Short Communications

Bacterial Carotenoids. XLV.*
Synthesis of Lycopene-20-al and Rhodopin-20(20')-al

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In the carotenoid field N-bromosuccinimide (NBS) has been frequently used for the introduction of carbon-carbon double bonds.1,2 Although no brominated carotenoid intermediates have been isolated, it is assumed that the reaction proceeds via allylic bromides, cf. Ref. 3. Thus allylic acetates or ethers are obtained in the presence of acetic acid or alcohol, respectively.4,5 A remarkable dehydrogenation is reported for canthaxanthin (1, Scheme 1), which provided the 15,15'-didehydro derivative with central triple bond.6,7

On the basis of this experience NBS-treatment of crocetindial (2) was expected to give either the acetylenic analogue or result in allylic substitution.

Under particular conditions NBS-treatment of crocetindial (2) resulted in allylic substitution of one of the central methyl groups. After chromatography of the product 3 on alumina, the allylic alcohol 4 was isolated. Characterization of 3 and 4 and a general study of the reaction between NBS and diapocarotenals are published separately.8

The dial 4, containing the desired hydroxy substituent, was used for the synthesis of lycopene-20-al (6) and an expected mixture of rhodopin-20-al (7a) and rhodopin-20'-al (7b), Scheme 1.

The hydroxy-dial 4 (9 mg) was reacted with the ylids of a mixed phosphonium salt (24%, 8 and 76%, 9, cf. Ref. 9) by a general procedure providing in good yield lycopene-20-al (10, 75% of recovered carotenoid) and a presumed mix-

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nature of rhodopin-20-ol and rhodopin-20'-ol (11a and 11b; 20% of recovered carotenoid).

Lycopene-20-ol (10, 5.4 mg), purified by TLC (kieselgel; 15% acetone in petroleum ether) had $\lambda_{\text{max}}$ (acetone) for the trans isomer (51% of the stereoisomeric mixture) 345, 363, 450, 471 and 500 nm, for neo U (27%) 345, 362, 442, 466 and 496 nm and for neo V (23%) 345, 363, (446), 467 and 495 nm; $\nu_{\text{max}}$ (KBr) 3300 and 1000 (OH) and 950 cm$^{-1}$ (trans CH = CH); $m/e$ 552 (M), M - 16, M - 18, M - 69, M - 92, M - 106, M - 108, M - 122, M - 158, M - 174.

Rhodopin-20(20')-ol (11a and 11b) which could not be separated, had $\lambda_{\text{max}}$ (acetone) 345, 363, 440, 468 and 495 nm (cis and trans); $m/e$ 570 (M), M - 2, M - 16, M - 18, M - 92, M - 106, M - 108, M - 158, M - 174 and was inseparable from natural rhodopin (ex. Thiocystis sp.) on alumina paper. On electron impact both 10 and 11 showed the elimination of 108, 122 and 174 mass units characteristic of aliphatic carotenoids with in-chain hydroxymethyl groups.18

Allylic oxidation of lycopene-20-ol (10), best achieved with DDQ,13,14 in dry ether at 0°C, gave lycopene-20-ol (6), but only in 7% yield. Previous attempts to oxidize such allylic alcohols have met with the same difficulties.14 The synthetic lycopene-20-ol (6) was obtained as two stereoisomers with $\lambda_{\text{max}}$ (acetone) 363, 502 (very broad) nm and 368, 492 (very broad) nm and $m/e$ 550 (M), M - 2, M - 16, M - 18, M - 69, M - 92, M - 106, M - 120, M - 158, M - 172, which could not be separated from those of authentic rhodopin (ex. Thiocystis sp.11). The synthetic lycopene-20-ol (6) was obtained as two stereoisomers with $\lambda_{\text{max}}$ (acetone) 363, 502 (very broad) nm and 368, 492 (very broad) nm and $m/e$ 550 (M), M - 2, M - 16, M - 18, M - 69, M - 92, M - 106, M - 120, M - 158, M - 172, which could not be separated from those of authentic rhodopin (ex. Thiocystis sp.11).

Rhodopin-20-ol (7a) and lycopene-20-ol (6) have been isolated from several Thiorhodaceae spp.11,13,14,15 Also the corresponding allylic alcohols rhodopin-20-ol (11a) and lycopene-20-ol (10) are naturally occurring.13,14,15 Structural studies led to derivatives of rhodopin and lycopene with one of the in-chain methyl groups oxidized.14 Subsequent mass-spectrometric analysis was consistent with structures 7a, 6, 11a and 10.11

The present small scale synthesis of lycopene-20-ol (6) and lycopene-20-ol (10) confirms the structures previously assigned to these carotenoids.

The properties of the mixed rhodopins (7a and 7b) confirm the previous chromatophore assignment, but add no proof for 20'-rather than 20'-substitution.

The same exceptional instability, failure to crystallize, characteristic broad electronic spectra with strong absorption in the cis-peak region, and the typical fragmentation pattern on electron impact, as well as identical chromatographic properties,13,14,15 were recorded for both the natural and synthetic pigments. The synthetic use of the hydroxy-dial 4 for the preparation of other, more stable cross-conjugated carotenoids is being pursued.16


Received September 9, 1974.