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CD CORRELATION OF C-2′ SUBSTITUTED MONOCYCLIC CAROTENOIDS

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Key Word Index—CD correlation of several monocyclic C-2′ substituted carotenoids; bacteria; blue-green algae; fungi; chirality; chemosystematics.

Abstract—The scope and limitation of circular dichroism (CD) correlations of several C-2′ substituted monocyclic monochiral, homodichiral and heterodichiral carotenoids have been investigated, aiming at the assignment of absolute configuration at C-2′ by using the diester and 2′-β-D-tetraacetylglucosyl derivative of (2′*R*)-plectaniaxanthin and a synthetic chiral C_{45}-carotene as key references. The correlations are based on the additivity hypothesis, the conformational rule and a comparison of CD spectra, preferably conservative ones. Quantitative aspects of the conformational rule are considered. Substituent effects at C-2′ and C-1′ have been studied. Absolute configurations are suggested for (2′*S*)-phleixanthophyll, (3*S*,2′*S*)-2′-hydroxyflexixanthin, (3*R*,2′*S*)-myxoxanthophyll, (3*S*,2′*S*)-4-ketomyxoxanthophyll, (3*R*,2′*S*)-myxol-2′-*O*-methyl methylpentoside and (2*R*,2′*S*)-*C.p.* 473 from relevant CD correlations. The chiralities of (2′*S*)-4-ketophleixanthophyll and (2*R*,6*R*,2′*S*)-*A.g.* 471 are suggested from biogenetic considerations. A chemosystematic consideration of chirality and source is included.

INTRODUCTION

Recently, the chirality of the fungal carotenoid plectaniaxanthin (**1**, Scheme 1) has been determined as 2′*R* by a synthetic approach [1].* Several other naturally occurring monocyclic carotenoids contain related C-2′ substituted aliphatic end-groups of unestablished chirality [2]. They comprise three structural types, namely (a) C-2′-ols such as phleixanthophyll (**2**), 4-ketophleixanthophyll (**3**) [3] and 2′-hydroxyflexixanthin (**4**) [4]; (b) C-2′-*O*-glycosides such as myxoxanthophyll (**5**) [5], 4-ketomyxoxanthophyll (**6**) [6] and myxol-2′-*O*-methyl methylpentoside (**7**) [7]; and (c) C-2′ isopentenylated higher carotenoids such as *C.p.* 473 (**8**) [8, 9] and *A.g.* 471 (**9**) [10].

In the present work the assignment of the absolute configurations of carotenoids **2**–**8** is attempted by using circular dichroism (CD) correlations with known structures.

RESULTS AND DISCUSSION

Theoretical basis for the CD correlations

The correlations are based on: (1) the additivity hypothesis; (2) the conformational rule; (3) comparison of CD spectra (preferably conservative); and (4) elucidation of substituent effects.

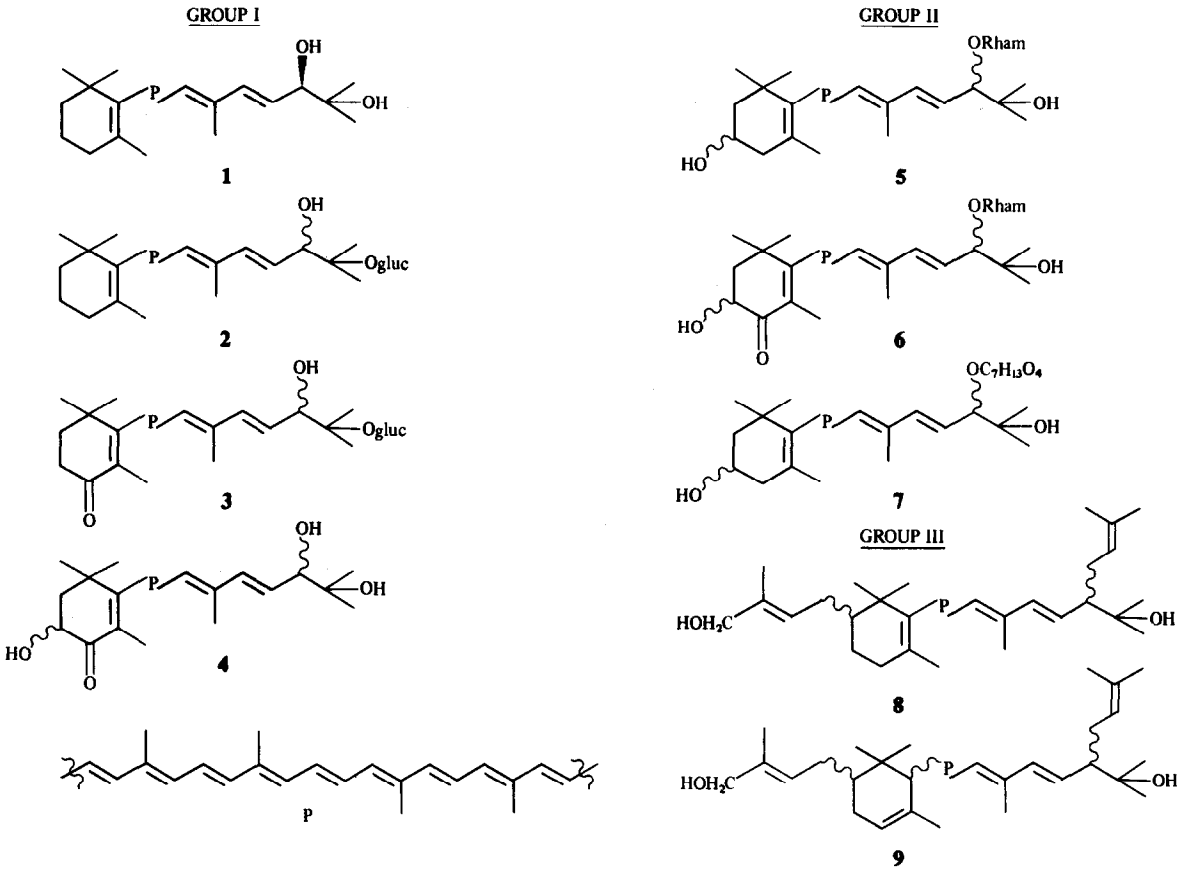
(1) The additivity hypothesis states that the ORD contributions from each of two chiral end-groups in a homodichiral or heterodichiral carotenoid are additive [11]. The validity of the hypothesis has, as expected, been demonstrated also for CD spectra, provided that homodichiral or heterodichiral carotenoids of identical chromophores are compared. For monochiral carotenoids, variations in the length of the polyene chain may result in predictable shifts of the maxima of the CD curves [12, 13].

(2) On the basis of earlier work by Mills [14], which was later elaborated by Eliel [15], the conformational rule has been developed, which states that the preferred chiral conformation of a cyclohexene ring determines the sign of the Cotton effect [12, 16]. Substituents at C-2 or C-3 in the β-rings of carotenoids determine the preferred conformation, whereas C-4 substituents have no marked influence [12, 16].

