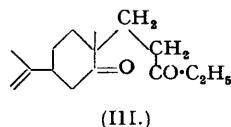
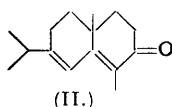
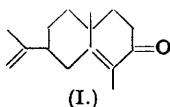


154. The Structure of β -Cyperone.

By F. J. McQUILLIN.

By comparison of the ultra-violet absorption of their derivatives, the sesquiterpene ketones α - and β -cyperone are shown to be structural isomers (I) and (II) and not stereoisomeric forms of structure (I) as proposed by Bradfield, Pritchard, and Simonsen (*J.*, 1937, 760).

α -CYPERONE, a sesquiterpene ketone, $C_{15}H_{22}O$, isolated from the tubers of *Cyperus rotundus* (Hegde and Rao, *J. Soc. Chem. Ind.*, 1935, 54, 387T; Bradfield, Hegde, Rao, Simonsen, and Gillam, *J.*, 1936, 667) was shown to possess the structure (I) (Bradfield *et al.*, *loc. cit.*; Bradfield, Pritchard, and Simonsen, *J.*, 1937, 760). A synthetic ketone, obtained by cyclisation of an intermediate (III) by means of sodium ethoxide, was found to be very closely similar to α -cyperone and to give closely similar derivatives (Adamson, McQuillin, Robinson, and Simonsen, *J.*, 1937, 1576).



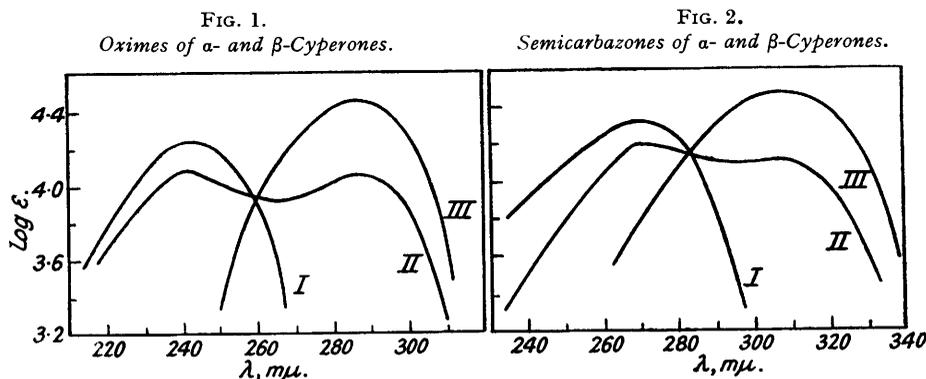
On digestion with acid or with alkali, α -cyperone is converted into an isomeric ketone (known as β -cyperone) of larger molecular refraction and optical rotation. Cyclisation of the diketone (III) by means of 50% sulphuric acid led to a synthetic ketone yielding derivatives generally similar to those of β -cyperone; the ketone itself, however, showed distinctly higher refraction and optical rotation (Adamson, McQuillin, Robinson, and Simonsen, *loc. cit.*).

The semicarbazones of α - and β -cyperone were found by Bradfield, Pritchard, and Simonsen (*loc. cit.*) to yield on ozonolysis the same main degradation product, $C_{15}H_{23}O_4N_3$, and these authors concluded that "the two ketones must presumably be stereo-isomerides, differing in the disposition of the angle methyl and the *isopropenyl* group." The physical properties of

α -cyperone and β -cyperone, obtained by isomerisation and synthetically, are, however, at variance with this conclusion:

α -Cyperone	n_D^{25} 1.5283	$[R_L]_D$ 67.5	$[\alpha]_{5461} + 138^\circ$
β -Cyperone, "N"	1.5414	68.9	+ 239°
" " "B"	1.5565	70.5	+ 111.7°
" " "O"	n_D^{16} 1.5590	70.4	+ 342°

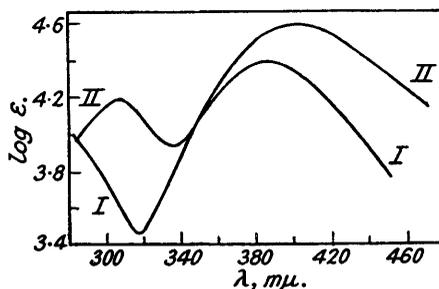
β -Cyperone "N" refers to the ketone from isomerisation of natural α -cyperone; "B" and "O" designate the synthetic specimens prepared by Adamson, McQuillin, Robinson, and Simonsen (*loc. cit.*).



