Preparation and (*E*/*Z*)-Isomerization of the Diastereoisomers of Violaxanthin

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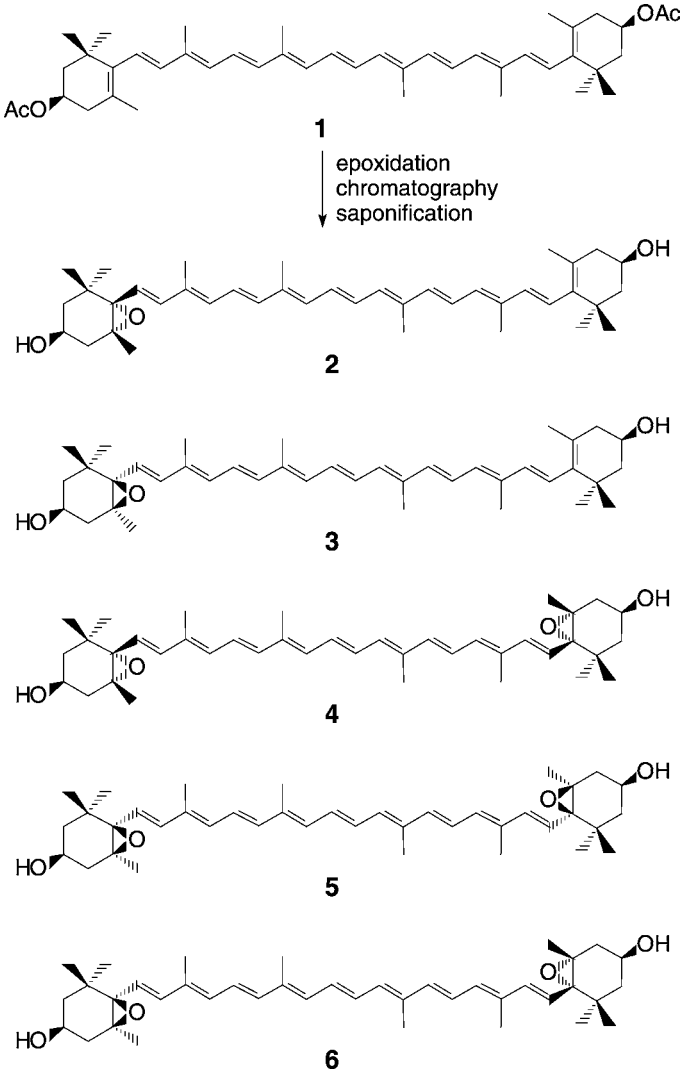
Violaxanthin A (=(all-*E*,3*S*,5*S*,6*R*,3′*S*,5′*S*,6′*R*)-5,6 : 5′,6′-diepoxy-5,6,5′,6′-tetrahydro-*β*,*β*-carotene-3,3′-diol = *syn*,*syn*-violaxanthin; **5**) and violaxanthin B (=(all-*E*,3*S*,5*S*,6*R*,3′*S*,5′*R*,6′*S*)-5,6 : 5′,6′-diepoxy-5,6,5′,6′-tetrahydro-*β*,*β*-carotene-3,3′-diol = *syn*,*anti*-violaxanthin; **6**) were prepared by epoxidation of zeaxanthin diacetate (**1**) with monoperphthalic acid. Violaxanthins **5** and **6** were submitted to thermal isomerization and I_2-catalyzed photoisomerization. The structure of the main products, *i.e.*, (9*Z*)-**5**, (13*Z*)-**5**, (9*Z*)-**6**, (9′*Z*)-**6**, (13*Z*)-**6**, and (13′*Z*)-**6**, was determined by their UV/VIS, CD, ^{1}H-NMR, ^{13}C-NMR, and mass spectra.

Introduction. – According to the classical experiments of *Karrer*'s school [1], epoxidation of zeaxanthin diacetate (=(all-*E*,3*R*,3′*R*)-*β*,*β*-carotene-3,3′-diol diacetate; **1**) with monoperphthalic acid yielded antheraxanthin A (=(all-*E*,3*S*,5*R*,6*S*,3′*R*)-5,6-epoxy-5,6-dihydro-*β*,*β*-carotene-3,3′-diol = *anti*-antheraxanthin = natural antheraxanthin; **2**), antheraxanthin B (=(all-*E*,3*S*,5*S*,6*R*,3′*R*)-5,6-epoxy-5,6-dihydro-*β*,*β*-carotene-3,3′-diol = *syn*-antheraxanthin = semisynthetic antheraxanthin; **3**), violaxanthin (=(all-*E*,3*S*,5*R*,6*S*,3′*S*,5′*R*,6′*S*)-5,6 : 5′,6′-diepoxy-5,6,5′,6′-tetrahydro-*β*,*β*-carotene-3,3′-diol = *anti*,*anti*-violaxanthin = natural violaxanthin; **4**), violaxanthin A (=(all-*E*,3*S*,5*S*,6*R*,3′*S*,5′*S*,6′*R*)-5,6 : 5′,6′-diepoxy-5,6,5′,6′-tetrahydro-*β*,*β*-carotene-3,3′-diol = *syn*,*syn*-violaxanthin = semisynthetic violaxanthin; **5**), and violaxanthin B (=(all-*E*,3*S*,5*S*,6*R*,3′*S*,5′*R*,6′*S*)-5,6 : 5′,6′-diepoxy-5,6,5′,6′-tetrahydro-*β*,*β*-carotene-3,3′-diol = *syn*,*anti*-violaxanthin = mesoviolaxanthin = semisynthetic violaxanthin; **6**) (*Scheme*)[1]). In our experiment and in agreement with the results of *Karrer*'s school, the naturally occurring antheraxanthin (**2**) and violaxanthin (**4**) were formed only as minor products. In other epoxidation experiments with different monoperoxy acids the exclusive formation of semisynthetic violaxanthins **5** and **6** was observed [2][3]. During our systematic research concerning the (*E*/*Z*)-isomerization of the polyene chain, the thermal isomerization and the I_2-catalyzed photoisomerization [4] of the natural *anti*,*anti*-violaxanthin (**4**) was investigated earlier. The (9*Z*)-, (13*Z*)-, and (15*Z*)-isomers of **4** were prepared by stereomutation and were isolated from the blossoms of *Viola tricolor* [5–7]. As part of a systematic investigation of the isolation, preparation, identification, and stereomutation of carotenoids [6–9], we now report the preparation

[1]) *syn*/*anti* refers to the position of the OH and epoxy group with respect to the mean ring plane of the *β*-end group.

Scheme



and structure elucidation of the isomerization products of semisynthetic violaxanthins **5** and **6**. Our previous experiments concerning the thermal isomerization and I_2-catalyzed photoisomerization of semisynthetic violaxanthins **5** and **6** on a semimicro scale confirmed that the end groups with different configuration influenced the composition of the stereoisomer equilibrium mixtures only slightly [8][9].

Results. – *Epoxidation*. The epoxidation of 800 mg of zeaxanthin diacetate (**1**) with monoperphthalic acid (Et_2O, room temperature, 40 h) gave, in agreement with the classical results of *Karrer*'s school [1], two diastereoisomeric antheraxanthins **2** and **3** and three diastereoisomeric violaxanthins **4**–**6** (for HPLC separation, see *Fig. 1*). The

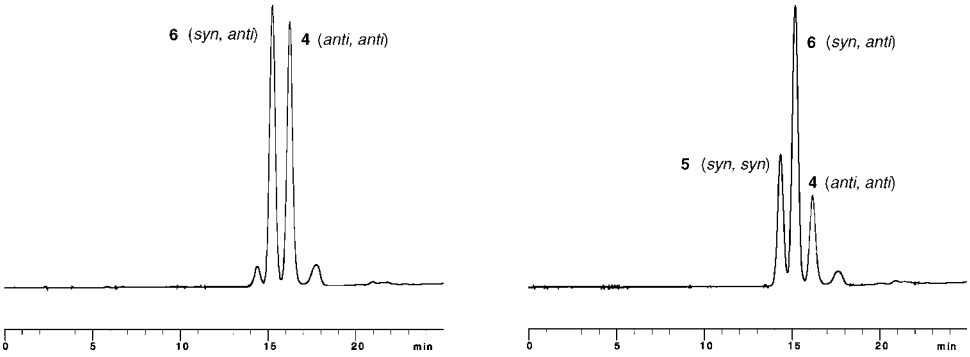


Fig. 1. *HPLC Separation of semisynthetic diastereoisomeric violaxanthins* **4**–**6**

separation of carotenoid esters was carried out by preparative column chromatography (CC; see *Exper. Part*). After saponification, the corresponding carotenoids were crystallized from benzene/hexane 1:5 to give 15 mg of **2**, 60 mg of **3**, 10 mg of **4**, 80 mg of **5**, and 75 mg of **6**.

Thermal Isomerization. The thermal isomerization of **5** and **6** (benzene, 80°, 2 h) gave, in agreement with the pioneering studies of *Zechmeister* [4] and with our recent results [6–9], (13*Z*)-**5** and (13*Z*)- and (13′*Z*)-**6**, respectively, as main products. In addition, two (di-*Z*)-isomers of **6** were observed in small quantities. The composition of the equilibrium mixtures of **5** and **6** was determined by HPLC (*Fig. 2*,*a* and *Fig. 3*,*a*) and CC [6][8][9]. The preparative separation was achieved by CC (see *Exper. Part*), and the fractions of the corresponding isomers were crystallized from benzene/hexane 1:5 to give 18 mg of (13*Z*)-**5**, 7 mg of (13*Z*)-**6**, and 5 mg of (13′*Z*)-**6**, respectively.

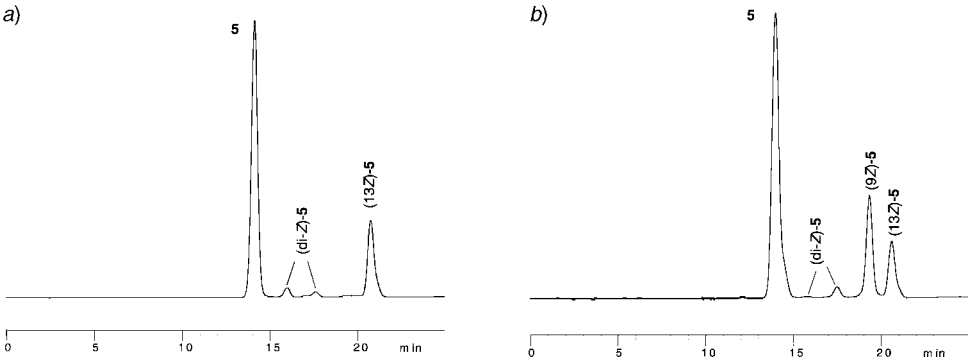
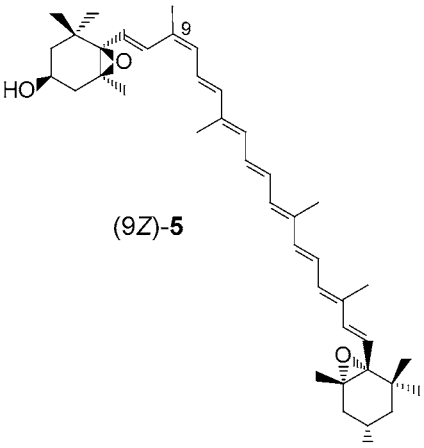
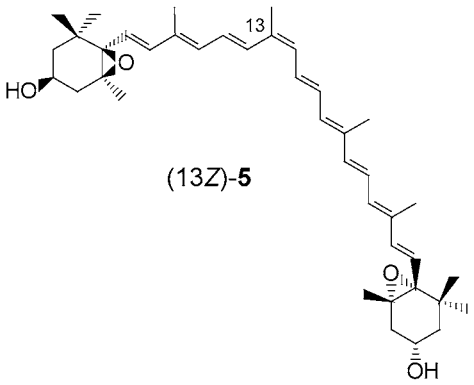


