A New Class of Carotenoids

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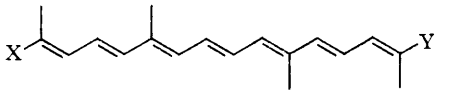
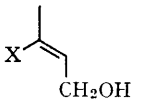
THREE novel carotenoids have been isolated from flagellates of the algal class Cryptophyceae.[1,2] The principal xanthophyll, "alloxanthin", from *Cryptomonas ovata* var. *palustris*, *Rhodomonas* Strain D3, and *Hemiselmis virescens* (Droop's Strain), is now regarded as the diacetylenic analogue (I) of zeaxanthin (II).



(I) X=Y=*a*; (II) X=Y=*b*; (III) X=*a*, Y=*c*; (IV) X=*a*, Y=*d*; (V) X=*a*, Y=*b*



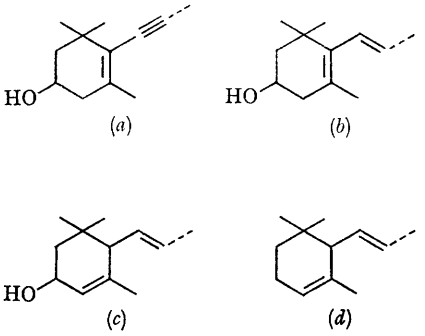
(VI) X=*a*

Alloxanthin‡ has the constitution $C_{40}H_{52}O_2$,§ and forms a diacetate. It exhibits visible light absorption[2] at slightly longer wavelengths than zeaxanthin (*cf.*, vitamin A and its 7,8-dehydro-analogue[3]), and weak absorption (in $CHCl_3$) at 2167 cm.$^{-1}$ attributable to acetylenic linkages. Its n.m.r. spectrum (in $CDCl_3$) includes bands at τ 8·86, 8·81 (geminal methyls at C-1 and C-1′), 8·10 (methyls at C-5 and C-5′), 8·06 (methyls at C-13 and C-13′), and 8·01 (methyls at C-9 and C-9′), and a

‡ Isolated independently in La Jolla and Aberystwyth; samples identified by mixed chromatograms, and by comparison of visible and i.r. light absorption spectra, n.m.r. spectra, and mass spectrometry.

§ All molecular formulae quoted were determined by precision mass spectrometry on an A.E.I. MS9 instrument.

doublet (J = 7 c./sec.) at 7·71 (allylic methylenes at C-4 and C-4′), with the correct relative intensities. No band was observed at τ 3·8 where vitamin A and related compounds exhibit absorption due to the protons at C-7 and C-8.[4] These n.m.r. properties agree well with those of the model (VI)[5] which has bands at τ 8·88, 8·83 (geminal methyls at C-1), 8·12, 8·10 (methyls at C-5 and C-9), and a doublet (J = 7 c./sec.) at 7·72 (allylic methylene at C-4).



The two minor xanthophylls,[2] "monadoxanthin", $C_{40}H_{54}O_2$, and "crocoxanthin", $C_{40}H_{54}O$, have spectral properties consistent with formulae (III) and (IV) respectively.

Diatoxanthin, $C_{40}H_{54}O_2$, a common pigment in diatoms[6] and Chrysophyceae,[7] was isolated[2] in the present studies from *Isochrysis galbana* for comparison purposes. Its spectral properties indicate that it has the structure (V).

Acetylenic carotenoids have not previously been reported in nature, but an acetylenic sesquiterpene[8] and three C_{14}-acetylenes, which can be regarded as degraded sesquiterpenes,[9] have been described recently.

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