

CYCLOSEYCHELLENE, A NEW TETRACYCLIC SESQUITERPENE FROM POGOSTEMON CABLIN

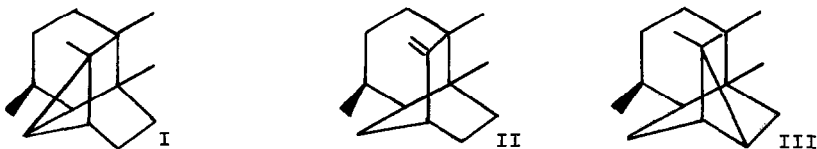
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We have isolated cycloseychellene I from the essential oil of Pogostemon cablin Benth. and have shown that it is related to seychellene (1,2) II, in the same way as sativene is related to cyclosativene (3).



AgNO₃/Al₂O₃ column chromatographic separation (4) of the sesquiterpene hydrocarbon fraction of P. cablin afforded a new sesquiterpene hydrocarbon M⁺=204. Its early elution from the column and IR spectrum (3021 and 845 cm⁻¹) suggests that it could be a tetracyclic hydrocarbon containing a cyclopropyl ring. Since seychellene has previously been found in the same oil (1,2), a tetracyclic structure based on the seychellene skeleton was proposed.

To confirm this hypothesis, cycloseychellene was synthesised from seychellene by a method similar to that used in the synthesis of cyclosativene (3,5) and longicyclene (6). Seychellene was heated (90°) with cupric acetate in acetic acid for fifty hours after which time 6% cycloseychellene was formed. As this reaction is one involving an equilibrium between the tricyclic and the tetracyclic molecules, it is obvious that, using the above conditions, it is greatly in favour of seychellene. To confirm this, cycloseychellene was heated (90°) with cupric acetate/acetic acid for forty hours to give 55% seychellene.

The NMR of cycloseychellene agrees with the proposed structure: Two cyclopropyl protons, one at δ 0.595, txd $J=8.0$ and ≈ 3 cps and one at δ 0.840 dxd $J=8.0$ and 3.6 cps. Three quaternary methyls at δ 0.754, 0.840 and 0.968 and one tertiary methyl δ 0.774, d, $J=6.0$ cps. The coincidental methyl and cyclopropyl protons (0.840) were completely resolved by using deuterated benzene instead of carbon tetrachloride as solvent. The cyclopropyl (0.595) collapsed to a doublet $J=8$ when the two protons at δ 1.69 were irradiated (FIG. 1)

Seychellene is unique in that it has two theoretically equivalent ways to cyclize to give either I or III. Examination of the molecular models of I and III reveals no steric reason why one structure should be favoured over the other. Yet, considering the NMR data, in particular the coupling of the cyclopropyl protons, structure III is ruled out. Because of this, we propose that cycloseychellene isolated from Pogostemon cablin has structure I.

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FIG. 1

