

VI (as the dibenzenesulfonamide) and VII (as barium carbonate) had respectively $51.8 \pm 1\%$ and $43.1 \pm 1\%$ of the radioactivity of V (as the semicarbazone or 2,4-dinitrophenylhydrazone). In a blank degradation of aniline-1- C^{14} (III),^{6,9} the corresponding percentage activity figures for VI and VII were 0.2 ± 1 and $96.7 \pm 1\%$, respectively. Since in the blank degradation the barium carbonate activity was consistently low, we consider the activity of VI to be the most reliable index of the amount of rearrangement in the amination of I.

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(9) Since I was prepared from III by Tracerlab, Inc., using the Sandmeyer reaction, this degradation constitutes a proof of the isotope position assignment for I.

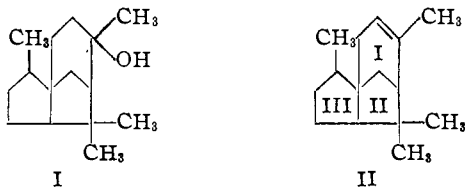
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THE STRUCTURE OF CEDRENE

Sir:

The tricyclic sesquiterpenes cedrene, $C_{15}H_{24}$, and cedrol, $C_{16}H_{26}O$, have been the object, since their isolation by Walter in 1841,¹ of a large number of chemical investigations² which have led to the proposal of no fewer than thirteen different structures for the tertiary alcohol cedrol and the related anhydro compound, cedrene.³

We have elucidated the structures of these two sesquiterpenes which can now be represented by I (cedrol) and II (cedrene).



(1) Ph. Walter, *Ann.*, **39**, 247 (1841).

(2) Reviews of the work in this field up to 1947 are found in J. Simonsen and D. H. R. Barton, *The Terpenes*, Vol. III, Cambridge University Press, London (1952); see also S. H. Harper, *Ann. Repts. Chem. Soc.*, **44**, 143 (1948).

(3) The last published proposals are by Pl. A. Plattner, *Chimia*, **2**, 248 (1948).

The presence of the grouping $-\text{CH}-\text{C}-\text{C}-$ in the unsaturated ring of cedrene is well established.² The size of that unsaturated ring (ring I, fig. II) has incorrectly been deduced to be five-membered by previous investigators^{4,4a} on the basis of observations which appeared to us to point clearly to a six-membered ring. We have confirmed our deduction by examination of the infrared spectrum of the anhydride of the bicyclic C_{13} diacid, norcedrenedicarboxylic acid (NCDA),⁵ which proved to be that of a glutaric anhydride, with peaks at 5.57 and 5.67 μ , while a succinic anhydride, derived from a six-membered ring I, would have absorption maxima at 5.40 and 5.63 μ .⁶ We have further prepared by the action of phenylmagnesium bromide on dimethyl norcedrenedicarboxylate a *diphenyl lactone*, m.p. 173–173.5°, which had its infrared band at 5.75 μ , in confirmation of the six-membered lactone structure corresponding to a glutaric acid.

The two carboxyls of NCDA are attached to a ring, the size of which we have proved by examination of the infrared spectrum of the anhydride of the monocyclic C_{11} dibasic acid obtained by further degradation of NCDA.⁴ Again this proved to be the anhydride of a glutaric acid and ring II is thus established to be five-membered. The position of the *gem* dimethyl group shown in fig. II is considered elsewhere.⁷ With respect to ring III two facts pointed strongly to the arrangement indicated in structure II: The isolation in high yield of *p*-cymene from the catalytic dehydrogenation of cedrene,⁸ indicating the probable presence of a potential isopropyl group *para* to the methyl group of ring I; and the obvious biogenetic relationship to β -curcumene, of which cedrol is a formal cyclization product. In any event, this surmise is confirmed by the fact that the dehydroacid obtained from the C_{11} dibasic acid^{4,5} is oxidized to α, α -dimethylhomotricarballylic acid,³ an important result, a possible structural implication of which was incorporated, together with previous erroneous structural deductions, into the last published proposals for the structure of cedrene.³ The full development of the necessarily sketchy outline presented here will be given in a subsequent paper.⁹

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(4) Pl. A. Plattner, G. W. Kusserow and H. Kläui, *Helv. Chim. Acta*, **25**, 1345 (1942).

(4a) L. Ruzicka, Pl. A. Plattner and G. W. Kusserow, *ibid.*, **25**, 85 (1942).

(5) Pl. A. Plattner and H. Kläui, *Helv. Chim. Acta*, **26**, 1553 (1943).

(6) We have established that the position of the diagnostically more important lower wave length band is not affected by the degree of substitution.

(7) G. Stork and R. Breslow, *THIS JOURNAL*, **75**, 3292 (1953).

(8) W. Treibs, *Ber.*, **68**, 1041 (1935).

(9) Structures I and II for cedrol and cedrene were first presented formally in a lecture given by one of us at Harvard on January 27, 1953.