19. Partial Synthesis and Characterization of the Mono- and Diepoxides of β-Cryptoxanthin

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β-Cryptoxanthin (**1**) was acetylated and then epoxidized with monoperoxyphthalic acid. After hydrolysis, repeated chromatography, and crystallization, (3*S*,5*R*,6*S*)-5,6-epoxy-β-cryptoxanthin (**3**), (3*S*,5*S*,6*R*)-5,6-epoxy-β-cryptoxanthin (**4**), (3*R*,5′*R*,6′*S*)-5′,6′-epoxy-β-cryptoxanthin (**5**), (3*S*,5*R*,6*S*,5′*R*,6′*S*)-5,6:5′,6′-diepoxy-β-cryptoxanthin (**6**), and (3*S*,5*S*,6*R*,5′*S*,6′*R*)-5,6:5′,6′-diepoxy-β-cryptoxanthin (**7**) were isolated as main products and characterized by their UV/VIS, CD, ^{1}H- and ^{13}C-NMR, and mass spectra. The comparison of the carotenoid isolated from yellow, tomato-shaped paprika (*Capsicum annuum* var. *lycopersiciforme flavum*) with **3**–**5** strongly supports the structure of **3** for the natural product.

1. Introduction. – The occurrence of the epoxides of β-cryptoxanthin ((3*R*)-β,β-caroten-3-ol; **1**), namely the 5,6-monoepoxide, the 5′,6′-monoepoxide and the 5,6:5′,6′-diepoxide as well as their 5,8- and 5′,8′-isomers, in natural sources, such as algae, vegetables, and fruits, has been reported by several authors [1–3]. In general, the elucidation of the constitution was mainly based on the chromatographic behaviour, the test for furanoid rearrangement, UV/VIS spectra, and partly the mass spectra. However, in many cases, the position of the epoxy group (C(5), C(6) or C(5′), C(6′)) remained uncertain. Recently, the isolation of the 5,6-monoepoxide from papaya was reported [4], and the constitution was established by ^{1}H-NMR spectroscopy.

The preparation of the epoxides of **1** by epoxidation of β-cryptoxanthin acetate (**2**) with monoperoxyphthalic acid has already been reported by *Karrer* and *Jucker* [5]. Based on the observation that the monoepoxide exhibited no vitamin-A activity, the constitution of the 5′,6′-monoepoxide was proposed for this compound [6]. Later, the partial synthesis was reinvestigated, and the products have been characterized by their chemical properties, UV/VIS spectra, and melting points [7]. Until today, the absolute configuration of the naturally occurring epoxides of β-cryptoxanthin (**1**) and of the products from the partial synthesis have not yet been established. The enzymatic deepoxidation of the 5,6-monoepoxide with violaxanthin-deepoxidase gave β-cryptoxanthin (**1**), and based on this observation, the (3*S*,5*R*,6*S*)-configuration was proposed [8].

From yellow, tomato-shaped paprika (*Capsicum annum* var. *lycopersiciforme flavum*), a yet unidentified carotenoid has recently been isolated in small amounts [9]. This compound had, in different HPLC systems, an identical t_R value as one of the compounds from the reaction mixture of the epoxidation of β-cryptoxantin (**1**). Based on this observation and the UV/VIS spectrum, structure **3** was proposed for this compound.

For the proper identification of a carotenoid in small amounts, the following minimal criteria have to be fulfilled [10]: *i*) The UV/VIS absorption spectrum (λ_{max} and fine structure in at least two different solvents) must be in agreement with the chromophore suggested, *ii*) chromatographic properties must be identical with those of an authentic sample in two different systems, preferably in TLC and HPLC, and co-chromatography with an authentic sample must be demonstrated, and *iii*) a mass spectrum should be obtained which allows at least confirmation of the molecular mass. Therefore, for the identification of carotenoids in small amounts, authentic reference samples (standards) are indispensable. These compounds which can be obtained by total or partial synthesis or by isolation from natural sources, must be fully characterized by modern spectroscopic methods, especially high-resolution NMR spectroscopy, and for chiral carotenoids, by their CD spectrum.

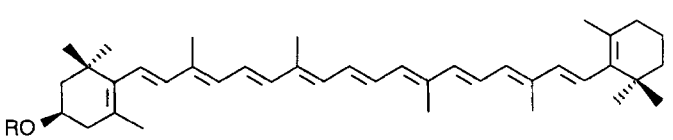
In view of the structure elucidation of the naturally occurring epoxides of β-cryptoxanthin (**1**), we report on the preparation and complete characterization of the main epoxidation products of β-cryptoxanthin acetate (**2**) after mild hydrolysis.

2. Results and Discussion. – For the epoxidation, crystalline β-cryptoxanthin (**1**) was transformed to acetate **2** which was reacted according to [5] with monoperoxyphthalic acid. The crude reaction mixture was directly hydrolysed with 30% KOH/MeOH. After normal workup, repeated column chromatography (see *Exper. Part*), and crystallization, the epoxides **3**–**7** were isolated. According to HPLC investigations, the purity of all compounds was > 95%.

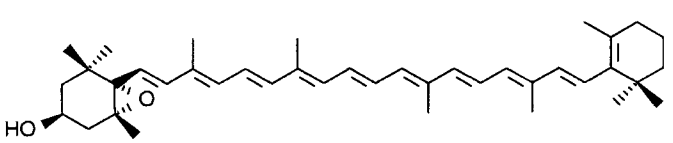
In the UV/VIS spectra, the maxima for **3**–**5** (435, 458, and 488 nm in benzene) as well as for **6** and **7** (427, 453, and 483 nm in benzene) and also the fine structures are in accordance with the data previously reported [2]. In addition, also the products from the furanoid rearrangement exhibits the expected absorption maxima.

In the mass spectra, the peak at *m/z* $[M - 80]^+$ is characteristic for 5,6-epoxides [2][3] and is observed with high intensity in the spectra of compounds **3**–**7**. The signals at *m/z* 181 and 221 which are typical for carotenoids with the 3-hydroxy-5,6-epoxy end group are observed in the mass spectra of **3**, **4**, **6**, and **7**. This allows the differentiation between the 5,6-epoxides **3** and **4** and the 5′,6′-epoxide **5**, respectively.

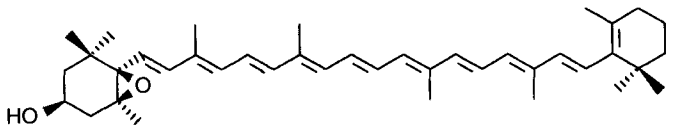
The NMR spectroscopic data of compounds **3**–**7** are summarized in *Tables 1* and *2*. Due to a rapid rearrangement to the 5,8-furanoid derivatives under the measuring conditions, no ^{1}H,^{1}H-COSY and ^{13}C-NMR data could be obtained for **3**. Therefore,



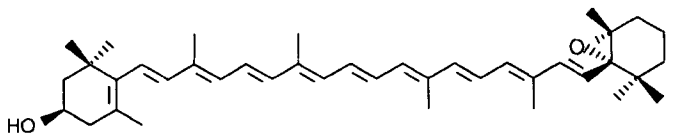
1 R = H (3*R*)-β-cryptoxanthin
2 R = Ac (3*R*)-β-cryptoxanthin acetate



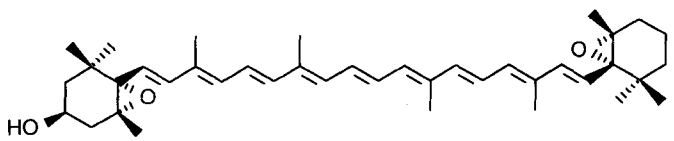
3 (3*S*,5*R*,6*S*)-5,6-epoxy-β-cryptoxanthin



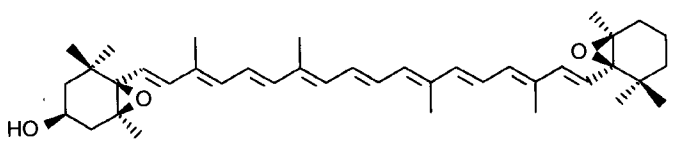
4 (3*S*,5*S*,6*R*)-5,6-epoxy-β-cryptoxanthin



