It is also possible from a stereochemical point of view that the guanidinium groups link together consecutive phosphates along the DNA helices, as has been proposed. The "strong" pair of hydrogen bonds can, however, in this case not be formed without strain, and we consider this possibility less likely than the one described above.

The bonding between lysine and phosphate diester. The -NH\textsuperscript{+} group of protonated lysine would be expected to form, if possible, three hydrogen bonds in roughly tetrahedral arrangement, as observed in compound (III) (Fig. 1) and also in crystals of amino acids. The \(P-O-N\) angles in (III) lie in the range 110–135° and the mean length of the three bonds is 2.80 Å.

The oxygen atoms receiving hydrogen bonds from an NH\textsuperscript{+} group are at distances of about 5 Å. The most favorable hydrogen bonding scheme in B-DNA-polylysine complexes would appear to be that the lysine NH\textsuperscript{+} groups are linked to an \textit{exo} oxygen atom (O3) in one phosphate and, by a weak bond, to an \textit{ester} oxygen atom (O4) in the next phosphate along the helix, these atoms being at a distance of 5.0 Å. \textit{Exo} oxygen atoms of consecutive phosphates seem to be too far apart. The third bond would then be formed to an \textit{exo} oxygen atom in the complementary helix in a neighbouring complex. The distance between complexes in fibres is consistent with this view.


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Algal Carotenoids. XI.* New Carotenoid Epoxides from Trentepohlia iolithus

GERD NYBRAATEN and SYNNØVE LIAAEN-JENSEN

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

A recent re-examination of the carotenoids of the green alga Trentepohlia iolithus\textsuperscript{*} demonstrated the natural occurrence of carotenoids containing 2-hydroxylated \(\beta\)-rings. Structures 1, 2, and 3 (Scheme 1) were established from full spectroscopic characterization. The absolute stereochemistry has subsequently been confirmed.

We now report the natural occurrence of the epoxides 4a and 7 (probably 7a) of \(\beta\)-\textit{e-caroten-2-ol} (1) and of \(\beta\)-\textit{\(\beta\)-caroten-2-ol} (2), comprising 0.2 % (0.4 mg) and 0.3 % (0.6 mg), respectively, of the total carotenoids of \(T.\) iolithus.

In order to include stereochemical considerations the partial synthesis of the 5,6-epoxides 4a and 4b from \(\beta\)-\textit{e-caroten-2-ol} (1), 3.6 mg) by m-chloroperoxybenzoic acid, Scheme 2, will be discussed first. Reported data for relevant cyclohexene model substances reveal a directive effect of a hydroxy substituent, resulting in preferential epoxidation \textit{cis} to the hydroxy substituent, explained by hydrogen bonding between the hydroxy group and the peracid.\textsuperscript{4} Similar results are observed with an acetox substituent.\textsuperscript{4} Thus zeaxanthin (\(\beta\)-\textit{\(\beta\)-caroten-3,3'-diol} diacetate gives preferentially \textit{cis} products (\textit{cis} relationship between the epoxy and acetox groups) on epoxidation.\textsuperscript{5}

On epoxidation of \(\beta\)-\textit{e-caroten-2-ol} (1) two diastereomeric products 4a (60 % of total) and 4b (40 % of total) were obtained. Both 4a and 4b exhibited \(\lambda_{max}\) (acetone) 419, 441.5, and 470 nm and \(m/e\) 568 (M), fragment ions M–16, M–80, 181, and 221 consistent with carotenoid epoxides, as well as common fragment ions M–92, M–106, M–16–92, M–16–106, M–80–92 ascribed to eliminations from the polyene chain, combined with losses of 16 and 80 mass units.\textsuperscript{48} Relative yields and adsorptive properties support the stereochemistry assigned to the epoxide products 4a and 4b, see Scheme 2. Thus 4a was chromatographically less strongly retained than 4b, compatible with intramolecular hydrogen bonding, and 4a indeed showed the predicted hydrogen bonding in IR (predominantly associated hydroxyl at 3509 cm\textsuperscript{−1} as expected for conformation A Scheme 2, cf. Ref. 6b).

On furanoid rearrangement with hydrogen chloride in ether the epoxide 4a, referred to

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as cis epoxide, gave two products 5a and 5b, assumed to be C-8 epimers on the basis of the favoured mechanism for furanoid rearrangement, not altering the stereochemistry at C-5. Scheme 2. The epoxide 6b, referred to as trans epoxide, likewise gave two furanoid products 5c and 5d. Relative Rf-values were 5a > 5c > 5b = 5d. However, in spite of identical Rf-values 5b and 5d are considered to be diastereomers. The furanoid products 5a, b, c, d all had λmax (methanol) at 396, 420, and 446 nm.