Fig. 2. *HPLC Separation of the equilibrium mixtures obtained* a) *by thermal isomerization and* b) *by* I_2*-catalyzed photoisomerization of* syn,syn-*violaxanthin* (**5**)

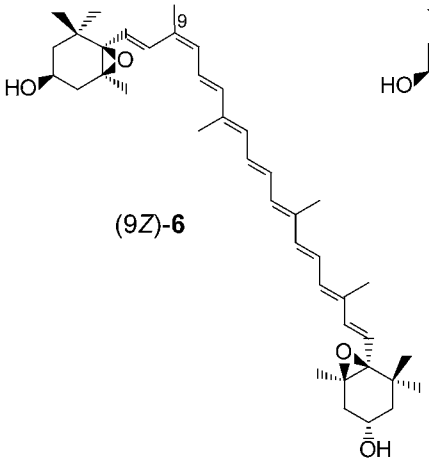
Iodine-Catalyzed Photoisomerization. In agreement with previous results for other carotenoids [4–12], the I_2-catalyzed photoisomerization of **5** (benzene, room temperature, 40 min in diffuse daylight, resulting in a thermodynamic equilibrium [12]) gave



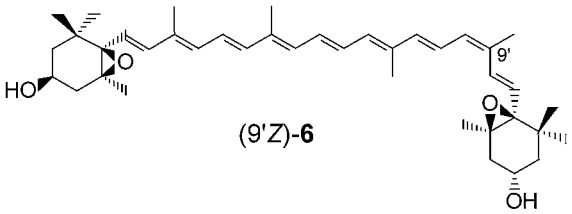
(9Z)-**5**



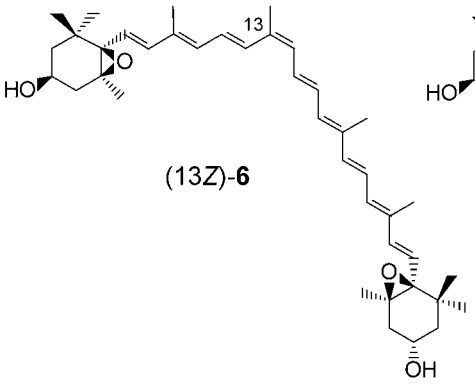
(13Z)-**5**



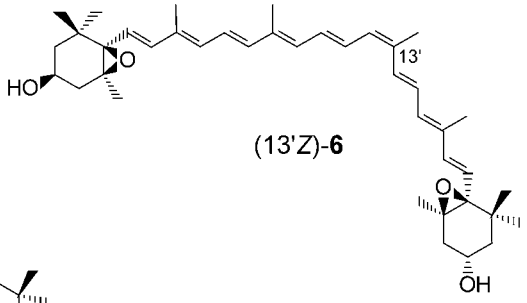
(9Z)-**6**



(9'Z)-**6**



(13Z)-**6**



(13'Z)-**6**

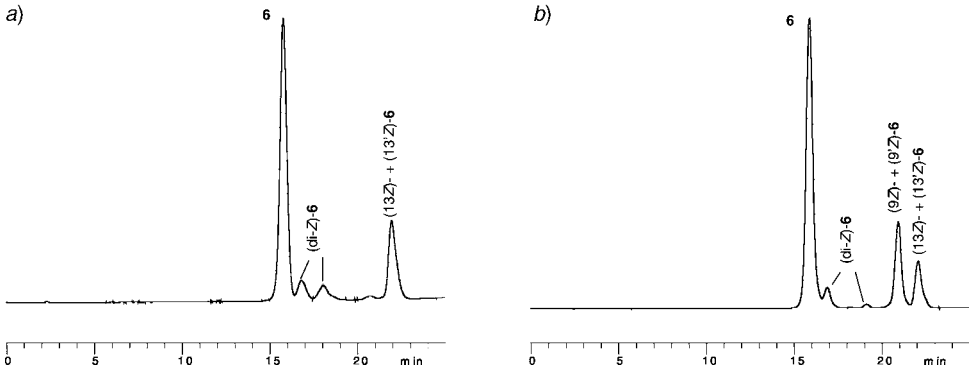


Fig. 3. *HPLC Separation of the equilibrium mixtures obtained by* a) *thermal isomerization and* b) *by I_2-catalyzed photoisomerization of* syn,anti-*violaxantin* (**6**)

(9*Z*)-**5** and (13*Z*)-**5**. In addition, the thermodynamic equilibrium mixture contained two (di-*Z*)-isomers in minor amounts (*Fig. 2,b*).

In accordance with the configurational asymmetry of semisynthetic *syn,anti*-violaxanthin (**6**), I_2-catalyzed photoisomerization of **6** gave four (mono-*Z*)-isomers, namely (9*Z*)-, (9′*Z*)-, (13*Z*)-, and (13′*Z*)-**6**. Furthermore, two additional (di-*Z*)-isomers were observed in the stereoisomer equilibrium mixture (*Fig. 3,b*), which were not identified.

The (*Z*)-isomers were separated on a preparative scale by CC (see *Exper. Part*) and then crystallized from benzene/hexane 1:5 to give 10 mg of (9*Z*)-**5**, 3 mg of (13*Z*)-**5**, 6 mg of (9*Z*)-**6**, 5 mg of (9′*Z*)-**6**, 2 mg of (13*Z*)-**6**, and 2 mg of (13′*Z*)-**6**.

Spectroscopic Characterization. A tentative determination of the position of the C=C bond with (*Z*)-configuration within the polyene chains was performed by the UV/VIS spectra of the isomerization products and their auroxanthin derivatives. The UV/VIS spectra of all geometrical isomers of semisynthetic violaxanthins, *i.e.*, of **5**, (9*Z*)-**5**, (13*Z*)-**5**, **6**, (9*Z*)-**6**, (9′*Z*)-**6**, (13*Z*)-**6**, and (13′*Z*)-**6**, with the main absorption maximum between 453–445 nm (in benzene) are in agreement with a nonaene chromophore. The characteristic UV/VIS data (λ_{max}, $\%A_{cis\text{-peak}}/A_{max}$ and λ_{max} after furanoid oxide reaction) are presented in *Table 1*. The occurrence of a week *cis*-peak and the small hypsochromic shift of λ_{max} ($\Delta\lambda_{max} = 5-6$ nm) is characteristic for (9*Z*)-**5**,

Table 1. *UV/VIS Spectroscopic Data of (all-*E*)- and Main (mono-*Z*)-Isomers of Semisynthetic Diastereoisomeric Violaxanthins* (**5**, (9*Z*)-**5**, (13*Z*)-**5**, **6**, (9*Z*)-**6**, (9′*Z*)-**6**, (13*Z*)-**6** and (13′*Z*)-**6**)

	λ_{max} in C_6H_6 [nm]	λ_{max} after acid treatment in C_6H_6 [nm]	$\%A_{cis\text{-peak}}/A_{max}$
5	483, 452, 427	437, 410, 387	< 5
(9*Z*)-**5**	477, 447, 423, 337, 323	435, 408, 385, 301, 289	8.73
(13*Z*)-**5**	475, 444, 419, 337, 323	434, 407, 384, 300, 288	51.55
6	483, 453, 427,	437, 410, 388	< 5
(9*Z*)-**6**	478, 448, 424, 337, 323	435, 408, 386, 302, 290	8.60
(9′*Z*)-**6**	477, 447, 423, 337, 323	436, 408, 385, 301, 289	8.76
(13*Z*)-**6**	475, 445, 420, 337, 323	434, 407, 384, 301, 289	51.02
(13′*Z*)-**6**	475, 444, 419, 337, 323	433, 406, 383, 300, 288	50.76

(9*Z*)-**6**, and (9′*Z*)-**6** (*Table 1*, *Figs. 4* and *5*) and is in agreement with geometrical isomers containing a (*Z*)-double bond in a peripheral position. (13*Z*)-**5**, (13*Z*)-**6**, and (13′*Z*)-**6** exhibit a strong *cis*-peak at *ca.* 337 and 323 nm and considerable $\Delta\lambda_{max}$-values ($\Delta\lambda_{max} = 7-8$ nm; *Table 1*, *Figs. 4* and *6*), characteristic for isomers with a (*Z*)-double bond in a more central position of the polyene chain [9][10].

The configuration of the C=C bonds of the polyene chain in **5**, (9*Z*)-**5**, (13*Z*)-**5**, **6**, (9*Z*)-**6**, (9′*Z*)-**6**, (13*Z*)-**6**, and (13′*Z*)-**6** was determined by NMR spectroscopy, applying ^{1}H-NMR, ^{1}H,^{1}H-COSY, ^{1}H,^{1}H-T-ROESY, ^{13}C-NMR, DEPT-135, and inverse HMQC techniques [13][14]. The data given in the *Exper. Part* and especially the characteristic values of ^{1}H- and ^{13}C-NMR isomerization shifts ($\Delta\delta = \delta(Z) - \delta$(all-*E*) (*Tables 2* and *3*) were identical with the corresponding data reported in [14] and confirmed the structure of the investigated (mono-*Z*)-isomers.

The CD spectrum of (all-*E*)-*syn*,*syn*-violaxanthin (**5**) is a mirror image of the CD spectrum of (all-*E*)-*anti*,*anti*-violaxanthin (**4**) [15]. The bands in the CD spectra of (9*Z*)- and (13*Z*)-*syn*,*syn*-violaxanthin at room temperature and at $-180°$ are opposite in sign to the corresponding (all-*E*)-*syn*,*syn*-violaxanthin (**5**) (*Fig. 7*). These data are in agreement with the data reported in [16–19]. The CD spectrum of (all-*E*)-*syn*,*anti*-violaxanthin (='mesoviolaxanthin'; **6**) is little meaningful and has signs exclusively with negative $\Delta\varepsilon$ values in the wavelength range of 200–550 nm (*Fig. 8*). It was established earlier that 'mesoviolaxanthin' (**6**) has no ORD spectrum [2]. The (9*Z*)-, (9′*Z*)-, (13*Z*)-, and (13′*Z*)-isomers of *syn*,*anti*-violaxanthin show weak CD bands (*Fig. 8*, note that the temperature is $-180°$!). The spectra of (9*Z*)-**6** and (9′*Z*)-**6** are opposite in sign in the wavelength range of 200–350 nm (mirror image) but they are identical in sign in the range of 350–550 nm (*Fig. 8*).

The mass spectra of all isomers showed the corresponding molecular ion peak at *m*/*z* = 600 and in addition signals at 582 $[M - H_2O]^+$, 564 $[M - 2\,H_2O]^+$, 520 $[M - 80]^+$, 508 $[M -$ toluene$]^+$, 352, 287, 274, 247 234, 221, 181, 91, 43, and 18 [2][20].

