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# SYNTHESIS OF CHLOROXANTHIN

P.S. Manchand and B.C.L. Weedon

Queen Mary College,
London, England.

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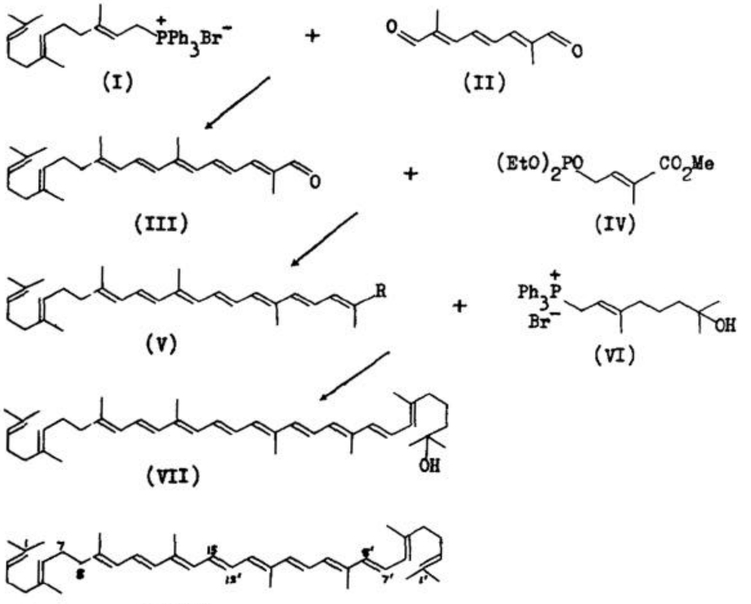
The unique carotenoids of the photosynthetic purple bacteria occur exclusively in one of two groups, "A" or "B", depending on the species.[1] The structures proposed by Weedon et al.[2] for chloroxanthin, spheroidene (pigment Y), and spheroidenone (pigment R), the principal pigments of the "B" group, are consistent with the view that these carotenoids, unlike those of the "A" group, are derived from neurosporene (VIII) by processes which preserve the 7,8-dihydro-feature characteristic of the latter. Chloroxanthin was assigned formula (VII), rather than that of 1-hydroxy-1,2-dihydro-neurosporene, on biogenetic grounds. The three related structures advanced for the "B" group of pigments now receive strong support from the total synthesis of chloroxanthin.

A Wittig reaction of farnesyl-triphenylphosphonium bromide (I)[2] with the trienedial (II)[3,4] gave the $C_{25}$-aldehyde (III); $\lambda_{max.}$ 408, 386, and 367 mμ; $\nu_{max.}$ 1664 and 978 $cm^{-1}$; τ 8.40, 8.34, 8.15, and 8.00, relative intensities ca. 2:1:2:1. Condensation of (III) with the phosphonate (IV) prepared from methyl ω-bromotiglate[4] yielded the ester (V, R = $CO_2Me$); $\lambda_{max.}$ 448, 419, and 398 mμ; $\nu_{max.}$ 1702 and 985 $cm^{-1}$; τ 8.41, 8.34, 8.20, 8.06, 8.03, and 6.27, relative intensities 2:1:1:2:1:1. Reduction with



(I) (II)

(III) (IV)

(V) (VI)

(VII)

(VIII)

lithium aluminium hydride gave the $C_{30}$-alcohol (V, R = $CH_2OH$), m.p. 99-101°; $\lambda_{max.}$ 426, 401, and 378 mμ; τ 8.40, 8.34, 8.20, and 8.05, relative intensities ca. 2:1:2:2. Oxidation with manganese dioxide furnished the corresponding aldehyde (V, R = CHO); $\lambda_{max.}$ 459, 431, and 408 mμ; $\nu_{max.}$ 1665 and 980 $cm^{-1}$; τ 8.40, 8.33, 8.18, 8.12, and 8.01, relative intensities ca. 2:1:1:1:2. The latter reacted with the Wittig reagent from (VI)$^5$ to give chloroxanthin, m.p. 140-141°; $\lambda_{max.}$ 469, 439, and 415 mμ; $\nu_{max.}$ 3580 and 975 $cm^{-1}$; τ 8.80, 8.41, 8.34, 8.20, and 8.04, relative intensities 2:2:1:2:3. The product was identical in all respects (mixed m.p.; comparison spectra; behaviour on iodine catalysed stereomutation; mixed chromatograms of the all-<u>trans</u> and three <u>cis</u>-isomers on thin layers of alumina, and on alumina impregnated paper) with a sample of the natural pigment isolated from a green mutant of Rhodopseudomonas spheroides.[6] Visible light absorption spectra were determined in petrol or hexane; infra-red and N.M.R. data in chloroform and deuterochloroform respectively.

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