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Short Communications

Bacterial Carotenoids. XLV.* Synthesis of Lycopen-20-al and Rhodopin-20(20′)-al

OLE PUNTERVOLD and
SYNNØVE LIAAEN-JENSEN

Organic Chemistry Laboratories, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim, Norway

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 lycopen-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 [10] providing in good yield lycopen-20-ol (*10*, 75 % of recovered carotenoid) and a presumed mix-

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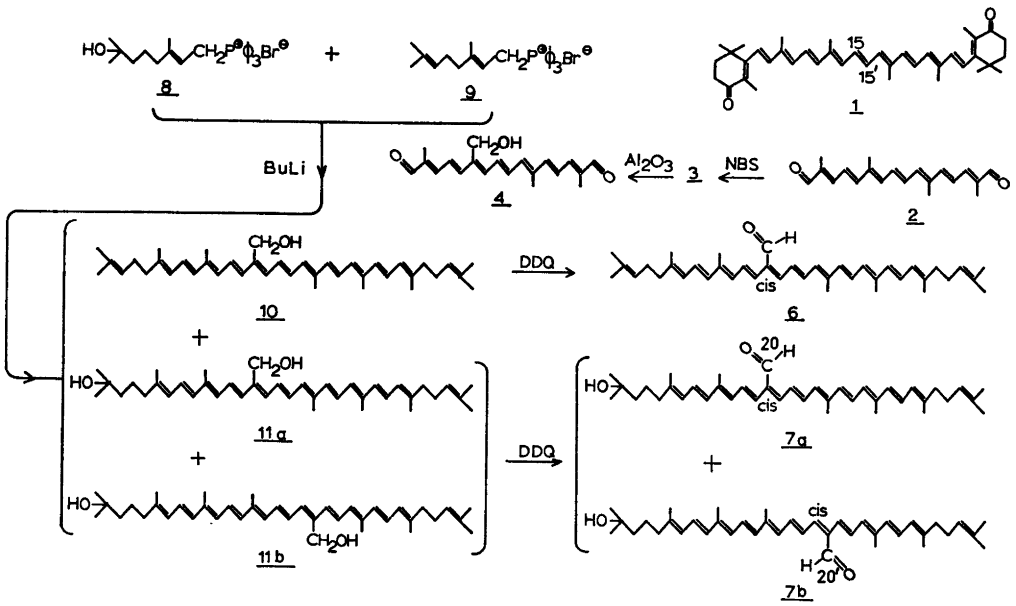

Scheme 1.

ture of rhodopin-20-ol and rhodopin-20′-ol (*11a* and *11b*; 20 % of recovered carotenoid).

Lycopen-20-ol (*10*, 5.4 mg), purified by TLC (kieselgel; 15 % acetone in petroleum ether) had λ_{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; ν_{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 λ_{max} (acetone) 345, 363, 440, 469 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 rhodopinol (*ex. Thiocystis* sp.[11]) 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.[12]

Allylic oxidation of lycopen-20-ol (*10*), best achieved with DDQ [13,14] in dry ether at 0 °C, gave lycopen-20-al (*6*), but only in 7 % yield. Previous attempts to oxidize such allylic alcohols have met with the same difficulties.[14] The synthetic lycopen-20-al (*6*) was obtained as two stereoisomers with λ_{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 rhodopinal *ex. Thiocystis* sp.[11]

Allylic oxidation of rhodopin-20(20′)-ol (*11a* and *11b*), effected with DDQ, gave a presumed mixture of *7a* and *7b* in 2 % yield. The cross-conjugated aldehyde (*7a* and *7b*) had λ_{max} (acetone) *ca.* 490 (very broad), *m/e* 568 (M), M−2, M−18, M−73, M−69−18, M−106, M−120, M−120−18, M−158, M−172 and could not be separated from rhodopinal *ex. Thiocystis* sp.[12]

Rhodopin-20-al (*7a*) and lycopen-20-al (*6*) have been isolated from several *Thiorhodaceae* spp.[11,14,15] Also the corresponding allylic alcohols rhodopin-20-ol (*11a*) and lycopen-20-ol (*10*) are naturally occurring.[12,14,15] 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*.[21]

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

The properties of the mixed rhodopinals (*7a* and *7b*) confirm the previous chromophore assignment, but add no proof for 20- rather than 20′-substitution.

The same exceptional instability, failure to crystallize,[14] characteristic broad electronic spectra with strong absorption in the *cis*-peak region,[14] and the typical fragmentation pattern on electron impact,[12] as well as identical chromatographic properties,[12,14,15] 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 carotenals is being pursued.[16]

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