Application of Diphenyl Diselenide as a New Catalyst for Photochemical Stereoisomerization of Carotenoids

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In a comparative study, diphenyl diselenide was shown to be an alternative to iodine as a catalyst for photochemical E/Z isomerization of carotenoids. Suitable conditions for the stereomutation of zeaxanthin, violaxanthin, canthaxanthin and fucoxanthin are reported.

Photochemical allenic isomerization with increased R to S conversion was achieved by employing diphenyl diselenide rather than iodine as the catalyst.

Reproducible and expedient artificial light conditions, avoiding insolation (sunlight), are reported.

Diphenyl diselenide tolerated the presence of Hünig's base upon stereoisomerization of acid-sensitive carotenoids.

Diphenyl ditelluride effected E/Z stereomutation, but no allenic R/S isomerization of fucoxanthin.

The presence of base decreased the isomerization rate in the absence of catalyst and may serve to decrease undesirable E/Z stereoisomerization of base-stable carotenoids.

Iodine has extensively and exclusively been used as a specific catalyst for promoting photoinduced E/Z stereomutation of carotenoids.[1–3] Isomerization of sterically unhindered double bonds (i.e., at C-9, C-13 and C-15; Scheme 1) takes place, and the same quasi-equilibrium mixture of geometrical isomers is obtained independent of the initial isomer.[1,4,5] More recently it has been demonstrated that iodine also promotes R/S photoisomerization of carotenoids containing a trisubstituted allenic bond.[6–8]

In the seventies Barton and co-workers employed diphenyl diselenide in combination with light to effect isomerization of the central double bond of the triene system of ergocalciferol, and suggested that the procedure may be applicable to polyenes.[9]

In the present paper we demonstrate the application of diphenyl diselenide as a new, base-tolerant catalyst for E/Z isomerization of carotenoids in a comparative study employing iodine or no catalyst as the reference, under standardized artificial light conditions avoiding irreproducible insolation (sunlight). Moreover, increased R to S allenic conversion has been achieved.

Results and discussion

Geometrical isomerization. As test carotenoids were selected the common carotenoid diol zeaxanthin (1), the

acid-sensitive diepoxide violaxanthin (2) and the conjugated dione canthaxanthin (3), Scheme 1.

The addition of base may, in principle, prevent artifact formation with acid-sensitive carotenoids during the isomerization. Since iodine (I_2) was found not to be compatible with Hünig's base, cf. Ref. 10, the effect of base is reported only for stereomutation experiments in the presence of diphenyl diselenide (Ph_2Se_2) or in the absence of catalyst.

The different scalar irradiances employed in the photoisomerization experiments are referred to as low light intensity (500–800 $\mu E\,m^{-2}\,s^{-1}$), medium light intensity ($\approx 1600\ \mu E\,m^{-2}\,s^{-1}$) and high light intensity (≈ 3100 $\mu E\,m^{-2}\,s^{-1}$), cf. summer sunlight $\approx 2500\ \mu E\,m^{-2}\,s^{-1}$ in the VIS region.

Zeaxanthin (1). Synthetic $(3R,3'R)$-zeaxanthin (1)[11] in benzene solution was submitted to stereoisomerization in artificial light without catalyst, with 2% I_2, 20% I_2, 2% Ph_2Se_2 or 20% Ph_2Se_2. The stereoisomerization was monitored by HPLC. Pigment recoveries were determined by VIS spectroscopy. The effect of base (Hünig's base, N-ethyldiisopropylamine, ≈ 1 vol%) was tested in the absence of catalyst and with 2% Ph_2Se_2. Reproducible results were obtained. Data are compiled in Table 1.

