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CHEMICAL TRANSFORMATION OF (+)-HIBAENE INTO (-)-KAURENE[*]

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Special interest attaches to the conversion of hibaene (I) into kaurene (II), as both of these are biogenetically linked through the precursor III, which in its stereochemically specified state[+] is the biogenetic progenitor for the various tetracarbocyclic diterpenes according to Wenkert scheme[1]. Though, at the time of the

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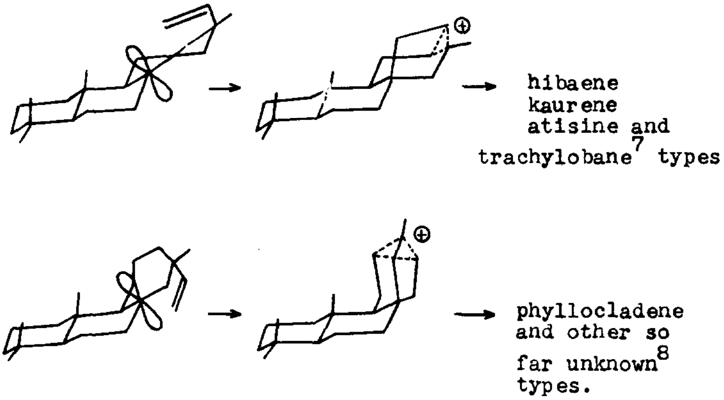
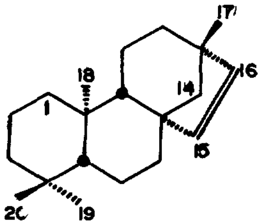
[*] Communication No. 767 , National Chemical Lab., Poona.

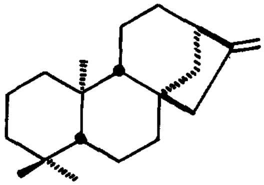
[+]



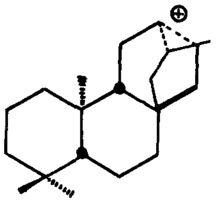
original proposal no diterpene of type I was known with certainty[2], several members of this class have been described[3,4,5,6] in recent years. We now report the chemical



I



II



III

transformation of (+)-hibaene (I)[6] into (-)-kaurene (II)[9].

(+)-Hibaene epoxide[6] on treatment with BF_3-Et_2O in benzene at 0° gave in 85% yield an unsaturated alcohol, $C_{20}H_{32}O$ (m.p. 134-135°, $[\alpha]_D$ -30.3°) with the following structural features: three quaternary methyl groups (PMR[*]: 3H sharp singlets at 50, 52 and 62 cps); one vinylic methyl (PMR: 3H doublet centred at 103 cps, J = 2 cps); one olefinic proton (PMR: 1H signal centred at 295 cps; IR: 1650, 865 cm^{-1}; positive tetranitromethane test); one secondary hydroxyl (PMR: 1H signal, essentially a singlet, at 240 cps; IR: 3400, 1052, 1044 cm^{-1}); these characteristics[+] are in accord with the structure IV, anticipated

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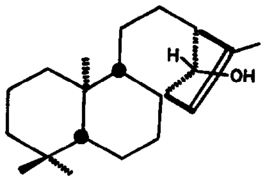
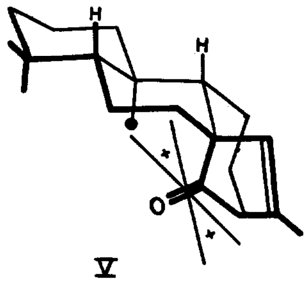
[*] All PMR spectra were measured in ~ 5-10% soln. in CCl_4 on a Varian A-60 Spectrometer; the signals are recorded in cps from tetramethylsilane (internal standard) as zero.

[+] Cf. e.g. the Me signals of isokaurene: 48, 51, 61 and 100 cps.

mechanistically. The above alcohol on oxidation with CrO_3-pyridine furnished the unsaturated ketone (V, m.p. 113-114°, $[\alpha]_D$ +16.0°; $\nu^{C=O}$ 1750 cm^{-1}; $\lambda_{max}^{ethanol}$ 273, ϵ 31, also a shoulder at 228 with ϵ 810) which, as required by structure V, showed the shielding of the C_{10}-Me by the carbonyl in its PMR spectrum (all the three quaternary methyls showing a composite 9H signal at 52 cps). The ketone on Wolff-Kishner reduction[10] gave in 62% yield a



IV



V

mixture of dihydrokaurene[*] (m.p. 84-85°, $[\alpha]_D$-30°) and kaurene (II)[+] (m.p. 50-50.5°, $[\alpha]_D$ -78.5°), readily

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[*] The reduction of an olefinic linkage during Wolff-Kishner reduction has been reported; for references see: R.Soman, Sukh Dev, R.Misra and R.C.Pandey, <u>Tetrahedron Letters</u> 3767 (1964).

[+] Apparently isomerisation of isokaurene to kaurene occurs with facility under these conditions.

separated over $AgNO_3$-silica gel[11] and identified by standard procedures.

The above rearrangement (Hibaene → isokaurene type) appears to be general. Thus (-)-monogynyl acetate[12] (19-acetoxy-I) could be readily converted into 19-acetoxy-IV (m.p. 151-152°, $[\alpha]_D^{27} = -31.7^\circ$) in an overall yield of 66% by this route.

In connection with the above work it should be mentioned that (+)-hibaene on being refluxed for 2.5 hr in a 1:1 mixture of dioxane-formic acid, was recovered essentially unchanged; only traces of some formate were produced. On treatment of (+)-hibaene with hydrogen chloride in C_6H_6-$CHCl_3$ at 0° the corresponding hydrochloride (m.p. 73-74°; $[\alpha]_D$ -29°. PMR: four quaternary methyl signals at 49, 51, 56 and 58.5 cps; $-C\underline{H}Cl-$ signal, as a multiplet centred at 265 cps) was obtained.

Acknowledgement. The authors wish to record their indebtedness to Prof. G. Ourisson for a sample of isokaurene and Prof. B.E. Cross for a specimen of (-)-kaurene.

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