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CONFIRMATION OF THE STRUCTURE OF PHYLLOCLADENE, MIRENE AND RIMUENE AND THE CONFIGURATION OF CUPRESSENE

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IN a previous paper[1] evidence for the constitution of the main naturally occurring crystalline diterpenes was summarized, while in a later paper[2] evidence was adduced for their absolute configuration. No direct chemical proof was given for the constitution of rings A and B nor for the position of the angular group which, on biogenetic grounds, was placed on C-12 although its position on C-11 could not theoretically be excluded.

These doubtful points in the constitution of rimuene, phyllocladene, mirene and cupressene have now been resolved and their absolute configuration confirmed by the conversion of rimuene into abieta-7:9(14)-diene of known constitution and absolute configuration.[3]

Earlier,[2] a mechanism, involving a Wagner - Meerwein transformation, was proposed for the conversion of rimuene into isophyllocladene. Ruzicka,

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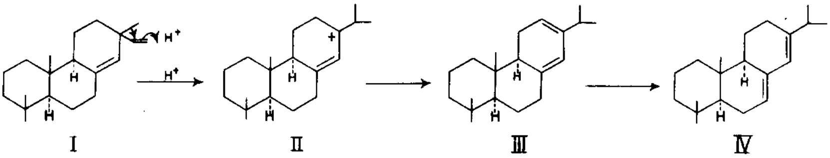
[1] L. H. Briggs, B. F. Cain, B. R. Davis and J. K. Wilmshurst, Tetrahedron Letters No. 8,p. 8 (1959).

[2] L. H. Briggs, B. F. Cain, B. R. Davis and J. K. Wilmshurst, Tetrahedron Letters No. 8, 13 (1959).

[3] W. Klyne, *J. Chem. Soc.* 3072 (1953).

however, has suggested[4] an alternative biogenetic scheme for the conversion of pimaradiene types of diterpenes into those of the levopimaric and neoabietic acid type. This has recently been realised in the laboratory by Wenkert and Chamberlin[5] with the conversion of both pimaric and isopimaric acid into abietic acid and now in our laboratory.

When rimuene is heated with formic acid for 2-3 days the major product, besides isophyllocladene, is an isomeric liquid hydrocarbon, b.p. 125°/0.3 mm, $[\alpha]_D^{25}$ - 196°, λ_{max}^{EtOH} 272.5 mμ (log ϵ 3.21) but with further reflux periods (5-10 days) the major product is another isomeric liquid hydrocarbon which, after distillation from sodium, had b.p. 138°/0.2 mm, $[\alpha]_D^{21}$ - 80.3° ± 3°, n_D^{22} 1.5320, λ_{max}^{EtOH} 239 mμ (log ϵ 4.30). The maxima correspond to diene systems of the levopimaric and abietic acid type respectively (λ_{max} 272.5 and 241 mμ) and the isomerization may be formulated (I) - (IV).



Obviously (III) is an intermediate in the reaction, isomerizing to the

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

[5] E. Wenkert and J. W. Chamberlin, J. Amer. Chem. Soc. 81, 688 (1959).

[6] L. Ruzicka, H. Waldmann, P. J. Meier and H. Hösli, Helv. Chim. Acta 16, 169 (1933).

more stable abietadiene type on longer treatment.

Abieta-7:9(14)-diene has been prepared from abietic acid by a modification of Ruzicka et al.[6] Reduction with lithium aluminium hydride afforded abieta-7:9(14)-dien-15-ol,[6] oxidized by t-butyl chromate[7] to the corresponding aldehyde.[6] Reduction of the derived semicarbazone by the Wolff - Kishner method gave abieta-7:9(14)-diene with properties similar to those recorded.[6] Our product, after distillation from sodium, had b.p. 133° (bath temp.)/0.1 mm, $[\alpha]_D^{21}$ - 86°, λ_{max}^{EtOH} 241 mμ (log ϵ 4.29) while Ruzicka et al.[6] record b.p. 135-138°/0.15 mm, n_D^{24} 1.5313. These properties indicate the identity of the dienes from both rimuene and abietic acid, confirmed by identical infra-red spectra.

Since the constitution and absolute configuration of abietic acid is known[3] and since rimuene, phyllocladene, mirene and cupressene can be isomerized to a common isomer, isophyllocladene, the constitutions and absolute configurations of rimuene, phyllocladene, mirene and the partial structure of cupressene, set out in the earlier papers[1,2] are confirmed while this evidence and biogenetic considerations support the constitution and absolute configuration proposed for kaurene.[2]

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[7] R. V. Oppenauer and H. Oberrauch, Anal. Assoc. Quim. Arg. **37**, 246 (1949).