The results demonstrated that the medium light intens-

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Zeaxanthin (1)

Violaxanthin (2)

Canthaxanthin (3)
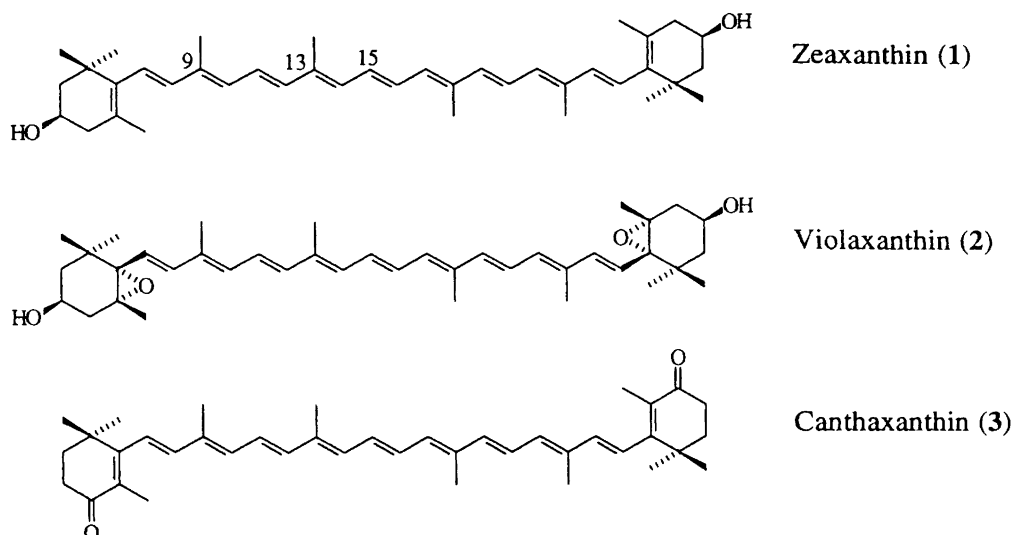
Scheme 1.

Table 1. Reaction conditions and results of seven stereomutation experiments with all-E-zeaxanthin (1, 50 μg) in benzene solution (40 μg ml^{-1}) at light intensity 1660 μE m^{-2} s^{-1}.

Base[a]	Catalyst	t/h	Recovery (%)	Geometrical isomer						
				di-Z	di-Z	di-Z	all-E	9Z	13Z	15Z
−	−	4	97	1	1	Trace	77	13	7	1
+	−	4	98	−	−	−	90	5	5	1
−	2% I$_2$	4	92	1	3	2	62	24	6	1
−	20% I$_2$[b]	4	80	3	4	3	56	21	10	2
−	2% Ph$_2$Se$_2$	4	85	3	4	3	53	21	14	2
+	2% Ph$_2$Se$_2$	4	89	3	4	4	52	21	14	2
−	20% Ph$_2$Se$_2$	4	82	3	4	3	55	20	14	1

[a] N-Ethyldiisopropylamine, 1 vol%. [b] Irreversible by-product formation observed.

ity conditions were expedient. Whereas the rate of isomerization was considerably lower in the absence of catalyst, photostationary quasi-equilibrium mixtures were obtained with 2% Ph$_2$Se$_2$ within 3 h and with 20% Ph$_2$Se$_2$ within 1 h with >82% pigment recovery. In comparison 20% I$_2$ caused artifact formation, whereas 2% I$_2$ caused quasi-equilibrium after 1 h with >92% pigment recovery. The presence of base reduced the isomerization rate in the absence of catalyst, but had no significant effect in the presence of 2% Ph$_2$Se$_2$.

Z-Isomers of zeaxanthin (1) have previously been identified and complete ^{1}H NMR assignments published.[12] The mono-Z-isomers (Tables 1 and 7) were here identified from λ_{max} shifts relative to the all-E-isomer (3–5 nm)[1,12] and increasing *cis*-peak (%D_B/D_{II})[13] intensities for Δ9, Δ13 and Δ15 Z-configurations respectively.[1,12]

Violaxanthin (2). HPLC-pure all-E-violaxanthin (2) was isolated from spinach[14] and characterized by VIS, MS and ^{1}H NMR data.

Stereomutation experiments were carried out in winter sunlight (63°N) and under weak or medium intensity artificial light conditions, in the absence of or with 5%

Ph$_2$Se$_2$ or 5% I$_2$ as the catalyst, without or in the presence of base. The results are compiled in Table 2.

