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BIOGENETIC-TYPE TRANSFORMATIONS IN DITERPENOIDS

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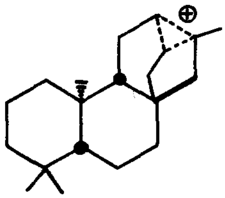
A recent publication by McAlees *et al.*[1] prompts us to place on record some of our experiments, which, though differing in approach, were directed towards a similar objective, *viz.* a study of tetracarbocyclic diterpene interconversions originating at an electron-deficient carbon.

The ion I occupies the central place in the biogenesis of tetracyclic diterpenoids according to Wenkert scheme[2] and its importance has been discussed earlier[3] and conversion of (+)-hibaene (II) into (-)-kaurene (III) described[3]. The present work, which is in continuation of the earlier one[3], deals with the *in vitro* fate of the ion I, under specified conditions.

Hydroboration[4] of (+)-hibaene furnished a 2:3 mixture of two alcohols, identified as IV (m.p. 103-103.5°: PMR[5]: quat. methyls, 48, 51, 53, 53 c/s; C<u>H</u>OH, broad doublet centred at 217 c/s, with J = 6 c/s) and V (m.p. 94-94.5°. PMR: quat. methyls 50, 52, 56.5, 58.5 c/s; C<u>H</u>OH, broad doublet centred at 250 c/s with J = 6 c/s) respectively, by chromic acid oxidation to the corresponding ketones, of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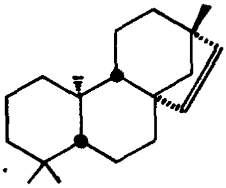
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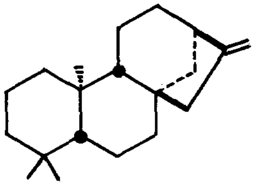
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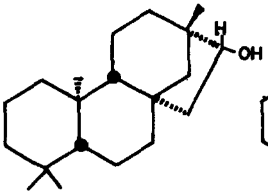
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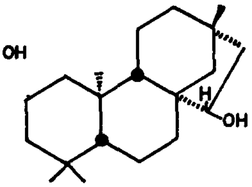
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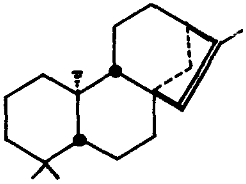
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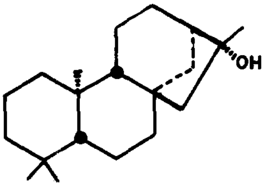
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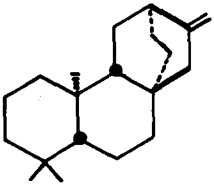
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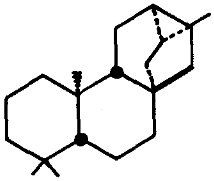
IX

known structure[6]. The tosylate (m.p. 89-90°. PMR: C$\underline{H}$OTs, broad doublet centred at 264 c/s with J = 6 c/s) derived from IV, on solvolysis in buffered (Li_2CO_3), 66% aq.dioxane furnished a reaction product (~80%), consisting of a hydrocarbon (40%) and alcohol (60%) portions, separated on a silica gel column. Silver nitrate-silica gel[7] TLC of the hydrocarbon part showed the presence of at least two components, which were separated by chromatography over silver nitrate-silica gel to give 42% (-)-kaurene, 29% isokaurene (VI) and 29% (+)-hibaene, all identified by comparison (TLC, IR) with authentic samples. The alcohol part was essentially homogeneous and after recrystallisations (ethyl acetate) gave a product (m.p. 204-206°; $[\alpha]_D$ -39.66°, dioxane; PMR, pyridine soln.: quat. methyls, 47.5, 49.5, 59 and 93 c/s) identified as kauran-16-ol (VII)[8], by comparison (mixed m.p., $[\alpha]_D$, IR) with an authentic sample.

When the above tosylate was shaken with alumina/I (pH 9-10) in hexane, only a hydrocarbon mixture resulted (yield ~ 71%), and this had a composition, virtually identical with that obtained by the solvolysis method.

The above experiments, which were carried out especially to see if any atiserene (VIII)[9] and trachylobane (IX)[10] result from such a reaction, clearly show the non-formation of these products under the reaction conditions studied.

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