Curve I— α -cyperone oxime. Curve II— β -cyperone oxime from isomerisation. Curve III—oxime of synthetic β -cyperone.

Curve I—semicarbazone of α -cyperone. Curve II—semicarbazone of β -cyperone from isomerised α -ketone. Curve III—semicarbazone of synthetic β -cyperone.

FIG. 3.
2 : 4-Dinitrophenylhydrazones of α - and β -cyperones.



Curve I—2 : 4-dinitrophenylhydrazone of α -cyperone.
Curve II—2 : 4-dinitrophenylhydrazone of β -cyperone from isomerisation of α -cyperone.

α -Cyperone shows the exaltation of molecular refraction to be expected of structure (I), $[R_L]_D$ calc. 66.15, whilst β -cyperone and particularly the synthetic specimens show values greatly in excess of those to be expected of a stereoisomer of (I). These properties were thought to indicate for β -cyperone a structure (II) (cf. McQuillin, *Chem. and Ind.*, 1937, 56, 514) which is *a priori* likely to result from acid or alkali-catalysed inversion at the centre carrying the isopropenyl group. Structure (II) is, however, consistent with Bradfield, Pritchard, and Simonsen's oxidation results (*loc. cit.*) only if the β -ketone and its semicarbazone prepared by these authors is regarded as a mixture containing a high proportion of the α -ketone from which the characteristic ozonolysis product was derived.

An examination of the ultra-violet absorption of the oximes, semicarbazones, and 2 : 4-dinitrophenylhydrazones of α - and β -cyperone has now shown this to be the case. The oxime and semicarbazone derived from the β -ketone made by isomerisation of natural α -cyperone show double absorption maxima (Figs. 1 and 2). The absorption peak at shorter wave-lengths corresponds with that shown by the corresponding derivative of α -cyperone and the longer-wave-length maximum with that of the derivative of the pure β -isomer obtained synthetically.

These results are in good agreement with the physical properties of the β -ketones noted above, and from inspection of the absorption curves it is clear that the β -semicarbazone used for ozonolysis by Bradfield, Pritchard, and Simonsen (*loc. cit.*) contained a sufficiently large proportion of the α -derivative to account for the isolation of the oxidation product corresponding to the α -ketone. In the case of the 2 : 4-dinitrophenylhydrazones (Fig. 3) the curve for the β -isomer shows a general shift of some 18 $m\mu$. towards longer wave-lengths, and this derivative clearly corresponds with an essentially pure β -isomer. The positions of the principal maxima are given below (solvent, ethyl alcohol).

<i>Oximes</i> :	$\lambda_{\max.}$	$\log \epsilon_{\max.}$	<i>Semicarbazones</i> :	$\lambda_{\max.}$	$\log \epsilon_{\max.}$
α -Cyperone	244 $m\mu$.	4.25	α -Cyperone	270 $m\mu$.	4.32
β -Cyperone, " N "	{ 244	4.09	β -Cyperone, " N "	{ 270	4.20
β -Cyperone, synthetic " O " ...	{ 286.5	4.05	β -Cyperone, synthetic " O " ...	{ 308	4.09
	286.5	4.47		307.5	4.45
	2 : 4-Dinitrophenylhydrazones :				
α -Cyperone	386	4.39	β -Cyperone, " N "	404	4.57

The ultra-violet absorption of α -cyperone has already been characterised as corresponding with an $\alpha\beta$ -unsaturated ketone structure [Bradfield, Hegde, Rao, Simonsen, and Gillam (*loc. cit.*)]. The absorption maxima of the derivatives of the α -ketone are also in good agreement with values for analogous derivatives of $\alpha\beta$ -unsaturated ketones (cf. Evans and Gillam, *J.*, 1943, 565; Braude and Jones, *J.*, 1945, 498; Braude, *Ann. Reports*, 1945, 42, 105). The longer wave-length absorption characteristic of the derivatives of the β -ketone implies a more extended dienone conjugation which, apart from some drastic rearrangement of the molecule for which there is no evidence, can be accommodated only in structure (II) for β -cyperone.

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