(3) Recently, Sturzenegger *et al.* [17] classified CD spectra of carotenoids as (i) essentially conservative, (ii) intermediate and (iii) essentially non-conservative. A conservative CD spectrum is characterized by five to six positive and negative maxima integrating to approximately zero at room temperature. *Trans*–mono-*cis* isomerization of the polyene chain results in inversion of the Cotton effect, a phenomenon associated by Noack and Thomson [18] with dicyclic, monochiral and dicyclic homo- or heterodichiral carotenoids. Essentially, non-conservative spectra have smaller Cotton effects of a constant sign, and the Cotton effect does not invert upon *cis*-isomerization.

(4) Substituent effects at a chiral centre, which determine the sign of the optical rotation and hence the circular dichroism, are also experienced in the carotenoid field [19]. Whereas the nature of the substituent at C-2 or C-3 of a β-ring is irrelevant according to the conformational rule, the change of an allylic C-2′ substituent in an aliphatic end-group from –OH to –*O*-glycosyl or isopentenyl may alter the CD in cases where the chirality is unchanged. Substituent effects at the achiral C-1′ (–OH,

*See note added in proof.



Scheme 1. Monocyclic dodecaene carotenoids with plectaniaxanthin (1) related end-groups.

–*O*-acyl, *O*-glucosyl, etc.) may in principle also influence the Cotton effect.

Quantitative aspects of the conformational rule

The conformational rule has previously been applied in a qualitative way. However, if the rule is applied in connection with the additivity hypothesis, quantitative values must be used. From the literature data compiled in Table 1, the CD contributions from C-3 substituted β-rings can be estimated as 2.4–2.8 times that of C-2 substituted β-rings. This result is consistent with the presumed conformational equilibria since inspection of models indicates that C-3 substituted β-rings have a stronger preference for quasi-equatorial arrangement than the corresponding C-2 derivatives.

Chiroptical models

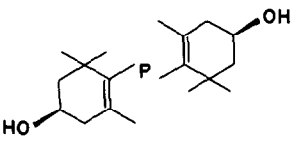
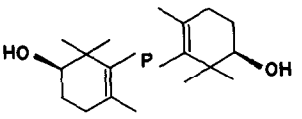
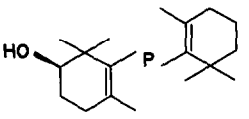
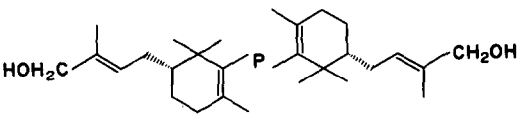
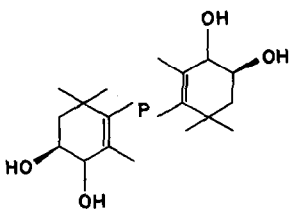
CD spectra of (2′*R*)-plectaniaxanthin (**1**), its natural diester (**1b**) and acetonide (**1c**) were available [1] (Scheme 2). The tetraacetate (**1d**) of plectaniaxanthin-2′-β-D-glucoside [20] was prepared by an improved procedure and was further characterized [21]. The pentaacetate of plectaniaxanthin 1′-β-D-glucoside (**1e**), with the same basic structure as phleixanthophyll tetraacetate [3], was also prepared [21]. The C_{45}-model (2′*R*)-3′,4′-didehydro-1′,2′-dihydro-2′-(3-methylbutyl)-β,ψ-carotene (**12**) was synthesized in a Wittig reaction from β-apo-8′-carotenal (**10**) and the appropriate phosphonium salt (**11**), available from a previous study [19] (Scheme 2). Another chiral C_{45}-carotene model (2′*S*)-2′-(3-methyl-2-butenyl)-1′,16′,3′,4′-tetradehydro-1′,2′-dihydro-β,ψ-carotene (**13**) was prepared as published elsewhere [22].

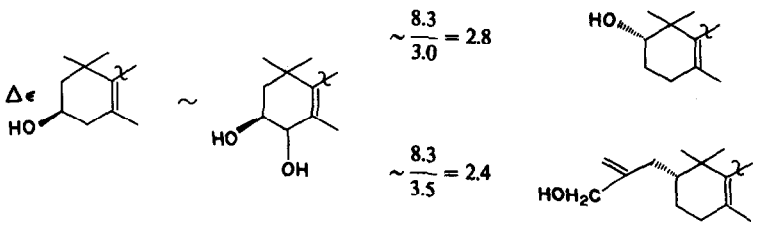
CD spectra of the models and substituent effects

The following discussion refers to Scheme 3, where the substituent effects on the CD spectra of the relevant models available in the C_{45}- and C_{40}-carotenoid series are summarized. The notations + Z and − Z refer to identical but opposite Cotton effects. The conclusions are based on CD comparison of pairs of monochiral carotenoids of established configuration with identical monocyclic dodecaene chromophores.

Plectaniaxanthin diester (**1b**, end-group B) exhibits an approximately conservative CD in contrast to the weak, non-conservative CD of plectaniaxanthin (**1**, end-group A, Fig. 1). Upon cooling to − 100°, the CD of the diol **1** becomes very similar to that of the diester **1b** [1]. For future work acylation of an allylic C-2′ hydroxy group is recommended for CD correlations.

Table 1. Quantitative contributions from chiral cyclohexene end-groups in carotenoid CD spectra

Carotenoid	Chirality	Δε 280 nm	Δε/one β-ring	Ref.
Zeaxanthin		÷16	÷8	16
β,β-Carotene-2,2'-diol		+5	+2, 5	12
β,β-Carotene-2-ol		+3	+3	12
C.p. 450		÷7	÷3.5	9, 34
$LiAlH_4$-reduced astaxanthin		÷17	÷8.5	16