Discussion. – The thermal isomerization of (all-*E*)-*syn*,*syn*-violaxanthin (**5**) and of (all-*E*)-*syn*,*anti*-violaxanthin (**6**) gave mainly the (13*Z*)-isomer of **5** and the (13*Z*)- and (13′*Z*)-isomers of **6**, respectively. Therefore, the thermal isomerization is a suitable method for the preparation of (13*Z*)-**5**, (13*Z*)-**6**, and (13′*Z*)-**6**. The I_2-catalyzed photoisomerization of **5** and **6** resulted in complex mixtures of (*Z*)-isomers, which were demanding to separate. As main products, the (mono-*Z*)-isomers, namely the (9*Z*)-**5**, (13*Z*)-**5**, (9*Z*)-**6**, (9′*Z*)-**6**, (13*Z*)-**6**, and (13′*Z*)-**6** were prepared and characterized.

The isomer composition of the equilibrium mixtures obtained from **5** and **6** were nearly identical (*Figs. 2* and *3*), showing that configurational differences have no appreciable influence on the process of stereomutation. In addition, each individual (mono-*Z*)-isomer was reconverted into the respective parent (all-*E*)-isomer by I_2-catalysis and into the corresponding auroxanthin epimers by acid treatment [2][4–9].

The *structure* of the main products of (*E*/*Z*)-isomerization of **5** and **6** correspond to those of the products of the (*E*/*Z*)-isomerization of other carotenoids containing the 5,6-epoxy-5,6-dihydro-3-hydroxy-β-end group with the same chromophore [5–10]. Also the *compositions* of the stereoisomer equilibrium mixtures were very similar for all compounds with the 5,6-epoxy-5,6-dihydro-3-hydroxy-β-end group, independent of the structure of the second end group (β-, 3-hydroxy-β-, 3,6-epoxy-5,6-dihydro-β-, 5,6-

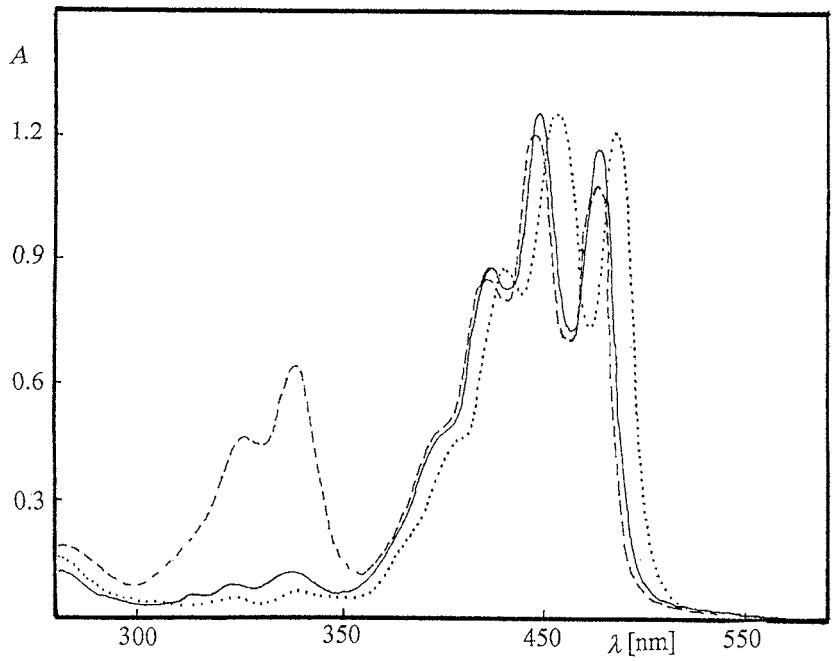


Fig. 4. *UV/VIS Spectra of (all-*E*)-*syn,syn-*violaxanthin* (**5**; ····), *(9*Z*)-*syn,syn-*violaxanthin* ((9*Z*)-**5**; —) *and (13*Z*)-*syn,syn-*violaxanthin* ((13*Z*)-**5**; – – –) *in benzene*

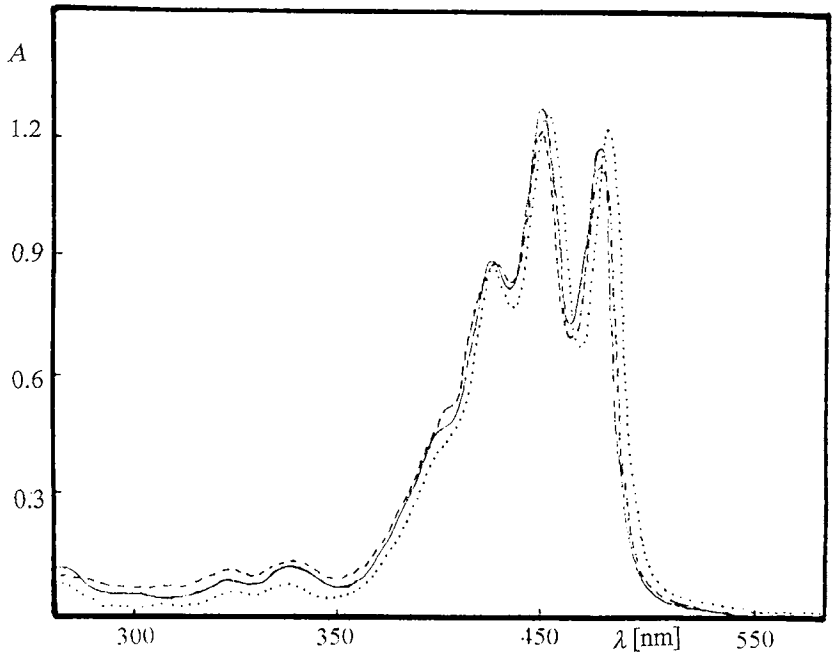


Fig. 5. *UV/VIS Spectra of (all-*E*)-*syn,anti-*violaxanthin* (**6**; ····), *(9*Z*)-*syn,anti-*violaxanthin* ((9*Z*)-**6**; —), *and (9′*Z*)-*syn,anti-*violaxanthin* ((9′*Z*)-**6**; – – –) *in benzene*

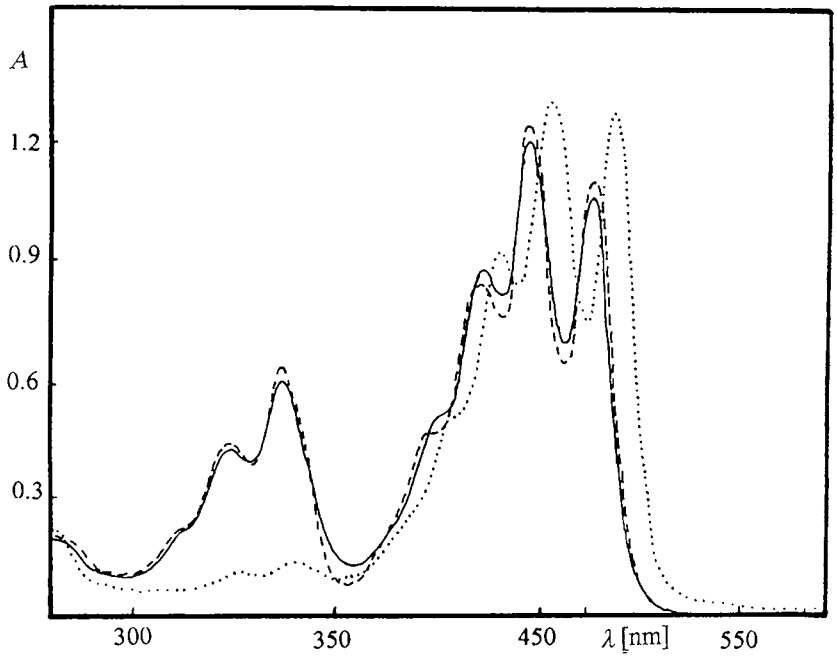


Fig. 6. *UV/VIS Spectra of (all-*E*)-*syn,anti-*violaxanthin* (**6**; ····), *(13*Z*)-*syn,anti-*violaxanthin* ((13*Z*)-**6**; —), *and (13′*Z*)-*syn,anti-*violaxanthin* ((13′*Z*)-**6**; – – –) *in benzene*

Table 2. *^{1}H- and ^{13}C-NMR Isomerization Shifts* ($\Delta\delta = \delta(Z) - \delta$(all-*E*)) *of* syn,syn-*Violaxanthin Isomers (9*Z*)-***5*** *and (13*Z*)-***5***

^{1}H-NMR isomerization shifts						^{13}C-NMR isomerization shifts		
H-atom	$\Delta\delta(^1H) = \delta(9Z) - \delta$(all-*E*)		H-atom	$\Delta\delta(^1H) = \delta(13Z) - \delta$(all-*E*)		C-atom	$\Delta\delta(^{13}C) = \delta(9Z) - \delta$(all-*E*)	
	measured	[14]		measured	[14]		measured	[14]
H–C(8)	+0.54	+0.54	H–C(10)	+0.04	+0.05	C(7)	+2.11	+1.6
H–C(10)	−1.12	−0.09	H–C(12)	+0.53	+0.52	C(8)	−7.90	−7.8
H–C(11)	+0.15	+0.10	H–C(14)	−0.14	−0.13	C(9)	−1.48	−1.4
H–C(12)	−0.08	−0.06	H–C(15)	+0.20	+0.16	C(10)	−1.47	−1.5
			H–C(15′)	−0.08	−0.08	C(11)	−1.02	−1.2
						C(12)	−0.74	−0.7
						Me(19)	+8.04	+8.0

[a]) The $\Delta\delta(^{13}C) = \delta(13Z) - \delta$(all-*E*) values could not be measured because the amount of the sample was insufficient.

dihydro-3,5,6-trihydroxy-β- and ε-end group) investigated before [5–10][21–24]. The *rate* of the (*E*/*Z*)-isomerization of **5** and **6** was in the same order as the rate of (*E*/*Z*)-isomerization of **4** and of other carotenoids containing a 5,6-dihydro-β end group [6][8][9]. The equilibrium was reached by thermal isomerization within 120 min and by I_2-catalyzed photoisomerization within 40 min [6–10].