Separate acetylation of the furanoxides 5a and 5b was slow (17 h, 55 % conversion, typical of 2-hydroxy substitution 4) and gave the monoacetates 6a and 6b, not separable in the systems tested. In general separation of the stereoisomeric epoxides and furanoxides was more difficult when acetylated.

Turning now to the naturally occurring epoxide 4a, the natural epoxide had electronic spectrum, mass spectrum and Rf-value (co-chromatography) consistent with semisynthetic 4a described above, and provided on standard acetylation slowly (cf. Ref. 8) a monoacetate (80 % conversion after 8 h) with unchanged electronic spectrum and m/e 610 (M), M-16,
M - 60, M - 80. Furanoïd rearrangement of \( 4a \) gave two products with electronic spectra, mass spectra, and \( R_F \)-values (co-chromatography) as \( 5a \) and \( 5b \) described above. Separate acetylation of the furanoïd products \( 5a \) and \( 5b \) gave 80% conversion to the corresponding acetates, inseparable in our chromatographic systems and from \( 5a,b \) derived from \( 1 \) in a special reaction discussed in the following paper.\(^6\) On this basis it is concluded that the natural epoxydiol has structure \( 4a \) (cis). It deserves comment that natural violaxanthin \((5,6,5',6'-di(epoxy)-5,6,5',6'-tetrahydro-\beta,\beta-caroten-3,3'-diol)\), has a \textit{trans} relationship between the 5,6-epoxy bridge and the 3-hydroxy substituent.\(^7\) However, the present epoxydiol \( 4a \) and violaxanthin both have the same axial/equatorial relationship between the hydroxy substituent and the polyene chain, see Scheme 2 for alternative conformations A and B of \( 4a \).

The second naturally occurring epoxydiol 7 exhibited \( \lambda_{\text{max}} \) (ether) 423, 443, and 472 nm consistent with data reported for the monooxoepoxide of \( \beta,\beta\)-carotene \(^8\) and mass spectrum like \( 4a \) except at \( M - 56 - 18 \) peak. Acetylation of 7 provided a monoacetate with unchanged electronic spectrum and mass spectrum as for \( 4a\)-monoacetate with no significant RDA-fragmentation. Furanoïd rearrangement of 7 gave two products both with \( \lambda_{\text{max}} \) (methanol) 404, 423, and 445 nm and \( m/e \) 568 (M), \( M - 16, M - 80, 221, \) inseparable from two furanoïd products obtained from \( \beta,\beta\)-caroten-2-ol (2) in the reaction discussed in the following paper.\(^6\) From the stereochemistry observed for the corresponding reaction of \( \beta,\delta\)-caroten-2-ol (1) \(^9\) and by analogy with the natural epoxydiol \( 4a \), the stereochemistry of \( 7a \) (cis) is considered likely for the second epoxydiol 7 isolated from \( T. \text{silithus} \).

Methods commonly employed in this laboratory were used. Experimental details are given elsewhere.\(^10\) The epoxydiols \( 4a \) and 7 were readily separated from 1, 2, and 3 on magnesium oxide columns (benzene). \( R_F \)-values (Schleicher & Schüll No. 287 circular, kieselguhr paper, 1% acetone in petroleum ether) were: \( 4a \) (0.56), \( 4b \) (0.35), \( 4a\)-acetate (0.88), \( 5a \) and \( 5b \) (0.48 and 0.18), \( 5c \) and \( 5d \) (0.33 and 0.18), \( 6a \) and \( 6b \) (0.72), 7 (0.53), 7-acetate (0.84), furanoïd 7 (0.22 and 0.55), and furanoïd 7-acetates (0.74). Purification for mass spectrometry was achieved by TLC on kieselgel, 20% acetone in petroleum ether).

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Algal Carotenoids. XII.* Chemical Reactions of Carotenoids with 2-Hydroxylated \( \beta \)-Rings

GERD NYBRAATEN and SYNNOVE LIASEN-JENSEN

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

Spectroscopic evidence alone was sufficient for the structural elucidation of the first carotenoids with 2-hydroxylated \( \beta \)-rings, namely \( \beta,\delta\)-caroten-2-ol (1a), \( \beta,\beta\)-caroten-2-ol (2a), and \( \beta,\beta\)-caroten-2,2'-diol (3), Scheme 1, from the green alga \textit{Trentepohlia silithus}\.\(^1,2\) We now report a chemical characterization of carotenoids possessing this end group (1a and 2a).

Models reveal steric hindrance of the 2-hydroxy-substituent of a \( \beta \)-ring. Lower reactivity than for analogous 3-hydroxy carotenoids was therefore predicted.

Standard acetylation\(^8\) of \( \beta,\beta\)-caroten-2-ol (2a) was slower than for \( \beta,\beta\)-caroten-3-ol (4a): 50 % and 100 % conversion, respectively, to the corresponding acetates \( 2b \) and \( 4b \) after 3.5 h, see Fig. 1. The 2-hydroxy compound