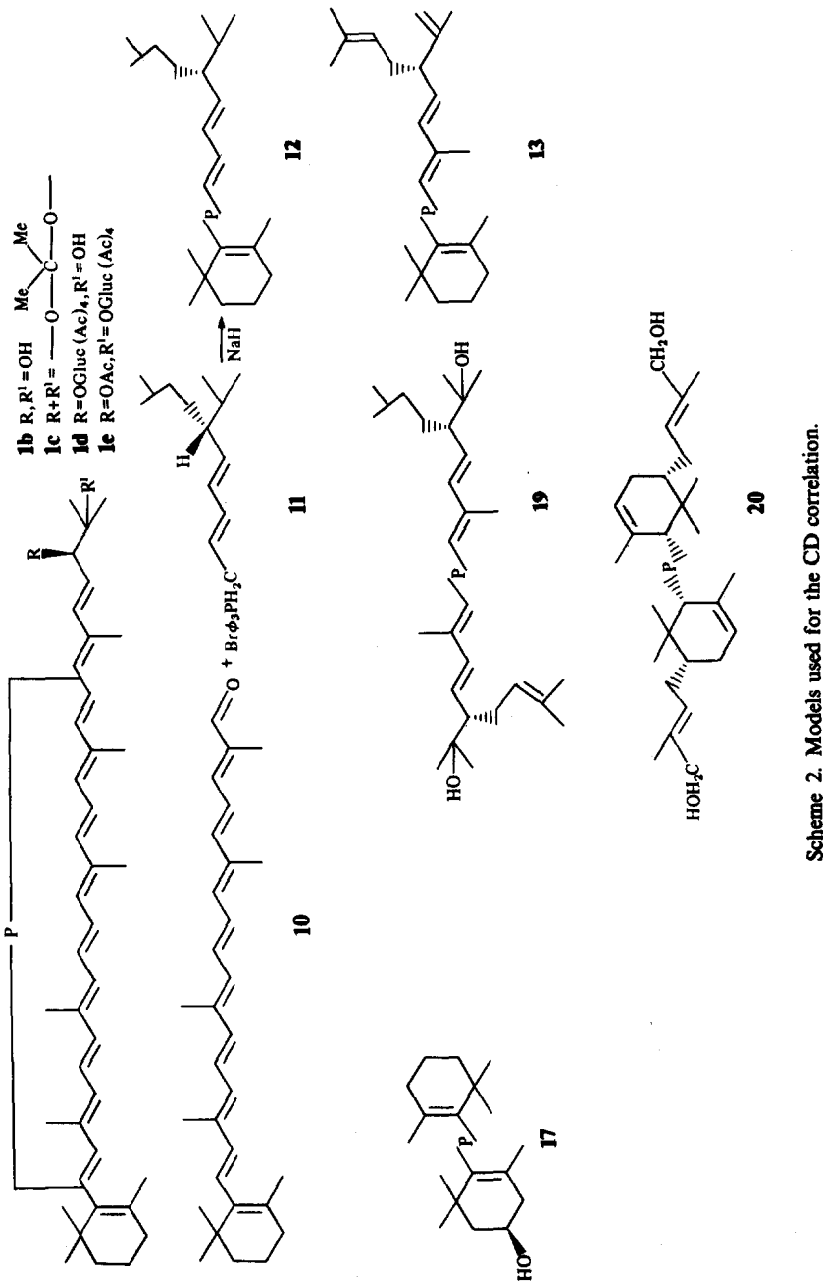


Plectaniaxanthin acetonide (**1c**, end-group F, Fig. 1) has a smaller and approximately opposite Cotton effect to that of the diester **1b** (end-group B) with the same configuration at C-2' [1] (Scheme 3).

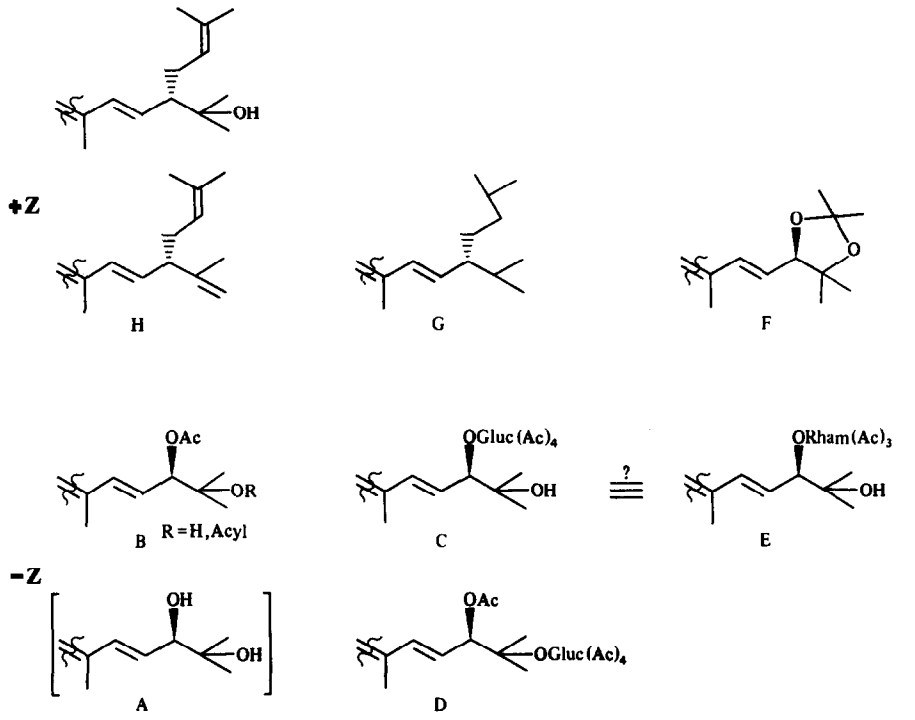
Plectaniaxanthin 2'-β-D-glucoside, as the tetraacetate **1d** (end-group C), showed a Cotton effect identical to that of the diester **1b**, (end-group B, Fig. 1, Scheme 3). This key relationship demonstrates that β-D-glucosidation of a 2'-ol does not invert the Cotton effect relative to the acetate. Moreover, the sign of the Cotton effect of the acetylated 1'-β-D-glucoside **1e** (end-group D) is the same as that for the diester **1b** (end-group B) and the acetylated 2'-β-D-glucoside **1d** (end-group C, Fig. 1).

The synthetic C_{45}-model **12** (Scheme 3, end-group G) had an approximately conservative CD, very similar, but opposite in sign, to that of plectaniaxanthin diester (**1b**, end-group B, R = acyl) [1] (Scheme 3, Fig. 2).

The other C_{45}-model **13** (Schemes 2 and 3, end-group H) exhibited the same Cotton effect as model **12** (Fig. 2). Models **12** and **13** thus serve to correlate C-2' isopentenylated and oxygen-substituted carotenoids with β,ψ-end groups.



Scheme 2. Models used for the CD correlation.



Scheme 3. Substituent effects on CD spectra of monocyclic dodecaene carotenoids with chiral centre at C-2'.

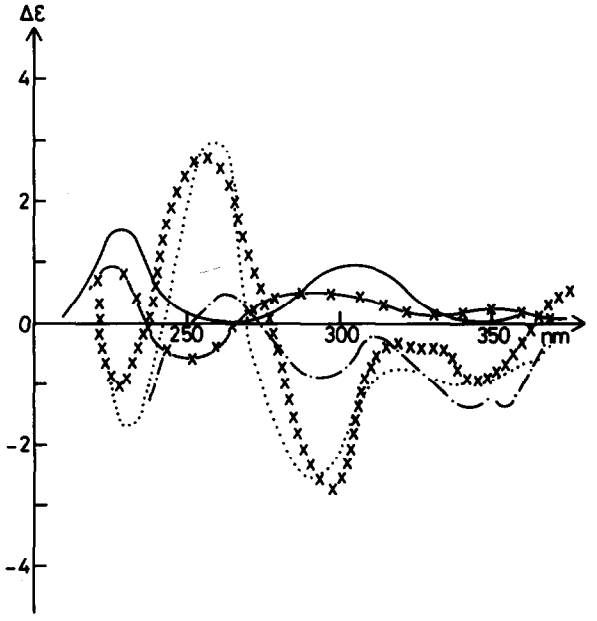


Fig. 1. CD spectra of plectaniaxanthin (**1**) (——), plectaniaxanthin diester (**1b**) (· · · ·), plectaniaxanthin acetonide (**1c**) (× —— ×), plectaniaxanthin 2'-β-D-glucoside tetraacetate (**1d**) (× × × ×) and plectaniaxanthin 1'-β-D-glucoside pentaacetate (**1e**) (— · — ·).

