Partial Synthesis and Characterization of Capsokarpoxanthins and 3,6-Epoxycapsanthins

by **József Deli**[a]), **Péter Molnár**[a]), **Zoltán Matus**[a]), **Gyula Tóth**[a])*, **Andrea Steck**[b]), and **Hanspeter Pfander**[b])*

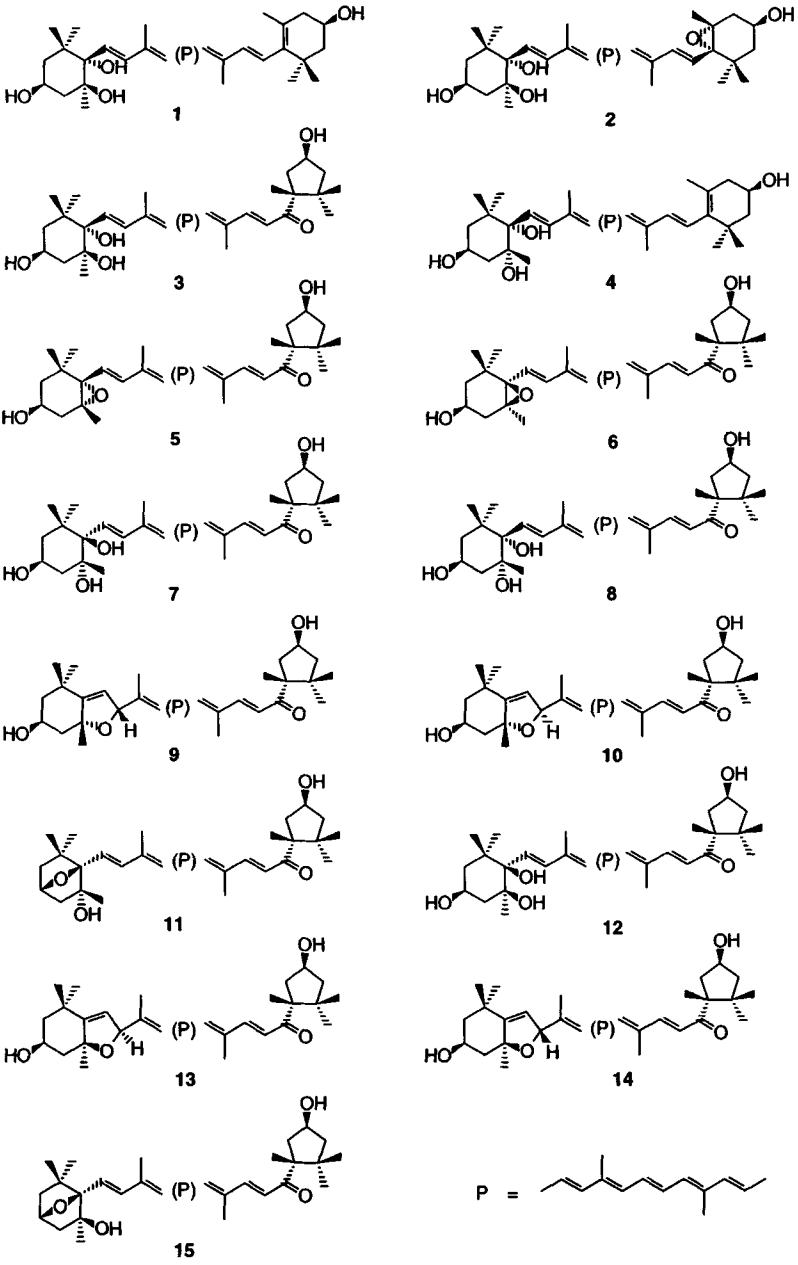
[a]) Department of Medical Chemistry, University Medical School of Pécs, P.O. Box 99, H-7601 Pécs
[b]) Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern

The acid-catalyzed hydrolysis of (3*S*,5*R*,6*S*,3'*S*,5'*R*)-5,6-epoxycapsanthin (**5**) led to (3*S*,5*R*,6*R*,3'*S*,5'*R*)- (**7**) and (3*S*,5*R*,6*S*,3'*S*,5'*R*)-capsokarpoxanthin (**8**). In addition, (3*S*,5*R*,8*R*,3'*S*,5'*R*)- (**9**), (3*S*,5*R*,8*S*,3'*S*,5'*R*)-capsochrome (**10**), and (3*S*,5*R*,6*R*,3'*S*,5'*R*)-3,6-epoxycapsanthin (**11**) were obtained. The acid-catalyzed hydrolysis of (3*S*,5*S*,6*R*,3'*S*,5'*R*)-5,6-epoxycapsanthin (**6**) afforded (3*S*,5*S*,6*R*,3'*S*,5'*R*)-capsokarpoxanthin (**12**), (3*S*,5*S*,8*S*,3'*S*,5'*R*)- (**13**) and (3*S*,5*S*,8*R*,3'*S*,5'*S*)-capsochrome (**14**) as well as (3*S*,5*S*,6*R*,3'*S*,5'*R*)-3,6-epoxyepicapsanthin (**15**). Compounds **5**–**15** were isolated in crystalline form and characterized by their UV/VIS, CD, ^{1}H- and ^{13}C-NMR, and mass spectra.

Introduction. – In the preceding paper [1], we described the isolation of 5,6-diepikarpoxanthin (**1**), 5,6-diepilatoxanthin (**2**), and 5,6-diepicapsokarpoxanthin (**3**), which all contain the (3*S*,5*S*,6*S*)-trihydroxy-5,6-dihydro-β-end group, and of 6-epikarpoxanthin (**4**) containing the (3*S*,5*R*,6*S*)-trihydroxy-5,6-dihydro-β-end group, from red paprika. In view of the structure elucidation of the natural 5,6-diepicapsokarpoxanthin (**3**), which was isolated for the first time, we report in the present paper the partial synthesis of several stereoisomers of **3** by acid-catalyzed hydrolysis of (3*S*,5*R*,6*S*,3'*S*,5'*R*)- (**5**) and (3*S*,5*S*,6*R*,3'*S*,5'*R*)-5,6-epoxycapsanthin (**6**) ('*anti*'-**5** and '*syn*'-**6**, resp.). For the structure elucidation of the 3,5,6-trihydroxy-5,6-dihydro-β-end groups, the partial synthesis by acid-catalyzed hydrolysis of 3-hydroxy-5,6-epoxy carotenoids has been successfully used before. By application of this method, heteroxanthin [2], karpoxanthin and 6-epikarpoxanthin [3], neoflor and 6-epineoflor [4] have been identified. It was demonstrated that, during the hydrolysis of 5,6-epoxy carotenoids, the configuration at C(5) is maintained, whereas at C(6) both configurations are obtained.