Again medium intensity artificial light conditions appeared to be adequate for reaching quasi-equilibrium (with 5% Ph$_2$Se$_2$). The rate of stereomutation was considerably lower in the absence of a catalyst. In these experiments 5% Ph$_2$Se$_2$ caused more extensive stereomutation than 5% I$_2$ but with comparable pigment recoveries. The presence of base reduced the rate of isomerization. Quasi-equilibrium composition appeared to be obtained with Ph$_2$Se$_2$ at medium light intensity. Mono-Z-isomers (Table 2 and 8) were identified by the same criteria as for zeaxanthin (1) above. The di-Z-isomers (Tables 2 and 8) had VIS properties compatible with the reported[15] 9,9'-di-Z- (%D_B/D_{II}=2) and 9,13(13')-di-Z- (%D_B/D_{II}=20) isomers.

Canthaxanthin (3). Synthetic canthaxanthin (3)[16] was available. Stereomutation experiments were performed only under medium light conditions, without catalyst or in the presence of 2% Ph$_2$Se$_2$, 20% Ph$_2$Se$_2$, 2% I$_2$ or 20% I$_2$, without or in the presence of base. The results are presented in Table 3.

Table 2. Reaction conditions and results of nine stereomutation experiments with all-*E*-violaxanthin (**2**)[a] in benzene solution (40 μg ml⁻¹) at different light intensities.

Base[b]	Catalyst	Light source	Light intensity /μE m⁻² s⁻¹	t/h	Recovery (%)	Geometrical isomer					
						di-Z	di-Z	all-E	9Z	13Z	Fur[c]
+	5% Ph₂Se₂	Sun 26.11.96	430	3	—	Trace	1	69	11	16	3
—	—	300W	910	3	—	—	2	89	2	7	2
		500W	1660	+27	79	1	2	74	16	6	3
—	5% I₂	300W	910	3	—	—	—	88	4	6	2
		500W	1660	+27	82	1	2	64	25	6	3
—	5% Ph₂Se₂	300W	910	3	—	—	Trace	74	7	16	3
		500W	1660	+27	82	3	2	56	27	9	4
+	5% Ph₂Se₂	300W	910	3	—	—	Trace	80	6	12	2
		500W	1660	+27	75	1	1	67	23	6	1

[a] 45–60 μg of **2** were used. [b] *N*-Ethyldiisopropylamine, 1 vol%. [c] Fur, Furanoid.

Table 3. Reaction conditions and results for seven stereomutation experiments with all-*E*-canthaxanthin (**3**)[a] in benzene solution (40 μg ml⁻¹) at 1660 μE m⁻² s⁻¹ light intensity.

Base[b]	Catalyst	t/h	Recovery (%)	Geometrical isomer						
				di-Z	di-Z	di-Z	all-E	9Z	13Z	15Z
—	—	4	92	Trace	1	1	83	7	7	1
+	—	4	96	—	—	—	96	2	3	—
—	2% I₂	1	87[c]	1	2	4	59	17	14	2
—	20% I₂	1	57[d]	1	2	4	60	17	14	1
—	2% Ph₂Se₂	4	81	1	2	4	62	15	13	2
+	2% Ph₂Se₂	4	95	1	2	5	60	16	14	2
—	20% Ph₂Se₂	4	83	1	3	7	59	17	14	2

[a] 34–52 μg of **3** were used. [b] *N*-Ethyldiisopropylamine, 1 vol%. [c] After 9.5 h. [d] After 8 h.

(6'*R*)-Fucoxanthin (**4**)

(6'*S*)-Fucoxanthin (**5**)
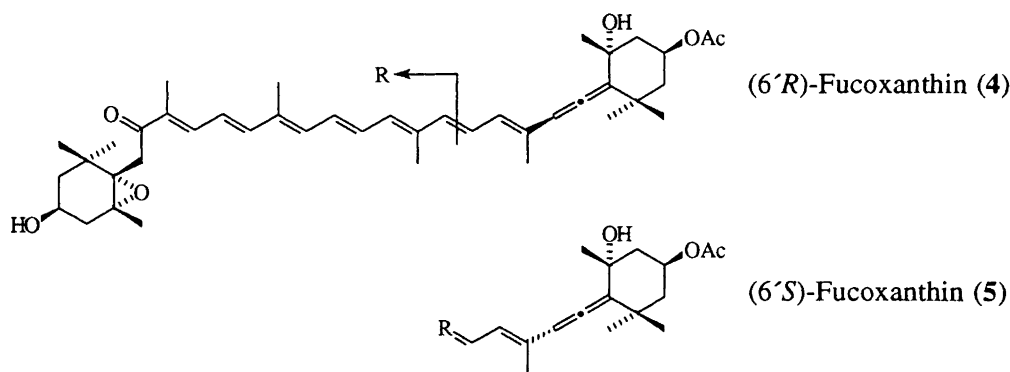
Scheme 2.

