Lincoln sequence operates in photosynthetic bacteria.

ζ -Carotene from tomato fruit or carrot root has absorption maxima in light petroleum at 378, 400 and 425nm., but the corresponding values for the *R. rubrum* heptaene are 376, 396 and 418nm., suggesting that the two heptaenes are different.

Chromatographic studies have eliminated the possibility of one of the heptaenes either having a different number of carbon atoms in the molecule or containing two β -ionone rings, and isomerization studies show that both have the all-*trans* configuration. The possibility that the *R. rubrum* heptaene has its chromophore located unsymmetrically in the molecule is strengthened by the close agreement between its absorption spectrum and that reported for a synthetic unsymmetrical isomer of ζ -carotene (Davis *et al.* 1966).

Mass spectrometry confirms that both the natural heptaenes are $C_{40}H_{60}$ and that the ζ -carotene from carrot root is symmetrical (7,8,7',8'-tetrahydrolycopene), showing fission at the C-3-C-4 and C-7-C-8 bonds. The heptaene from *R. rubrum*, however, shows additional fission at the C-11-C-12 bond, confirming that it is the unsymmetrical isomer (7,8,11,12-tetrahydrolycopene).

Thus, in these bacteria, there is a novel dehydrogenation sequence, involving two consecutive dehydrogenations at one side of the central chromophore followed by two at the other, so that phytofluene, 7,8,11,12-tetrahydrolycopene and neurosporene are the intermediates in the formation of lycopene from phytoene.

We are grateful to Mrs J. H. Warren for skilled technical assistance and to Professor B. C. L. Weedon, Dr T. P. Toube and Mr D. E. Loeber for carrying out the mass spectrometric analyses in the Department of Chemistry, Queen Mary College, University of London.

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Trisporic Acid Biosynthesis and Carotenogenesis in *Blakesleea trispora*

By D. G. AUSTIN, J. D. BU'LOCK and D. J. WINSTANLEY. (*Microbial Chemistry Laboratory, Department of Chemistry, University of Manchester*)

Trisporic acids form only in mixed cultures of (+) and (-) strains of *B. trispora* and related Phycoc-

mycetes, where they mediate increased carotenoid synthesis by an inducer-like action on the (-) strain. They are oxidized unsaturated derivatives of 1,1,3-trimethyl-2-(3-methyloctyl)cyclohexane, and biogenetically they could be classed as elaborated sesquiterpenes, or as degraded diterpenes, or as degraded carotenoids. However, synthesis of the trimethylcyclohexyl system has so far only been demonstrated to occur at the C_{40} level, i.e. in cyclic carotenoids.

With pre-mated cultures on malt-extract media, to optimize trisporic acid yields, added $[2-^{14}C]$ -mevalonate was incorporated into both β -carotene and trisporic acids. Degradation of the latter by reductive ozonolysis revealed four equally labelled C_5 units in the C_{18} molecule, which must therefore be derived either from a diterpenoid or from carotenoid precursor. Plausible mechanisms can be proposed for the formation of trisporic acids from a dicyclic diterpene or from β -carotene but currently we prefer the latter suggestion for the following reasons.

Labelled β -carotene is a better precursor of trisporic acids than is $[2-^{14}C]$ -mevalonate. Moreover, when the conversion of phytoene into β -carotene is blocked with diphenylamine the trisporic acids are not formed. This suggests that the trisporic acids are formed from the carotenoids whose synthesis they promote. Similar biogenetic origins seem equally probable for related trimethylcyclohexane derivatives in other organisms, such as β -ionone, the abscisins, and various insect products.

