The Structure of Perezone

By D. A. ARCHER and R. H. THOMSON
(*Department of Chemistry, University of Aberdeen*)

FOLLOWING a recent publication[1] on the structure of α- and β-pipitzol, the rearrangement products of perezone, we now report that the structure (I), hitherto accepted for this sesquiterpene quinone, is incorrect.

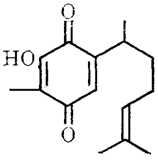
Kögl and Boer[2] established that perezone is a 2,5-dialkylbenzoquinone and the acidic hydroxyl group was located, as shown, on reasonable chemical evidence. The n.m.r. spectrum of perezone is consistent with structure (I) *except* that the quinonoid methyl group appears as a clearly defined doublet at τ 7·94 and the quinonoid proton shows up as a quartet centred at τ 3·53. Similarly, the spectrum of dihydroperezone (II according to ref. 2) shows a doublet at τ 7·93 and a quartet at τ 3·5. These data imply that the quinonoid position adjacent to the methyl group is unsubstituted and consequently perezone has structure (III). We have now prepared a synthetic compound of structure (II) which is different from dihydroperezone. Its n.m.r. spectrum is almost identical with that of dihydroperezone (IV)

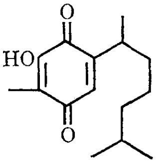
---

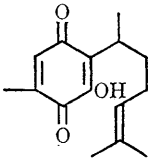
[1] F. Walls, J. Padilla, P. Joseph-Nathan, F. Giral, and J. Romo, *Tetrahedron Letters*, 1965, 1577.
[2] F. Kögl and A. G. Boer, *Rec. Trav. chim.*, 1935, **54**, 779.

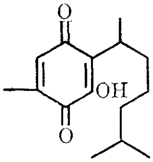
except for the signals from the quinonoid methyl group (a sharp singlet at τ8·05) and the quinonoid proton (a singlet at τ3·5).

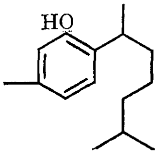
Compound (II) was synthesised by reaction of 4-methylpentylmagnesium bromide with 2-acetyl-5-methylanisole. Dehydration, reduction, and demethylation then gave the phenol (V) which was converted into its 2,4-dinitro-derivative, reduced to the diamine, and oxidised with ferric chloride to the hydroquinone (II), m.p. 103—104°. Authentic dihydroperezone has m.p. 95—96° (lit.[3] 95°) and the mixed m.p. is considerably depressed. (The synthetic dihydroperezone claimed by Yamaguchi[3] had m.p. 130—132°.)

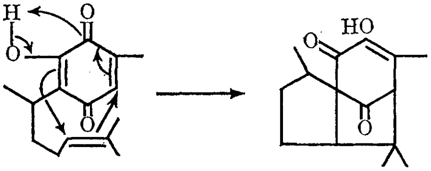

(I)


(II)


(III)


(IV)


(V)


(VI) (VII)

A synthesis of DL-perezone (III) is in progress. Using this structure the rearrangement of perezone to the pipitzols (VII) can now be represented by (VI) (*cf.* ref. 1).

(*Received, June* 28*th*, 1965; *Com.* 401.)

K. Yamaguchi, *J. Pharm. Soc. Japan*, 1942, **62**, 491.