Tricyclovetivene

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THE structure (I) has been suggested for tricyclovetivene, one of the sesquiterpene hydrocarbons of vetiver oil, by Chiurdoglu and Tullen,[1] and Romanuk and Herout[2] have isolated this sesquiterpene in a more pure state. We have also isolated pure tricyclovetivene† ($[\alpha]_D$ +40·4°, *c* 5·2 in chloroform) from vetiver oil and re-examined its structure.

The infrared spectrum exhibits absorptions due to an exocyclic methylene group at 1641 and 889 cm.$^{-1}$ as reported earlier; however the n.m.r. spectrum is incompatible with the structure (I). This spectrum shows a secondary methyl signal (0·94 p.p.m., doublet, *J* 6·5 c./sec., 3H), instead of the signal due to an isopropyl group, two tertiary methyl groups, and an exocyclic methylene group.

Osmium tetroxide oxidation of tricyclovetivene afforded the glycol (VII), m.p. 84—84·5°, in good yield, and the latter yielded the nor-ketone (VI), ν_{max} 1708 cm.$^{-1}$, by lead tetra-acetate oxidation. On the other hand, tricyclovetivene gave the nor-ketone as a mixture of epimers‡ by ozonisation followed by treatment with sodium iodide in acetic acid. The infrared spectra of both the pure nor-ketone (VI) and the epimeric mixture were

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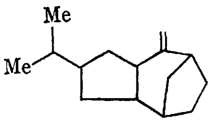
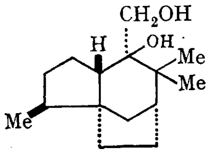
† We thank Professor V. Herout (Czechoslovak Academy of Science, Institute of Organic Chemistry and Biochemistry, Prague) for identification of tricyclovetivene and to Mr. Y. Ueno (Ogawa Perfumery Co., Osaka, Japan) for supplying vetiver oil.

‡ The epimeric mixture of nor-ketones was also obtained from zizanoic acid (ref. 3).

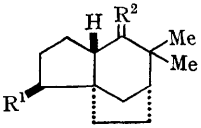
not superimposable with that of the nor-ketone obtained by Chiurdoglu and Tullen.[1] The Belgian authors have mentioned the formation of cyclopentane-1,3-dicarboxylic acid by stepwise degradation through the nor-ketone as an important evidence for the structure (I). The homogeneity of their nor-ketone, however, has not been ascertained.



(I)



(VII)



(II) R^1=Me, R^2=CH_2
(III) R^1=CO_2H, R^2=CH_2
(IV) R^1=CH_2OH, R^2=CH_2
(V) R^1=CH_2OTs, R^2=CH_2
(VI) R^1=Me, R^2=O

Recently the structure of zizanoic acid (III) and khusimol (IV), which are also constituents of vetiver oil, have been established,[3] and it has been reported that an olefin (II) corresponding to zizanoic acid was obtained by lithium aluminium hydride reduction of the tosylate (V) and tentatively named "zizaene". We found that the infrared, n.m.r., and mass spectra and optical rotation of tricyclovetivene are totally identical with those of zizaene.§ Consequently, the structure (I) of tricyclovetivene should be revised to (II).

The presence of impurity may be responsible for the reported formation of vetizazulene upon dehydrogenation of tricyclovetivene,[1] since our numerous attempts to obtain either vetivazulene or eudalene from pure tricyclovetivene by dehydrogenation[3] failed.

(*Received, November 10th,* 1967; *Com.* 1219.)

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§ According to a private communication, E. Klein (Dragoco, Holzminden, Germany) has also observed that tricyclovetivene is identical with the parent olefin derived from vetivenic acid, a sesquiterpenic carboxylic acid isolated from vetiver oil. It was confirmed by direct comparison that vetivenic acid is synonymous with zizanoic acid.

[1] G. Chiurdoglu and P. Tullen, *Bull. Soc. chim. belges.*, 1957, **66**, 169.

[2] M. Romanuk and V. Herout, *Coll. Czech. Chem. Comm.*, 1960, **25**, 2540.

[3] F. Kido, H. Uda, and A. Yoshikoshi, *Tetrahedron Letters*, 1967, 2815; for the stereochemistry, see *Tetrahedron Letters*, in the press.