Artificial medium light conditions were reproducible and sufficient. Again a lower isomerization rate was observed in the absence of a catalyst. However, similar quasi-equilibrium mixtures were obtained under medium light conditions with 2% Ph₂Se₂, 20% Ph₂Se₂, 2% I₂ or 20% I₂ after 4 h, with pigment recoveries >81%, except for 20% I₂ with 63% recovery. The presence of base decreased the isomerization rate in the absence of catalyst.

Z-Isomers of canthaxanthin (**3**), obtained by heating crystals, have been characterized by ¹H NMR spectroscopy,[17] cf. also Ref. 18. Mono-Z-isomers (Tables 3 and 9) were identified by the same criteria as for zeaxanthin

(1) above. The minor di-Z-isomers obtained here most likely represent the 9,9'-di-Z-, 9,13-di-Z- and 13,13'-di-Z-isomers.

R/S Allenic isomerization. The allenic acid[19]- and base[20]-labile carotenoid fucoxanthin (**4**), isolated from brown seaweeds,[21] was chosen for a study of (6'*R*)→(6'*S*) allenic isomerization, Scheme 2.

Fucoxanthin (**4**) was characterized by HPLC, VIS, MS and ¹H NMR data. Geometrical isomers belonging to the allenic (6'*R*)-(**4**) and (6'*S*)-(**5**) series have previously been fully characterized.[8,22]

Several stereoisomerization experiments varying dif-

ferent parameters were carried out. Under milder conditions (combination of catalyst and light intensity) E/Z geometrical isomerization (Table 4) could be obtained as a separate process without allenic isomerization as previously observed for I_2-catalyzed stereomutation.[8,22] Results for 2% Ph_2Se_2 under medium and strong light conditions in comparison with data for 2% I_2 at low light intensity are compiled in Table 4. Similar quasi-equilibrium mixtures were obtained. In darkness 100% Ph_2Se_2 caused only geometrical isomerization.

Experiments resulting in E/Z as well as allenic R/S isomerization are presented in Tables 5 and 6. The all-E-(6'R) (4):all-E-(6'S) (5) ratio is here employed as a measure for (6'R)→(6'S) allenic isomerization. The corresponding HPLC peaks are well separated and exhibit the same λ_{max}. The distribution of E/Z-isomers within the (6'R)- and (6'S)-series is not included in Tables 5 and 6.

The results demonstrated that allenic R/S isomerization, previously achieved for 4 in sunshine,[8] could be effected in artificial light. This process required the

presence of Ph_2Se_2 or I_2, preferably at $\geqslant$20% concentration at high light intensity.

Indeed Ph_2Se_2 represents an alternative to I_2 as a catalyst. The somewhat lower reaeaction rate for Ph_2Se_2 could be compensated by increasing the catalyst concentration. The quasi-equilibrium reached with Ph_2Se_2 as the catalyst differed from that obtained with I_2, in containing increased amounts of the (6'S) isomers, up to 75% of total fucoxanthin (4+5).

Diphenyl ditelluride (100%) was tested as an alternative catalyst for allenic isomerization of fucoxanthin (4) at high light intensity. HPLC analysis revealed that no allenic R/S isomerization had occurred during 8 h, but a quasi-equilibrium (cf. Table 4) of E/Z-isomers was reached.

General discussion/conclusions

The availability of efficient and relatively fast HPLC separations for monitoring the isomerization reactions was essential.

Table 4. Geometrical isomerization observed for all-E-fucoxanthin (4)[a] in benzene solution (40 µg ml⁻¹) in eight experiments at different conditions, not resulting in allenic (6'R) to (6'S) isomerization.

