The Allenic Ketone from Grasshoppers

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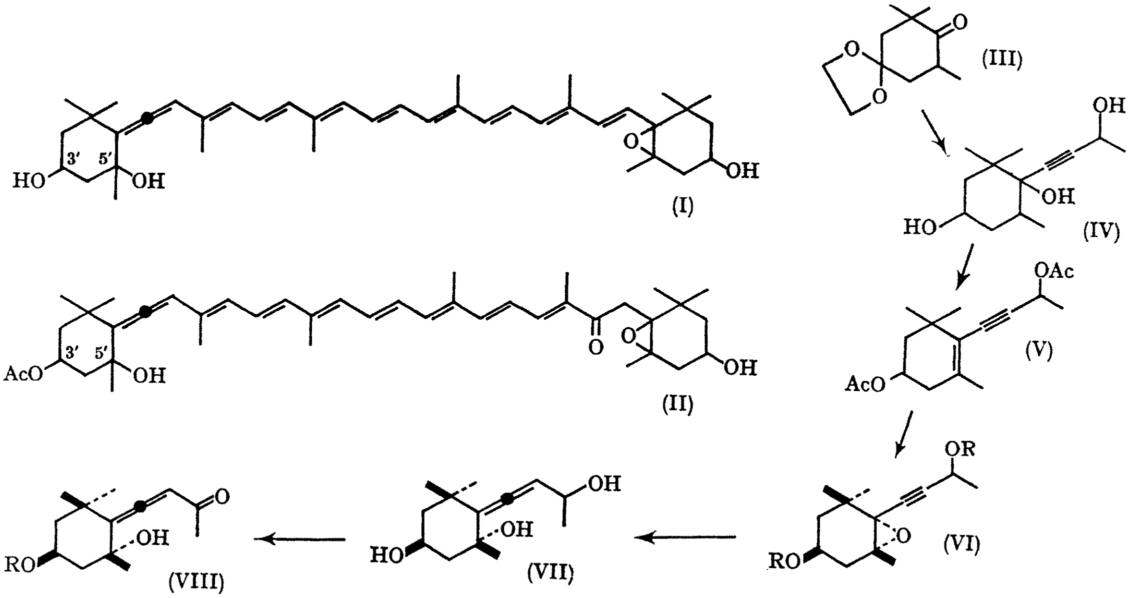
MEINWALD *et al.*[1] recently suggested structure (VIII; R = H) for a crystalline ketone which they isolated from an ant repellant secretion of the large flightless grasshopper, *Romalae microptera*. It is conceivable that the ketone is formed from neoxanthin (I),[2] a constituent of all green leaves, by an oxidative degradation *in vivo* formally analogous to that which has been carried out *in vitro* with fucoxanthin (II).[3,4] In connection with studies on (I), (II), and related allenic terpenes,[3,5] we have synthesised racemic forms of the ketones (VIII; R = H and R = Ac).



A Grignard reaction between but-3-yn-2-ol and (III),[6] liberation of the protected keto-group in the product, and reduction with sodium borohydride, gave the acetylenic triol (IV), m.p. 122°. Treatment of the latter with acetic anhydride yielded the enyne diacetate (V); λ_{max} (EtOH) 229 nm., $10^{-3}\,\epsilon$ 11·2; ν_{max} 2220, 1741, and 1245 cm.$^{-1}$; τ ($CDCl_3$) 8·85 (6H), 8·48 (3H, d, *J* 7 Hz), 8·14 (3H) 7·98 (3H), 7·94 (3H), 5·01 (1H, complex), and 4·40 (1H, q, *J* 7 Hz). Oxidation with monoperphthalic acid furnished a mixture of epoxides which was separated by chromatography on silica gel. Reaction of the minor, more strongly adsorbed product, tentatively formulated as the *trans*-isomer (VI; R = Ac), with lithium aluminium hydride at $< 20°$, gave the epoxy-diol (VI; R = H); ν_{max} 2240 cm.$^{-1}$; τ ($CDCl_3$) 8·89 (3H), 8·75 (3H), 8·53 (3H, d, *J* 7 Hz), 8·50 (3H), 6·17 (1H, m), and 5·41 (1H, q, *J* 7 Hz); *m/e* 224 (*M*; $C_{13}H_{20}O_3$ requires 224). Vigorous treatment of the latter with lithium aluminium hydride in boiling tetrahydrofuran led to the allenic triol (VII), m.p. 166°; ν_{max} (KBr) 1955 (C=C=C) cm.$^{-1}$; τ ($CD_3{\cdot}CO{\cdot}CD_3$) 8·96 (3H), 8·80 (3H, d, *J* 6 Hz), 8·72 (3H), 8·70 (3H), 6·36 (1H, m), 5·80 (1H; doublet of quartets, J_1 5·5; J_2 6 Hz), and 4·79 (1H; d, *J* 5·5 Hz); *m/e* 226·157 (*M*; $C_{13}H_{22}O_3$ requires 226·157). Selective oxidation of (VII) in acetone with manganese dioxide yielded the ketone (VIII; R = H), m.p. 111°; λ_{max} (EtOH) 233 nm., $10^{-3}\,\epsilon$ 13·1; ν_{max} ($CHCl_3$) 3600, 3420 (O–H), 1945 (C=C=C), and 1678 (C=O) cm.$^{-1}$; τ ($CDCl_3$) 8·85 (3H), 8·64 (3H), 8·58 (3H), 8·34 (4H; m), 7·83 (3H), 571· (1H, m), and 4·17 (1H); τ ($CD_3{\cdot}CO{\cdot}CD_3$) 8·87 (3H), 8·62 (6H), 8·20 (4H; m), 7·87 (3H), 6·46 (1H, m), and 4·33 (1H); *m/e* 224·142 (M; $C_{13}H_{20}O_3$ requires 224·141). The light-absorption and n.m.r. properties of the synthetic racemate agree well with those reported[1] for the natural product, m.p. 128°, which is presumably optically active.

Acetylation (Ac_2O–C_5H_5N) of the racemate yielded the acetate (VIII; R = Ac), τ ($CDCl_3$) 8·84 (3H), 8·57 (6H), 7·97 (3H), 7·82 (3H), 4·84 (1H, m,), and 4·18 (1H); *m/e* 266·152 (*M*; $C_{15}H_{22}O_4$ requires 266·152). The n.m.r. bands agree well with those of the fucoxanthin oxidation product[3] from which the synthetic acetate did not separate on mixed t.l.c. (Kieselgel HF254; 25% acetone in petrol). This indicates that the oxygen substituents at C-3′ and C-5′ in fucoxanthin, and hence in neoxanthin,[7] are probably *trans* to one another. It has previously been shown[2,3] that the absolute configuration at C-3′ in both allenic carotenoids is the same as that in zeaxanthin.

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