Results. – *Preparation and Characterization of 5,6-Epoxycapsanthins.* For the epoxidation, 800 mg of crystalline capsanthin (*ex.* paprika) was transformed into the diacetate [5], then treated with monoperoxyphthalic acid according to [6], and afterwards the reaction mixture was directly hydrolyzed with 30% KOH/MeOH. After usual work-up, the mixture was separated by column chromatography to give 84 mg of (3*S*,5*R*,6*S*,3'*S*,5'*R*)-5,6-epoxycapsanthin (**5**), 212 mg of (3*S*,5*S*,6*R*,3'*S*,5'*R*)-5,6-epoxycapsanthin (**6**), and 116 mg of the mixture of capsochrome epimers, all in crystalline form. In the UV/VIS spectra, the maxima for **5** and **6** (507 and 481 nm in benzene) are in accordance with the data reported in [7]. The mass spectra of **5** and **6** exhibited the same molecular ion (*m/z* 600) and fragments at *m/z* 582 ($[M - H_2O]^+$), 221, 181 [8] indicating a 3-hydroxy-5,6-epoxy-5,6-dihydro-β-end group, and at *m/z* 109 characteristic for a

κ-end group. Detailed structure information about the constitutions and configurations of **5** and **6** were derived from various NMR experiments, which allowed complete ^{1}H and ^{13}C signal assignments. The spectral data fully correspond to the stereoisomers **5** and **6** and to the data given in [9][10].



The CD spectra of the 5,6-epoxycapsanthin **5** and **6** are opposite, demonstrating the different configuration of the 5,6-epoxy-end groups which are mainly responsible for the sign of the *Cotton* effect and are in agreement with the data reported before [7].

Hydrolysis of 5,6-Epoxycapsanthins **5** *and* **6**. The 5,6-epoxycapsanthins **5** and **6** were hydrolyzed according to *Eugster*'s method [3] in a mixture of THF and H_2O in the presence of 0.001N H_2SO_4. The reaction mixtures were separated by repeated column chromatography, and then the products were crystallized.

The hydrolysis of 84 mg of (3*S*,5*R*,6*S*,3′*S*,5′*R*)-5,6-epoxycapsanthin (**5**) gave two trihydroxy compounds, namely, 3.8 mg of (3*S*,5*R*,6*R*,3′*S*,5′*R*)-capsokarpoxanthin (**7**) and 1.3 mg of (3*S*,5*R*,6*S*,3′*S*,5′*R*)-capsokarpoxanthin (**8**). In addition, 16.3 mg of (3*S*,5*R*,8*R*,3′*S*,5′*R*)- (**9**) and 11 mg of (3*S*,5*R*,8*S*,3′*S*,5′*R*)-capsochrome (**10**), and unexpectedly also 0.7 mg of (3*S*,5*R*,6*R*,3′*S*,5′*R*)-3,6-epoxycapsanthin (**11**) were obtained.

The hydrolysis of 106 mg of (3*S*,5*S*,6*R*,3′*S*,5′*R*)-5,6-epoxycapsanthin (**6**) gave 7 mg of (3*S*,5*S*,6*R*,3′*S*,5′*R*)-capsokarpoxanthin (**12**), 21.5 mg of (3*S*,5*S*,8*S*,3′*S*,5′*R*)- (**13**) and 11.2 mg of (3*S*,5*S*,8*R*,3′*S*,5′*R*)-capsochrome (**14**), as well as 4.1 mg of (3*S*,5*S*,6*R*,3′*S*,5′*R*)-3,6-epoxyepicapsanthin (**15**). The formation of two trihydroxy compounds, **7** and **8**, from the '*anti*'-epoxide **5**, but only one trihydroxy compound, **12**, starting from the '*syn*'-epoxide has been observed previously by *Eugster* and coworkers [11].

On acid treatment, the 3,6-epoxy compound **15** and the 3,5,6-trihydroxy compound **12** underwent a furanoid-oxide reaction, and, for both reactions, the products were identical with **13** and **14** in HPLC.

Spectroscopic Characterization of the Capsokarpoxanthins **7**, **8**, *and* **12**. In each case, the mass spectra exhibited the corresponding molecular-ion peaks at *m/z* 618. In addition to the signals typical for hydroxy carotenoids ($[M - H_2O]^+$; $[M -$ toluene$]^+$), strong peaks at *m/z* 221 and 181, characteristic for the 3,5,6-trihydroxy-end group, were observed. Diagnostically relevant ^{1}H-NMR data for compounds with the (3*S*,5*R*,6*R*)-, (3*S*,5*R*,6*S*)-, (3*S*,5*S*,6*R*)-, and (3*S*,5*S*,6*S*)-3,5,6-trihydroxy-5,6-dihydroxy-β-end group have been reported by *Eugster* and co-workers [11]. Based on these results, the configuration of the 3,5,6-trihydroxy-end group of the capsokarpoxanthins obtained by partial synthesis can be confirmed as (3*S*,5*R*,6*R*) for **7**, as (3*S*,5*R*,6*S*) for **8**, and as (3*S*,5*S*,6*R*) for **12**, whereas the natural capsokarpoxanthin isolated from paprika possesses the (3*S*,5*S*,6*S*)-configuration (**3**). By comparing the ^{1}H 'fingerprints' of **7** and **8** with the corresponding data in [11], contrary assignments of Me(17) and Me(18) can be noticed: strong Me(16) << Me(17) COSY cross-peaks, however, rendered our spectral analysis correct. The separation of the stereoisomers **3**, **7**, **8**, and **12** on a reversed-phase HPLC column confirm that **3**, isolated from paprika, is not identical with the stereoisomers obtained by partial synthesis.

CD Spectra of the capsokarpoxanthins **7**, **8**, and **12** are presented in *Fig. 1*. Due to their saturated cyclic end group, they show relatively weak nonconservative CD. The features of the spectra are strongly influenced by the absolute configuration of the OH substituents, whereas conformation changes at C(5) are more sensitive than at C(6).

Spectroscopic Characterization of the 3,6-Epoxycapsanthins **11** *and* **15**. In both cases the mass spectra showed the corresponding molecular-ion peaks at *m/z* 600. In addition to the signals typical for hydroxy carotenoids ($[M - H_2O]^+$; $[M -$ toluene$]^+$), strong peaks at *m/z* 286, 221, 160, 155, and 43, characteristic for the 3,6-epoxy-end group, were

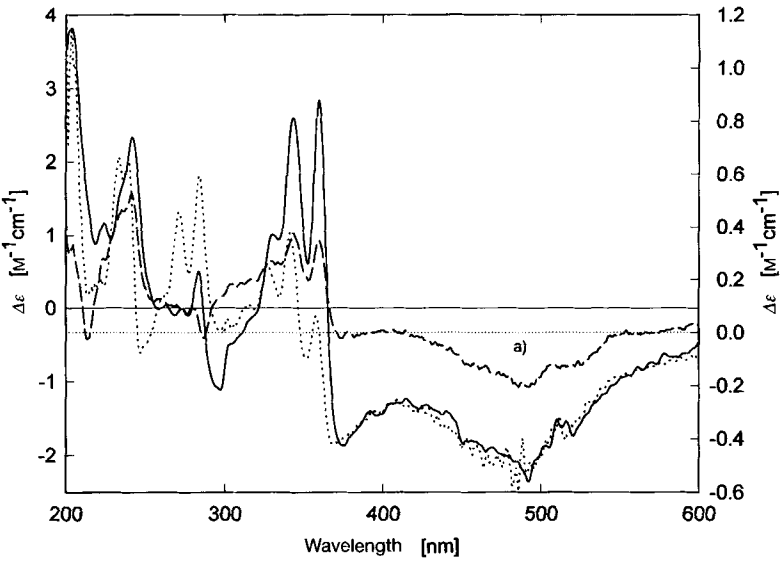


Fig. 1. *CD Spectra of (3*S,5R,6R,3′S,5′R*)-capsokarpoxanthin* (**7**; solid line), *(3*S,5R,6S,3′S,5′R*)-capsokarpoxanthin* (**8**; dashed line), *and (3*S,5S,6R,3′S,5′R*)-capsokarpoxanthin* (**12**; dotted line) *in Et_2O/isopentane/EtOH 5:5:2 at −180°*. a) Null line for (3*S*,5*S*,6*R*,3′*S*,5′*R*)-capsokarpoxanthin (**12**).