Catalyst	Light intensity /µE m⁻² s⁻¹	t/h	Recovery (%)	(6'R) Geometrical isomers					
				13,9'-di-Z	9',13'-di-Z +13,13'-di-Z	all-E	13Z	13'Z	9'Z
—	3150[b]	11	100	1	2	68	5	7	17
2% Ph_2Se_2	Sun 16.09.96	2.5	78	2	4	60	9	10	16
2% I_2	500[b]	11	84	2	5	56	10	10	15
2% Ph_2Se_2	1660[b]	11	100	1	3	64	6	9	17
2% Ph_2Se_2	3150[b]	11	78	2	5	58	9	11	16
10% Ph_2Se_2	500[b]	12	84	2	4	60	7	10	17
100% Ph_2Se_2	Darkness	2400	82	Trace	1	78	6	10	5
100% Ph_2Te_2	3150[b]	8	78	2	3	64	5	7	18

[a] 0.09-0.36 mg of 4 was used. [b] By use of a 1000 W halogen lamp.

Table 5. Reaction conditions and results for six isomerization experiments with all-E-(6'R)-fucoxanthin (4)[a] in sunlight or artificial light resulting in geometrical (E/Z) as well as allenic (6'R to 6'S) isomerization, employing iodine as catalyst.

I_2 (%)	Light intensity /µE m⁻² s⁻¹	t/h	Recovery (%)	all-E-(6'R):all-E-(6'S)
2	Sun 12.09.96	2.5	73	85:15
20	Sun 12.09.96	2.5	72	59:41
2	1660[b]	1	—	91: 9
		3	—	69:13
		5	—	57:43
		8	—	54:46
		11	84	53:47
20	3150[b]	1	—	82:18
		3	—	65:35
		5	—	56:44
		8	—	52:48
		11	91	52:48
100	500[b]	1	59[c]	58:42
100	3150[b]	1	—	Decomp.

[a] 0.09-0.44 mg of 4 was used. [b] By use of a 1000 W halogen lamp. [c] After 8 h.

Table 6. Reaction conditions and results from four isomerization experiments with all-*E*-(6'*R*)-fucoxanthin (**4**)[a] in sunlight or artificial light resulting in geometrical (*E/Z*) as well as allenic (6'*R* to 6'*S*) isomerization, employing diphenyl diselenide as catalyst.

Ph_2Se_2 (%)	Light intensity /$\mu E\ m^{-2}\ s^{-1}$	*t*/h	Recovery (%)	all-*E*-(6'*R*) : all-*E*-(6'*S*)
20	Sun 16.09.96	2.5	—	70:30
		4.5	52	53:47
20	3150[b]	15	63	70:30
100	500[b]	10	76	84:16
100	3150[b]	1	—	97: 3
		3	—	84:16
		5	—	59:41
		6	—	50:50
		7	—	43:57
		10	—	32:68
		13	—	25:75
		15	27	25:75

[a] 0.10–0.28 mg of **4** was used. [b] By use of a 1000 W halogen lamp.

Table 7. Characterization of individual geometrical isomers of zeaxanthin (**1**) by HPLC (system 1,[12] Spherisorb S5W, eluent hexane–dichloromethane–isopropyl alcohol–*N*-ethyldiisopropylamine 90.9:6.5:2.5:0.1) and VIS properties.

t_R/min	λ_{max}/nm in HPLC-eluent	%III/II[13]	%D_B/D_{II}[13]	Isomer
15.9	340, (420), 439, 466	30	19	di-*Z*
16.6	340, (420), 439, 466	28	8	di-*Z*
17.9	340, (420), 438, 465	28	14	di-*Z*
18.8	(430), 450, 478	38	—	all-*E*
34.1	340, (424), 445, 475	38	6	9*Z*
39.8	340, (422), 442, 470	22	43	13*Z*
42.4	340, (425), 445, 475	25	58	15*Z*

Table 8. Characterization of individual geometrical isomers of violaxanthin (**2**) by HPLC (system 3, Techsphere 5CN, eluent hexane–dichloromethane–methanol 75:23.5:1.5) and VIS properties.