5 (3*R*,5′*R*,6′*S*)-5′,6′-epoxy-β-cryptoxanthin



6 (3*S*,5*R*,6*S*,5′*R*,6′*S*)-5,6:5′,6′-diepoxy-β-cryptoxanthin



7 (3*S*,5*S*,6*R*,5′*S*,6′*R*)-5,6:5′,6′-diepoxy-β-cryptoxanthin

signal assignments are restricted to the protons for the end groups in **3**. The assignments of the ^{1}H-NMR signals of the olefinic and in-chain Me groups were obtained by ^{1}H,^{1}H-COSY (**4**–**7**) and by one-dimensional NOE difference experiments (**4**, **5**, and **7**). The identification of the ^{13}C-NMR signals was deduced from ^{13}C/DEPT-135 measurements (**4**–**7**), from ^{13}C,^{1}H shift-correlation experiments (**4**, **5**, and **7**) and, in case of the quaternary C-atom resonances, by comparison with data previously reported [11][12]. The data in *Tables 1* and *2* for **3**–**7** are in agreement with the proposed structure and literature data [11–13]. In the 3-hydroxy β-end group, the δ(H) and δ(C) of CH_2(4) differ significantly for the *cis*- and *trans*-epoxide (rel. to OH) and, therefore, prove the (3*S*,5*R*,6*S*)-configuration of **3** and **6** and the (3*S*,5*S*,6*R*)-configuration of **4** and **7**. As the enantiomeric (5′*S*,6′*R*)- and (5′*R*,6′*S*)-epoxy β-end groups cannot be distinguished in the ^{1}H- and ^{13}C-NMR spectra, the elucidation of the configuration at the non-hydroxylated end group was based on the chiroptical data.

The structure elucidation of **3**–**7** was completed and confirmed by their CD spectra. Carotenoid 5,6-epoxides exhibit strongly conservative CD spectra comparable to those of other carotenoids with a substituted β-end group. The influence of additional substituents like OH groups at C(3) or C(3′) is rather small [14]. Therefore, from the CD spectra of the epoxides, conclusions can only be drawn about the absolute configuration of the epoxy group. The CD spectra of **3** and **4** (*Fig. 1*) can be compared to those of (5*R*,6*S*)- and (5*S*,6*R*)-5,6-epoxy-β-carotene [13][15] and confirm the structure elucida-

Table 1. *^{1}H-NMR Data of the β-Cryptoxanthin Epoxides* **3**–**7**[a])

	3	**4**	**5**	**6**	**7**
H_{ax}–C(2)	1.27 (J = 3.5)	1.61 (J = 6.7)	1.48	*ca.* 1.25	1.61
H_{eq}–C(2)	1.62 (J = 1.7)	1.35 (J = 2.7)	1.79	*ca.* 1.63	1.35 (J = 1.2)
H–C(3)	3.91; 1.25 (OH)	3.88; 1.62 (OH)	4.00; 1.26 (OH)	3.91; 1.25 (OH)	3.88; 1.60 (OH)
H_{ax}–C(4)	1.63	1.89 (J = 8.5)	2.05	1.63	1.89
H_{eq}–C(4)	2.39 (J = 2.0)	2.20 (J = 6.3)	2.39	2.39	2.20 (J = 1.0)
H–C(7)	5.88 (J = 15.5)	5.82 (J = 15.6)	6.11	5.88 (J = 15.4)	5.82 (J = 15.5)
H–C(8)	6.29 (J = 15.5)	6.30 (J = 15.6)	6.15	6.29 (J = 15.4)	6.30 (J = 15.5)
H–C(10)	[b])	6.20 (J = 10.6)	6.16 (J = 11)	6.20 (J = 11.4)	6.20 (J = 11.3)
H–C(11)	[b])	6.59 (J = 10.6, 14.9)	6.64 (J = 11, 14.9)	6.59 (J = 11.4, *ca.* 15)	6.60 (J = 11.3, 15.0)
H–C(12)	[b])	6.38 (J = 14.9)	6.36 (J = 14.9)	6.36 (J = 15)	6.37 (J = 15.0)
H–C(14)	[b])	6.25	6.26	6.26	6.26
H–C(15)	[b])	6.64	6.63	6.64	6.64
Me(16)	0.98	1.16	1.07	0.98	1.16
Me(17)	1.15	1.01	1.07	1.15	1.01
Me(18)	1.19	1.19	1.74	1.19	1.19
Me(19)	1.93	1.93	1.97	1.93	1.93
Me(20)	1.97	1.97	1.96	1.96	1.96
CH_2(2′)	*ca.* 1.46	1.46	1.48, 1.07[d])	1.47, *ca.* 1.08[d])	*ca.* 1.48, 1.06[d])
CH_2(3′)	1.57	1.62	1.43	1.42	*ca.* 1.43
CH_2(4′)	2.02 (J = 5.7)	2.02	1.75, 1.91[d])	1.74, 1.89[d])	1.74, 1.90[d])
H–C(7′)	[c])	6.16	5.88 (J = 15.6)	5.88 (J = 15.4)	5.88 (J = 15.5)
H–C(8′)	[c])	6.14	6.29 (J = 15.6)	6.29 (J = 15.4)	6.29 (J = 15.5)
H–C(10′)	[b])	6.16 (J = 11.5)	6.19 (J = 11)	6.19 (J = 11.4)	6.19 (J = 11.1)
H–C(11′)	[b])	6.66 (J = 11.5, 15.0)	6.61 (J = 11, 14.9)	6.60 (J = 11.4, *ca.* 15)	6.61(J = 11.4, 14.9)
H–C(12′)	[b])	6.35 (J = 15.0)	6.37 (J = 14.9)	6.36 (J = 15)	6.36 (J = 14.9)
H–C(14′)	[b])	6.27	6.26	6.26	6.26
H–C(15′)	[b])	6.63	6.63	6.64	6.63
Me(16′)	1.03	1.03	0.94[e])	0.94[e])	0.94[e])
Me(17′)	1.03	1.03	1.10[e])	1.10[e])	1.10[e])
Me(18′)	1.72	1.72	1.15	1.15	1.15
Me(19′)	1.96	1.96	1.93	1.93	1.93
Me(20′)	1.97	1.97	1.96	1.96	1.96