observed. The ^{1}H- and ^{13}C-NMR results fully confirm the constitutions and configurations of both 3,6-epoxycapsanthins. A comparison of the ^{1}H-NMR data of the (3*S*,5*R*,6*R*)-3,6-epoxy-end group in **11** with the data in [12] showed identity, and the majority of the ^{13}C chemical shifts were obtained by ^{13}C- and inverse HMQC experiments. The NMR data of the (3*S*,5*S*,6*R*)-3,6-epoxy-end group of the stereoisomer **15** deviate significantly from those of **11**, affecting the ^{1}H and ^{13}C chemical shifts of all the end-group nuclei but mainly the ^{1}H chemical shift of H–C(8) and the ^{13}C chemical shift of C(5), an influence expected for an inversion at C(5).

The saturated cyclic end group of **11** and **15** led to nonconservative CD spectra as shown in *Fig. 2*. Here, the chiral perturbation introduced by the OH group at C(5) is apparently stronger for the absolute configuration (5*S*) than for (5*R*).

Spectroscopic Characterization of the Capsochrome Stereoisomers **9**, **10**, **13**, *and* **14**. In each case, the mass spectra showed the corresponding molecular-ion peaks at *m*/*z* 600. In addition to the signals typical for hydroxy carotenoids ($[M - H_2O]^+$; $[M -$ toluene$]^+$), strong peaks at *m*/*z* 221 and 181 were found, indicating the 3-hydroxy-5,8-epoxy-end group.

The ^{1}H- and ^{13}C-NMR data were found to be identical with corresponding information from the literature [9], and established the constitutions and configurations of the four stereoisomers.

Discussion. – Our results confirm the results of *Eugster* and co-workers [3][4][11] and show that the configuration of 3,5,6-trihydroxy carotenoids originating from 3-hydroxy-5,6-epoxy carotenoids by hydrolysis does not depend on the remote end group. The same two (3*S*,5*R*,6*S*)- and (3*S*,5*R*,6*R*)-3,5,6-trihydroxy-5,6-dihydro-β-end groups have been

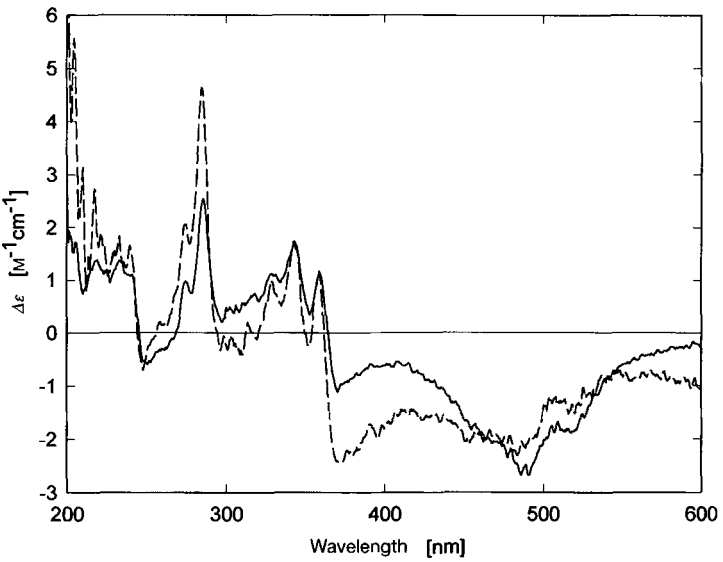


Fig. 2. *CD Spectra of (3S,5R,6R,3'S,5'R)-3,6-epoxycapsanthin* (**11**; solid line) *and (3S,5S,6R,3'S,5'R)-3,6-epoxyepicapsanthin* (**15**; dashed line) *in Et_2O/isopentane/EtOH 5:5:2 at −180°*

obtained from (3*S*,5*R*,6*S*)-antheraxanthin containing the 3-hydroxy-β-end group, from (3*S*,5*R*,6*S*)-5,6-epoxylutein containing the 3-hydroxy-ε-end group, and from (3*S*,5*R*,6*S*)-5,6-epoxycapsanthin containing the 3-hydroxy-κ-end group. In the acid-catalyzed hydrolysis, the configuration of the 3-hydroxy-5,6-epoxy-β-end group is decisive for the configuration of the 3,5,6-trihydroxy-5,6-dihydro-β-end group. The proposed mechanism for the formation of 3,5,6-trihydroxy-carotenoids is shown in the *Scheme*. The formation of 3,6-epoxy carotenoids in the acid-catalyzed hydrolysis has not been reported previously, and further investigations of this new reaction are in progress.

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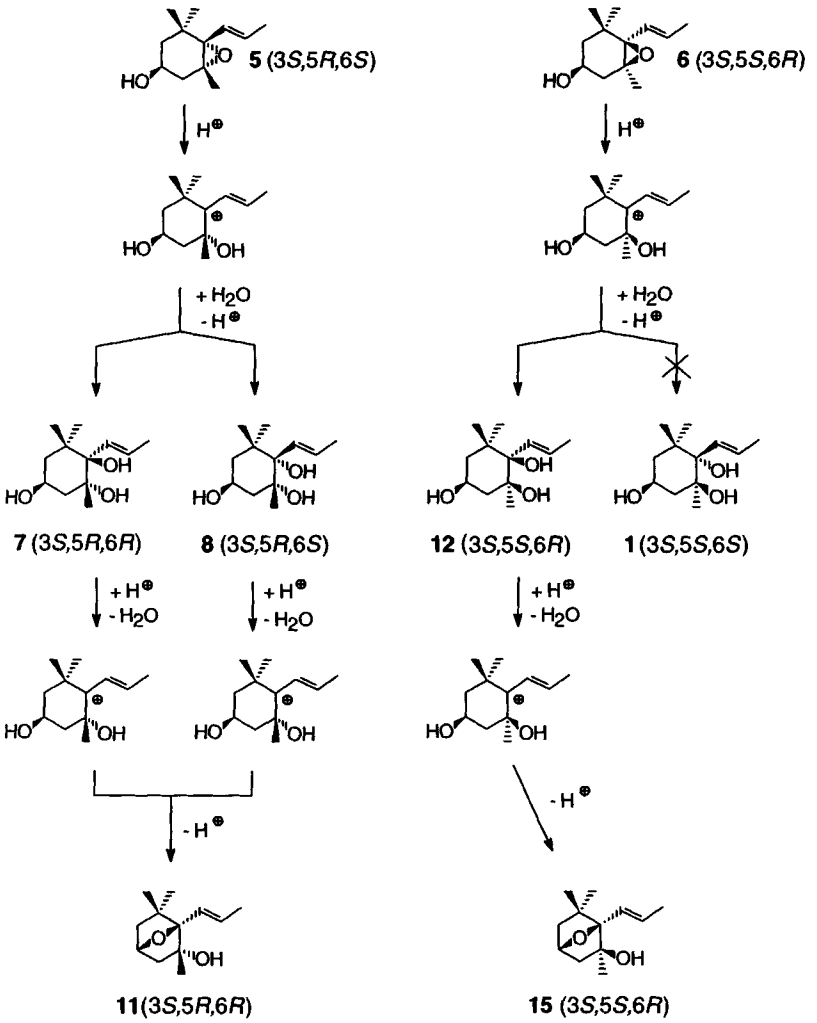
Experimental Part