New Pathways of Methoxy Carotenoid Formation in *Rhodospirillum rubrum*

By B. H. DAVIES and E. ANN HOLMES. (*Department of Biochemistry and Agricultural Biochemistry, University College of Wales, Aberystwyth*)

In *Rhodospirillum rubrum*, spirilloxanthin is normally formed from lycopene by a series of consecutive reactions that involves the hydration of an isopropylidene end group to form a tertiary alcohol, the introduction of a double bond in conjugation with the polyene chain at the hydroxylated end, and the methylation of the tertiary hydroxyl group. These reactions convert lycopene first into anhydorrhodovibrin and then, by occurring at the unchanged end of the molecule, convert anhydorrhodovibrin into spirilloxanthin (Jensen, 1961; Jensen, Cohen-Bazire & Stanier, 1961).

In the present work on the pigments of diphenylamine-inhibited cultures of *R. rubrum*, two carotenoids that were described by Goodwin & Osman (1954) and designated P450 and P412 by Jensen,

Cohen-Bazire, Nakayama & Stanier (1958) were examined. The former has been shown, on the basis of its absorption spectrum, chromatographic behaviour and mass spectrum, to be identical with a sample of spheroidene isolated from an anaerobic culture of *Rhodospseudomonas spheroides*. The second has a chromophore of eight conjugated double bonds and bears the same chromatographic relationship to spheroidene as spheroidene does to anhydrorhodovibrin. The mass spectrum of this new carotenoid shows that it is 11',12'-dihydro-spheroidene.

These two carotenoids must be formed in *R. rubrum* by sequences of consecutive reactions, analogous to that used in the formation of anhydrorhodovibrin from lycopene, but operating at a different level in the dehydrogenation sequence described by Davies & Holmes (1969). Thus 7,8,11,12-tetrahydrolycopene is converted into 11',12'-dihydrospheroidene and spheroidene is formed, as in *Rps. spheroides* (Jensen *et al.*, 1961) from neurosporene. Eimhjellen & Jensen (1964) showed that spheroidene is dehydrogenated to anhydrorhodovibrin in *Rhodospseudomonas gelatinosa*; this same reaction, together with the analogous conversion of 11',12'-dihydrospheroidene into spheroidene, probably occurs in *R. rubrum*.

In addition, the existence in diphenylamine-inhibited cultures of *R. rubrum* of a carotenoid with the chromatographic behaviour (before and after silylation) and absorption spectrum of hydroxy-spheroidene indicates that spheroidene may also act as a precursor of spirilloxanthin in a pathway that does not involve anhydrorhodovibrin; such a pathway has been established in *Rps. gelatinosa* (Eimhjellen & Jensen, 1964).

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On the Presence of Plastochromanols in Plants

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The green tissue of plants is known to contain several chromanols including α -, β -, γ - and δ -tocopherols as well as plastochromanol-8, a cyclic relative of plastoquinone-9 (Dunphy, Whittle & Pennock, 1966). This communication reports on a number of chromanols apparently related to the plastoquinones PQB, PQC and PQZ. Following the characterization of plastoquinone-9 (PQA) Kegel, Henninger & Crane (1962) described two other plastoquinones, PQB and PQC, and recently another member of the family, PQZ, has been recognized (Wallwork & Pennock, 1968). It was later realized that the PQB and PQC groups were mixtures and not single components (Griffiths, Wallwork & Pennock, 1966) and Griffiths (1966) showed that PQB species contained an ester group in the side chain. It was suggested that two types of PQC could occur, one with a secondary hydroxyl group:

and the other with a tertiary hydroxyl group:

(Wallwork & Pennock, 1968). Perhaps eight compounds of each type occurred, and the PQB species were thought to be esters of the secondary type. PQZ species had the characteristics of both ester and hydroxyl compounds.

Investigation of lipids from *Lingustrum* and *Polygonum* yielded three groups of chromatographically distinguishable chromanols which all gave a blue-grey colour with diazotized *o*-dianisidine, characteristic of a 7,8-dimethylchromanol. The u.v. and i.r. spectra were similar to those of plastochromanol-8 and from the other physicochemical properties it was clear that these compounds were plastochromanols related to PQB, PQC and PQZ species. In particular the plastochromanol B species showed evidence of the group: