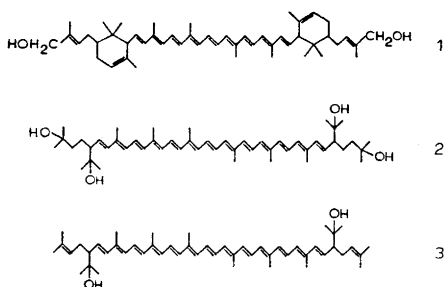


C_{50} -Carotenoids8.* Circular Dichroism and Relative Configuration of C_{50} -CarotenoidsG. BORCH,^a S. NORGDÅRD^b and
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Recently Bartlett *et al.*¹ published the optical rotatory dispersion (ORD) curves of more than forty carotenoids. Among these was decaprenoxanthin (1)²⁻⁴ isolated from *Flavobacterium dehydrogenans*.

In the present communication we report on the circular dichroism (CD) of bacterioruberin (2)⁵ from *Halobacterium salinarium* and bisanhydrobacterioruberin (3)⁶ isolated from *Corynebacterium poinsettiae*. Both are C_{50} -carotenoids, with chiral centers in 2,2'-position. The identity of natural 3 with semi-synthetic bisanhydrobacterioruberin was confirmed by means of mass spectroscopy and co-chromatography.⁶ CD curves of 2 and 3 are presented in Fig. 1. The CD curve (Fig. 2) of decaprenoxanthin (1) was recorded for comparison. The ORD spectrum, calculated from the CD curve, was in agreement with the one previously reported.¹ The computer program used (approximation of Kuhn function to Cotton effect) will be published elsewhere.⁷



In the point group C_2 , both the electric dipole moment and the magnetic dipole moment transform according to the irre-

ducible representation A and B⁸ (in Schoenflies notation) and therefore, substances belonging to this point group are capable of showing optical activity.

The assumption that C_{40} -carotenoids have a two-fold axis of symmetry (C_2 symmetry) through the central double bond is supported by X-ray studies for, *e.g.*, canthaxanthin.⁹

Assuming that the C_{50} -carotenoids have C_2 symmetry, optically active transitions to various singlet A and singlet B states are expected.^{10,11} Transitions to triplet states rather than singlet states seems less likely. In transitions of species A, the electric dipole and magnetic dipole transition moments lie parallel or antiparallel to the C_2 -axis (z-axis), whereas in transitions of species B they lie in the plane of the polyene chain (xy-plane). With a fixed chirality (unknown in the present case), Cotton effects of species A will generally have opposite signs to those of species B.¹¹

The CD curves of 2 and 3 (Fig. 1) show both positive and negative signs, and thus meet well with the situation involving both A and B transitions described above. Moreover, the curves in Fig. 1 are very

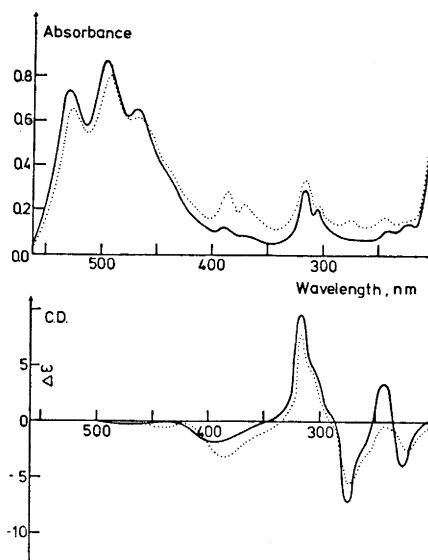


Fig. 1. Electronic spectra and circular dichroism spectra in EPA solution of — bisanhydrobacterioruberin (3) ex *Corynebacterium poinsettiae* and ... bacterioruberin (2) ex *Halobacterium salinarium*.

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similar, indicating that bacterioruberin (2) and bisanhydrobacterioruberin (3) have the same absolute configuration in 2,2'-position.

Identical relative configuration of 2 and 3 from different biological sources is taken to support a common biosynthetic formation and indicates a stereospecific addition of the two extra C_5 -units to the traditional C_{40} -carotenoid skeleton.¹²

The CD curve of decaprenoxanthin (1, Fig. 2) shows essentially only negative

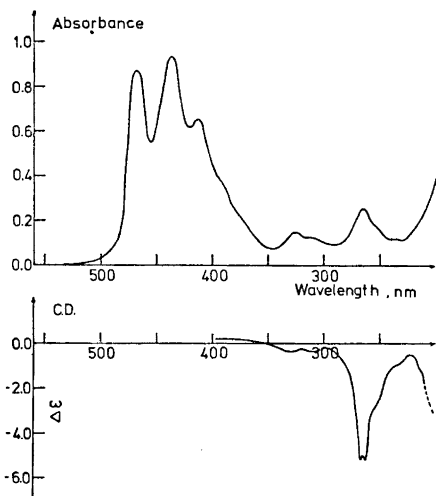


Fig. 2. Electronic spectrum and circular dichroism spectrum in EPA solution of decaprenoxanthin (1) ex *Flavobacterium dehydrogenans*.

signs, suggesting predominance of A or B-type transitions, provided that the assumption of C_2 symmetry for this compound is maintained. Direct comparison of the CD-curves shown in Figs. 1 and 2, respectively, are therefore not informative. This conclusion could also be reached from the fact that decaprenoxanthin (1) possesses two helical rings, each with two asymmetric carbon atoms, and a different chromophore from 2 and 3, the influence of which, at the present stage of investigation, cannot be judged.

Experimental. Crystalline specimens^{5,6} were used. CD spectra were recorded in EPA (diethyl ether, isopentane, ethanol 5:5:2) solution (conc. $\sim 10^{-4}$ mol/l, 0.1 cm cell path length) on a Roussel-Jouan Dicrographe in the region 200–600 nm. The experimental uncertainty for the $\Delta\epsilon$ values is estimated to be ca. 15%. Electronic spectra were recorded in the same solvent on a dual beam Cary 14 R spectrophotometer.

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