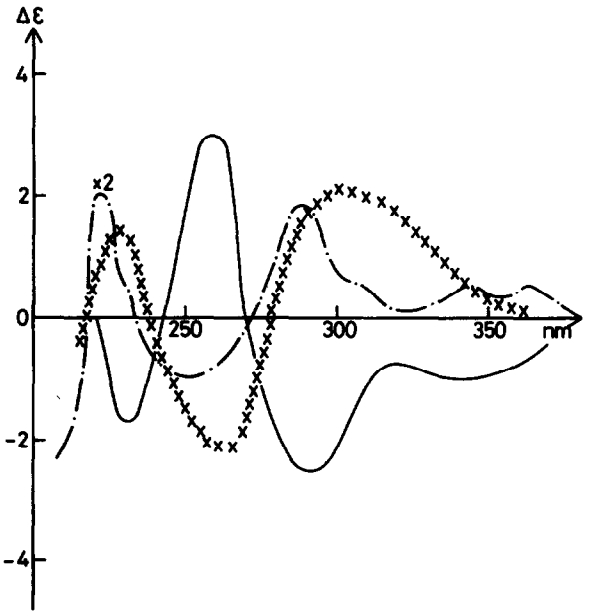


Fig. 2. CD spectra of plectaniaxanthin diester (**1b**) (——) and synthetic C_{45}-carotenes **12** (× × ×) and **13** (— · —).

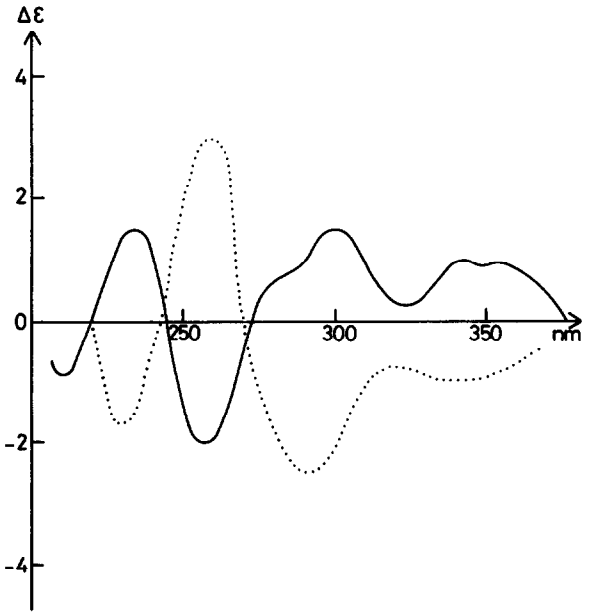


Fig. 3. CD spectra of phleixanthophyll pentaacetate (**2b**) (——) and plectaniaxanthin diester (**1b**) (· · · ·).

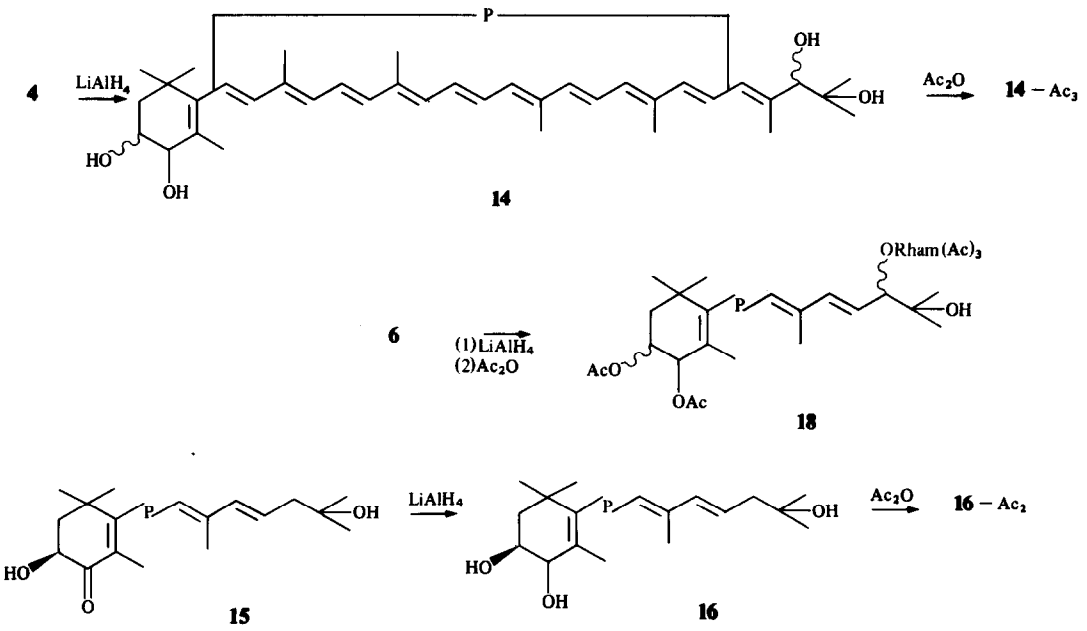
End-group H caused quite similar qualitative effects as end group I in the CD spectra of both aliphatic monochiral dodecaenes [22] and aliphatic homodichiral tridecaenes [19]. A corresponding situation will be assumed for the monocyclic dodecaene to be considered here. We will furthermore make the assumption that the acetylated end-groups C (β-D-glucosyl) and E (α-L-rhamnosyl), Scheme 3, cause the same Cotton effects, relevant for the chiralities of the glycosides from blue-green algae (**5**–**7**).

From the correlations made in Scheme 3 the chirality of monocyclic dodecaenes with end-groups A–I can be deduced.

Assignment of chirality to individual carotenoids by CD correlation

Group I (*Scheme* 1). The approximately conservative CD spectrum of the pentaacetate **2b** of the β-D-glucoside phleixanthophyll (**2**) [3] is nearly the mirror image of that of plectaniaxanthin diester (**1b**, Fig. 3), and the pentaacetate (**1e**, Fig. 1) of plectaniaxanthin with the same basic structure as phleixanthophyll (**2**) pentaacetate. Hence, plectaniaxanthin (**1**) and phleixanthophyll (**2**) have opposite chiralities at C-2′ and 2′*S* configuration for phleixanthophyll (**2**) may be concluded. Thus, 4-ketophleixanthophyll (**3**), also produced together with **2** by *Mycobacterium phlei* strain Vera [3], is likely to have the same 2′*S* chirality.

