# α-Vetivone[1]

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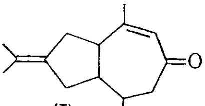
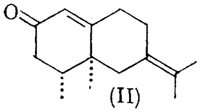
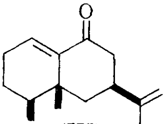
THE constitutions of α- and β-vetivone have been generally accepted as being represented by stereoisomeric modifications of the structure (I). The n.m.r. spectrum of β-vetivone is in accord with its assigned structure: that of α-vetivone* is not. This is because of the absence of a signal which can be 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.

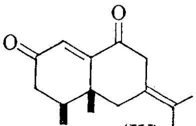
Despite "an extraordinary resemblance to β-vetivone in its chemical reactions and in most of its physical properties",[3] the significant facts upon which the structure (I) was based were: (a) the presence of an isopropylidene group, (b) the similarity of ultraviolet spectra, (c) a parallel behaviour 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.

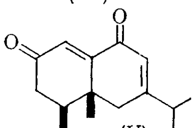
Conversion of eremophilone (III)[4]† into the enol acetate (during which migration of the ethylenic linkage to the isopropylidene position occurred) oxidation with sodium dichromate to (IV), and isomerisation with base gave (V). Acetylation of α-vetivone (II) also gave an enol acetate, but oxidation of this with sodium dichromate led to the formation of (VI). Base-catalysed air oxidation[5] of (II) gave, though in poor yield, the optical antipode of (V).

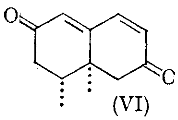

(I)


(II)


(III)


(IV)


(V)


(VI)

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

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* The α-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,[6] indicates that terpenoids, at least, are not necessarily known by the company they keep.[7]

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[1] Satisfactory analyses have been obtained for all compounds characterised.

[2] J. L. Simonsen and D. H. R. Barton, "The Terpenes", vol. III, Cambridge University Press, 1952, p. 224.

[3] Ref. 2, p. 231.

[4] L. H. Zalkow, Fr. X. Markley, and C. Djerassi, *J. Amer. Chem. Soc.*, 1960, **82**, 6354.

[5] R. Howe and F. J. McQuillin, *J. Chem. Soc.*, 1958, 1513.

[6] C. J. W. Brooks and G. H. Draffen, *Chem. Comm.*, 1966, 701.

[7] Seventeenth century proverb.