The Structure and Stereochemistry of a New Sesquiterpene of the Acorane Type

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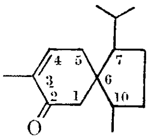
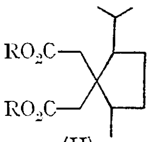
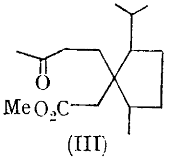
THE steam-volatile oil of a hybrid grass prepared from two parent races of *Bothriochloa intermedia* has been found to contain as a major component the new sesquiterpene, acorenone-B ($C_{15}H_{24}O_2$, M^+ 220). Acorenone-B is similar to acorenone (I),[1] both in physical properties and in its i.r. spectrum; its n.m.r. and u.v. spectra are consistent with the structural features in (I). However, hydrogenation of acorenone-B under the conditions reported[1] for acorenone gave a mixture of two dihydro-derivatives, neither of which are identical with dihydro-acorenone. Acorenone-B was degraded to a diacid with melting point identical with that reported[1] for (II; R = H) obtained from acorenone. In addition, the diester (II; R = Me) obtained from acorenone-B had an identical i.r. spectrum with the corresponding compound obtained from acorenone.[1] Acorenone-B was transformed into the keto-ester (III) by sequential Baeyer–Villiger oxidation, reduction with lithium aluminum hydride, Jones oxidation, and finally esterification. In the n.m.r. spectrum of (II; R = Me) the two methylene groups adjacent to the methoxycarbonyl groups appeared at 137 and 172 c./sec. downfield from tetramethylsilane while in (III) the corresponding methylene group appeared at 126 c./sec.



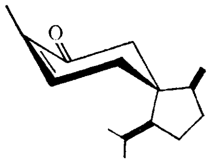
(I)



(II)



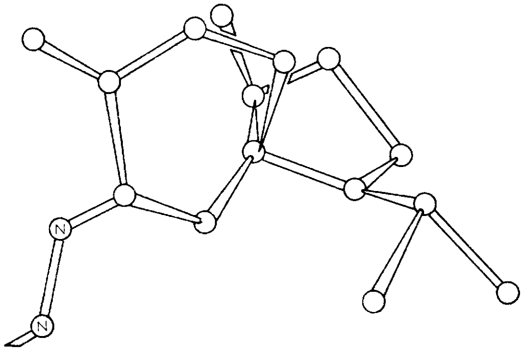
(III)



(IV)

An *X*-ray crystallographic determination was carried out on acorenone-B 4-iodo-2-nitrophenylhydrazone ($C_{21}H_{24}O_2N_2I$, M^+ 481). The crystals were orthorhombic, space group $P2_12_12$, a = 20·81, b = 7·18, c = 14·81 Å, Z = 4, D_c = 1·44, D_m = 1·40 (by flotation), Mo-K_α radiation, precess camera data. The iodine atoms were located by a three-dimensional Patterson synthesis and the structure was solved by successive Fourier syntheses. With use of full-matrix least-squares refinement with isotropic temperature factors and individual layer scale factors, the R index converged to 0·107 for 465 independent non-zero reflections. The structure is shown in the Figure.

The relative configuration of acorenine-B is as depicted in (IV) while acorenone presumably differs in relative configuration at the spiro-carbon atom. Another reported[2] difference is that acorenone (carbonyl group *cis* to methyl and isopropyl groups) does not give a crystalline carbonyl derivative whereas acorenone-B readily gives such derivatives.



FIGURE

Acorone,[3] which has the same carbon skeleton as (I) without the double bond and with an additional carbonyl group at C-8, has been shown by X-ray analysis[4] to have the relative configuration in which the methyl and isopropyl groups are *trans* and the carbonyl group is *trans* to the methyl group as opposed to being *cis* as in acorenone-B.

On the basis of this X-ray data we suggest that the methyl acetate residues in (II, with high field CH_2 group) and (III) have a *trans* relationship to the *cis*-oriented methyl and isopropyl groups in the five-membered ring.

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[2] J. Vrokc, V. Herout, and F. Sorm, *Coll. Czech. Chem. Comm.*, 1961, **26**, 1021.

[3] J. Vrkoc, J. Jonas, V. Herout, and F. Sorm, *Coll. Czech. Chem. Comm.*, 1964, **29**, 539.

[4] C. E. McEachan, A. T. McPhail, and G. A. Sim, *Chem. Comm.*, 1965, 276.