2′-Hydroxyflexixanthin (**4**) [4] was reduced with lithium aluminium hydride to the tetrol **14** for CD correlation with the triol **16**, obtained by a similar reduction of (3*S*)-flexixanthin (**15**) [23, 24] (Scheme 4). As expected from the low Cotton effect of plectaniaxanthin (**1**), the difference curve between the CD of the tetrol **14** and the triol **16** (Fig. 4A) is very small. Since it is nearly quantitatively opposite to the CD of plectaniaxanthin (**1**) in the 280–370 nm region, opposite chiralities for plectaniaxanthin (**1**) and 2′-hydroxyflexixanthin (**4a**) were tentatively considered, but not proved. The relatively small differences in the CD curves would demand highly accurate Δε values in order to be conclusive. Since the acylated end-group B was shown to cause a larger Cotton effect for plectaniaxanthin (**1**), the acetylated derivative **14**-triacetate of 2′-hydroxyflexixanthin (**4**) was subsequently prepared [24] and its CD spectrum compared



Scheme 4. Derivations carried out for the CD correlations.

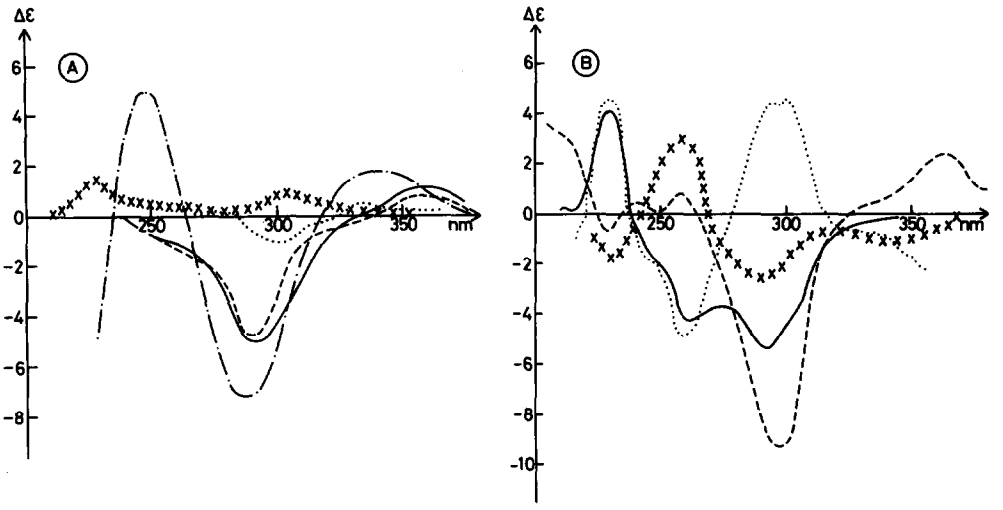


Fig. 4. (A) CD spectra of $LiAlH_4$-reduced 2-hydroxyflexixanthin (**14**) (——), $LiAlH_4$-reduced flexixanthin (**16**) (– – – –), of plectaniaxanthin (**1**) (× × × ×) and of β-cryptoxanthin (**17**) (— · — ·) [18]. (· · · ·) Difference curve (Δε **14** – Δε **16**). (B) CD spectra of **14**-triacetate (——), **16**-diacetate (– – –) and of plectaniaxanthin diester (**1b**) (× × × ×). (· · · ·) Difference curve (Δε **14** – Δε **16**).

with that of the corresponding diacetate (**16**-diacetate) prepared from (3*S*)-flexixanthin (**15**, Scheme 4, Fig. 4B). The difference curve between **14**-triacetate and **16**-diacetate corresponds well to the mirror image of the CD spectrum of plectaniaxanthin (**1**) diester (**1b**) and is consequently taken as proof for 2′*S* configuration for 2′-hydroxyflexixanthin.

Group II. The Cotton effect of myxoxanthophyll tetraacetate (**5b**, Fig. 5), is negative around 280 nm, suggesting 3*R* chirality of the β-ring in comparison with the known CD of (3*R*)-cryptoxanthin (**17**, Fig. 4) [18]. According to the conformational rule and the additivity hypothesis, the Cotton effect of the chiral β-ring may be eliminated by subtracting the Cotton effect of lithium aluminium hydride-reduced flexixanthin (**16**). The difference curve is approximately conservative, very similar in shape and opposite in sign to that of plectaniaxanthin diester (**1b**) and plectaniaxanthin 2′-β-D-glucoside tetraacetate (**1d**, Fig. 5). Provided the Cotton effect of end-groups C and E, Scheme 3, are the same, this leads to the opposite chirality at C-2′ for myxoxanthophyll (**5**) and plectaniaxanthin (**1**) at the 2′-position. Myxoxanthophyll should consequently have 3*R*,2′*S*-configuration (**5a**).

4-Ketomyxoxanthophyll (**6**) was reduced with lithium aluminium hydride and acetylated to provide the pentaacetate **18** for direct CD correlation with myxoxanthophyll tetraacetate (**5b**, Fig. 6). The CD spectra are very similar, supporting identical chiralities at C-3 and C-2′ (3*S*,2′*S*) for **6a**. Further support for this assignment is obtained from the difference curve obtained by subtracting the CD spectrum of lithium aluminium hydride-reduced flexixanthin (**16**) from that of the pentaacetate **18**. The difference curve is very similar to the mirror image of the Cotton effect of plectaniaxanthin diester (**1b**) and the tetraacetate of plectaniaxanthin 2′-β-D-glucoside (**1d**, Fig. 6).

The Cotton effect of the triacetate of myxol-2′-*O*-methyl methylpentoside (**7b**) in comparison with that of myxoxanthophyll tetraacetate (**5b**, Fig. 7) is taken as support of the same chirality at C-3 and C-2′ (3*R*,2′*S*); compare with the general conclusion below.

