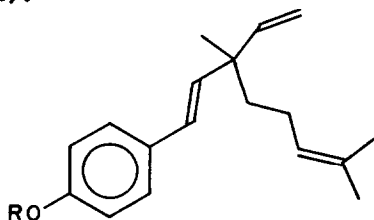


SYNTHESIS OF (+)-BAKUCHIOL METHYL ETHER

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THE isolation and structure determination of Bakuchiol, a novel monoterpene phenol (I), from Psoralea corylifolia Linn., has been recently reported by us¹. We now describe an unambiguous three-step synthesis of its methyl ether (II).

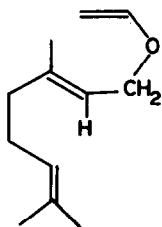


I, R = H

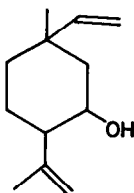
II, R = Me

Interaction of geraniol and ethyl vinyl ether in the presence of mercuric acetate² proceeded smoothly to give, in 56% yield, geranyl vinyl ether (III; b.p. 71-72°/2 mm, n_D^{30} 1.4641), the structure of which is fully supported by the spectral data (IR spectrum: vinyl ether 1630, 1205, 1060 cm^{-1} . PMR spectrum³: three vinylic methyls, 3H singlets at 96, 100, 100 c/s; =CH-CH₂-O- and CH₂=CH-O-, overlapping multiplets located between 228-255 c/s; CH₂=CH-O-, 1H quartet centred at 383 c/s; two >=CH-CH₂, 1H triplets centred at 304 and 321 c/s). Heating III at 200° (3 hr) gave a mixture, in which an alcohol, considered to be IV on spectral grounds, predominated. Since IV could arise from the expected aldehyde, V, by a further thermal reaction, the pyrolysis of III under various conditions was studied. Heating III at 182 ± 2°

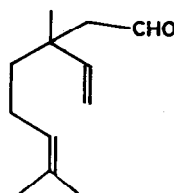
for 30 min. furnished, in 90% yield, the required aldehyde (V; b.p. 92-94°/5 mm; semicarbazone, m.p. 108-110°) of Claisen rearrangement⁴ (IR spectrum: HC=O 2700, 1725 cm^{-1} . PMR spectrum: one quaternary methyl, 3H singlet at 69 c/s; two vinylic methyls, singlets at 95.5 and 100 c/s; $\text{C-CH}_2\text{-CHO}$, 2H doublet centred at 138.5 c/s, $J = 3$ c/s; four olefinic protons, one triplet centred at 305 c/s, and three H coupled in an ABC pattern between 290-367 c/s; $\text{-CH}_2\text{-CHO}$, 1H triplet centred at 597 c/s, $J = 3$ c/s). Action of p-methoxyphenyl magnesium bromide on V, gave an alcohol, which on dehydration with



III



IV



V

alumina⁵ at $175 \pm 5^\circ$ furnished a product, identified (TLC, IR, PMR) as the racemic II.

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