Stereochemistry of Allenes Formed by Photochemical Oxidation: an *X*-Ray Crystallographic Study

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Summary The stereochemistry of the allene formed by photochemical oxidation of *trans*-3-hydroxy-β-ionol has been determined by *X*-ray crystallographic analysis of a suitable derivative.

SMALL amounts of allenic hydroperoxides are formed during the photochemical oxidation of some β-ionone derivatives, and subsequent reduction gives the corresponding alcohols (II).[1-3] Attention has been drawn to the similarity between these products and the allenic end-groups in neoxanthin (I) and fucoxanthin, which might conceivably arise in Nature by oxidation of the terminal diene unit in zeaxanthin or a related carotenoid.† Since the *in vitro* reactions were believed to occur by attack of singlet oxygen at C-5 concerted with abstraction of the ethylenic hydrogen at C-7,‡ the products were assigned the (relative) stereochemistry indicated in (II).[1-3] As this contrasts with the (absolute) stereochemistry (III) recently established for the natural allenic carotenoids,[4] it seemed desirable to confirm the stereochemistry of the *in vitro* process.

Photochemical oxidation of *trans*-3-hydroxy-β-ionol (IV)[5] in methanol in the presence of Rose Bengal, reduction of the resulting crude allenic hydroperoxides with sodium

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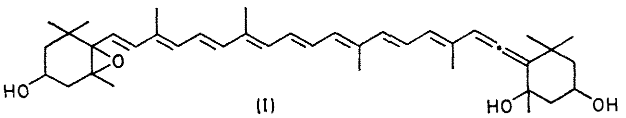
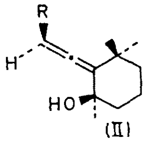
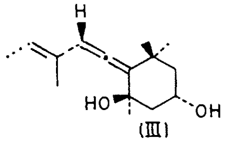
† It has been claimed in a recent note [K. Tsukida, S.-C. Chô, and M. Yokota, *Chem. and Pharm. Bull.* (*Japan*), **1969**, **17**, 1755] that an allene is among the products formed on photochemical oxidation of β-carotene, using chlorophyll as photosensitiser.

‡ Carotenoid numbering. 1,2-Dioxetan intermediates have been suggested for related photochemical oxidations of olefins (W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, 1969, **91**, 3396; D. R. Kearns, *ibid.*, p. 6554).

borohydride, and selective oxidation of the product with manganese dioxide, gave the allenic ketone (V), m.p. 151—152°; ν_{max} ($CHCl_3$) 3590, 3390, 1941, and 1670 cm^{-1}; τ ($CDCl_3$) 8·88 (s, 3H), 8·60 (s, 3H), 8·58 (s, 3H), 7·75 (s, 3H), 6·27 (m, 1H), and 4·03 (s, 1H); *m/e* 224·141 $M^{+\cdot}$; $C_{13}H_{20}O_3$ requires 224·141). That this had the predicted stereochemistry was shown by *X*-ray crystallographic analysis of its *p*-bromobenzoate (VI), m.p. 172—173°.


(I)


(II)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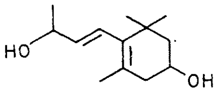
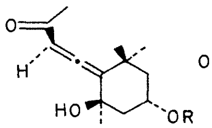
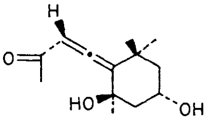

(IV)


(V) R = H
(VI) R = COC_6H_4Br-*p*


(VII)

Crystals of the *p*-bromobenzoate (VI) are monoclinic, space group $P2_1/a$ with $a = 8·786$, $b = 10·776$, $c = 20·922$ Å, $\beta = 101·85°$. Its structure was determined by conventional techniques using *ca.* 1350 independent reflections collected on a General Electric XRD6 manual diffractometer with Cu-K_α radiation. *R* is currently 0·10.

It has been suggested that the allenic ketone from the large flightless grasshopper, *Romalea microptera*, is an enantiomer of (V).[6] However, comparison of the n.m.r. properties reported for the natural allene with those of the racemate (V), and of the epimeric racemate (VII) prepared earlier,[7,8] confirms that the grasshopper ketone belongs to the latter series. This supports the view that the grasshopper ketone results from an *in vivo* degradation of the leaf pigment, neoxanthin (I).[7]

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[7] S. W. Russell and B. C. L. Weedon, *Chem. Comm.*, 1969, 85.

[8] T. E. DeVille, M. B. Hursthouse, S. W. Russell, and B. C. L. Weedon, *Chem. Comm.*, 1969, 754.