Table 3. *^{1}H- and ^{13}C-NMR Isomerization Shifts ($\Delta\delta = \delta(Z) - \delta(all\text{-E})$) of* syn,anti-*Violaxanthin Isomers (9Z)-**6**, (9′Z)-**6**, (13Z)-**6**, and (13′Z)-**6***

^{1}H isomerization shifts												
H-atom	$\Delta\delta(^1H) = \delta(9Z) - \delta(\text{all-}E)$		H-atom	$\Delta\delta(^1H) = \delta(9'Z) - \delta(\text{all-}E)$		H-atom	$\Delta\delta(^1H) = \delta(13Z) - \delta(\text{all-}E)$		H-atom	$\Delta\delta(^1H) = \delta(13'Z) - \delta(\text{all-}E)$	
	measured	[14]		measured	[14]		measured	[14]		measured	[14]
H−C(8)	+0.54	+0.54	H−C(8′)	+0.54	+0.54	H−C(10)	+0.05	+0.05	H−C(10′)	+0.05	+0.05
H−C(10)	−0.11	−0.09	H−C(10′)	−0.1	−0.09	H−C(12′)	+0.54	+0.52	H−C(12′)	+0.52	+0.52
H−C(11)	+0.14	+0.10	H−C(11′)	+0.15	+0.10	H−C(14)	−0.13	−0.13	H−C(14′)	−0.16	−0.13
H−C(12)	−0.09	−0.06	H−C(12′)	−0.07	−0.06	H−C(15)	+0.13	+0.16	H−C(15′)	+0.16	+0.16
						H−C(15′)	−0.08	−0.08	H−C(15)	−0.08	−0.08

^{13}C-NMR isomerization shifts											
C-atom	$\Delta\delta(^{13}C) = \delta(9Z) - \delta(\text{all-}E)$		C-atom	$\Delta\delta(^{13}C) = \delta(9'Z) - \delta(\text{all-}E)$		C-atom	$\Delta\delta(^{13}C) = \delta(13Z) - \delta(\text{all-}E)$		C-atom	$\Delta\delta(^{13}C) = \delta(13'Z) - \delta(\text{all-}E)$	
	measured	[14]		measured	[14]		measured[a])	[14]		measured[a])	[14]
C(7)	+2.01	+1.6	C(7′)	+2.09	+1.6	C(11)	+0.9	+1.3			
C(8)	−7.95	−7.8	C(8′)	−8.07	−7.8	C(12)	−8.3	−8.0			
C(9)	−1.51	−1.4	C(9′)	−1.53	−1.4	C(13)	not available	−1.2			
C(10)	−1.53	−1.5	C(10′)	−1.50	−1.5	C(14)	−1.8	−1.6			
C(11)	−1.10	−1.2	C(11′)	−1.09	−1.2	C(15)	−1.9	−1.3			
C(12)	−0.82	−0.7	C(12′)	−0.79	−0.7	C(15′)	−1.2	−0.9			
C(19)	+8.00	+8.0	C(19′)	+8.00	+8.0	C(20)	+8.0	+8.0	C(20′)	+8.0	+8.0

a) These data were gained on the basis of the HMQC experiments.

It was established earlier that carotenoids with 5,6-epoxy-5,6-dihydro-β-end groups have strongly conservative CD spectra. Also, it is known that CD spectra of carotenoids in which the chromophoric portions belong to the C_2 point group conform to the so-called C_2-rule: if the overall conjugated system acquires right-handed helicity (*i.e.*, dihedral angles around bonds C(6)–C(7) and C(6′)–C(7′) are negative), then transitions of symmetry *A* lead to negative *Cotton* effects (CE), and transitions of symmetry *B* lead to positive CE [25][26]. Epoxy groups and the polyene backbone of violaxanthin form a common chromophore with C_2 symmetry due to the conjugative interaction between them. Accordingly, the C(5)–C(6) and C(5′)–C(6′) bonds can be treated as C=C bonds, whose spatial positions relative to the polyene chain will determine the overall helicity of the molecule and, consequently, the signs of the individual CD bands. The structure of (all-*E*)-*syn*,*syn*-violaxanthin (**5**) shows that its C(5)–C(6) and C(5′)–C(6′) bonds are behind the plane of the paper so the molecules has right-handed helicity. In agreement with this configuration and the C_2 rule, negative (transition symmetry *A*) and positive (transition symmetry *B*) *Cotton* bands appears in the CD spectrum centered at 328.5 and 267 nm (*Fig. 7*). Due to the restricted

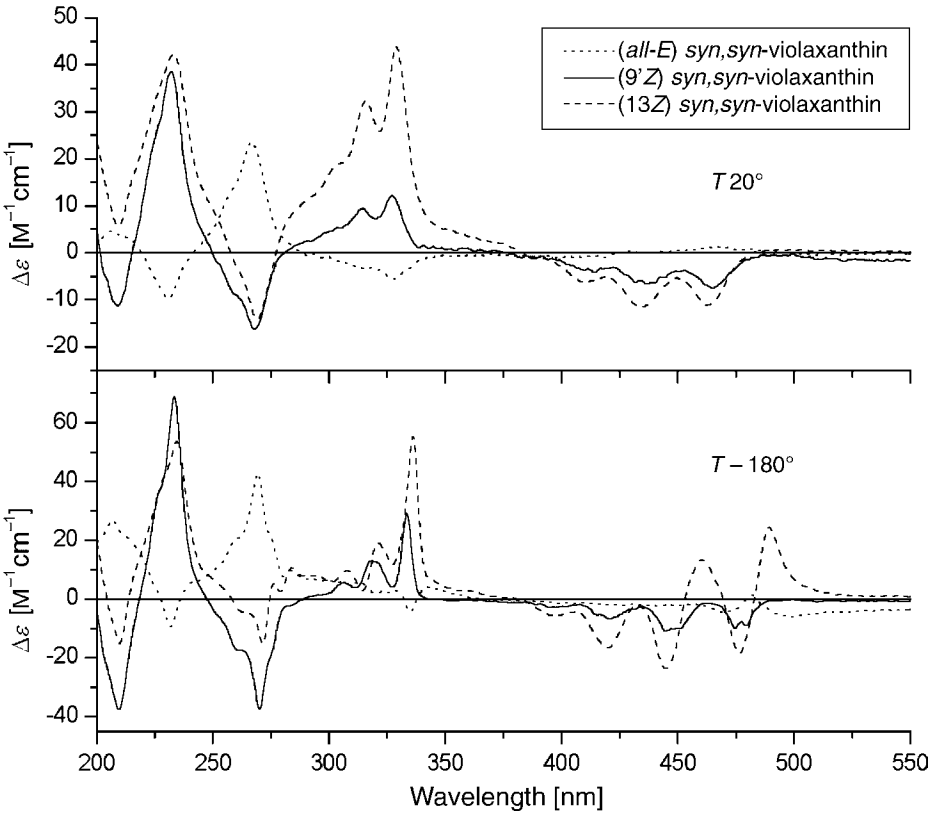


Fig. 7. *CD Spectra of (all-*E*)-, (9*Z*)-, and (13*Z*)-*syn,syn-*violaxanthins* (**5**, (9*Z*)-**5**, and (13*Z*)-**5**, resp.) *in* Et_2O/*isopentane/EtOH 5 :5 :2 at room temperature and at* $-180°$

conformational motions, CD spectra obtained at $-180°$ show more resolved vibrational fine structure, and the band maxima are shifted toward lower wavelengths. Since in the geometrical isomers of *syn*,*syn*-violaxanthin (**5**) helicity of the overall conjugated system is changed from right- to left-handed, the (9*Z*)- and (13*Z*)-isomers give mirror-image CD spectra (*Fig. 7*).

The CD curve of (all-*E*)-*syn*,*anti*-violaxanthin (='mesoviolaxanthin'; **6**) exhibits much weaker bands, even at $-180°$ (*Fig. 8*), due to the opposite chiral influences of the epoxy groups. The same holds for the (*Z*)-isomers of *syn*,*anti*-violaxanthin. The presence of the (3*S*) and (3′*S*) stereogenic centers is responsible for the weak 'residual' optical activity.

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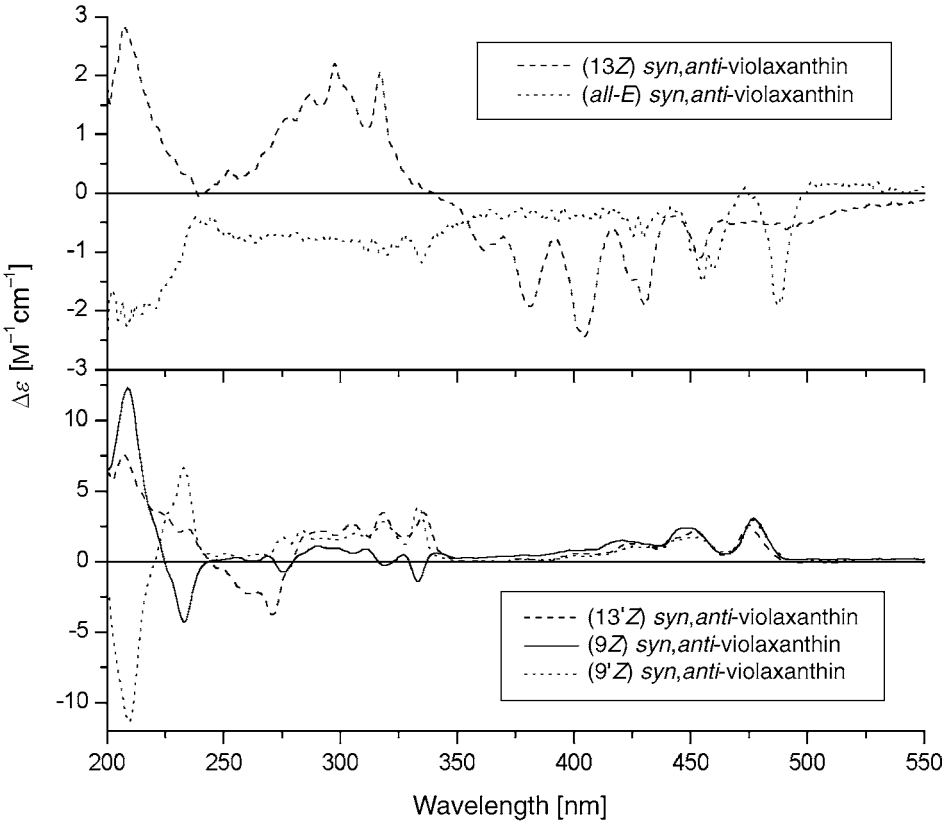

Fig. 8. *CD Spectra of (all*-E*)-, (9Z)-, (9′*Z*)-, (13*Z*)- and (13′*Z*)-*syn,anti-*violaxanthins* (**6**, (9*Z*)-**6**, (9′*Z*)-**6**, (13*Z*)-**6**, and (13′*Z*)-**6**), resp. *in* Et_2O*/isopentane/EtOH 5 : 5 : 2 at* $-180°$

Experimental Part

1. *General.* See [27]. EPA = Et_2O/isopentane/EtOH 5:2:2. Asterisks (*,**) mean that assignments may be interchanged.

2. *HPLC.* See [27].

3. *Diastereoisomeric Semisynthetic Violaxanthins* **5** *and* **6**. A soln. of 800 mg of (all-*E*)-zeaxanthin diacetate (**1**; m.p. 124°; purity (HPLC) > 95%) in 1600 ml of Et_2O (free of H_2O and peroxides) was epoxidized with 0.65N monoperphthalic acid (24 ml) at r.t. during 40 h under N_2 in the dark [1][2] (reaction monitoring by UV/VIS spectra and paper chromatography (*Whatman AH-81*, benzene)). After the usual workup [28], the mixture was separated by CC (30 columns, 6 × 30 cm; with $CaCO_3$, hexane). Picture after development: 5 mm yellow (unidentified); 10 mm of intermediate zone; 15 mm yellow (*Zone 1*; diacetate of **5**); 3 mm of intermediate zone; 20 mm yellow (*Zone 2*; diacetate of **4** and **6**); 3 mm of intermediate zone; 8 mm ochre (*Zone 3*; diacetate of **2**); 5 mm of intermediate zone; 16 mm of ochre (*Zone 4*; diacetate of **3**); 6 mm of intermediate zone; 10 mm ochre (*Zone 5*; **1**). The fraction of *Zone 2* was submitted to repeated CC (10 columns, 6 × 30 cm; $CaCO_3$, 0.5% acetone/hexane). Picture after development: 3 mm pale yellow (unidentified); 10 mm of intermediate zone; 6 mm yellow (*Zone 21*; diacetate of **4**); 3 mm of intermediate zone; 25 mm yellow (*Zone 22*; diacetate of **6**). After saponification (30% KOH/MeOH in heterogeneous phase) and the usual workup [28], the carotenoids were crystallized from benzene/hexane 1:5 to give 30 mg of **1** (m.p. 193–194°), 15 mg of **2** (m.p. 170–171°), 60 mg of **3** (m.p. 113–115°), 10 mg of **4** (m.p. 196–198°), 80 mg of **5**, and 75 mg of **6**.

