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THE BIOSYNTHESIS OF CITRONELLAL AND OF CINEOLE IN EUCALYPTUS

A.J.Birch, D.Boulter, R.I.Fryer, (Mrs) P.J.Thomson and J.L.Willis.

Manchester University, Liverpool University,
and Museum of Applied Arts and Sciences, Sydney.

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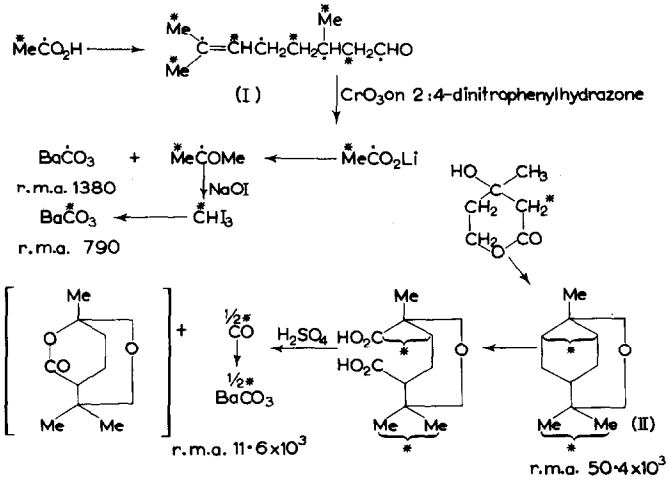
LITTLE work has been done on the biosynthesis of plant terpenes, and in order to investigate the experimental techniques of incorporation we have fed $Me^{14}CO_2H$ into citronellal in Eucalyptus citriodora Hook and 2-^{14}C-mevalonic lactone into cineole in E.globulus.Lab. Terminal branchlets (total weight about 50 g) were allowed to absorb by transpiration acqueous solutions (about 30 cc) containing the labelled precursor, assisted if necessary by a current of warm air. The oils were obtained by steam-distillation (cohobation technique), citronellal being isolated as its 2:4-dinitrophenylhydrazone, and cineole as the resorcinol complex. Dilution with inactive material (about 200 mg) assisted purification and provided sufficient material for degradation. The incorporations were small, but sufficient for further investigation.

The pattern expected for citronellal is (I) and with $Me^{14}CO_2H$ as precursor the activity should be zero if no randomisation occurs. The result shown, based on Kuhn-Roth oxidation, supports the expected distribution although randomisation is considerable, the accuracy being good in view of rather low activities [Found for the whole molecule: r.m.a. 11 x 10^3; calc. from the sum of the r.m.a. contributions based on

(I) and the results of the Kuhn-Roth oxidation: r.m.a. 10 x 10^3]. The randomisation may occur through formation of $^{14}CO_2$ and photosynthesis.

The pattern expected for cineole from 2-^{14}C-mevalonic lactone is (II) and is supported by the degradation shown: little if any randomisation appears to have occurred. The degradation assumes that the isotope effect in the oxidation to cineolic acid is small.



Clearly, this technique can be used for other leaf terpenes, especially with mevalonic lactone. While this work was in progress Stanley [1] showed that mevalonic acid could be incorporated into α-pinene, but did not degrade the product.

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[1] R. G. Stanley, Nature, Lond. 182, 738 (1958).