Group III. Considering now the C-2′ isopentenylated carotenoids, the Cotton effect of *C.p.* 473 (**8**) shown in Fig. 8 could be rationalized assuming 2*R*,2′*S*-chirality (**8a**). Thus, the CD spectrum of **8a** is compatible with the one calculated from (1/2.4) Δε for lithium aluminium hydride-reduced flexixanthin (**16**) diacetate (to account for the substituted β-end) plus Δε for the β-monocyclic

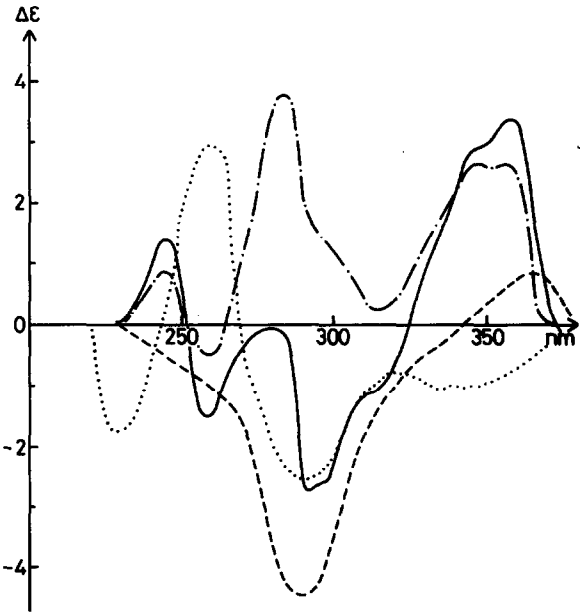


Fig. 5. CD spectra of myxoxanthophyll tetraacetate (**5b**) (——), $LiAlH_4$-reduced flexixanthin (**16**) (– – –), and of plectaniaxanthin diester (**1b**) (· · · ·). (— · — ·) Difference curve (Δε **5b** – Δε **16**).

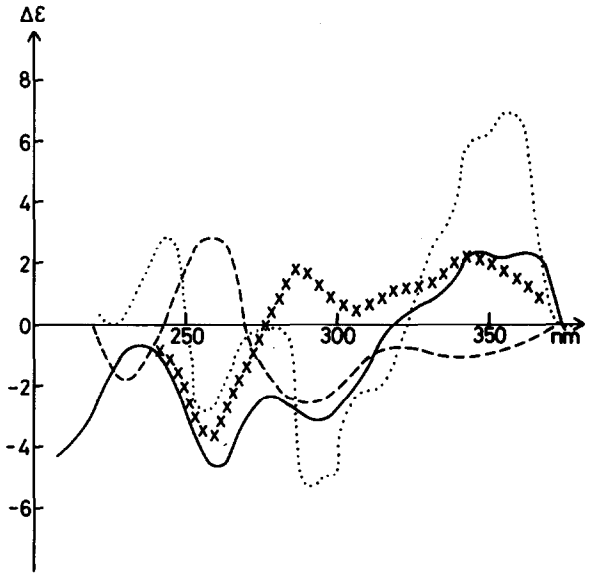


Fig. 6. CD spectra of $LiAlH_4$-reduced 4-ketomyxoxanthophyll pentaacetate (**18**) (——), myxoxanthophyll tetraacetate (**5b**) (· · · ·) and of plectaniaxanthin diester (**1b**) (——) (× × × ×). Difference curve (Δε **18** − Δε **5b**).

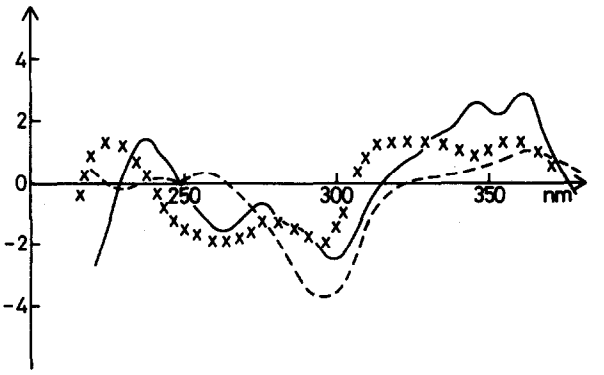


Fig. 8. CD spectra of *C.p.* 473 (**8**) (——), calculated curve for (1/2.4) Δε $LiAlH_4$-reduced flexixanthin (**16**) diacetate plus Δε C_{45}-model **13** (– – – –) and calculated curve for (1/2.4) Δε $LiAlH_4$-reduced flexixanthin (**16**) diacetate plus Δε C_{45}-model **12** (× × ×).

C_{45}-model **13** with end-group H. This approach uses the additivity hypothesis and takes into account the quantitative aspects of 3- versus 2-substitution of the β-ring (see Fig. 8 and Table 1). If we take into account that dehydration of end-group I (as in *C.p.* 473) to H in the aliphatic series is known to reduce the Δε value, particularly of the nagative peak at *ca* 260 nm [19, 22], a closer fit in the 260 nm region may be achieved. Moreover, the CD curve calculated from (1/2.4) Δε for lithium aluminium hydride-reduced flexixanthin (**16**) diacetate plus Δε for the β-monocyclic C_{45}-model **12** with end-group G is also compatible with the experimental result for *C.p.* 473 (**8**, Fig. 8).

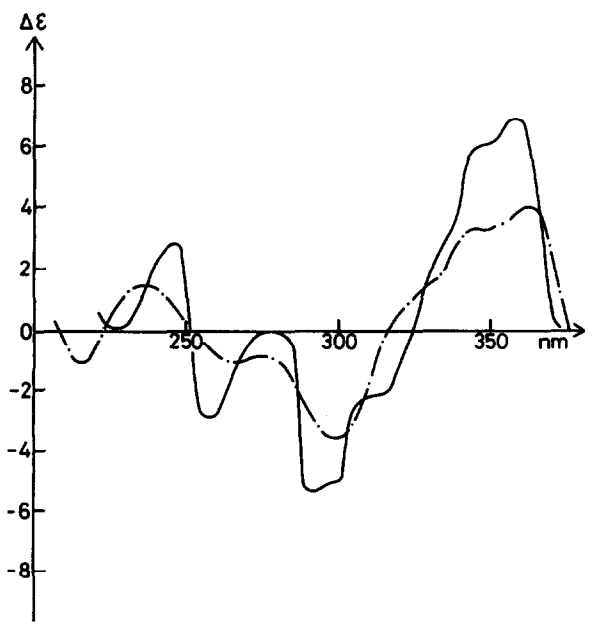


Fig. 7. CD spectra of myxoxanthophyll tetraacetate (**5b**) (——) and of myxol-2′-*O*-methyl pentoside triacetate (**7b**) (— · —).

Whereas the enantiomeric 2*S*,2′*R*-chirality would require an opposite Cotton effect, the alternative combination 2*R*,2′*R* (or its enantiomer 2*S*,2′*S*) would not fit the experimental CD curve for *C.p.* 473 (**8**).

The CD spectrum of the trichiral *A.g.* 471 (**9**, Scheme 1) has been published [10]. The futility of adding half of each of the CD spectra of bisanhydrobacterioruberin (**19**, Scheme 2) and decaprenoxanthin (**20**, Scheme 2) to obtain the observed CD spectrum of *A.g.* 471 (**9**) [10] can now be explained since carotenoids of different chromophores were involved. However, on biogenetic grounds, *A.g.* 471 is likely to possess the same 2*R*,6*R*,2′*S* chirality as the symmetrical carotenoids bisanhydrobacterioruberin (**19**) [19] and decaprenoxanthin (**20**) [25] occurring in the same organism [10].

