reaction. The U.V. spectra of a number of fractions isolated from the hydrocarbon mixture by gas chromatography were similar to those of substituted diphenyls. Thus the trisubstituted double bond is in ring B.

The diol (II), was cleaved when treated with Jones' reagent, and gave a keto-acid, m.p. 164 - 165°, $C_{20}H_{34}O_3$. The mass spectrum of this acid can only be explained if it is assigned structure (III).



I



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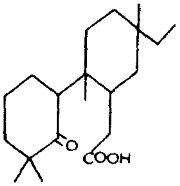


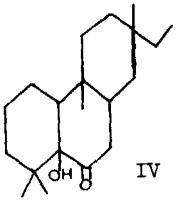
III

Rimuene therefore has structure (I) with the trisubstituted double bond in the C(5) - C(6) position and a methyl group at C(9) rather than in themore usual C(10) position. The n.m.r. spectra of rimuene and dihydrorimuene are consistent with this formulation, the two methyl peaks at unexpectedly low field (8.92τ, 8.98τ) being due to shielding of the C(4) methyl groups by the C(5) - C(6) double bond while the broad unresolved nature of the peak due to the olefinic proton is caused by spin-spin interaction with the allylic proton at C(10). The mass spectrum of rimuene is also consistent with a double bond in this position. On biogenetic grounds this is not unexpected, since the majority of triterpenes having a C(5) - C(6) double bond (alnusenone, cucurbitacins) have a methyl radical linked to C(9) rather than to C(10) and a plausible mechanism for the biogenesis of this type of system has been advanced (9).

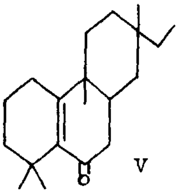
The correctness of this structure has been confirmed by the following reactions.

Rimuane-5,6-diol (II), with chromic acid in pyridine gave the hydroxy ketone, rimuan-5-ol-6-one (IV), m.p. 142.5 - 143°, $C_{20}H_{34}O_2$, λ_{max}^{EtOH} 305 mμ(ε 48). Dehydration of (IV) with thionyl chloride in pyridine gave an α:β-unsaturated ketone (V), rimu-5:(10)-en-6-one, m.p. 103 - 103.5°; $C_{20}H_{32}O$, λ_{max}^{EtOH} 249.5 mμ (ε 11,400).

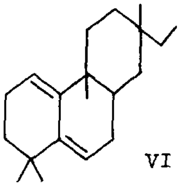
Dehydration of rimuan-5-ol-6-acetate gave a labile unsaturated acetate which with acid gave rimua-1:(10),5:6 diene (VI), m.p. 51.5 - 52.5°, $C_{20}H_{32}$, λ_{max}^{EtOH} 232, 239, 247 (infl)mμ (ε 16,100). This diene absorption is typical of a heteroannular diene and agrees very closely with that reported for the analogous alnusadienes (10). Hydrogenation of (VI) gave rimuane (identical m.p. mixed m.p. and infrared spectrum) and so established that molecular rearrangement had not taken place during this reaction sequence. Hydroboration of dihydrorimuene gave an alcohol, rimuan-6-ol, m.p. 148.5 - 149°, $C_{20}H_{36}O$, which with Jones' reagent gave the ketone rimuan-6-one, m.p. 98.5 - 99°, $C_{20}H_{34}O$, (positive Cotton effect).



IV



V



VI

By comparison with the established stereochemistry of the related triterpenes and on biogenetic grounds it would be expected that in rimuene the methyl at C(9) would be β and the hydrogen at C(10) would be α with the configuration at C(8) rather uncertain. However, rimuene on vigorous treatment with formic acid gave isophyllocladene (4). This rearrangement may be formulated as a series of 1:2 shifts initiated by protonation of the C(5) - C(6) double bond followed by ring closure to give the five membered ring system (Fig. 1). Since these shifts are almost certainly stereospecific the substituents at C(8), C(9) and C(10) may be assigned the α,β and α configurations respectively. For the formation of the β five-membered phyllocladene-type ring system to be stereochemically feasible the C(13) vinyl group must be α orientated (11).

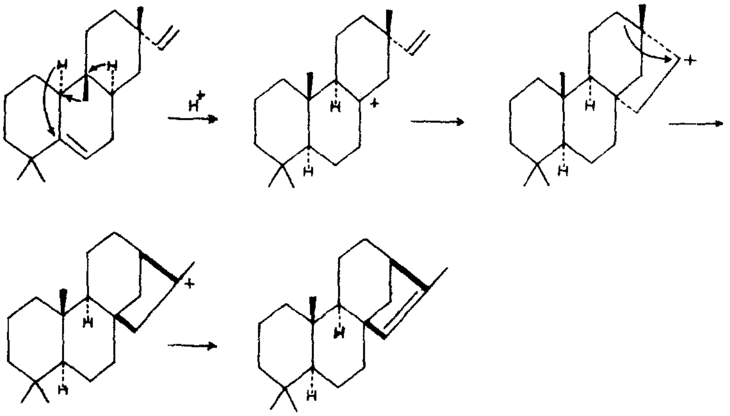
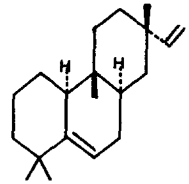


FIG.1

The formation of abieta-7:13-diene on prolonged acid treatment of rimuene can be explained by a similar series of shifts induced by protonation of the nuclear and vinyl double bonds.

The complete stereostructure of rimuene is therefore (VII).



VII

The stereostructures and n.m.r. spectra of the intermediates will be described in a full account of this work to be published elsewhere. All new compounds gave satisfactory analyses.

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