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Short Communications

Bacterial Carotenoids. XLVII. * C_{50}-Carotenoids. 15. ** Absolute Configuration of Decaprenoxanthin

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Hitherto the constitutions of 16 C_{50}-carotenoids have been reported.[1–5] They all exhibit extra five carbon substituents in 2,2′-positions of a traditional C_{40}-carotenoid, suggesting common biosynthetic pathways.[6,7]

Recently, we assigned the absolute configuration to *C.p.* 450 (*1*, Scheme 1)[8] from CD-correlation with (2R,2′*R*)-2,2′-dimethyl-β,β-carotene (*2*).[9]

We now present evidence for assignment of the absolute configuration *3* to decaprenoxanthin.[10,11]

Decaprenoxanthin (*3*) has two chiral centers in each ε-ring (C-2, C-6 and C-2′, C-6′). Since decaprenoxanthin is optically active,[12] it is not a *meso* compound, and the chirality of each end-group is from biosynthetic considerations likely to be the same. This is supported by the ^{1}H NMR spectrum,[10] demonstrating that decaprenoxanthin is centro-symmetric.

Four stereochemical alternatives, consisting of two enantiomeric pairs (A, ent. A (2,6-*trans*); B, ent B (2,6-*cis*)) for these end-groups exist. In principle, CD-spectra of two model carotenoids with end groups A or ent. A, B or ent. B should allow a differentiation between these four possibilities.

Two optically active 2,2′-dimethyl-carotenes of type A,A (*4*) and B,B (*5*) have been synthesized[13] from the irones *6* and *7* by routes known to retain the stereo-integrity of the optically active irones[14] *via* the C_{15}-alcohols *8* and *9*. Irone *7* is a natural constituent of Iris oil; *6* was isolated after base-catalyzed isomerization of natural irones according to Rautenstrauch and Ohloff.[15]

The similarities of the CD spectra (Fig. 1) of the 2,6-*trans* model dimethyl-carotene

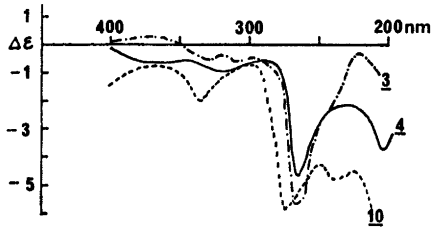
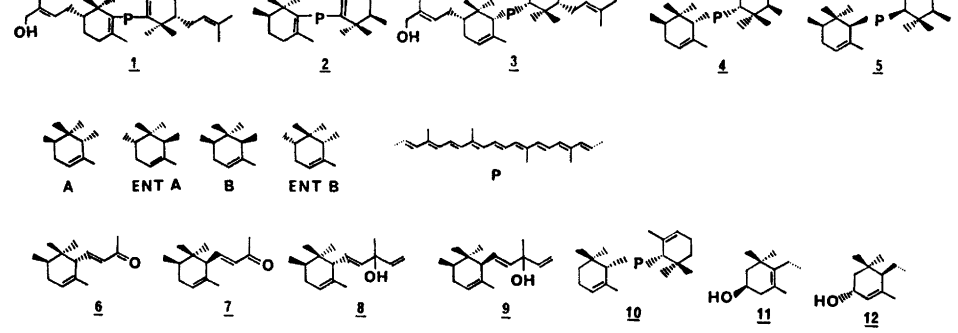


Fig. 1. CD-spectra of *4* (EPA = ether, isopentane, ethanol 5:5:2———; *10* (dioxane)[14] — — —, and decaprenoxanthin (*3*, EPA)[10] — · —.



Scheme 1.

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Table 1. δ-values ($CDCl_3$) of the *gem.* dimethyl signals of some model compounds and of decaprenoxanthin.

Compound		δ *gem.* dimethyl		Difference in chemical shift Δ
7		0.72	0.87	0.15
9	2,6-*cis*	0.63	0.85	0.22
5		0.68	0.87	0.19
6		0.83	0.87	0.04
8	2,6-*trans*	0.77	0.81	0.04
4		0.81	0.82	0.01
Decaprenoxanthin [10]		0.75	0.95	0.20

