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.[7] 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 $-NH_3^+$ 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_3^+ 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_3^+ groups are linked to an *oxo* oxygen atom (O3) in one phosphate and, by a weak bond, to an *ester* oxygen atom (O4) in the next phosphate along the helix, these atoms being at a distance of 5.0 Å. *Oxo* oxygen atoms of consecutive phosphates seem to be too far apart. The third bond would then be formed to an *oxo* 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*

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

We now report the natural occurrence of the epoxides *4a* and *7* (probably *7a*) of β,ε-caroten-2-ol (*1*) and of β,β-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 β,ε-caroten-2-ol (*1*, 3.6 mg) by *m*-chloroperbenzoic acid,[3] 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 *cis* to the hydroxy substituent, explained by hydrogen bonding between the hydroxy group and the peracid.[4] Similar results are observed with an acetoxy substituent.[5] Thus zeaxanthin (β,β-caroten-3,3′-diol) diacetate gives preferentially *cis* products (*cis* relationship between the epoxy and acetoxy groups) on epoxidation.[5]

On epoxidation of β,ε-caroten-2-ol (*1*) two diastereomeric products *4a* (60 % of total) and *4b* (40 % of total) were obtained. Both *4a* and *4b* exhibited λ_{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.[6a] Relative yields and adsorptive properties support the stereochemistry assigned to the epoxidic 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^{-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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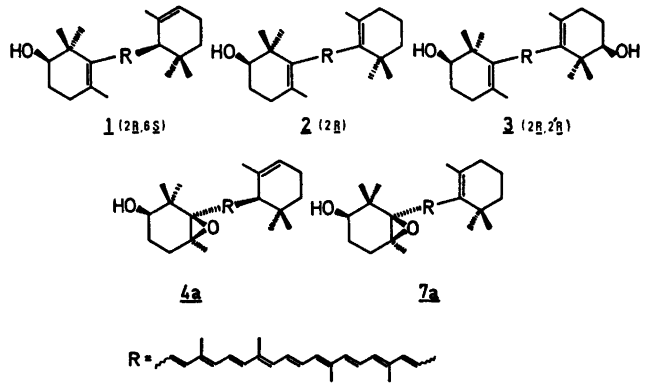
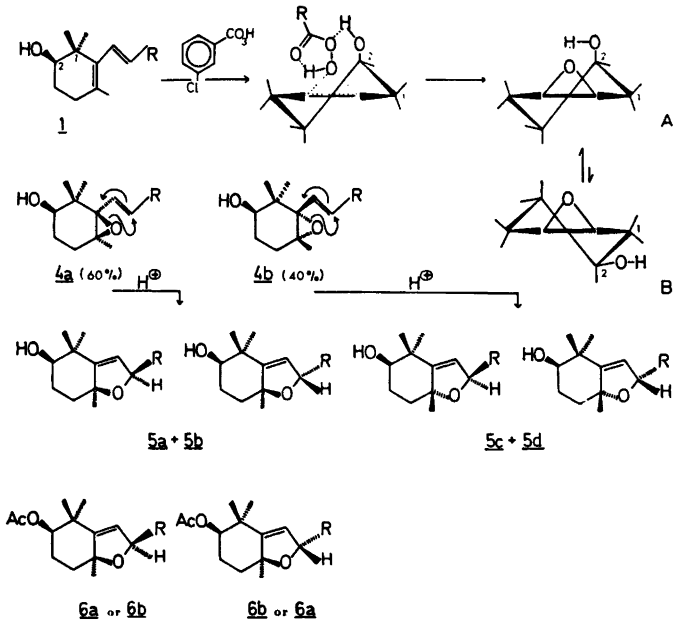


Scheme 1.



Scheme 2.

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,[7] Scheme 2. The epoxide *4b*, referred to as *trans* epoxide, likewise gave two furanoid products *5c* and *5d*. Relative R_F-values were *5a* > *5c* > *5b* = *5d*. However, in spite of identical R_F-values *5b* and *5d* are considered to be diastereomers. The furanoid products *5a*, *b*, *c*, *d* all had λ_{max} (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 [8]) 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 R_F-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. Furanoid 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 furanoid products *5a* and *5b* gave 60 % 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.[8] On this basis it is concluded that the natural epoxide has structure *4a* (*cis*). It deserves comment that natural violaxanthin (5,6,5′,6′-diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-3,3′-diol), has a *trans* relationship between the 5,6-epoxy bridge and the 3-hydroxy substituent.[4,7] However, the present epoxide *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 epoxide *7* exhibited λ_{max} (ether) 423, 443, and 472 nm consistent with data reported for the mono-epoxide of β,β-carotene [9] and mass spectrum like *4a* except an (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. Furanoid rearrangement of *7* gave two products both with λ_{max} (methanol) 404, 423, and 445 nm and *m/e* 568 (M), M−16, M−80, 221, inseparable from two furanoid products obtained from β,β-caroten-2-ol (*2*) in the reaction discussed in the following paper.[8] From the stereochemistry observed for the corresponding reaction of β,ε-caroten-2-ol (*1*) [8] and by analogy with the natural epoxide *4a*, the stereochemistry of *7a* (*cis*) is considered likely for the second epoxide *7* isolated from *T. iolithius*.

Methods commonly employed in this laboratory were used. Experimental details are given elsewhere.[10] The epoxides *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), furanoid *7* (0.22 and 0.55), and furanoid *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 β-Rings

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Spectroscopic evidence alone was sufficient for the structural elucidation of the first carotenoids with 2-hydroxylated β-rings, namely β,ε-caroten-2-ol (*1a*), β,β-caroten-2-ol (*2a*), and β,β-carotene-2,2′-diol (*3*), Scheme 1, from the green alga *Trentepohlia iolithus*.[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 β-ring. Lower reactivity than for analogous 3-hydroxy carotenoids was therefore predicted.

Standard acetylation [3] of β,β-caroten-2-ol (*2a*) was slower than for β,β-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

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