4. *Violaxanthin A* (= *(all-*E*,3*S*,5*S*,6*R*,3′*S*,5′*S*,6′*R*)-5,6:5′,6′-Diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-3,3′-diol* = syn,syn-*Violaxanthin*; **5**). M.p. 190–192°. Purity (HPLC): >95%. UV/VIS (benzene): *Table 1*, *Fig. 4*. CD (EPA, r.t.): 206.5 (+4.6), 219.5 (0.0), 231.0 (−9.9), 242.0 (0.0), 267.0 (+23.7), 288.5 (0.0), 328.5 (−5.6); *Fig. 7*. CD (EPA, −180°): 207.0 (+27.0), 227.5 (+0.1), 232.0 (−9.5), 236.0 (−0.3), 269.5 (+42.9), 284.5 (+9.7), 332.0 (+0.4), 335.0 (−4.7), 338.0 (+0.3), 342.5 (+4.0), 482.0 (+1.3); *Fig. 7*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.01 (*s*, Me(16)); 1.01 (*s*, Me(16′)); 1.17 (*s*, Me(17)); 1.17 (*s*, Me(17′)); 1.19 (*s*, Me(18)); 1.19 (*s*, Me(18′)); 1.35 (*dd*, J_{gem} = 12.4, J(2eq,3) = 2.8, H_{eq}–C(2)); 1.35 (*dd*, J_{gem} = 12.4, J(2′eq,3′) = 2.8, H_{eq}–C(2′)); *ca.* 1.61 (*dd*, J_{gem} = 12.4, J(2ax,3) ≈ 4, H_{ax}–C(2)); *ca.* 1.61 (*dd*, J_{gem} = 12.4, J(2′ax,3′) ≈ 4, H_{ax}–C(2′)); 1.89 (*dd*, J_{gem} = 14.8, J(4ax,3) = 8.5, H_{ax}–C(4)); 1.89 (*dd*, J_{gem} = 14.8, J(4′ax,3′) = 8.5, H_{ax}–C(4′)); 1.92 (*s*, Me(19)); 1.92 (*s*, Me(19′)); 1.96 (*s*, Me(20)); 1.96 (*s*, Me(20′)); 2.20 (*dd*, J_{gem} = 14.8, J(4eq,3) = 6.3, H_{eq}–C(4)); 2.20 (*dd*, J_{gem} = 14.8, J(4′eq,3′) = 6.3, H_{eq}–C(4′)); 3.87 (*m*, H–C(3)); 3.87 (*m*, H–C(3′)); 5.82 (*d*, J(7,8) = 15.6, H–C(7)), 5.82 (*d*, J(7′,8′) = 15.6, H–C(7′)); 6.20 (*d*, J(10,11) = 11.4, H–C(10)), 6.20 (*d*, J(10′,11′) = 11.4, H–C(10′)); 6.26 (H–C(14)); 6.26 (H–C(14′)); 6.30 (*d*, J(8,7) = 15.6, H–C(8)); 6.30 (*d*, J(8′,7′) = 15.6, H–C(8′)); 6.37 (*d*, J(12,11) = 14.9, H–C(12)); 6.37 (*d*, J(12′,11′) = 14.9, H–C(12′)); 6.60 (*dd*, J(11,10) = 11.4, J(11,12) = 14.9, H–C(11)); 6.60 (*dd*, J(11′,10′) = 11.4, J(11′,12′) = 14.9, H–C(11′)); 6.64 (H–C(15)); 6.64 (H–C(15′)). ^{13}C-NMR (100 MHz, $CDCl_3$): 12.74 (C(20,20′)); 12.91 (C(19,19′)); 21.18 (C(18,18′)); 26.03 (C(17,17′)), 26.81 (C(16,16′)); 35.03 (C(1,1′)); 39.17 (C(4,4′)); 43.74 (C(2,2′)); 64.04 (C(3,3′)); 65.23 (C(5,5′)); 71.27 (C(6,6′)); 122.45 (C(7,7′)); 124.01 (C(11,11′)); 130.16 (C(15,15′)); 132.38 (C(10,10′)); 132.87 (C(14,14′); 134.10 (C(9,9′)); 136.39 (C(13,13′)); 138.07 (C(8,8′)); 138.24 (C(12,12′)). EI-MS: 600 (58, M^+), 582 (3, $[M - H_2O]^+$), 520 (12, $[M - 80]^+$), 508 (24, $[M$ − toluene$]^+$), 440 (13), 352 (12), 287 (9), 274 (24), 247 (14), 234 (23), 221 (100), 208 (19), 181 (38), 91 (100), 43 (21, 18 (19).

5. *Violaxanthin B* (= *(all-*E*,3*S*,5*S*,6*R*,3′*S*,5′*R*,6′*S*)-5,6:5′,6′-Diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-3,3′-diol* = syn,anti-*Violaxanthin* = '*Mesoviolaxanthin*'; **6**). M.p. 203–205°. Purity (HPLC): 95%. UV/VIS (benzene) *Table 1*, *Figs. 5* and *6*. CD (EPA, r.t.): 222.0 (0.0), 230.5 (+0.7), 254.0 (0.0), 266.5 (−1.2), 279.5 (0.0), 440.5 (−0.4), 476 (−0.7). CD (EPA, −180°): 335.0 (−1.2), 425.5 (−0.7), 430.0 (−0.8), 455.0 (−1.5), 459.5 (−1.3), 488.0 (−1.9); *Fig. 8*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.98 (*s*, Me(16′)); 1.01 (*s*, Me(17)); 1.154 (*s*, Me(16)); 1.147 (*s*, Me(17′)); 1.19 (*s*, Me(18)); 1.19 (*s*, Me(18′)); 1.25 (*dd*, J_{gem} ≈ 13, J(2′ax,3′) ≈ 11, H_{ax}–C(2′)), 1.25 (br., OH–C(3′)); 1.35 (*ddd*, J_{gem} = 12.53, J(2eq,3) = 3.81, J(2eq,4eq) = 1.15, H_{eq}–C(2)); 1.57 (br., OH–C(3)); 1.60 (*m*, J_{gem} = 12.53, H_{ax}–C(2)); 1.63 (*m*, J_{gem} ≈ 13, J(2′eq,4′eq) = 1.64, H_{eq}–C(2′)); 1.63 (*dd*, J_{gem} = 14.08, J(4′ax,3′) = 8.54, H_{ax}–C(4′)); 1.89 (*dd*, J_{gem} = 14.80, J(4ax,3) = 8.43, H_{ax}–C(4)); 1.92 (*s*, Me(19)); 1.92 (*s*, Me(19′)); 1.96 (*s*, Me(20)); 1.96 (*s*, Me(20′)); 2.20 (*ddd*, J_{gem} = 14.80, J(4eq,3) = 5.57, J(4eq,2eq) = 1.15, H_{eq}–C(4)); 2.39 (*ddd*, J_{gem} = 14.08, J(4′eq,3′) = 5.19, J(4′eq,2′eq) = 1.64, H_{eq}–C(4′)); 3.89 (*m*, H–C(3)); 3.91 (*m*, H–C(3′)); 5.82 (*d*, J(7,8) = 15.66, H–C(7)); 5.88 (*d*, J(7′,8′) = 15.67, H–C(7′)); 6.19 (*d*, J(10,11) = 10.71, H–C(10)); 6.19 (*d*, J(10′,11′) = 11.71, H–C(10′)); 6.27 (H–C(14)); 6.27 (H–C(14′)); 6.29 (*d*, J(8′,7′) = 15.67, H–C(8′)); 6.30 (*d*, J(8,7) = 15.66, H–C(8)); 6.37 (*d*, J(12,11) = 14.75, H–C(12)); 6.37 (*d*, J(12′,11′) = 14.75, H–C(12′)); 6.61 (*dd*, J(11,10) = 11.71, J(11,12) = 14.75, H–C(11)); 6.61 (*dd*, J(11′,10′) = 11.71, J(11′,12′) = 14.75, H–C(11′)); 6.64 (H–C(15)); 6.64 (H–C(15′)). ^{13}C-NMR (100 MHz, $CDCl_3$): 12.79 (C(20,20′)); 12.95 (C(19))*; 12.98 (C(19′))*; 20.04 (C(18′)); 21.25 (C(18)); 25.00 (C(16′)); 26.09 (C(16)); 26.88 (C(17)); 29.57 (C17′)); 35.12

(C(1)); 35.36 (C(1′)); 39.34 (C(4)); 41.08 (C(4′)); 43.92 (C(2)); 47.22 (C(2′)); 64.12 (C(3′)); 64.34 (C(3)); 65.24 (C(5′)); 66.86 (C(5)); 70.34 (C(6′)); 71.31 (C(6)); 122.54 (C(7)); 123.87 (C(7′)); 124.67 (C(11)); 124.74 (C(11′)); 130.19 (C(15′)); 130.27 (C(15)); 132.26 (C(10′)); 132.45 (C(10)); 132.84 (C(14′)); 132.94 (C(14)); 134.15 (C(9)); 134.33 (C(9′)); 136.40 (C(13))**; 136.48 (C(13′))**; 137.44 (C(8′)); 138.21 (C(8)); 138.21 (C(12′)); 138.33 (C(12′)). EI-MS: 600 (37, M^+), 582 (10, $[M-H_2O]^+$), 520 (14, $[M-80]^+$), 508 (8, $[M-\text{toluene}]^+$), 440 (12), 352 (16), 299 (20), 287 (27), 274 (26), 247 (25), 234 (32), 221 (100), 181 (51), 165 (35), 145 (31), 119 (34), 91 (26), 43 (23), 18 (11).

6. *Thermal Isomerization*. A soln. of 80 mg of violaxanthin A (=(all-*E*)-*syn*,*syn*-violaxanthin; **5**) in 800 ml of benzene and a soln. of 75 mg of violaxanthin B (=(all-*E*)-*syn*,*anti*-violaxanthin; **6**) in 750 ml of benzene were refluxed during 2 h under N_2 in the dark [4][6][9][23], and after the usual workup [28], the equilibrium mixtures were submitted to CC.

7. *I_2-Catalyzed Photoisomerization*. A soln of 50 mg of violaxanthin A (=(all-*E*)-*syn*,*syn*-violaxanthin; **5**) in 500 ml of benzene or a soln. of 45 mg of violaxanthin B (=(all-*E*)-*syn*,*anti*-violaxanthin; **6**) in 450 ml of benzene was isomerized under N_2 in scattered daylight in the presence of 1 mg of I_2 (*ca.* 2% rel. to the carotenoid) [4][6][8][23] (monitoring by UV/VIS [6][8]). When the thermodynamic equilibrium was reached after *ca.* 40 min, the mixture was washed free of I_2 with 5% $Na_2S_2O_3$ soln. and, after the usual workup [28], submitted to CC.

