

THE FORMATION OF RING C OF THE DITERPENES

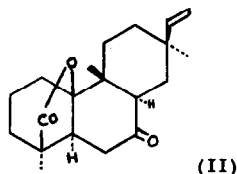
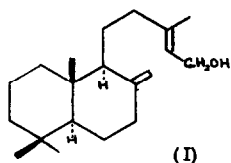
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The intervention of a bicyclic intermediate (I) in the biosynthesis of the tricyclic diterpenes forms a key feature in a number of biogenetic schemes (1). We now wish to present experimental evidence in support of this.

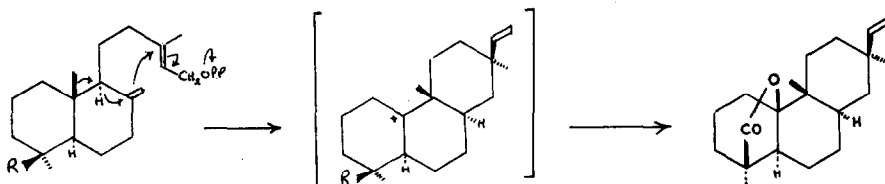
The alcohol (I) was prepared from sclareol by dehydration and allylic rearrangement (2). It was oxidized to the aldehyde with manganese dioxide and reduced with sodium borohydride-T. The labelled alcohol solubilized in Tween 80, was then fed to Tricothecium roseum (3). This was harvested after 13 days. Isolation of the rosenonolactone (II) showed after crystallization to constant activity, an incorporation of 0.13%.



The hydrocarbon, (+)-pimaradiene (III) was prepared (4) and tritiated by reduction of pimonic acid methyl ester to the alcohol, and oxidation with chromium trioxide to the aldehyde (IV). The semicarbazone was exchanged with T_2O and subjected in the presence of T_2O to a Wolff-Kishner reduction.



The labelled hydrocarbon was fed to T. roseum. However on several occasions no consistent incorporation was observed. This suggests that methyl migration occurs at the bicyclic stage without however defining the oxidation level of the intermediate that rearranges.



The biosynthesis and the degradation of the labelled rosenonolactone is the subject of further study.

REFERENCES

1. Inter alia
 L. Ruzicka, Experientia **9**, 357 (1953); Proc. Chem. Soc. 341 (1959).
 A. J. Birch, R. W. Richards, H. Smith, A. Harris and W. B. Whalley, Tetrahedron **7**, 241 (1959).
 D. Arigoni, CIBA Foundation Symposium Biosynthesis of Terpenes and Sterols, ed. Wolstenholme and O'Connor, p. 231, London (1959).
 A. J. Birch, ibid., p. 245.
 A. I. Scott, F. McCapra, F. Comer, S. A. Sutherland, D. W. Young, G. A. Sim and G. Ferguson, Tetrahedron **20**, 1339 (1964).
2. G. Ohloff, Ann. **617**, 134 (1958).
3. A. Robertson, W. R. Smithies and E. Tittensor, J. Chem. Soc. 879 (1949).
 G. A. Ellestad, B. Green, A. Harris, W. B. Whalley and H. Smith, J. Chem. Soc. 7246 (1965) (and previous refs.).
4. R. E. Ireland and P. W. Schiess, J. Org. Chem. **28**, 6 (1963).