[a]) Chemical shifts δ [ppm] and in parentheses averaged coupling constant J(H,H) values [Hz].
[b]) Not assigned.
[c]) Signals overlapped.
[d]) No assignment to axial or equatorial position.
[e]) Assignment may be interchanged.

tion by NMR spectroscopy. The 5′,6′-epoxide **5** is a carotenoid with two different chiral end groups, and its CD spectrum can be compared with the sum of the CD spectra of β-cryptoxanthin (**1**) and **3**. These two compounds exhibit maxima and minima in the same region which results in a spectrum with more or less the same shape and wavelengths of the maxima and minima but with different itensities. This establishes the (5′*R*,6′*S*)-configuration of **5**. In addition, also the comparison of the CD spectra of **1** and (5*R*,6*S*)-5,6-epoxy-β,β-carotene with the spectrum of **5** supports this assignment. In analogy, the (3*S*,5*R*,6*S*,5′*R*,6′*S*)-configuration for **6** and the (3*S*,5*S*,6*R*,5′*S*,6′*R*)-configuration for **7** can be deduced from the comparison of their CD spectra (*Fig. 2*) with those of the monoepoxides **3** and **4**, respectively.

Table 2. *^{13}C-NMR Data of the β-Cryptoxanthin Epoxides* **4**–**7**

	4	**5**	**6**	**7**
C(1)	35.11	37.13	35.37	35.11
C(2)	43.84	48.46	47.23	43.84
C(3)	64.12	65.09	64.34	64.11
C(4)	39.27	42.58	41.05	39.27
C(5)	65.28	126.17	66.95	65.28
C(6)	71.33	137.78	70.33	71.33
C(7)	122.46	125.59	123.84	122.49
C(8)	138.17	138.51	137.38	138.17
C(9)	134.06	135.69	134.28	134.12
C(10)	132.49	131.32	132.29	132.45
C(11)	124.53	124.95	124.66	124.61
C(12)	138.37	137.57	138.23	138.35
C(13)	136.78	136.37[a])	136.37[a])	136.33[a])
C(14)	132.33	132.58[b])	132.72[b])	132.71[b])
C(15)	130.41[a])	130.04[c])	130.25	130.30
Me(16)	26.11	28.73[d])	24.93[c])	26.10
Me(17)	26.88	30.26[d])	29.60[c])	26.88
Me(18)	21.26	21.62	20.02	21.26
Me(19)	12.97	12.75	13.01	13.00[c])
Me(20)	12.80[b])	12.80	12.81	12.81
C(1′)	34.30	33.84	33.86	33.86
C(2′)	39.68	35.76	35.77	35.77
C(3′)	19.29	17.11	17.13	17.13
C(4′)	35.14	30.11	30.12	30.13
C(5′)	129.41	65.51	65.52	65.53
C(6′)	137.94	71.39	71.40	71.41
C(7′)	126.75	124.16	124.20	124.20
C(8′)	137.77	137.25	137.25	137.26
C(9′)	136.16	134.48	134.54	134.55
C(10′)	130.82	131.94	131.93	131.93
C(11′)	125.20	124.77	124.85	124.86
C(12′)	137.19	137.96	137.95	137.95
C(13′)	136.78	136.54[a])	136.53[a])	136.56[a])
C(14′)	133.05	132.76[b])	132.90[b])	132.98[b])
C(15′)	129.84[a])	130.18[c])	130.10	130.09
Me(16′)	29.37	25.99[e])	25.91[d])	25.91[d])
Me(17′)	29.37	25.90[e])	26.00[d])	26.00[d])
Me(18′)	21.78	21.16	21.18	21.17
Me(19′)	12.84	12.99	13.01	12.98[c])
Me(20′)	12.78[b])	12.80	12.81	12.81