8. *Separation of* (*E*/*Z*)-*Isomers*. The reaction mixtures were separated by CC (6 × 30 cm columns, $CaCO_3$). The separation of the thermal isomerization mixture from **5** (4 columns, benzene, 1–2% acetone/benzene) resulted in the following picture after development: 4 mm pale yellow (unidentified), 3 mm of intermediate zone, 20 mm yellow (*Zone 1*; (13*Z*)-**5**), 4 mm of intermediate zone, 3 mm pale yellow (*Zone 2*; (9*Z*)-**5**), 50 mm of intermediate zone, 8 mm pale yellow (unidentified; probably (di-*Z*)-isomer of **5**), 20 mm of intermediate zone, 40 mm yellow (*Zone 3*; **5**). Picture after development for I_2-catalyzed photoisomerization of **5** (3 columns; benzene, 1–3% acetone/benzene): 3 mm pale yellow (unidentified), 4 mm of intermediate zone, 10 mm yellow (*Zone 1*; (13*Z*)-**5**), 4 mm of intermediate zone, 20 mm yellow (*Zone 2*; (9*Z*)-**5**), 4 mm of intermediate zone, 4 mm pale yellow (*Zone 3*; (di-*Z*)-**5**), 20 mm of intermediate zone, 12 mm pale yellow (*Zone 4*; (di-*Z*)-**5**), 15 mm of intermediate zone, 15 mm pale yellow (*Zone 5*; (di-*Z*)-**5**), 20 mm of intermediate zone, 10 mm pale yellow (*Zone 6*; (di-*Z*)-**5**), 20 mm of intermediate zone, 12 mm pale yellow (*Zone 7*; (di-*Z*)-**5**), 25 mm of intermediate zone, 40 mm yellow (*Zone 8*; **5**).

The separation of the thermal isomerization mixture of **6** (4 columns, benzene and 0.2–4% acetone/benzene) resulted in the following picture after development: 2 mm pale yellow (unidentified), 20 mm yellow (*Zone 1*; (13*Z*)- and (13′*Z*)-**6**), 25 mm of intermediate zone, 8 mm pale yellow (unidentified), 30 mm of intermediate zone, 40 mm yellow (*Zone 2*; **6**). Picture after development for the mixture obtained by I_2-catalyzed photoisomerization of **6** (3 columns, benzene and 3–6% acetone/benzene): 2 mm pale yellow (unidentified), 10 mm of intermediate zone, 10 mm yellow (*Zone 1*; (13*Z*)- and (13′*Z*)-**6**), 10 mm of intermediate zone, 3 mm pale yellow (unidentified), 15 mm of intermediate zone, 30 mm yellow (*Zone 2*; (9′*Z*)-**6**), 4 mm of intermediate zone, 25 mm yellow (*Zone 3*; (9*Z*)-**6**), 10 mm of intermediate zone, four pale yellow zones (10–12 mm one after the other) with intermediate zones (*Zone 4*; mixture of (di-*Z*)-isomers of **6**), 10 mm of intermediate zone, 50 mm yellow (*Zone 5*; **6**). *Zone 1* ((13*Z*)- and (13′*Z*)-**6**; obtained by CC of thermal- and I_2-catalyzed photoisomerization equilibrium mixtures of **6**) was submitted to repeated CC (4 columns, 4%, 8%, and 12% acetone in benzene/hexane 1:1). Picture after development: 80 mm of intermediate zone, 25 mm yellow (*Zone 11*; (13′*Z*)-**6**), 2 mm of intermediate zone, 20 mm yellow (*Zone 12*; (13*Z*)-**6**), 10 mm of intermediate zone, 10 mm pale yellow (unidentified).

After the usual workup [28], the corresponding fractions were combined, and the carotenoid isomers were crystallized from benzene/hexane 1:5 to give 10 mg of (9*Z*)-**5**, 21 mg of (13*Z*)-**5**, 6 mg of (9*Z*)-**6**, 5 mg of (9′*Z*)-**6**, 9 mg of (13*Z*)-**6**, and 7 mg of (13′*Z*)-**6**.

9. *(9Z,3S,5S,6R,3′S,5′S6′R)-5,6:5′,6′-Diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-3,3′-diol*, (=*(9Z)*-syn,syn-*Violaxanthin*; (9*Z*)-**5**). M.p. 111–113°. Purity (HPLC): 97%. UV/VIS (benzene) see *Table 1*, *Fig. 4*. CD (EPA, r.t.): 201.5 (+0.4), 209.0 (−11.3), 215.5 (+0.4), 232.0 (+38.5), 250.0 (0.0), 268.0 (−16.2), 281.0 (0.0), 315.0 (+9.4), 320.0 (+7.2), 327.0 (+12.1), 376.0 (0.0), 414.4 (−4.2), 422.5 (−3.1), 437.5 (−6.6), 453.5 (−3.7), 465.5 (−7.6); *Fig. 7*. CD (EPA, −180°): 209.5 (−37.7), 218.5 (0.0), 233.5 (+68.7), 247.5 (0.0), 270.0 (−37.4), 289.0 (0.0), 307.0 (+5.6), 311.5 (+3.7), 318.5 (+12.9), 327.5 (+4.0), 333.5 (+29.0), 421.0 (−6.8), 434.5 (−2.4), 445.0 (−11.1), 463.5 (−1.6), 475.0 (−10.0); *Fig. 7*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.01 (*s*, Me(16′)), 1.03 (*s*, Me(16)); 1.15 (*s*, Me(17′)); 1.17 (*s*, Me(17)); 1.19 (*s*, Me(18′)); 1.21 (*s*, Me(18)); 1.37 (*m*, $J_{gem} \approx 12.5$, H_{eq}–C(2′)); *ca.* 1.37 (*m*, $J_{gem} \approx 12.5$, H_{eq}–C(2)); 1.61 (*dd*, $J_{gem} \approx 12.5$, J(2'ax,3′) = 4.2, H_{ax}–C(2′)); 1.62 (*dd*, $J_{gem} \approx 12.5$, J(2ax,3) = 4.2, H_{ax}–C(2)); 1.88 (*dd*, J_{gem} = 14.8, J(4ax,3) = 8.7, H_{ax}–C(4)); 1.89 (*dd*, $J_{gem} \approx 14.8$, J(4′ax,3′) = 8.5,

H_{ax}–C(4′)); 1.92 (*s*, Me(19′)); 1.93 (*s*, Me(19)); 1.956 (*s*, Me(20′)); 1.964 (*s*, Me(20)); 2.20 (*dd*, $J_{gem} \approx 14.8$, $J(4'eq,3') \approx 6$, H_{eq}–C(4′)); 2.22 (*dd*, $J_{gem} = 14.8$, $J(4eq,3) \approx 6$, H_{eq}–C(4)); 3.87 (*m*, H–C(3′)); 3.88 (*m*, H–C(3)); 5.81 (*d*, $J(7',8') = 15.6$, H–C(7′)); 5.87 (*d*, $J(7,8) = 15.5$, H–C(7)); 6.08 (*d*, $J(10,11) = 11.5$, H–C(10)); 6.20 (*d*, $J(10',11')$); 6.23 (H–C(14)); 6.26 (H–C(14′)); 6.29 (*d*, $J(12,11) = 14.9$, H–C(12)); 6.29 (*d*, $J(8',7') = 15.6$, H–C(8′)); 6.37 (*d*, $J(12',11') = 14.9$, H–C(12′)); 6.59 (*dd*, $J(11',10') = 11.6$, $J(11',12') = 14.9$, H–C(11′)); 6.61 (H–C(15)); 6.64 (H–C(15′)); 6.75 (*dd*, $J(11,10) = 11.5$, $J(11,12) = 14.9$, H–C(11)); 6.84 (*d*, $J(8,7) = 15.5$)). ^{13}C-NMR (100 MHz, $CDCl_3$): 12.78 (C(20′)); 12.95 (C(19′)); 12.99 (C(20)); 20.95 (C(19)); 21.22 (C(18)); 21.24 (C(18′)); 26.02 (C(17)); 26.07 (C(17′)); 26.85 (C(16′)); 26.94 (C(16)); 35.01 (C(1)); 35.08 (C(1′)); 39.23 (C(4,4′)); 43.79 (C(2,2′)); 64.01 (C(3)); 64.08 (C(3′)); 65.27 (C(5′)); 65.29 (C(5)); 71.31 (C(6′)); 71.44 (C(6)); 122.45 (C(7′)); 123.59 (C(11)); 124.56 (C(7), C(11′)); 129.97 (C(15)); 130.32 (C(15′)); 130.91 (C(10)); 132.44 (C(10′)); 132.62 (C(9),C(14)); 132.95 (C(14′)); 134.08 (C(9′)); 136.26 (C(13′)); 136.59 (C(13)); 137.50 (C(12)); 138.13 (C(8′)); 138.32 (C(12′)). EI-MS: 600 (65, M^+), 582 (4, $[M - H_2O]^+$), 564 (2, $[M - 2H_2O]^+$), 520 (33, $[M - 80]^+$), 508 (19 $[M$ – toluene$]^+$), 440 (33), 352 (28), 299 (28), 287 (39), 274 (53), 247 (23), 234 (34), 221 (100), 208 (23), 181 (41), 165 (30), 119 (24), 105 (17), 91 (30), 43 (17), 18 (10).