1. *General.* The solvents (*puriss.* or *p.a.*) were freshly distilled before use. The acetylation of capsanthin was performed according to [13], the furanoid rearrangement according to [14]. HPLC: *Gynkotek* pump model *300 B* with *Gynkotek* gradient former; detector, *Waters-991*, photodiode array. Column: 250 × 4.6 mm i.d., *Chromsyl* C_{18}, 6 μm, endcapped. Mobile phase: eluent *A*: 12% H_2O in MeOH, eluent *B*: MeOH, eluent gradient program: 0–2 min: 100% *A*; 2–10 min: to 80% *A*/20% *B*; 10–18 min: to 50% *A*/50% *B*; 18–25 min: to 100% *B*; 25–31 min: 100% *B* (linear steps). CC: $CaCO_3$ (*Biogal*, Hungary) columns 6 × 30 cm. After development, the columns were extruded and cut into pieces. TLC: Silica F_{254} (*Merck 5554*); benzene/AcOEt/MeOH 7:2:1. UV/VIS: *Beckman DU-65*. CD: *Jobin-Yvon Dichrograph CD-6* in EPA (Et_2O/isopentane/EtOH 5:5:2) at r.t. and −180°. NMR: *Bruker AM 400* and *Bruker DRX 400* (^1H: 400.14 MHz, ^{13}C: 100.61 MHz); chemical shifts (δ) in ppm (relative to the solvent signal), *J* in Hz; solvent: $CDCl_3$, purified by passing two times through a column with Al_2O_3 before use. MS: *Varian MA-CH 7A*; *m/z* (rel. intensity in %).

Scheme



2. *Preparation of 5,6-Epoxycapsanthins.* To a soln. of 900 mg of capsanthin diacetate in 3000 ml of Et_2O were added, at r.t., 12 ml of 0.775M monoperoxyphthalic acid in Et_2O. The mixture was kept under N_2 in the dark, and, after 22, 53, and 69 h, an additional 15, 18, and 8 ml, respectively, of the monoperoxyphthalic acid soln. were added. The reaction was monitored by UV/VIS and TLC. After 75 h, the mixture was washed with 5% aq. $NaHCO_3$ soln., the org. phase was dried (Na_2SO_4), and afterwards 600 ml of a 30% KOH/MeOH soln. were added. After 16 h, the Et_2O soln. was washed with H_2O until neutral, dried (Na_2SO_4), and evaporated. The residue was dissolved in benzene and submitted to CC: 35 columns; eluent, benzene. Picture after development: 25 mm ochre (zone *1*, mixture of capsochromes and (*Z*)-compounds); 80 mm orange (**5**); 30 mm orange reddish (**6**), 15 mm intermediate zone; 60 mm red (capsanthin). After the CC separation, the pigments were crystallized from benzene/hexane to give 84 mg of **5**, 212 mg of **6**, 200 mg of capsanthin, and 212 mg of a mixture of capsochromes and (*Z*)-isomers.

3. *(3*S,*5*R,*6*S,*3'*S,*5'*R*)-5,6-Epoxycapsanthin* (*(all*-E,*3*S,*5*R,*6*S,*3'*S,*5'*R*)-5,6-Epoxy-5,6-dihydro-3,3'-dihydroxy-β,κ-caroten-6'-one*; **5**): 84 mg. M.p. 176–178°. UV/VIS (benzene): 507, 478; after acid treatment: 486, 464 nm. CD (EPA, r.t.): 216 (−12.10), 243 (+ 2.98), 282 (−13.29), 348 (+ 3.83). CD (EPA, −180°): 217 (−16.85), 244

(+ 13.63), 276 (−9.22), 279 (−8.17), 286 (−19.76), 345 (+ 7.17), 353 (+ 3.21), 360 (+ 9.75). ^{1}H-NMR ($CDCl_3$): 0.84 (*s*, Me(16′)); 0.98 (*s*, Me(17)); 1.15 (*s*, Me(16)); 1.19 (*s*, Me(18)); 1.21 (*s*, Me(17′)); 1.25 (*dd*, J_{gem} = 14.7, J(2ax,3) = 10.2, H_{ax}–C(2)); 1.37 (*s*, Me(18′)); 1.49 (*dd*, J_{gem} = 14.4, J(4′ax,3′) = 3.2, H_{ax}–C(4′)); 1.63 (*ddd*, J_{gem} = 14.7, J(2eq,3) = 3.6, J(2eq,4) = 1.7, H_{eq}–C(2)); 1.63 (*dd*, J_{gem} = 14.2, J(4ax,3) = 8.8, H_{ax}–C(4)); 1.71 (*dd*, J_{gem} = 13.7, J(2′ax,3′) = 4.6, H_{ax}–C(2′)); 1.93 (*s*, Me(19)); 1.96 (*s*, Me(19′)); 1.98 (*s*, Me(20,20′)); 2.00 (*dd*, J_{gem} = 13.7, J(2′eq,3′) = 7.8, H_{eq}–C(2′)); 2.39 (*ddd*, J_{gem} = 14.2, J(4eq,3) = 4.9, J(4eq,2) = 1.6, H_{eq}–C(4)); 2.96 (*dd*, J_{gem} = 14.4, J(4′eq,3′) = 8.5, H_{eq}–C(4)); 3.91 (*m*, H–C(3)); 4.51 (*m*, H–C(3′)); 5.90 (*d*, J(7,8) = 15.5, H–C(7)); 6.20 (*d*, J(10,11) = 11.6, H–C(10)); 6.27 (*m*, H–C(14)); 6.30 (*d*, J(8,7) = 15.5, H–C(8)); 6.34 (*m*, H–C(14′)); 6.37 (*d*, J(12,11) = 13.0, H–C(12)); 6.44 (*d*, J(7′,8′) = 15.0, H–C(7′)); 6.51 (*d*, J(12′,11′) = 14.6, H–C(12′)); 6.56 (*d*, J(10′,11′) = 11.4, H–C(10′)); 6.61 (*dd*, J(11′,10′) = 11.4, J(11′,12′) = 14.6, H–C(11′)); 6.63 (*dd*, J(11,10) = 11.6, J(11,12) = 13.0, H–C(11)); 6.64 (*m*, H–C(15)); 6.69 (*m*, H–C(15′)); 7.33 (*d*, J(8′,7′) = 15.0, H–C(8′)). ^{13}C-NMR ($CDCl_3$)[1]): 12.75 (C(19))*; 12.86 (C(20,20′)); 13.04 (C(19′))*; 20.02 (C(18)); 21.31 (C(18′)); 24.93 (C(17)); 25.11 (C(17′)); 25.88 (C(16′)); 29.59 (C(16)); 35.37 (C(1)); 41.03 (C(4)); 43.98 (C(1′)); 45.33 (C(4′)); 47.20 (C(2)); 50.90 (C(2′)); 58.96 (C(5′)); 64.31 (C(3)); 66.98 (C(5)); 70.33 (C(6)); 70.38 (C(3′)); 120.94 (C(7′)); 124.13 (C(7)); 124.17 (C(11′)); 125.22 (C(11)); 129.91 (C(15)); 131.55 (C(15′)); 132.20 (C(10)); 132.69 (C(14)); 133.70 (C(9′)); 134.69 (C(9)); 135.19 (C(14′)); 136.05 (C(13)); 137.33 (C(8)); 137.42 (C(13′)); 138.05 (C(12)); 140.67 (C(10′)); 141.94 (C(12′)); 146.86 (C(8′)); 202.92 (C(6′)). EI-MS: 600 (5, M^+), 582 (3, $[M - H_2O]^+$), 520 (1), 508 (1), 492 (3), 221 (37), 181 (18), 109 (96), 91 (100).

