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THE CONSTITUTION AND STEREOCHEMISTRY OF RIMUENE

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The constitution of rimuene has been the subject of protracted controversy in recent years and indeed represents an outstanding unsolved problem in diterpene chemistry. Our recent interest in the constituents of Erythroxylon monogynum (1) has caused us to re-examine the published evidence on rimuene and at the same time furnished us with a means of testing our conclusions. On the basis of the observations which follow, we now wish to propose for rimuene the constitution and stereochemistry (I).

The salient recorded facts are as follows:-

Rimuene, $C_{20}H_{32}$, is tricyclic and contains two double bonds. N.M.R. data (2) show that one is a vinylidene group as in the pimaric acids, the other trisubstituted with an adjacent methylene group. Dehydrogenation of dihydro-

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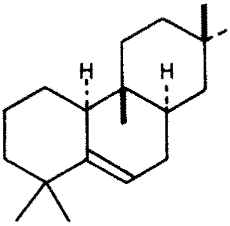
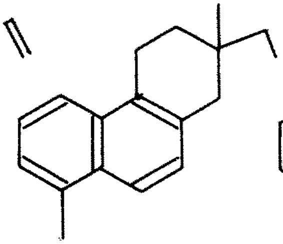
-rimuene (3) affords a hydrocarbon (II) also obtainable from the pimaric acids.



I



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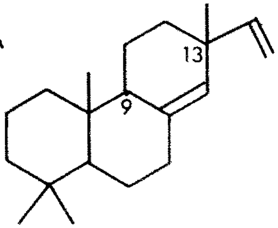
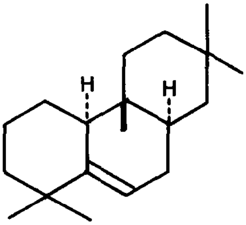


III

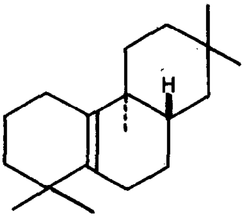
It has been conclusively shown by synthesis (4) that rimuene is not one of the four isomeric $\Delta^{8(14),15}$- pimaradienes (III), epimeric at C-9 and C-13, as previously suggested. It is therefore difficult to account for the reported (3) conversion of dihydrorimuene into 1,2,8-trimethyl phenanthrene by successive epoxidation, reaction with methyl Grignard reagent and dehydrogenation. We have been unable to confirm the reported transformation (5), even in minor amount, of G.L.C.-pure rimuene into isophyllocladene on prolonged exposure to refluxing formic acid. We cannot comment on the formation of abieta-8(14),12- or 7,13-diene (5) under the same conditions because we do not possess authentic samples of these compounds. Finally, it has been observed (6) that rimuene is unaffected by dry chloroformic hydrogen chloride, which transforms the pimaradienes into the $\Delta^{8(9)}$-isomers. However, change of the reaction conditions (see below) does result in isomerisation of rimuene also.

The combined evidence and biogenetic considerations point to a rearranged pimarane structure (I) (or the $\Delta^{1(10)}$, $5\alpha H$-isomer) for rimuene.

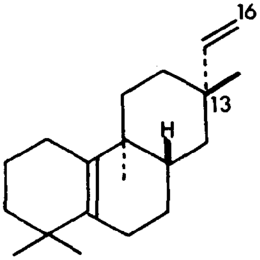
This we have confirmed as follows. Exposure of rimuene to moist chloroformic hydrogen chloride at 20° for 16 hr. results in a mixture of hydrocarbons, showing two peaks of almost equal intensity on G. L. C. The diene (VI) from erythroxydiol Y (1) under the same conditions affords a similar mixture, both components however showing slightly longer retention times. When carbon atom 16 is removed in both cases by standard procedures (via the diol, nor-aldehyde and thioketal), the nor-rimuene (IV) so obtained gives on acid treatment a mixture of isomers (10% Ap. L.; 175°: 16.5 and 19 min.), whose less retained component was isolated by chromatography on $AgNO_3$-silica gel. This was identical in all respects [including mass spectrum, G. L. C. (10% Ap. L., 10% PEGA and 5% Q. F. 1) and T. L. C. ($AgNO_3$-silica gel) properties], with the C_{19}-hydrocarbon (V) from diene (VI). Both compounds had m.p. (needles from methanol) 61-63°; $\epsilon_{205\ m\mu}$ 3600, $\epsilon_{220\ m\mu}$ 950; N.M.R. signals at 9.17 (3H), 9.05 (6H), 9.01 (6H) τ, no vinyl H; $[\alpha]_D$ - 112° (from rimuene), + 116° [from diene (VI)]. Moreover, the two nor-hydrocarbons gave with acid identical (on the above G. L. C. columns) mixtures of isomers.



IV



V



VI

We prefer the Δ5(6)-position of the nuclear double bond in rimuene to the alternative Δ1(10)-position on the basis of mass-spectrometric results to be detailed in our full paper [in particular a strong peak at m/e 136 in rimuene (7)], and a signal from one methyl group at high field (τ 9.38) in rimuene and dihydro- but not in tetrahydrorimuene, which we attribute (8) to the methyl group attached at C-9.

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REFERENCES

(1) J. D. Connolly, R. McCrindle, R.D.H. Murray, K. H. Overton and A. Melera, Tetrahedron Letters, 000, (1964).

(2) R. M. Carman, Austral. J. Chem., 16, 1104 (1963).

(3) L. H. Briggs, B. F. Cain and J. K. Wilmshurst, Chem. and Ind., 599 (1958).

(4) R. E. Ireland and P. W. Schiess, J. Org. Chem., 28, 6 (1963);
R. F. Church and R. E. Ireland, ibid., p. 17.

(5) L. H. Briggs, B. F. Cain and R. C. Cambie, Tetrahedron Letters, 8, 17 (1959).

(6) R. F. Church and R. E. Ireland, Tetrahedron Letters, 14, 493 (1961).

(7) H. Budzikiewicz, J. M. Wilson and C. Djerassi, J. Amer. Chem. Soc., 85, 3688 (1963).

(8) W. A. Ayer, C. E. McDonald and J. B. Stothers, Canad. J. Chem., 41, 1113 (1963).