10. *(13Z,3S,5S,6R,3′S,5′S,6′R)-5,6:5′,6′-Diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-3,3′-diol* (= *(13Z)*-syn,syn-*Violaxanthin*; (13*Z*)-**5**). M.p. 121–123°. Purity (HPLC): 94%. UV/VIS (benzene) *Table 1*, *Fig. 4*. CD (EPA, r.t): 209.5 (+5.6), 233 (+42.1), 257.5 (+0.3), 269.0 (−14.3), 277.5 (+0.2), 316.0 (+32.3), 321.5 (+25.7), 329.0 (+43.9), 382.5 (0.0), 409.5 (−6.2), 419.5 (−5.2), 434.5 (−11.5), 449.5 (−5.4), 462.5 (−11.2); *Fig. 7*. CD (EPA, −180°): 204.5 (−0.1), 210.0 (−15.2), 214.0 (+0.2), 234.5 (+53.6), 258.0 (+0.3), 271.5 (−15.5), 274.5 (−0.6), 276.5 (+5.3), 279.5 (+2.37), 284.0 (+10.5), 301.0 (+5.6), 308.0 (+9.7), 314.5 (+3.0), 321.0 (+19.1), 327.5 (+11.4), 336.5 (+55.1), 380.5 (+0.1), 397.5 (−5.8), 407.0 (−4.7), 420.0 (−16.7), 432.5 (−2.3), 445.0 (−23.6), 453.5 (+0.9), 460.5 (+13.2), 469.5 (+0.3), 476.5 (−18.7), 483.0 (−0.5), 489.5 (+24.4); *Fig. 7*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.013 (*s*, Me(17′)); 1.018 (*s*, Me(17)); 1.155 (*s*, Me(16′)); 1.161 (*s*, Me(16)); 1.190 (*s*, Me(18′)); 1.196 (*s*, Me(18)); *ca.* 1.36 (*ddd*, $J_{gem} = 12.5$, $J(2eq,3) = 3.6$, $J(2eq,4eq) = 1.8$, H_{eq}–C(2), H_{eq}–C(2′)); 1.611 (*dd*, $J_{gem} = 12.5$, $J(2'ax,3') = 11.3$, H_{ax}–C(2′)); 1.614 (*dd*, $J_{gem} = 12.5$, $J(2ax,3) = 11.3$, H_{ax}–C(2)); 1.891 (*dd*, $J_{gem} = 14.9$, $J(4'ax,3') = 8.6$, H_{ax}–C(4′)); 1.896 (*dd*, $J_{gem} = 15.0$ $J(4ax,3) = 8.7$, H_{ax}–C(4)); 1.92 (*s*, Me(19′)); 1.93 (*s*, Me(19)); 1.95 (*s*, Me(20′)); 1.98 (*s*, Me(20)); 2.20 (*m*, H_{eq}–C(4), H_{eq}–C(4′)), 3.88 (*m*, H–C(3), H–C(3′)); 5.82 (*d*, $J(7',8') = 15.5$, H–C(7′)); 5.84 (*d*, $J(7,8) = 15.6$, H–C(7)); 6.12 (*d*, $J(12,11) = 12.1$, H–C(14)); 6.20 (*d*, $J(10',11') = 11.5$, H–C(10′)); 6.24 (*d*, $J(10,11) = 11.3$, H–C(10)); 6.26 (*d*, $J(14',15') = 12.9$, H–C(14′)); 6.30 (*d*, $J(8',7') = 15.5$, H–C(8′)); 6.32 (*d*, $J(8,7) = 15.6$, H–C(8)); 6.38 (*d*, $J(12',11') = 15.3$, H–C(12′)); 6.56 (*dd*, $J(15',14') = 12.9$, $J(15',15) = 14.0$, H–C(15′)); 6.60 (*dd*, $J(11',10') = 11.5$, $J(11',12') = 15.3$, H–C(11′)); 6.61 (*dd*, $J(11,10) = 11.3$, $J(11,12) = 15.1$, H–C(11)); 6.80 (*dd*, $J(15,14) = 12.1$, $J(15,15') = 14.0$, H–C(15)); 6.90 (*d*, $J(12,11) = 15.1$). ^{13}C-NMR: no data due to the small sample amount and instability of (13*Z*)-**5** in $CDCl_3$. EI-MS: 600 (44, M^+), 582 (2, $[M - H_2O]^+$), 520 (20, $[M - 80]^+$), 508 (11, $[M$ – toluene$]^+$), 440 (27), 352 (17), 299 (20), 287 (24), 274 (48), 247 (18), 234 (25), 221 (100), 203 (23), 181 (34), 165 (25), 119 (22), 105 (15), 91 (45), 43 (15), 18 (25).

11. *(9Z,3S,5S,6R,3′S,5′R,6′S)-5,6:5′,6′-Diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-3,3′-diol* (= *(9Z)*-syn,anti-*Violaxanthin*; (9*Z*)-**6**). M.p. 94–96°. Purity (HPLC): 96%. UV/VIS (benzene): *Table 1*, *Fig. 5*. CD (EPA, r.t.): 208.0 (+6.4), 224.0 (0.0), 232.0 (−2.3), 241.0 (0.0), 274.0 (−0.3), 279.0 (−0.1), 284.0 (+0.7), 312.0 (0.0), 328.0 (−0.7), 335.0 (0.0), 436.0 (+1.5), 452.0 (+1.2), 465.0 (+1.7). CD (EPA, −180°): 209.0 (+12.3), 225.0 (0.0), 233.0 (−4.3), 243.0 (0.0), 262.0 (0.00), 269.0 (+0.4), 275.0 (−0.7), 290.0 (+1.1), 311.0 (+0.9), 319.0 (−0.3), 327.0 (+0.5), 333.0 (−1.4), 341.0 (+0.6), 401.0 (+0.8), 421.0 (+1.5), 436.0 (+1.1), 447.0 (+2.4), 464.0 (+0.5), 477.0 (+3.0); *Fig. 8*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.976 (*s*, Me(16′)); 1.030 (*s*, Me(17)); 1.147 (*s*, Me(17′)); 1.170 (*s*, Me(16)); 1.186 (*s*, Me(18′)); 1.211 (*s*, Me(18)); 1.23 (*dd*, H_{ax}–C(2′)); 1.33 (*ddd*, H_{eq}–C(2)); 1.62 (*dd*, H_{ax}–C(2)); 1.63 (*ddd*, H_{eq}–C(2′)); 1.89 (*dd*, $J(4ax,4eq) = 14.8$, $J(4ax,3) = 8.8$, H_{ax}–C(4)); 1.925 (*s*, Me(19′)); 1.929 (*s*, Me(19)); 1.958 (*s*, Me(20′)); 1.967 (*s*, Me(20)); 2.22 (*m*, $J(4eq,4ax) = 14.8$, $J(4eq,3) = 7.1$, H_{eq}–C(4)); 2.38 (*m*, $J(4'eq,4'ax) = 13.4$, $J(4'eq,3') = 4.2$, H_{eq}–C(4)); 3.89 (*m*, H–C(3)); 3.90 (*m*, H–C(3′)); 5.87 (*d*, $J(7,8) =$ 15.6, H–C(7)); 5.88 (*d*, $J(7',8') = 15{,}6$, H–C(7′)); 6.08 (*d*, $J(10,11) = 11.3$, H–C(10)); 6.18 (*d*, $J(10',11') \approx 11$, H–C(10′)); 6.24 (*m*, H–C(14)); 6.26 (*m*, H–C(14′)); 6.28 (*d*, $J(12,11) = 15.0$, H–C(12)); 6.29 (*d*, $J(8',7') = 15.6$, H–C(8′)); 6.37 (*d*, $J(12',11') = 14.7$, H–C(12′)); 6.60 (*dd*, $J(11',10') \approx 11$, $J(11',12') = 14.7$, H–C(11′)); 6.62 (*m*, H–C(15), H–C(15′)); 6.75 (*dd*, $J(11,10) = 11.3$, $J(11,12) = 15.0$, H–C(11)); 6.84 (*d*, $J(8,7) = 15.6$, H–C(8)). ^{13}C-NMR (100 MHz, $CDCl_3$): 12.79 (C(20)); 12.99 (C(18′), C(19′), C(20′)); 20.96 (C(19)); 21.22 (C(18)); 24.89 (C(16′)); 26.03 (C(16)); 26.95 (C(17)); 29.58 (C(17′)); 35.01 (C(1)); 35.35 (C(1′)); 39.23 (C(4)); 41.00 (C(4′)); 43.79 (C2)); 47.19 (C(2′)); 64.03 (C(3)); 64.30 (C(3′)), 65.29 (C(5′)); 66.96 (C(5)); 70.30 (C(6′)); 71.45 (C(6)); 123.57 (C(11)); 123.81 (C(7′)); 124.55 (C(7)); 124.61 (C(11′)); 129.99 (C(15)); 130.19 (C(15′)); 130.26 (C(8)); 130.92 (C(10)); 132.26 (C(10′)); 132.62 (C(14)); 132.64 (C(9)); 132.88 (C(14′)); 134.24 (C(9′)); 136.29 (C(13));

136.55 (C(13′)); 137.34 (C(8′)); 137.51 (C(12)); 138.21 (C(12′)). EI-MS: 600 (11, M^+), 520 (23, $[M-80]^+$), 440 (0.12), 287 (25), 274 (17), 247 (5), 234 (12), 221 (100), 181 (28), 165 (21), 119 (30), 105 (29), 91 (64), 56 (28), 43 (42), 18 (17).

12. *(9′Z,3S,5S,6R,3′S,5′R,6′S)-5,6:5′,6′-Diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-3,3′-diol* (= *(9′Z)*-syn,anti-*Violaxanthin*; (9′*Z*)-**6**). M.p. 93–95°. Purity (HPLC): 94%. UV/VIS (benzene): *Table 1*, *Fig. 5*. CD (EPA, r.t.): 210.0 (−7.1), 223.0 (+0.1), 232.0 (+2.1), 239.0 (+0.6), 271.0 (+2.4), 282.0 (+1.9), 313.0 (+1.6), 321.0 (+1.0), 327.0 (+1.4), 343.0 (+0.1), 441.0 (+1.8), 454.0 (+1.5), 463.0 (+2.0). CD (EPA, −180°): 210.0 (−11.4), 221.0 (+0.2), 233.0 (+6.7), 275.0 (+1.8), 284.0 (+2.2), 298.0 (+1.53), 307.0 (+2.0), 312.0 (+1.6), 318.0 (+2.8), 328.0 (+1.2), 334.0 (+3.85), 429.0 (+1.0), 453.0 (+1.7), 465.0 (+0.6), 477.0 (+2.9); *Fig. 8.* ^{1}H-NMR (400 MHz, $CDCl_3$): 1.005 (*s*, Me(16′)); 1.009 (*s*, Me(17)); 1.152 (*s*, Me(16)), 1.161 (*s*, Me(17′)); 1.186 (*s*, Me(18)); 1.242 (*s*, Me(18′)), 1.25 (*dd*, J(2′ax,2′eq) ≈ 13, J(2′ax,3′) ≈ 11, H_{ax}−C(2′)); 1.35 (*ddd*, J(2eq,2ax) = 12.4, J(2eq,3) = 4.1, J(2eq,4eq) = 1.0, H_{eq}−C(2′)); 1.60 (*m*, J(2ax,2eq) = 12.4, H_{ax}−C(2)); 1.63 (*ddd*, H_{eq}−C(2′)); 1.64 (*dd*, J(4′ax,4′eq) = 14.3, J(4′ax,3′) = 8.8, H_{ax}−C(4′)); 1.89 (*dd,* J(4ax,4eq) = 14.9, J(4ax,3) = 8.5, H_{ax}−C(4)); 1.921 (*s*, Me(19)); 1.929 (*s*, Me(19′)); 1.954 (*s*, Me(20)); 1.960 (*s*, Me(20′)); 2.20 (*ddd*, J(4eq,4ax) = 14.9, J(4eq,3) = 6.6, J(4eq,2eq) = 1.0, H_{eq}−C(4)); 2.40 (*ddd*, J(4′eq,4ax) = 14.3, J(4′eq,3′) = 5.1, J(4′eq,2′eq) = 1.7, H_{eq}−C(4′)); 3.87 (*m*, H−C(3)); 3.92 (*m*, H−C(3′)); 5.81 (*d*, J(7,8) = 15.6, H−C(7)); 5.93 (*d*, J(7′,8′) = 15.3, H−C(7′)); 6.07 (*d*, J(10′,11′) = 11.7, H−C(10′)); 6.20 (*d*, J(10,11) = 11.8, H−C(10)); 6.23 (*m*, H−C(14′)); 6.27 (*m,* H−C(14)); 6.28 (*d*, J(8,7) = 15.6, H−C(8)); 6.30 (*d*, J(12′,11′) = 14.8, H−C(12′)); 6.37 (*d*, J(12,11) = 15.0, H−C(12)); 6.59 (*dd*, J(11,10) = 11.8, J(11,12) = 15.0, H−C(11)); 6.61 (*m*, H−C(15′)); 6.64 (*m*, H−C(15)); 6.76 (*dd*, J(11′,10′) = 11.7, J(11′,12′) = 14.8, H−C(11′)); 8.83 (*d*, J(8′,7′) = 15.3, H−C(8′)). ^{13}C-NMR (100 MHz, $CDCl_3$): 12.78 (C(20′)); 12.95 (C(20)); 13.00 (C(19)); 19.97 (C(18′)); 21.00 (C(19′)); 21.24 (C(18)); 24.93 (C(16′)); 26.07 (C(16)); 26.85 (C(17)); 29.56 (C(17′)); 35.08 (C(1)); 35.29 (C(1′)); 39.22 (C(4)); 40.98 (C(4′)); 43.78 (C(2)); 47.20 (C(2′)); 64.09 (C(3)); 64.29 (C(3′)); 65.27 (C(5′)); 67.06 (C(5)); 70.48 (C(6′)); 71.31 (C(6)); 122.44 (C(7)); 123.65 (C(11′)); 124.54 (C(11)); 125.96 (C(7′)); 129.37 (C(8′)); 129.93 (C(15′)); 130.33 (C(15)); 130.76 (C(10′)); 132.44 (C(10)); 132.56 (C(14′)); 132..80 (C(9′)); 132.96 (C(14)); 134.06 (C(9)); 136.23 (C(13′)); 136.63 (C(13)); 137.42 (C(12′)); 138.13 (C(8)); 138.33 (C(12)). EI-MS: 600 (35, M^+), 274 (11), 247 (1), 234 (5), 221 (54), 181 (17), 157 (18), 123 (31), 109 (14), 91 (52), 83 (19), 69 (28), 56 (45), 43 (100), 18 (55).