4. *(3S,5S,6R,3′S,5′R)-5,6-Epoxycapsanthin* (*(all-*E*,3S,5S,6R,3′S,5′R)-5,6-Epoxy-5,6-dihydro-3,3′-dihydroxy-β,κ-caroten-6′-one*; **6**): 212 mg. M.p. 171–173°. UV/VIS (benzene): 508, 479 nm; after acid treatment: 486, 465. CD (EPA, r.t.): 216 (+ 9.18), 242 (−5.49), 282 (+ 17.80), 350 (−4.72). CD (EPA, −180°): 217 (+ 18.16), 244 (−11.83), 276 (+ 15.83), 279 (+ 14.47), 286 (+ 32.27), 346 (−4.82), 353 (−3.85), 361 (−9.44). ^{1}H-NMR ($CDCl_3$): 0.84 (*s*, Me(16′)); 1.01 (*s*, Me(17)); 1.16 (*s*, Me(16)); 1.19 (*s*, Me(18)); 1.21 (*s*, Me(17′)); 1.36 (*ddd*, J_{gem} = 12.6, J(2eq,3) = 3.9, J(2eq,4) = 1.3, H_{eq}–C(2)); 1.37 (*s*, Me(18′)); 1.49 (*dd*, J_{gem} = 14.4, J(4′ax,3′) = 3.2, H_{ax}–C(4′)); 1.61 (*dd*, J_{gem} = 12.6, J(2ax,3) = 10.8, H_{ax}–C(2)); 1.71 (*dd*, J_{gem} = 13.6, J(2′ax,3′) = 4.7, H_{ax}–C(2′)); 1.89 (*dd*, J_{gem} = 14.8, J(4ax,3) = 8.5, H_{ax}–C(4)); 1.93 (*s*, Me(19)); 1.96 (*s*, Me(19′)); 1.98 (*s*, Me(20,20′)); 2.00 (*dd*, J_{gem} = 13.6, J(2′eq,3′) = 7.8, H_{eq}–C(2′)); 2.20 (*ddd*, J_{gem} = 14.8, J(4eq,3) = 6.8, J(4eq,2) = 1.3, H_{eq}–C(4)); 2.96 (*dd*, J_{gem} = 14.4, J(4′eq,3′) = 8.5, H_{eq}–C(4′)); 3.88 (*m*, H–C(3)); 4.51 (*m*, H–C(3′)); 5.84 (*d*, J(7,8) = 15.6, H–C(7)); 6.20 (*d*, J(10,11) = 11.5, H–C(10)); 6.27 (*m*, H–C(14)); 6.30 (*d*, J(8,7) = 15.6, H–C(8)); 6.34 (*m*, H–C(14′)); 6.38 (*d*, J(12,11) = 14.8, H–C(12)); 6.44 (*d*, J(7′,8′) = 15.1, H–C(7′)); 6.52 (*d*, J(12′,11′) = 14.8, H–C(12′)); 6.55 (*d*, J(10′,11′) = 12.0, H–C(10′)); 6.62 (*dd*, J(11′,10′) = 12.0, J(11′,12′) = 14.8, H–C(11′), H–C(15)); 6.63 (*dd*, J(11,10) = 11.5, J(11,12) = 14.8, H–C(11)); 6.69 (*m*, H–C(15′)); 7.33 (*d*, J(8′,7′) = 15.1, H–C(8′)). ^{13}C-NMR ($CDCl_3$)[1]): 12.74 (C(19))*; 12.85 (C(20,20′)); 12.99 (C(19′))*; 21.24 (C(18′)); 21.31 (C(18)); 25.10 (C(17′)); 25.87 (C(16′)); 26.07 (C(16)); 26.87 (C(17)); 35.10 (C(4)); 39.25 (C(1)); 43.81 (C(2)); 43.97 (C(1′)); 45.32 (C(4′)); 50.88 (C(2′)); 58.94 (C(5′)); 64.07 (C(3)); 65.29 (C(5)); 70.36 (C(3′)); 71.31 (C(6)); 120.94 (C(7′)); 122.77 (C(7)); 124.18 (C(11′)); 125.16 (C(11)); 129.95 (C(15)); 131.53 (C(15′)); 132.37 (C(10)); 132.76 (C(14)); 133.71 (C(9′)); 134.52 (C(9)); 135.17 (C(14′)); 136.08 (C(13)); 137.37 (C(13′)); 138.11 (C(8)); 138.15 (C(12)); 140.66 (C(10′)); 141.92 (C(12′)); 146.85 (C(8′)); 202.92 (C(6′)). EI-MS: 600 (3, M^+), 582 (3, $[M - H_2O]^+$), 520 (1), 508 (1), 492 (1), 221 (38), 181 (21), 109 (10), 91 (67).