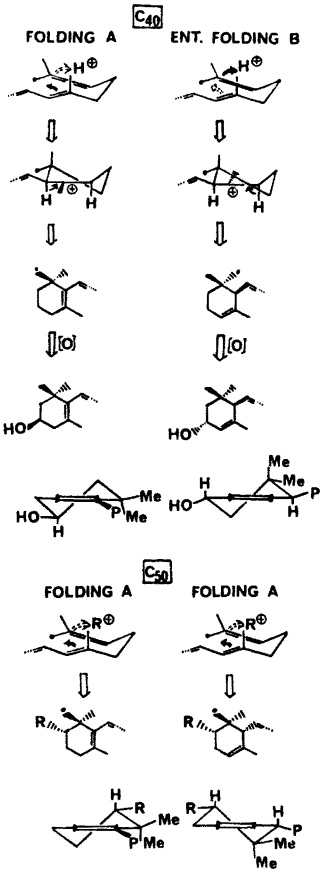
(*4*)[13] and of decaprenoxanthin is striking and could be taken to support the same (2*S*,6*R*,2′*S*,6′*R*) configuration for decaprenoxanthin.

However, the ^1H NMR signals of the *gem.* dimethyl groups of the model compounds *4*–*9* (Table 1) clearly demonstrate a smaller shielding of one of the *gem.* dimethyl groups in the 2,6-*trans* than the 2,6-*cis* derivatives. Assuming that the influence on the *gem.* dimethyl signals caused by a 2-methyl group is comparable with that of a 2-(4-hydroxy-3-methyl-2-butenyl) substituent, the situation (Table 1) for decaprenoxanthin[10] clearly favours 2,6-*cis*. The CD results therefore need further consideration. When comparing the CD spectrum (Fig. 1) of unnatural (6*S*,6′*S*)-ε,ε-carotene (*10*)[16] with that of *4* it becomes evident that the chiral center at C-2 does not contribute significantly to the *CD*. This is compatible with the concept of preferred helicity of the chiral cyclohexene half-chair[17,18] The conformation with the polyene chain quasiequatorial is expected to be dominant for *10*, *4* and particularly stabilized for *3* with the isopentenyl substituent equatorial. The CD spectrum of decaprenoxanthin (Fig. 1) is therefore compatible with structure *3* (2,6-*cis*, 2′,6′-*cis*; ent B, ent B).

That the CD of 2-substituted ε-rings is dictated nearly exlusively by the C-6 center has already been observed by Rautenstrauch and Ohloff for α-ionone and the corresponding epimeric irones.[15] The same appears to be true for a 3-substituted ε-ring.[19]

Attempts to confirm assignment *3* for decaprenoxanthin by base-catalyzed isomerization[20,21] to the β-analogue were made. Decaprenoxanthin was reisolated from *Flavobacterium dehydrogenans*.[10] Base-catalyzed isomerization of the ε- to β-end groups, successful with ε,ε-carotene and lutein, did not yield the expected products when applied to decaprenoxanthin. Chromatographic, spectroscopic and mass spectrometric evidence indicated that isomerization was accompanied by other fundamental changes in structure (probably involving the additional 5-carbon units at the 2-positions). As a result correlation of the configuration at C-2 of decaprenoxanthin with that of *C.p.* 450 failed.

Decaprenoxanthin (2*R*,6*R*,2′*R*,6′*R*)-2,2′-bis(4-hydroxy-3-methyl-2-butenyl)-ε,ε-carotene thus has the same absolute configuration at C-2,2′ as *C.p.* 450 (*1*) isolated from *Corynebacterium poinsettiae*[8] and opposite configuration at C-6 to all C_{40}-carotenoids with ε-end groups,[1] which leads to the following biosynthetic considerations depicted in Scheme 2.



Scheme 2.

From work on the trisporic acid biosynthesis[22,23] cyclization resulting in β- and ε-end groups must proceed through enantiomeric foldings of the chain forms if the cyclizations involve loss of axial H and are analogous with other terpenoids. Subsequent equatorial hydroxylation of half-chairs of the same helicity is consistent with the stereochemistry of the zeaxanthin (*11*) and lutein (*12*) end groups.

In the C_{50}-series addition of 2 five-carbon units (probably isopentenyl or dimethylallyl pyrophosphate) could precede or initiate cyclization. No cyclic C_{40}-carotenoids have as yet been found in organisms producing C_{50}-carotenoids. Folding A, followed by 5-carbon addition/cyclization and loss of the axial H at C-4 would give the observed stereochemistry for the *C.p.* 450 (*1*) end groups and the same folding is required to give the decaprenoxanthin (*3*) end group. In the ε-series the half-chairs are stabilized by extra equatorial substituents (OH in *12* and alkyl in *3*). Different enzymes must be responsible for cyclization to ε-rings in carotenoids in the C_{40}-series and in the C_{50}-series; the latter so far being restricted to non-photosynthetic, spherical or rod-shaped, aerobic bacteria.

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