[a]) to [e]) Assignment may be interchanged.

Although our investigations do not represent a quantitative analysis of the reaction products, our results demonstrate that, as expected, at the hydroxylated end group, the (3*S*,5*S*,6*R*)-isomer is formed in preference compared to the (3*S*,5*R*,6*S*)-isomer. However, it is remarkable that also the latter configuration is formed in significant amounts in **3** and **6** under the described experimental conditions, *i.e.*, oxidation with monoperoxy-

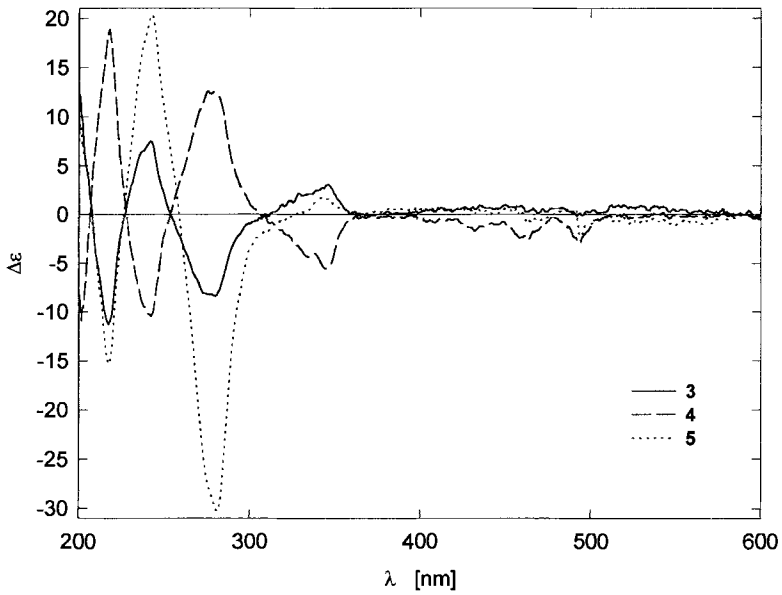


Fig. 1. *CD Spectra* (Et_2O/isopentane/EtOH 5:5:2) *of monoepoxides* **3**–**5**

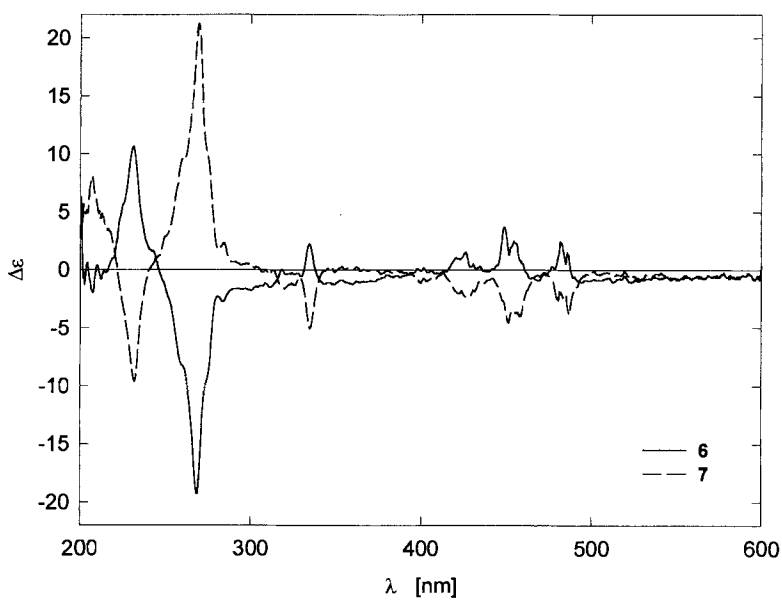


Fig. 2. *CD Spectra* (Et_2O/isopentane/EtOH 5:5:2) *of diepoxides* **6** *and* **7**

phthalic acid. On the other hand, the epoxidation of the diacetate of zeaxanthin (= (3*R*,3′*R*)-β,β-carotene-3,3′-diol) with perbenzoic acid gave 'mesoviolaxanthin' only in a small amount, and no violaxanthin with the (3*S*,5*R*,6*S*)-configuration at both end groups was detected [16].

With the fully characterized reference compounds in hand, the monoepoxide of cryptoxanthin (**1**) isolated from yellow, tomato-shaped paprika [9] was compared with **3**–**5**. The co-chromatography in different HPLC systems showed identity with **3**, and, therefore, the proposed structure of (3*S*,5*R*,6*S*)-5,6-epoxy-cryptoxanthin with the same configuration as violaxanthin for the natural product is strongly supported.

In view of the identification of further naturally occurring oxygenated derivatives of β-cryptoxanthin (**1**), the structure elucidation of the minor products of the epoxidation of **2** is under investigation.