5. *Hydrolysis of* **5**. To a soln. of 84 mg of **5** in 500 ml of THF and 250 ml of H_2O, 250 ml of 0.0005M H_2SO_4 soln. were added at r.t. The mixture was kept under N_2 in the dark. The reaction was monitored by UV/VIS. After 4.5 h, the mixture was diluted with Et_2O, and washed wtih 5% aq. $NaHCO_3$ soln., the Et_2O phase was dried (Na_2SO_4), and then evaporated. The residue was dissolved in benzene and submitted to CC: 5 columns; eluent, benzene. Picture after development: 15 mm pale-yellow (zone *1*, mixture, not identified); 20 mm red (zone *2*, mixture **7**/**8**); 10 mm intermediate zone; 40 mm reddish-ochre (zone *3*, **9**); 30 mm orange (zone *4*, **10**); 20 mm pink (zone *5*, **11**). The zone *2* was submitted to a second CC: 2 columns, 10% acetone in benzene. Picture after development: 15 mm pale-yellow unidentified; 30 mm pink (**7**); 20 mm intermediate zone; 20 mm pink (**8**). Also the zone *5* containing **11** was submitted to a second CC: 1 column (30 × 5 cm), 3.5% acetone in hexane. Picture after development: 5 mm pale-reddish (unidentified); 10 mm intermediate zone; 15 mm pink (**11**). After CC separation, the pigments were crystallized from benzene/hexane to give 3.8 mg of **7**, 1.3 mg of **8**, 16.3 mg of **9**, 11.0 mg of **10**, and 0.7 of mg **11**.

6. *Hydrolysis of* **6**. To a soln. of 106 mg of **6** in 500 ml of THF and 250 ml of H_2O, 250 ml of 0.0005M H_2SO_4 soln. were added at r.t. The mixture was kept under N_2 in the dark. The reaction was monitored by UV/VIS. After

[1]) *: Signal assignments may be interchanged.

22.5 h, the mixture was diluted with Et_2O, and washed with 5% aq. $NaHCO_3$ soln., the Et_2O phase was dried (Na_2SO_4) and was evaporated. The residue was dissolved in benzene and submitted to CC: 6 columns; eluent, 1% acetone in benzene. Picture after development: 5 mm lemon-yellow (zone *1*, not identified); 15 mm red (zone *2*, **12**); 15 mm intermediate zone; 40 mm orange-red (zone *3*, **13**); 10 mm intermediate zone; 15 mm orange-red (zone *4*, **14**); 40 mm intermediate zone; 20 mm pink (zone *5*, **15**). The zone *2* was submitted to a second CC: 2 columns; 9% acetone in benzene. Picture after development: 4 mm pink ((*Z*)-**12**); 10 mm intermediate zone; 60 mm red (**12**). After separation, the pigments were crystallized from benzene/hexane to give 7.7 mg of **12**, 21.5 mg of **13**, 11.2 mg of **14**, and 4.1 mg of **15**.

7. *(3S,5R,6R,3'S,5'R)-Capsokarpoxanthin* (*(all-*E*,3S,5R,6R,3'S,5'R)-5,6-Dihydro-3,5,6,3'-tetrahydroxy-β,κ-caroten-6'-one*; **7**): 3.8 mg. M.p. 160–162°. UV/VIS (benzene): 506, 479 nm. CD (EPA, r.t.): 205 (+ 1.42), 224 (−0.06), 256 (+ 0.33), 275 (0.00), 278 (+ 0.20), 295 (−1.05), 339 (+ 0.35), 344 (+ 0.31), 348 (+ 0.31), 375 (−0.70), 396 (−0.51), 485 (−1.27). CD (EPA, −180°): 203 (+ 3.83), 224 (+ 1.16), 242 (+ 2.34), 263 (+ 0.04), 273 (−0.01), 283 (+ 0.50), 297 (−1.12), 330 (+ 1.01), 343 (+ 2.60), 352 (+ 0.61), 359 (+ 2.84), 375 (−1.87). ^{1}H-NMR ($CDCl_3$)[2]): 0.84 (*s*, Me(16')); 0.87 (*s*, Me(16)); 1.18 (*s*, Me(18)); 1.20 (*s*, Me(17')); 1.25 (*s*, Me(17)); 1.36 (*s*, Me(18')); 1.48 (*dd*, J_{gem} = 14.3, J(4'ax,3') = 3.1, H_{ax}–C(4')); 1.54 (*m*, H_{eq}–C(2)); 1.63 (*m*, H_{ax}–C(2)); 1.71 (*dd*, J_{gem} = 13.6, J(2'ax,3') = 4.4, H_{ax}–C(2')); 1.81 (*Ψt*, $J_{gem} \approx$ (4ax,3) = 11.3, H_{ax}–C(4))*; 1.88 (*dd*, J_{gem} = 11.3, J(4eq,3) = 4.7, H_{eq}–C(4))*; 1.96 (*s*, Me(19')); 1.97 (*s*, Me(19)); 1.98 (*s*, Me(20')); 1.99 (*s*, Me(20)); 1.99 (*dd*, J_{gem} = 13.6, J(2'eq,3') = 7.8, H_{eq}–C(2')); 2.95 (*dd*, J_{gem} = 14.3, J(4'eq,3') ≈ 8.6, H_{eq}–C(4')); 4.16 (*m*, H–C(3)); 4.51 (*m*, H–C(3')); 6.14 (*d*, J(7,8) = 16.1, H–C(7)); 6.23 (*d*, J(10,11) = 11.8, H–C(10)); 6.28 (*d*, J(14,15) = 10.8, H–C(14)); 6.35 (*d*, J(14',15') ≈ 10.5, H–C(14')); 6.38 (*d*, J(12,11) ≈ 15.0, H–C(12)); 6.40 (*d*, J(8,7) = 16.1, H–C(8)); 6.44 (*d*, J(7',8') = 15.0, H–C(7')); 6.52 (*d*, J(12',11') = 14.4, H–C(12')); 6.55 (*d*, J(10',11') = 10.7, H–C(10')); 6.62 (*dd*, J(11',10') = 10.7, J(11',12') = 14.4, H–C(11')); 6.63 (*dd*, J(15',14') ≈ 10.5, J(15',15) = 14.2, H–C(15')); 6.66 (*dd*, J(11,10) = 11.8, J(11,12) ≈ 15.0, H–C(11)); 6.70 (*dd*, J(15,14) = 10.8, J(15,15') = 14.2, H–C(15)); 7.33 (*d*, J(8',7') = 15.0, H–C(8')). ^{13}C-NMR ($CDCl_3$)[1]): 12.73 (C(19')); 12.84 (C(20))*; 12.86 (C(20'))*; 13.32 (C(19)); 21.28 (C(18')); 25.08 (C(17')); 25.56 (C(17)); 25.85 (C(16')); 26.71 (C(16)); 27.51 (C(18)); 40.27 (C(1)); 43.96 (C(1')); 45.30 (C(4')); 45.40 (C(4)); 45.74 (C(2)); 50.85 (C(2')); 58.94 (C(5')); 64.57 (C(3)); 70.37 (C(3')); 77.49 (C(5)); 78.61 (C(6)); 120.92 (C(7')); 124.15 (C(11')); 125.25 (C(11)); 128.96 (C(7)); 129.88 (C(15')); 131.52 (C(15)); 131.90 (C(10)); 132.63 (C(14)); 133.70 (C(9')); 134.93 (C(9)); 135.16 (C(14')); 135.29 (C(8)); 136.04 (C(13)); 137.42 (C(13')); 137.90 (C(12)); 140.65 (C(10')); 141.91 (C(12')); 146.83 (C(8')); 202.91 (C(6')). EI-MS: 618 (3, M^+), 600 (14, $[M - H_2O]^+$), 582 (4, $[M - 2H_2O]^+$), 494 (14), 221 (33), 181 (13), 145 (20), 119 (19), 109 (51), 91 (100), 83 (22), 43 (19).