Conclusion for the CD correlations

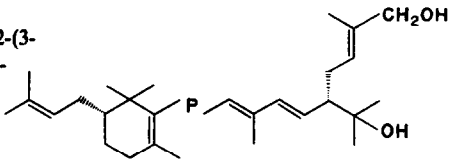
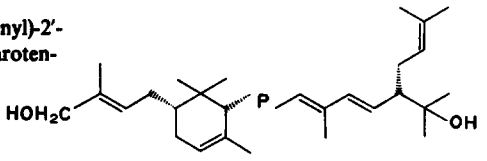
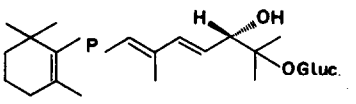
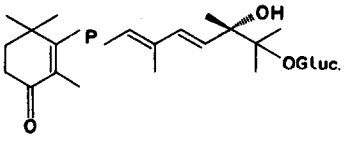
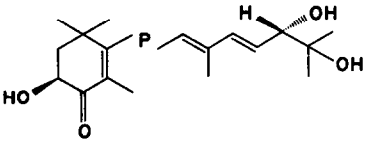
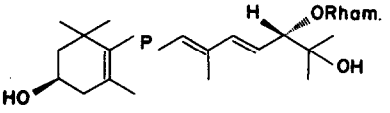
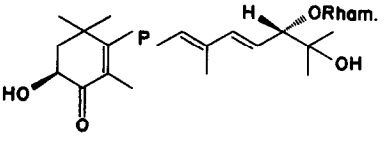
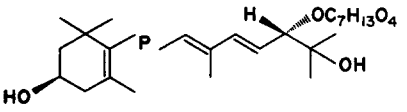
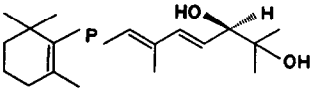
The similarity of the CD spectra of *C.p.* 473 (**8a**, Fig. 8), of myxoxanthophyll tetraacetate (**5b**, Figs. 5 and 6), and of acetylated lithium aluminium hydride-reduced 2′-hydroxyflexixanthin (**14**-Ac_2, Fig. 4B) is striking. These carotenoids all represent heterodichiral monocyclic dodecaene carotenoids with different substituents at C-2′ in the aliphatic end and at C-2 or C-3 in the β-ring.

For **8a**, **5b** and **16**-diacetate above, the negative peak at 290 nm is clearly caused by the chirality of the β-ring as reflected by lithium aluminium hydride-reduced (3*S*)-flexixanthin (**16**) or its diacetate (Fig. 4).

The negative peak at 260 nm in the CD spectra of the same carotenoids (**8a**, **5b**, **16**-Ac_2) is caused by the chirality at the C-2′ centre exemplified by the monochiral (disregarding the glycosyl substituent) (2′*S*)-phleixanthophyll pentaacetate (**2b**, Fig. 3).

On the basis of the present study it may now be possible to make CD predictions and correlations for mono- and dichiral β-monocyclic carotenoids with dodecaene chromophores.

Table 2. Sources, names and suggested chiralities of the C-2′ substituted carotenoids studied (P as in Schemes 1, 2, 3 and 4)

Source	Carotenoid	
BACTERIA		
Corynebacterium poinsettiae	*C.p.* 473 (**9a**); (2*R*,2′*S*)-2′-(4-hydroxy-3-methyl-2-butenyl)-2-(3-methyl-2-butenyl)-3′,4′-didehydro-1′,2′-dihydro-β,ψ-caroten-1′-ol	
Arthrobacter glacialis	*A.g.* 471 (**9**); (2*R*,6*R*,2′*S*)-2-(-4-hydroxy-3-methyl-2-butenyl)-2′-(3-methyl-2-butenyl)-3′,4′-didehydro-1′,2′-dihydro-ε, ψ-caroten-1′-ol	
Mycobacterium phlei	Phleixanthophyll (**2a**); (2′*S*)-1′-(β-D-glucopyranosyloxy)-3′,4′-didehydro-1′,2′-dihydro-β,ψ-caroten-2′-ol	
	4-ketophleixanthophyll (**3a**); (2′*S*)-1-β-D-glucopyranosyloxy)-2′-hydroxy-3′,4′-didehydro-1′,2′-didehydro-β,ψ-caroten-4-one	
Flexibacterium sp. RXC/NIVA	2-Hydroxyflexixanthin (**4a**); (3*S*,2′*S*)-3′,4′-didehydro-1′,2′-dihydro-3,1′,2′-trihydroxy-β,ψ-caroten-4-one	
BLUE-GREEN ALGA		
Phormidium luridum	Myxoxanthophyll (**5a**); (3*R*,2′*R*)-2′-rhamnosyloxy-3′,4′-didehydro-1′,2′-dihydro-β,ψ-carotene-3,1′-diol	
Oscillatoria limosa	4-Ketomyxoxanthophyll (**6a**); (3*S*′,2′*R*)-3,1′-dihydroxy-2′-rhamnosyloxy-3′,4′-dihydro-1′,2′-dihydro-β,ψ-caroten-4-one	
	Myxol-2′-*O*-methyl methylpentoside (**7a**); (3*R*,2′*S*)-2′-(*O*-methyl-5-C-methylpentosyloxy)-3′,4′-didehydro-1′,2′-dihydro-β,ψ-carotene-3,1′-diol	
FUNGI		
Plectania coccinea	Plectaniaxanthin (**1**); (2′*R*)-3′,4′-didehydro-1′,2′-dihydro-β,ψ-carotene-1′,2′-diol	

Chemosystematic considerations

The stereochemical suggestions for carotenoids **2–9** (Scheme 1) are summarized in Table 2, including full rational names and sources of the carotenoids examined.

The aliphatic and cyclic C_{45}- and C_{50}-carotenoids from non-photosynthetic bacteria studied previously [19, 22, 25, 26] and **8** and **9** considered here all appear to have the same chirality at C-2 and C-2′, which represent the biosynthetic isopentenylation site.

The two bacterial carotenoids (**2a** and **4a**) with allylic C-2 hydroxy groups are assigned the same chirality at C-2′, opposite to that of the fungal plectaniaxanthin (**1**). It is interesting to note that also the chiralities of other fungal carotenoids differ from those in other organisms: (3*R*,3′*R*)-astaxanthin from *Phaffia rhodozyma* [27] and (6*S*)-β,γ-carotene from *Caloscypha fulgens* [28, 29].

The C-2′ *O*-glucosides from blue-green algae studied here also have identical chiralities at C-2′, as expected from biosynthetic considerations. That the parent carotenol has bacterial type chirality is consistent with the classification of blue-green algae as cyanobacteria [30].