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Experimental Part

General. The solvents (*puriss.* or *p.a.*) were freshly distilled before use. The acetylation of **1** was performed according to [17], the furanoid rearrangement according to [18]. HPLC: *Gynkotek* pump model *300 B* with *Gynkotek* gradient former; *Waters-991* detector, photo-diode array; column 250 × 4.6 mm i.d., *Chromsyl* C_{18}, 6 μm, endcapped; mobile phase: eluent *A*, 6% H_2O in MeOH; eluent *B*, MeOH; eluent *C*, MeOH/acetone 1:1; gradient program: 0–4 min 100% *A*, 4–10 min → 100% *B*, 10–12 min 100% *B*, 12–19 min → 100% *C*, 19–25 min 100% *C* (linear steps). CC: $CaCO_3$ (*Biogal*, Hungary), columns 6 × 30 cm; after development, the columns were extruded and cut into pieces. UV/VIS: *Beckman-DU 65*. CD: *Jobin-Yvon Dichrograph-6*; in EPA (Et_2O/isopentane/EtOH 5:5:2) at r.t. and − 180°. NMR: *Bruker AC 300* (^1H 300.13 MHz, ^{13}C 75.47 MHz) and *Bruker AM 400* (^1H 400.14 MHz, ^{13}C 100.61 MHz); chemical shifts δ in ppm (rel. to the solvent signal), coupling constants *J* in Hz; $CDCl_3$ was purified by passing two times through a column (Al_2O_3) before use. Mass spectra: *Varian MA-CH 7A*; *m/z* (rel. intensity in %).

Epoxidation of **2**. To a soln. of **2** (270 mg; m.p. 130–132°) in Et_2O (800 ml) was added at r.t. *ca.* 0.05M monoperoxyphthalic acid in Et_2O (50 ml). The mixture was kept under N_2 in the dark, and after 24 and 53 h, resp., additional monoperoxyphthalic acid soln. (25 and 20 ml) was added. After 70 h, the mixture was washed with 5% aq. $NaHCO_3$ soln., the org. phase dried (Na_2SO_4), and 30% KOH/MeOH soln. (100 ml) added. After 16 h, the soln. was washed with H_2O until neutral, dried (Na_2SO_4), and evaporated.