Derivatization. Reduction of **7** with $NaBH_4$ yielded a mixture of the epimers of 5,6-dihydro-β,κ-carotene-3,5,6,3',6'-pentol. UV/VIS (benzene): 481, 451, 426. EI-MS: 620 (17, M^+), 221 (28), 181 (34), 145 (39), 119 (23), 109 (43), 91 (83), 83 (46), 43 (26).

8. *(3S,5R,6S,3'S,5'R)-Capsokarpoxanthin* (*(all-*E*,3S,5R,6S,3'S,5'R)-5,6-Dihydro-3,5,6,3'-tetrahydroxy-β,κ-caroten-6'-one*; **8**): 1.3 mg. M.p. 115–117°. UV/VIS (benzene): 506, 478. CD (EPA, r.t.): 213 (−0.72), 230 (−0.04), 236 (−0.10), 242 (−0.07), 261 (+ 0.001), 285 (−0.10), 339 (+ 0.25), 485 (−0.28). CD (EPA, −180°): 213 (−0.43), 224 (+ 0.68), 241 (+ 1.58), 286 (−0.41), 343 (+ 1.03), 353 (+ 0.38), 360 (+ 0.92). ^{1}H-NMR ($CDCl_3$): 0.81 (*s*, Me(16)); 0.84 (*s*, Me(16')); 1.10 (*s*, Me(18)); 1.20 (*s*, Me(17')); 1.26 (*s*, Me(17)); 1.37 (*s*, Me(18')); 1.48 (*dd*, J_{gem} = 14.3, J(4'ax,3') = 3.2, H_{ax}–C(4')); 1.53 (*m*, H_{ax}–C(2)); *ca.* 1.62 (*m*, H_{ax}–C(4)); 1.71 (*dd*, J_{gem} = 13.5, J(2'ax,3') = 4.8, H_{ax}–C(2')); 1.76 (*ddd*, J_{gem} = 13.2, J(2eq, 3) = 4.2, J(2eq,4eq) = 2.8, H_{eq}–C(2)); 1.92 (*s*, Me(19)); 1.96 (*s*, Me(19')); 1.97 (*s*, Me(20')); 1.98 (*s*, Me(20)); 1.99 (*dd*, J_{gem} = 13.5, J(2'eq,3') = 7.6, H_{eq}–C(2')); 2.11 (*ddd*, J_{gem} = 13.4, J(4eq,3) = 4.3, J(4eq,2eq) = 2.8, H_{eq}–C(4)); 2.96 (*dd*, J_{gem} = 14.3, J(4'eq,3') = 8.5, H_{eq}–C(4')); 4.27 (*m*, H–C(3')); 4.51 (*m*, H–C(3)); 5.88 (*d*, J(7,8) = 15.9, H–C(7)); 6.22 (*d*, J(10,11) = 10.9, H–C(10)); 6.27 (*d*, J(14,15) = 10.8, H–C(14)); 6.35 (*d*, J(14',15') = 10.5, H–C(14')); 6.37 (*d*, J(12,11) = 15.2, H–C(12)); 6.42 (*d*, J(8,7) = 15.9, H–C(8)); 6.44 (*d*, J(7',8') = 15.1, H–C(7')); 6.52 (*d*, J(12',11') = 14.7, H–C(12')); 6.55 (*d*, J(10',11') = 10.8, H–C(10')); 6.62 (*dd*, J(11',10') = 10.8, J(11',12') = 14.7, H–C(11')); 6.63 (*dd*, J(15',14') = 10.5, J(15',15) = 14.6, H–C(15')); 6.64 (*dd*, J(11,10) = 10.9, J(11,12) = 15.2, H–C(11)); 6.69 (*dd*, J(15,14) = 10.8, J(15,15') = 14.6, H–C(15)); 7.33 (*d*, J(8',7') = 15.1, H–C(8')). ^{13}C-NMR ($CDCl_3$)[3]): 12.74 (C(19')); 12.86 (C(20,20')); 13.22 (C(19)); 21.28 (C(18')); 24.63 (C(17)); 25.08 (C(17')); 25.85 (C(16')); 27.79 (C(18)); 28.63 (C(16)); 39.69 (C(1)); 43.96 (C(1')); 45.30 (C(4')); 45.74 (C(4)); 46.86 (C(2)); 50.85 (C(2')); 58.93 (C(5')); 64.38 (C(3)); 70.37 (C(3')); 79.27 (C(6)); 120.90 (C(7')); 124.14 (C(11'));

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[2]) Assignments to axial/equatorial positions not established.

[3]) The C(5) signal is overlapped by the solvents signal.

125.25 (C(11)); 129.57 (C(7)); 129.84 (C(15')); 131.54 (C(15)); 131.92 (C(10)); 132.59 (C(14)); 133.10 (C(8)); 133.68 (C(9')); 134.77 (C(9)); 135.18 (C(14')); 136.01 (C(13)); 137.42 (C(13')); 137.83 (C(12)); 140.66 (C(10')); 141.92 (C(12')); 146.84 (C(8')); 202.91 (C(6')). EI-MS: 618 (2, M^+), 600 (48, $[M - H_2O]^+$), 582 (5, $[M - 2H_2O]^+$), 494 (44), 221 (87), 181 (24), 145 (28), 119 (17), 109 (62), 91 (100), 83 (22), 43 (18).

Derivatization. Reduction of **8** with $NaBH_4$ yielded a mixture of the epimers of 5,6-dihydro-β,κ-carotene-3,5,6,3',6'-pentol. UV/VIS (benzene): 481, 451, 426. EI-MS: 620 (8, M^+), 602 (1, $[M - H_2O]^+$), 584 (5, $[M - 2H_2O]^+$), 221 (22), 181 (28), 145 (31), 119 (17), 109 (33), 91 (100), 83 (35), 43 (19).