The 2′*S* chirality concluded here for myxoxanthophyll (**5a**) casts doubt on the opposite chirality suggested elsewhere for the homodichiral aliphatic tridecaene 2,2′-dirhamnoside oscillaxanthin [20] and will be discussed further elsewhere.

EXPERIMENTAL

CD spectra. Figs. 1–8 were recorded with a Roussel Jouan Dichrographe in EPA (Et_2O–*i*-pentane–EtOH, 5:5:2) soln at room temp. Concns used for calculation of Δε values were based on known extinction coefficients for the absorption spectra in visible light.

Chiroptical models. (2′*R*)-Plectaniaxanthin (**1**) was obtained from *Plectania coccinea* [1, 31]; CD: Fig. 1. Note that the Δε values quoted elsewhere [20] have been corrected.

(2′*R*)-Plectaniaxanthin diester (**1b**). The natural diester was reisolated from *Plectania coccinea* [1, 31]; CD: Fig. 1.

(2′*R*)-Plectaniaxanthin acetonide (**1c**). The acetonide was synthesized as reported elsewhere [1]; CD: Fig. 1.

(2′*R*)-Plectaniaxanthin 2′-β-D-glucoside tetraacetate (**1d**). Details of the partial synthesis from plectaniaxanthin (**1**) have been reported elsewhere [1, 21]; CD: Fig. 1.

(2′*R*)-Plectaniaxanthin 1′-β-D-glucoside pentaacetate (**1e**). The partial synthesis from plectaniaxanthin (**1**) has been reported elsewhere [21]; CD: Fig. 1.

(2′*R*)-3′,4′-Didehydro-1′,2′-dihydro-2′-(3-methylbutyl)-β,ψ-carotene (**12**). NaH (55–60% in mineral oil, 50 mg) was washed with hexane and suspended in CH_2Cl_2. β-Apo-8′-carotenal (**10**, 20 mg) and (6*R*)-3,9-dimethyl-6-isopropyl-2,4-decadienyl triphenylphosphonium bromide (**11**, 90 mg) [19] was added with stirring. The reaction mixture was stirred with aq. NH_4Cl, after 28 hr extracted with Et_2O and dried over Na_2SO_4. TLC (silica gel) provided **12** (25 mg, 83%); vis. λ_{max}^{hexane} nm: 444.470 and 500, % III/II [32] = 39; CD: Fig. 2; ^1H NMR ($CDCl_3$): δ0.83, 0.86 and 0.89 (12H, Me-16′, 17′ and gem. Me in C-2′ substituent), 1.03 (6H, *s*, Me-16, 17), 1.1–2.3 (CH_2, *m*, CH), 1.71 (3H, *s*, Me-18), 1.92 (3H, *s*, Me-18′), 1.97 (12H, *s*, Me-19, 20, 19′, 20′) 5.1–6.9 (*ca.* 17H, *m*, olefinic); MS *m/z* (rel. int.): 606 $[M]^+$ (100), 514 $[M-92]^+$ (7), 500 $[M-106]^+$ (9), 448 $[M-158]^+$ (2), 435 m* (*m/z* 606 to *m/z* 514).

(2′*S*)-2′-(3-Methyl-2-butenyl)-1′,3′,4′,16′-tetradehydro-β,ψ-carotene (**13**) was synthesized and characterized as described elsewhere [22], CD: Fig. 2.

Carotenoids utilized for CD correlations. Derivatives. Acetylations of primary and secondary hydroxy groups with Ac_2O in pyridine and $LiAlH_4$-reduction in dry Et_2O of keto groups were carried out by standard procedure [33]. Reductions with $NaBH_4$ were effected in MeOH–Et_2O.

Phleixanthophyll (**2**) in mixture with 4-ketophleixanthophyll (**3**) from *Mycobacterium phlei* strain Vera [3] was acetylated. TLC (silica gel) provided phleixanthophyll pentaacetate (**2b**), 8.5 mg [3]; CD: Fig. 3.

2′-Hydroxyflexixanthin (**4**) was reisolated from *Flexibacterium* strain NIVA [4], yield 0.7 mg. Compound **4** had vis. $\lambda_{max}^{Me_2CO}$ nm: 479 and (505); CD nm (Δε): 240 (0), 292 (−5.3), 335 (0) and 370 (−0.8); MS *m/z* (rel. int.): 598 $[M]^+$ (2) 582 $[M-16]^+$ (1), 580 $[M-18]^+$ (1), 564 $[M-16-18]^+$ (1), 562 $[M-18-18]^+$ (1), 508 $[M-90]^+$ (2), 506 $[M-92]^+$ (2), 492 $[M-106]^+$ (4), 283 (100). Compound **4** was reduced with $NaBH_4$, yield of the tetrol (**14**) 0.2 mg after TLC (silica gel); vis. $\lambda_{max}^{Me_2CO}$ nm: (443), 469 and (498); CD: Fig. 4A.

14-Triacetate was prepared and characterized as described elsewhere [24]; CD: Fig. 4B.

Myxoxanthophyll (**5**) was reisolated from *Phormidium luridum* [6] and converted to the tetraacetate **5b**, yield 0.6 mg; vis. $\lambda_{max}^{Me_2CO}$ nm: (445), 471 and 503; CD: Figs. 6 and 7; MS *m/z*: 898 $[M]^+$, 840 $[M-58]^+$, 806 $[M-92]^+$, 792 $[M-106]^+$, 273.

4-Ketomyxol-2′-methylpentoside (**6**) from *Oscillatoria limosa* was available as the tetraacetate **6b** [7]. Brief $LiAlH_4$-reduction followed by acetylation provided the pentaacetate **18**; $\lambda_{max}^{Me_2CO}$ nm: 450, 474, 506; CD: Fig. 7.

Myxol-2′-*O*-methyl methylpentoside (**7**) *ex Oscillatoria limosa* [7] was available as the triacetate **7b**; CD: Fig. 7.

C.p. 473 (**8**) was obtained from *Corynebacterium poinsettiae* [8, 9]; CD: Fig. 8.

Flexixanthin (**15**) was reisolated from *Flexibacterium* strain NIVA [4, 34], yield 0.7 mg; vis. $\lambda_{max}^{Me_2CO}$ nm: 478 and (503); MS *m/z* (rel. int.): 582 $[M]^+$ (3), 566 $[M-16]^+$ (1), 490 $[M-92]^+$ (2), 476 $[M-106]^+$ (6). Reduction with $LiAlH_4$ provided the triol **16**, yield 0.3 mg after TLC (silica gel); vis. $\lambda_{max}^{Me_2CO}$ nm: (440), 467 and 495; CD: ref. [24].

16-Diacetate was prepared and characterized as described elsewhere [24]; CD: Fig. 4B.

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NOTE ADDED IN PROOF

Recent total synthesis of (2′*S*)-plectaniaxanthin [R. Dümont and H. Pfander, *Helv. Chim. Acta* **67**, 1283 (1984)] has confirmed the 2′*R*-chirality of natural plectaniaxanthin.