t_R/min	λ_{max}/nm in HPLC-eluent	%III/II[13]	%D_B/D_{II}[13]	Isomer
7.0	331, 411, 434, 463	85	2	9,9'-di-*Z*
7.1	331, 410, 433, 461	72	20	9,13(13')-di-*Z*
7.4	329, 404, 426, 454	72	5	Monofuranoid
7.8	419, 444, 473	93	—	all-*E*
9.2	330, 415, 439, 469	91	5	9*Z*
10.4	331, 413, 437, 466	77	44	13*Z*

Table 9. Characterization of individual geometrical isomers of canthaxanthin (**3**) by HPLC (system 4,[26] Techsphere 5 Sil, eluent benzene–hexane–acetone 94:5:1) and VIS properties.

t_R/min	λ_{max}/nm in HPLC-eluent	%D_B/D_{II}[13]	Isomer
7.2	(368), 468	<1	di-*Z*
7.8	368, 466	5	di-*Z*
8.6	368, 467	5	di-*Z*
9.4	483	—	all-*E*
13.5	368, 474	10	9*Z*
16.9	368, 472	32	13*Z*
18.2	368, 472	50	15*Z*

Pigment yields were estimated at the end of each experiment using the same $E_{1cm}^{1\%}$ value at λ_{max} as for the all-*E*-isomer. This represents minimum yields since

Z-isomers generally have lower, but unknown, $E_{1cm}^{1\%}$. However, because the all-*E*-isomers represented as much as 60–70% of the quasi-equilibrium mixtures, the error is reduced. Pigment recoveries decreased on increased exposure time and with high (20%) iodine concentrations. The Ph_2Se_2 concentrations (2%, 5%, 20%, 100%) did not systematically reduce the recovered carotenoid (generally >75%).

This investigation demonstrated that Ph_2Se_2 is an alternative mediator for photochemical stereomutation of common carotenoids such as zeaxanthin (**1**), violaxanthin (**2**) and canthaxanthin (**3**). As for I_2, allenic *R/S* isomerization can be achieved, but with higher *R→S* conversion.

The presence of Hünig's base is compatible with Ph_2Se_2-mediated stereomutation and is recommended

for acid-labile carotenoids, including epoxides.[23] Furthermore, base was found to reduce the rate of stereoisomerization in the absence of catalyst and might serve to prevent undesirable isomerization of base-stable carotenoids.

Irreproducible insolation conditions can be replaced by reproducible artificial light for Ph_2Se_2- as well as for I_2-catalyzed E/Z stereomutations and for R to S isomerization of the allenic bond.

Experimental

Carotenoid substrates. All-E-($3R,3'R$)-zeaxanthin (**1**) of synthetic origin[11] was purified by TLC (silica, 40% acetone in heptane). HPLC (system 1) revealed a purity of >98%, VIS λ_{max} (benzene): (437), 461, 490 nm, %III/II[13] = 26; MS (210 °C) and ^{1}H NMR ($CDCl_3$, 400 MHz) were consistent with published data.[11,12]

All-E-($3S,5R,6S,3'S,5'R,6'S$)-violaxanthin (**2**) was isolated from spinach (*Spinacia oleracea*)[14] by extraction (7:3 acetone–methanol containing 0.1% N-ethyldiisopropylamine), saponification (5% KOH in methanol–ether), TLC on alkaline plates[24] and preparative HPLC (system 2). Analytical HPLC (system 3) revealed a purity of >98%. VIS λ_{max} (benzene): 419, 443, 474 nm, %II/II = 94; MS [210 °C; m/z (rel. int.)]: 600 (M, 81), 598 ($M-2$, 25), 584 ($M-16$, 10), 582 ($M-18$, 8), 566 ($M-16-18$, 6), 564 ($M-18-18$, 5), 520 ($M-80$, 11), 508 ($M-92$, 4), 504 ($M-16-80$, 4), 221 (100), 181 (25); ^{1}H NMR ($CDCl_3$, 400 MHz) was consistent with reported data.[25]

All-E-canthaxanthin (**3**): Synthetic all-E-canthaxanthin (**3**)[16] was employed. HPLC analysis (system 4) demonstrated the presence of 98% all-E, 1% 9Z and 1% 13Z. VIS λ_{max} (benzene) 479 nm, MS (210 °C) and ^{1}H NMR ($CDCl_3$, 400 MHz) were consistent with reported data.[17,18]