Column Chromatography of Epoxide Mixture. The residue was dissolved in hexane and submitted to CC (10 columns, eluent benzene/hexane 15:85 and 20:80). Picture after development: 5 mm bright yellow (*Zone 1*, complex mixture, not identified); 10 mm intermediate zone; 60 mm bright yellow (*Zone 2*, mixture); 10 mm pale ochre (*Zone 3*, not identified); 20 mm intermediate zone; 10 mm ochre (*Zone 4*, mixture); 5 mm ochre (*Zone 5*, not identified); 20 mm orange-yellow (*Zone 6*). The *Zone 2* was submitted to a second CC (10 columns, benzene/hexane 15:85). Picture after development: 2 mm yellow (epimers of β-cryptochrom); 5 mm intermediate zone; 10 mm yellow (epimers of β-cryptoflavin); 3 mm intermediate zone; 10 mm bright yellow (complex mixture); 15 mm intermediate zone; 20 mm yellow (mixture containing **3** and **5**–**7**). The last zone was submitted to a third CC (9 columns, benzene/hexane 20:80). Picture after development: 5 mm intermediate zone; 1 mm lemon yellow; 1 mm intermediate zone; 1 mm lemon yellow; 2 mm intermediate zone; 8 mm yellow (**7**); 2 mm intermediate zone; 5 mm yellow (**6**); 20 mm intermediate zone; 8 mm ochre (**3**); 30 mm intermediate zone; 7 mm ochre (**5**). Also *Zone 4* was submitted to a second CC (18 columns, benzene/hexane 20:80). Picture after development: 1 mm bright yellow; 5 mm intermediate zone; 16 mm yellow to bright yellow (mixture containing **4**); 10 mm intermediate zone; 40 mm yellow (mixture of **1** and **5**); 40 mm ochre (**1**). The zone containing **4** was submitted to a third CC (10 columns, benzene/hexane 25:75). Picture after development: 5 mm bright yellow, 10 mm intermediate zone; 10 mm yellow (**4**); 8 mm bright yellow. Also the zone containing **1** and **5** was submitted to a third CC (10 columns, benzene/hexane 15:85). Picture after development: 6 mm lemon yellow; 25 mm intermediate zone; 20 mm yellow

(**5**), 20 mm intermediate zone; 15 mm orange-yellow (**1**). After the CC separation, the epoxides were crystallized from benzene/hexane to give 1.7 mg of **3**, 5.2 mg of **4**, 21.2 mg of **5**, 2.0 mg of **6**, and 7.4 mg of **7**.

*(all-*E,*3*S,*5*R,*6*S*)*-5,6-Epoxy-β-cryptoxanthin* (= *(all-*E,*3*S,*5*R,*6*S*)*-5,6-Epoxy-5,6-dihydro-β,β-caroten-3-ol*; **3**): M.p. 154–156°. UV/VIS (benzene): 435, 458, 488; after furanoid rearrangement: 416, 438, 465. CD ($1.14 \cdot 10^{-4}$ mol/l, 0.1 cm, −180°): 217.5 (−1.12), 242 (+ 7.50), 280 (−8.40), 346 (+ 3.06). NMR: *Tables 1* and *2*. EI-MS: 568 (100, M^+), 488 (83, $[M-80]^+$), 476 (19, $[M-92]^+$), 422 (17), 396 (13), 365 (11), 352 (45), 325 (8), 299 (12), 287 (7), 284 (8), 247 (8), 234 (8), 221 (47), 209 (9), 208 (8), 203 (11), 197 (11), 105 (10), 181 (16), 173 (10), 171 (12), 165 (14), 159 (17), 157 (16), 145 (17), 133 (14), 121 (15), 119 (22), 107 (12), 105 (15).

*(all-*E,*3*S,*5*S,*6*R*)*-5,6-Epoxy-β-cryptoxanthin* (= *(all-*E,*3*S,*5*S,*6*R*)*-5,6-Epoxy-5,6-dihydro-β,β-caroten-3-ol*; **4**): M.p. 158–159°. UV/VIS (benzene): 434, 458, 488; after furanoid rearrangement: 416, 438, 465. CD ($1.13 \cdot 10^{-4}$ mol/l, 0.1 cm, −180°): 218 (+ 1.89), 242.5 (−1.04), 275.5 (+ 1.25), 344.5 (−5.49), 463.5 (−2.65), 478 (−0.33), 493.5 (−3.03). NMR: *Tables 1* and *2*. EI-MS: 568 (100, M^+), 480 (41, $[M-80]^+$), 476 (10, $[M-92]^+$), 422 (10), 352 (19), 325 (6), 299 (11), 287 (9), 286 (20), 247 (8), 234 (7), 221 (35), 209 (11), 208 (7), 203 (11), 197 (16), 185 (10), 181 (21), 173 (9), 171 (14), 161 (12), 159 (16), 157 (17), 147 (11), 145 (20), 133 (14), 121 (15), 119 (24), 109 (10), 107 (13), 105 (16).