13. *(13Z,3S,5S,6R,3′S,5′R,6′S)-5,6:5′,6′-Diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-3,3′-diol* (= *(13Z)*-syn,anti-*Violaxanthin*; (13*Z*)-**6**). M.p. 104–105°. Purity (CC): 94%. UV/VIS (benzene) *Table 1*, *Fig. 6*. CD (EPA, r.t.): 207.5 (+2.5), 238.5 (+0.2), 284.5 (+1.25), 294.0 (+1.5), 306.0 (+0.9), 312.5 (+1.1). CD (EPA, −180°): 207.0 (+2.8), 240.0 (−0.1), 257.5 (+0.2), 279.0 (+1.3), 281.0 (+1.2), 287.5 (+1.7), 292.0 (+1.5), 297.5 (+2.2), 311.0 (+1.1), 317.0 (+2.05), 340.0 (0.0), 362.0 (−1.0), 370.0 (−0.7), 381.5 (−1.9), 392.0 (−0.8), 404.5 (−2.5), 416.0 (−0.6), 430.5 (−1.9), 443.0 (−0.4), 455.0 (−1.1), 491.0 (−0.6); *Fig. 8.* ^{1}H-NMR (400 MHz, $CDCl_3$): 0.99 (*s*, Me(16′)); 1.03 (*s*, Me(17)); 1.158 (*s*, Me(17′)); 1.170 (*s*, Me(16)); 1.20 (*s*, Me(18), Me(18′)); 1.24 (*dd,* H_{ax}−C(2′)); 1.35 (*ddd*, H_{eq}−C(2)); 1.60 (*dd*, H_{ax}−C(2)); 1.63 (*ddd,* H_{eq}−C(2′)); 1.63 (*dd*, H_{ax}−C(4′)); 1.89 (*dd*, H_{ax}−C(4)); 1.932 (*s*, Me(19′)); 1.940 (*s*, Me(19)); 1.961 (*s*, Me(20′)); 1.989 (*s*, Me(20)); 2.21 (*m*, J(4eq,4ax) ≈ 15, J(4eq,3) ≈ 6, 2.39 (*ddd*, H_{eq}−C(4)); 3.88 (*m*, H−C(3)); 3.91 (*m*, H−C(3′)); 5.85 (*d*, J(7,8) ≈ 15, 5, H−C(7)); 5.89 (*d*, J(7′,8′) = 15.6, H−C(7′)); 6.14 (*d*, J(14,15) = 11.2, H−C(14)); 6.20 (*d*, J(10′,11′) ≈ 11, H−C(10′)); 6.24 (*d*, overlapped, H−C(10)); 6.25 (*d*, J(14′,15′) = 11.0, H−C(14′)), 6.30 (*d*, J(8,7) ≈ 15, H−C(8)); 6.33 (*d*, J(8′,7′) = 15.6, H−C(8′)); 6.37 (*d*, J(12′,11′) = 15.2, H−C(12′)); 6.56 (*m*, J(15′,14′) = 11.0, H−C(15′)); 6.60 (*dd,* overlapped, J(11,12) = 15.0, H−C(11)); 6.60 (*dd*, J(11′,10′) ≈ 11, J(11′,12′) = 15.2, H−C(11′)); 6.77 (*m*, J(15,14) = 11.2, H−C(15)); 6.91 (*d*, J(12,11) = 15.0, H−C(12)). ^{13}C-NMR *via* HSQC/HMBC (100 MHz, $CDCl_3$): 12.3 (C(20′)); 12.6 (C(19), C(19′)); 19.8 (C(18′)); 20.2 (C(20)); 21.0 (C(18)); 24.7 (C(16′)); 25.8 (C(16)); 26.6 (C(17)); 29.3 (C(17′)); 38.8 (C(4)); 43.5 (C(2)); 46.8 (C2′)); 63.9 (C(3), C(3′)); 122.7 (C(7)); 123.7 (C(7′)); 124.3 (C(11′)); 125.6 (C(11)); 128.4 (C(15)); 129.0 (C(15′)); 129.2 (C(12)); 131.1 (C(14)); 132.0 (10′)); 132.4 (C(14′)); 132.5 (C(10)); 137.2 (C(8)); 138.0 (C(8′)); 138.2 (C(12′)); some signals could not be extracted due to the small sample amount. EI-MS: 600 (35, M^+), 582 (6, $[M-H_2O]^+$), 520 (18, $[M-80]^+$), 508 (8, $[M-$ toluene$]^+$), 440 (13), 352 (20), 299 (22), 287 (25), 274 (18), 247 (11), 234 (12), 221 (42), 181 (42), 135 (12), 125 (15), 119 (16), 109 (14), 95 (26), 91 (31), 83 (17), 69 (23), 56 (35), 43 (100), 18 (26).

14. *(13′Z,3S,5S,6R,3′S,5′R,6′S)-5,6:5′,6′-Diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-3,3′-diol* (= *(13′Z)*-syn,anti-*Violaxanthin*; (13′*Z*)-**6**). M.p. 110–111°. Purity: 95% (CC). UV/VIS (benzene): *Table 1*, *Fig. 6*. CD (EPA, r.t.): 202 (+2.0), 208 (+3.4), 230.0 (0.0), 233.0 (−0.2), 236 (−0.1), 260.0 (−1.4), 268.0 (−1.9), 279.0 (0.0), 290.0 (+1.0), 295.0 (+0.8), 300.0 (+1.0), 308 (+0.7), 314.0 (+1.05), 322.0 (+0.3), 328.0 (+0.6), 338.0 (0.0), 343.0 (−0.2), 350.0 (0.0), 437.0 (+1.8), 456 (+1.4), 465.0 (+1.7). CD (EPA, −180°): 202.0 (+5.8), 207.0 (+7.5), 231.0 (+2.05), 234.0 (+2.35), 244.0 (+0.1), 260.0 (−2.3), 265.0 (−2.2), 271.0 (−3.8), 280.0 (+0.1), 291.0 (+2.1), 298.0 (+1.8), 305.0 (+2.6), 312.0 (+1.8), 318.0 (+3.5), 327.0 (+1.7), 336.0 (+3.5), 351.0 (0.0), 378.0 (+0.2),

388.0 (0.0), 402 (+0.6), 410.0 (+0.5), 427.0 (+1.3), 436.0 (+0.9), 452.0 (+2.1), 464.0 (+0.4), 475.0 (+2.6); *Fig. 8*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.98 (*s*, Me(16′)); 1.01 (*s*, Me(17)); 1.15 (*s*, Me(16), Me(17)); 1.189 (*s*, Me(18)); 1.193 (*s*, Me(18′)); 1.25 (*dd*, H_{ax}–C(2′)), 1.36 (*ddd*, J(2eq,2ax) ≈ 12, J(2eq,3) ≈ 4, J(2eq,4eq) ≈ 1, H_{eq}–C(2)); 1.61 (*m*, J(2ax,2eq) ≈ 12, H_{ax}–C(2)); 1.63 (*ddd*, H_{eq}–C(2′)), 1.63 (*dd*, H_{ax}–C(4′)); 1.89 (*dd*, J(4ax,4eq) = 14.9, J(4ax,3) = 6.4, J(4ax,2eq) ≈ 1, H_{ax}–C(4)); 1.92 (*s*, Me(19)); 1.93 (*s*, Me(19′)); 1.95 (*s*, Me(20)); 1.98 (*s*, Me(20′)); 2.20 (*ddd*, J(4eq,4ax) = 14.9, J(4eq,3) = 6.4, J(4eq,2eq) ≈ 1, H_{eq}–C(4)); 2.39 (*ddd*, J(4′eq,4′ax) = 14.2, J(4′eq,3′) = 4.8, J(4′eq,2′eq) = 1.4, H_{eq}–C(4′)); 3.88 (*m*, H–C(3)); 3.92 (*m*, H–C(3′)); 5.81 (*d*, J(7,8) = 15.6, H–C(7)); 5.90 (*d*, J(7′,8′) = 15.5, H–C(7′)); 6.11 (*d*, J(14′,15′) = 11.6, H–C(14′)); 6.20 (*d*, J(10,11) = 11.4, H–C(10)); 6.24 (*d*, J(10′,11′) = 11.7, H–C(10′)), 6.27 (*d*, overlapped, H–C(14)); 6.30 (*d*, J(8,7) = 15.6, H–C(8)); 6.31 (*d*, J(8′,7′) = 15.5, H–C(8′)); 6.38 (*d*, J(12,11) = 15.0, H–C(12)); 6.56 (*m*, J(15,15′) = 14.4, H–C(15)); 6.60 (*dd*, J(11,10) = 11.4, J(11,12) = 15.0, H–C(11)); 6.61 (*dd*, J(11′,10′) = 11.7, J(11′,12′) = 14.9, H–C(11′)); 6.80 (*dd*, J(15′,14′) = 11.6, J(15′,15) = 14.4, H–C(15′)); 6.89 (*d*, J(12′,11′) = 14.9, H–C(12′)). ^{13}C-NMR *via* HSQC/HMBC (100 MHz, $CDCl_3$): 12.6 (C(19′)); 12.9 (C(19)); 12.9 (C(20)); 19.7 (C(18)); 20.3 (C(20′)); 20.9 (C(18′)); 25.8 (C(16), C(16′)); 26.6 (C(17)); 29.4 (C(17′)); 38.9 (C(4)); 41.3 (C(4′)); 43.5 (C(2)); 47.9 (C(2′)); 64.3 (C(3), C(3′)); 122.3 (C(7)); 124.1 (C(7′)); 124.2 (C(11)); 130.4 (C(14)); 132.2 (C(10)); 132.8 (C(10′)); *ca.* 137.2 (C(8′)); *ca.* 137.4 (C(8)); some signals could not be extracted due to the small sample amount. EI-MS: 600 (30, M^+), 582 (6, $[M - H_2O]^+$), 520 (10, $[M - 80]^+$), 508 (5, $[M$ – toluene$]^+$), 287 (17), 274 (49), 247 (8), 234 (12), 221 (100), 208 (16), 181 (42), 125 (18), 119 (19), 91 (91), 56 (26), 43 (44), 18 (31).

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