All-E-($3S,5R,6S,3'S,5'R,6'R$)-fucoxanthin (**4**) was isolated from *Fucus serratus* by extraction and chromatography (CC and TLC) according to previous procedures.[21] Analytical HPLC (system 5) demonstrated the following composition all-E (93%), 13Z (3%), 13'Z (4%) and 9'Z (trace). VIS λ_{max} (benzene) 458, (483) nm, %D_B/D_{II} = 4; MS (210 °C) and ^{1}H NMR ($CDCl_3$, 300 MHz) were consistent with reported data.[22]

Isomerization experiments. Carotenoids were stored in frozen stock solutions in *p.a.* benzene. Experiments were carried out in benzene solution in Quickfit test tubes MF 24/1/6 in 1–11 ml of solvent, carotenoid concentration 40 µg ml^{-1}. The carotenoid amount and concentration of catalyst (% by weight) is specified for each experiment. The solutions were carefully flushed with pure N_2 for 2–3 min by bubbling the gas through the solution via a capillary, and the glass stopper was sealed with tape. Experiments with artificial light were carried out in a windowless cold room (temp. 3–4 °C) with strong air circulation. The air temperature around the test tube reached 23–33 °C during prolonged irradiation experi-

ments. The distance between the light source and the test tube was adjusted to obtain the desired light intensity, generally 19–30 cm. A 300 W (Osram), a 500 W (Osram) or a 1000 W halogen lamp (Osram) was employed. When low intensity conditions were provided with a 1000 W lamp, the distance was increased to ca. 1 m. Light intensities in the visible region were measured with a QSL-100 (Biospherical Instruments Inc., USA) quantum meter with a spherical sensor.

Some isomerization experiments were carried out outdoors in sunlight (63°N, date specified). The intensity of sunlight was recorded as 2500 µE m^{-2} s^{-1} in June–August, 2000 µE m^{-2} s^{-1} in October and 430 µE m^{-2} s^{-1} in November.

Analysis. Samples (20 µl) were withdrawn with a syringe and immediately analyzed by use of a Hewlett Packard instrument equipped with a quaternary pump (type 1050) and a diode array detector (type 1040A or 1050) with simultanous recording of VIS spectra of each stereoisomer. The HPLC systems used were for zeaxanthin (**1**): system 1, t_R = 15–43 min; violaxanthin (**2**): system 3, t_R = 6–12 min, canthaxanthin (**3**): system 4, t_R = 7–19 min, and fucoxanthin (**4**+**5**): system 5, t_R = 20–50 min. The HPLC systems are specified as follows: system 1:[12] Spherisorb S5W (4.6 × 250 mm) column, eluent hexane–dichloromethane–isopropyl alcohol–N-ethyldiisopropyl amine (90.9:6.5:2.5:0.1), flow 1.5 ml min^{-1}, detection wavelength 450 nm. System 2: Techsphere 5CN (10 × 250 mm) column, eluent hexane–dichloromethane–methanol (75:23.5:1.5), flow 3 ml min^{-1}, detection wavelength 445 nm. System 3: Techsphere 5CN (4.6 × 250 mm) column, eluent as for system 2, flow 1.5 ml min^{-1}, detection wavelength 445 nm. System 4:[26] Techsphere 5 Sil (4.6 × 250 mm) column, eluent benzene–hexane–acetone (94:5:1), flow 1.5 ml min^{-1}, detection wavelength 480 nm. System 5:[22] column as in system 4, eluent hexane–isopropyl acetate–isopropyl alcohol–N-ethyldiisopropylamine (83.9:14:2:0.1), flow 1.5 ml min^{-1}, detection wavelength 445 nm.

Retention times and VIS data (λ_{max}, %D_B/D_{II}[13] and %III/II[13]) for individual stereoisomers of zeaxanthin (**1**), violaxanthin (**2**) and canthaxanthin (**3**) are listed in Tables 7, 8 and 9. For the identification of geometrical isomers of the (6'R)- and (6'S)-series of fucoxanthin (**4**), see Refs. 8 and 22.

Pigment recoveries were estimated at the end of each experiment by VIS spectroscopy using the same $E_{1cm}^{1\%}$ value at λ_{max} as for the all-E-isomer.

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