

## $\alpha$ -Vetivone<sup>1</sup>

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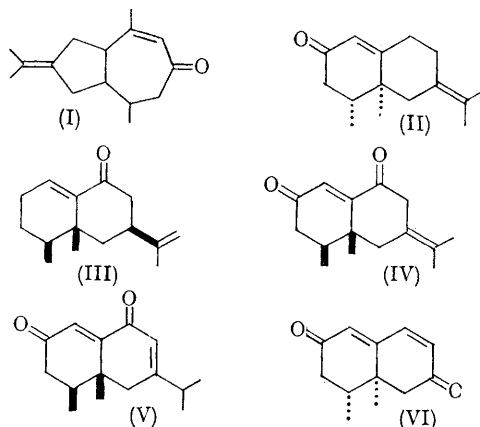
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THE constitutions of  $\alpha$ - and  $\beta$ -vetivone have been generally accepted as being represented by stereoisomeric modifications of the structure (I). The n.m.r. spectrum of  $\beta$ -vetivone is in accord with its assigned structure: that of  $\alpha$ -vetivone\* is not. This is because of the absence of a signal which can be attributed to a vinylic methyl group and the presence of a singlet (three protons, 0.97 p.p.m.) compatible with expectation for a methyl group attached to an unperturbed  $sp^3$  carbon.

Despite "an extraordinary resemblance to  $\beta$ -vetivone in its chemical reactions and in most of its physical properties",<sup>3</sup> the significant facts upon which the structure (I) was based were: (a) the presence of an isopropylidene group, (b) the similarity of ultraviolet spectra, (c) a parallel behaviour in hydrogenation and (d) the formation of vetivazulene on dehydrogenation. The co-existence of the substances in the same oil was, no doubt, a powerful emotive factor in the general acceptance of the structural assignment.

Conversion of eremophilone (III)<sup>4†</sup> into the enol acetate (during which migration of the ethylenic linkage to the isopropylidene position occurred) oxidation with sodium dichromate to (IV), and isomerisation with base gave (V). Acetylation of

$\alpha$ -vetivone (II) also gave an enol acetate, but oxidation of this with sodium dichromate led to the formation of (VI). Base-catalysed air oxidation<sup>5</sup> of (II) gave, though in poor yield, the optical antipode of (V).



The reported dehydrogenation to vetivazulene is, therefore, misleading. Dehydrogenation of the

\* The  $\alpha$ -vetivone agreed in properties with all published physical data, and gave a 2,4-dinitrophenylhydrazone of the correct m.p. 151°.

† We are very grateful indeed to Dr R. A. Massey-Westropp (Adelaide) for a generous supply of eremophilone.

saturated alcohols, in which opportunities for rearrangement are curtailed, gave from  $\beta$ -vetivanol, 8% of vetivazulene (estimated spectroscopically) and from  $\alpha$ -vetivanol, nil.

The revised structure of  $\alpha$ -vetivone, which now

places it in a rapidly expanding group of eremophiloids,<sup>6</sup> indicates that terpenoids, at least, are not necessarily known by the company they keep.<sup>7</sup>

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<sup>1</sup> Satisfactory analyses have been obtained for all compounds characterised.

<sup>2</sup> J. L. Simonsen and D. H. R. Barton, "The Terpenes", vol. III, Cambridge University Press, 1952, p. 224.

<sup>3</sup> Ref. 2, p. 231.

<sup>4</sup> L. H. Zalkow, Fr. X. Markley, and C. Djerassi, *J. Amer. Chem. Soc.*, 1960, **82**, 6354.

<sup>5</sup> R. Howe and F. J. McQuillin, *J. Chem. Soc.*, 1958, 1513.

<sup>6</sup> C. J. W. Brooks and G. H. Draffen, *Chem. Comm.*, 1966, 701.

<sup>7</sup> Seventeenth century proverb.