*(all-*E,*3*R,*5*'R,*6*'S*)*-5',6'-Epoxy-β-cryptoxanthin* (= *(all-*E,*3*R,*5*'R,*6*'S*)*-5',6'-Epoxy-5',6'-dihydro-β,β-caroten-3-ol*; **5**): M.p. 158–160°. UV/VIS (benzene): 434, 459, 488; after furanoid rearrangement: 416, 437, 465. CD ($9.7 \cdot 10^{-5}$ mol/l, 0.1 cm, −180°): 217.5 (−1.53), 243 (+ 2.04), 281 (−3.03), 342 (+ 1.71), 494 (−2.69). NMR: *Tables 1* and *2*. EI-MS: 568 (100, M^+), 488 (90, $[M-80]^+$), 476 (24, $[M-92]^+$), 422 (16), 396 (13), 349 (11), 336 (44), 284 (12), 283 (17), 271 (11), 231 (10), 218 (12), 209 (9), 205 (57), 197 (11), 192 (11), 185 (10), 183 (10), 173 (11), 171 (13), 165 (21), 159 (16), 157 (18), 147 (12), 145 (18), 143 (10), 135 (14), 133 (13), 121 (14), 119 (21), 109 (11), 107 (12), 105 (13).

*(all-*E,*3*S,*5*R,*6*S,*5*'R,*6*'S*)*-5,6:5',6'-Diepoxy-β-cryptoxanthin* (= *(all-*E,*3*S,*5*R,*6*S,*5*'R,*6*'S*)*-5,6:5',6'-Diepoxy-5,6,5',6'-tetrahydro-β,β-caroten-3-ol*; **6**): M.p. 162–164°. UV/VIS (benzene): 427, 453, 483; after furanoid rearrangement: 388, 410, 436. CD ($1.3 \cdot 10^{-4}$ mol/l, 0.1 cm, −180°): 204.5 (+ 6.12), 207 (−12.87), 231 (+ 1.06), 268.5 (−1.92), 334.5 (+ 2.28), 449 (+ 3.71), 468.5 (−0.92), 482 (+ 2.27). NMR: *Tables 1* and *2*. EI-MS: 584 (100, M^+), 504 (22, $[M-80]^+$), 492 (6, $[M-92]^+$), 336 (8), 283 (8), 271 (6), 247 (6), 221 (20), 210 (7), 209 (10), 205 (22), 197 (11), 185 (11), 181 (10), 173 (10), 171 (16), 165 (14), 159 (15), 157 (18), 147 (11), 145 (17), 143 (9), 135 (10), 133 (12), 123 (10), 121 (13), 119 (15), 109 (16), 107 (12), 105 (11).

*(all-*E,*3*S,*5*S,*6*R,*5*'S,*6*'R*)*-5,6:5',6'-Diepoxy-β-cryptoxanthin* (= *(all-*E,*3*S,*5*S,*6*R,*5*'S,*6*'R*)*-5,6:5',6'-Diepoxy-5,6,5',6'-tetrahydro-β,β-caroten-3-ol*; **7**): M.p. 174–175°. UV/VIS (benzene): 427, 453, 483; after furanoid rearrangement: 388, 410, 436. CD ($9.9 \cdot 10^{-5}$ mol/l, 0.1 cm, −180°): 203 (+ 4.79), 207 (+ 7.72), 231 (−9.47), 269 (+ 2.11), 334.5 (−5.02), 451 (−4.41), 472 (−0.21), 486.5 (−3.75). NMR: *Tables 1* and *2*. EI-MS: 584 (100, M^+), 504 (29, $[M-80]^+$), 492 (10, $[M-92]^+$), 336 (10), 286 (12), 283 (9), 271 (9), 247 (10), 234 (9), 221 (31), 218 (11), 209 (12), 205 (31), 203 (8), 197 (15), 185 (13), 181 (18), 173 (12), 171 (18), 169 (10), 165 (17), 161 (11), 159 (20), 157 (22), 147 (13), 145 (23), 143 (13), 135 (12), 133 (16), 123 (13), 121 (16), 119 (19), 109 (20), 107 (15), 105 (15).

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