9. *(3S,5S,6R,3'S,5'R)-Capsokarpoxanthin* (*(all-E,3S,5S,6R,3'S,5'R)-5,6-Dihydro-3,5,6,3'-tetrahydroxy-β,κ-caroten-6'-one*; **12**): 7.7 mg. M.p. 152–154°. UV/VIS (benzene): 507, 479; after acid treatment: 487, 462. CD (EPA, r.t.): 241 (−0.01), 269 (+ 0.63), 273 (+ 0.61), 280 (+ 0.71), 352 (−0.18), 392 (−0.07), 481 (−0.36). CD (EPA, −180°): 203 (+ 1.14), 214 (+ 0.14), 233 (+ 0.66), 239 (+ 0.64), 247 (−0.08), 271 (+ 0.46), 284 (+ 0.59), 297 (0.00), 327 (+ 0.25), 341 (+ 0.38), 352 (−0.10), 358 (+ 0.06), 368 (−0.42). ^{1}H-NMR ($CDCl_3$): 0.83 (*s*, Me(16')); 1.02 (*s*, Me(16)); 1.06 (*s*, Me(17)); 1.20 (*s*, Me(17')); 1.35 (*s*, Me(18)); 1.36 (*s*, Me(18')); 1.48 (*dd*, J_{gem} = 14.4, J(4'ax,3') = 3.2, H_{ax}–C(4')); 1.62 (*dd*, J_{gem} = 13.0, J(2eq,3) = 3.1, H_{eq}–C(2)); 1.71 (*dd*, J_{gem} = 13.6, J(2'ax,3') = 4.6, H_{ax}–C(2')); 1.82 (*dd*, J_{gem} = 13.0, J(2ax,3) = 9.2, H_{ax}–C(2)); 1.88 (*dd*, J_{gem} = 12.8, J(4ax,3) = 1.3, H_{ax}–C(4)); 1.93 (*dd*, J_{gem} = 12.8, J(4eq,3) = 1.6, H_{eq}–C(4)); 1.94 (*s*, Me(19)); 1.96 (*s*, Me(19')); 1.976 (*s*, Me(20)); 1.981 (*s*, Me(20')); 1.99 (*dd*, J_{gem} = 13.6, J(2'eq,3') = 7.81, H_{eq}–C(2')); 2.93 (*dd*, J_{gem} = 14.4, J(4'eq,3') = 8.5, H_{eq}–C(4')); 3.98 (*m*, H–C(3)); 4.51 (*m*, H–C(3')); 5.84 (*d*, J(7,8) = 15.5, H–C(7)); 6.25 (*d*, J(10,11) = 12.2, H–C(10)); 6.28 (*d*, J(14,15) ≈ 11, H–C(14)); 6.35 (*d*, J(14',15') = 10.6, H–C(14')); 6.38 (*d*, J(12,11) = 14.9, H–C(12)); 6.44 (*d*, J(7',8') = 15.0, H–C(7')); 6.52 (*d*, J(12',11') = 14.6, H–C(12')); 6.55 (*d*, J(10',11') = 11.2, H–C(10')); 6.56 (*d*, J(8,7) = 15.5, H–C(8)); 6.62 (*dd*, J(11',10') = 11.2, J(11',12') = 14.6, H–C(11')); 6.64 (*m*, H–C(15')); 6.64 (*dd*, J(11,10) = 12.2, J(11,12) = 14.9, H–C(11)); 6.69 (*m*, H–C(15)); 7.33 (*d*, J(8',7') = 15.0, H–C(8')). ^{13}C-NMR ($CDCl_3$): 12.74 (C(19')); 12.84 (C(20,20')); 13.25 (C(19)); 21.29 (C(18')); 25.09 (C(17')); 25.86 (C(16')); *ca.* 26.9 (C(18)); 26.93 (C(17)); 27.09 (C(16)); 38.71 (C(1)); 43.97 (C(4)); *ca.* 44.0 (C(1')); 45.18 (C(2)); 45.32 (C(4')); 50.87 (C(2')); 58.94 (C(5')); 66.30 (C(3)); 70.37 (C(3')); 76.30 (C(5)); 79.41 (C(6)); 120.93 (C(7')); 124.18 (C(11')); 125.16 (C(11)); 127.86 (C(7)); 129.93 (C(15')); 131.51 (C(15)); 132.36 (C(10)); 132.74 (C(14)); 133.71 (C(9')); 134.52 (C(9)); 135.16 (C(14')); 136.01 (C(8)); 136.07 (C(13)); 137.35 (C(13')); 138.11 (C(12)); 140.64 (C(10')); 141.91 (C(12')); 146.83 (C(8')); 202.90 (C(6')). EI-MS: 618 (2, M^+), 600 (10, $[M - H_2O]^+$), 582 (6, $[M - 2H_2O]^+$), 494 (12), 221 (55), 181 (31), 145 (40), 119 (28), 109 (100), 91 (67), 83 (47), 43 (33).

Derivatization. Reduction of **12** with $NaBH_4$ yielded a mixture of the epimers of 5,6-dihydro-β,κ-carotene-3,5,6,3'-6'-pentol. UV/VIS (benzene): 481, 451, 426.

10. *(3S,5R,6R,3'S,5'R)-3,6-Epoxycapsanthin* (*(all-E,3S,5R,6R,3'S,5'R)-3,6-Epoxy-5,6-dihydro-5,3'-dihydroxy-β,κ-caroten-6'-one*; **11**): 0.7 mg. M.p. 148–150°. UV/VIS (benzene): 507, 480; after $NaBH_4$ reduction (benzene): 482, 452, 426. CD (EPA, r.t.): 213 (−0.34), 226 (+ 0.16), 240 (−0.58), 282 (+ 2.80), 350 (−0.40), 387 (−0.13), 480 (−1.65). CD (EPA, −180°): 210 (+ 0.74), 218 (+ 1.36), 227 (+ 0.97), 234 (+ 0.73), 251 (−0.60), 261 (−0.32), 275 (+ 0.96), 278 (+ 0.75), 286 (+ 2.54), 330 (+ 1.10), 343 (+ 1.74), 359 (+ 1.14), 370 (−1.12), 407 (−0.54), 490 (−2.70), 520 (−1.85). ^{1}H-NMR: ($CDCl_3$): 0.84 (*s*, Me(16')); 0.88 (*s*, Me(17)); 1.20 (*s*, Me(17')); 1.21 (*s*, Me(18)); 1.37 (*s*, Me(18')); 1.43 (*s*, Me(16)); 1.48 (*dd*, J_{gem} = 14.4, J(4'ax,3') = 3.3, H_{ax}–C(4')); 1.61 (*d*, J_{gem} = 11.6, H_{eq}–C(2)); 1.67 (*d*, J_{gem} = 11.9, H_{eq}–C(4)); 1.71 (*dd*, J_{gem} = 13.5, J(2'ax,3') = 4.9, H_{ax}–C(2')); 1.84 (*ddd*, J_{gem} = 11.6, J(2ax,3) = 5.9, J(2ax,4ax) = 2.3, H_{ax}–C(2)); 2.00 (*dd*, J_{gem} = 13.5, J(2'eq,3') = 7.7, H_{eq}–C(2')); 1.96 (*s*, Me(19,19')); 1.97 (*s*, Me(20')); 1.98 (*s*, Me(20)); 2.06 (*ddd*, J_{gem} = 11.9, J(4ax,3) = 6.0, J(4ax,2ax) = 2.3, H_{ax}–C(4)); 2.96 (*dd*, J_{gem} = 14.4, J(4'eq,3') = 8.6, H_{eq}–C(4')); 4.39 (*Ψt*, J(3,2ax) = 2.9, J(3,4ax) = 6.0, H–C(3)); 4.51 (*m*, H–C(3')); 5.75 (*d*, J(7,8) = 16.0, H–C(7)); 6.20 (*d*, J(10,11) = 11.3, H–C(10)); 6.27 (*d*, J(14,15) = 11.0, H–C(14)); 6.35 (*d*, J(14',15') ≈ 12, H–C(14')); 6.36 (*d*, J(12,11) = 15.4, H–C(12)); 6.38 (*d*, J(8,7) = 16.0, H–C(8)); 6.44 (*d*, J(7',8') = 15.0, H–C(7')); 6.52 (*d*, J(12',11') = 14.6, H–C(12')); 6.55 (*d*, J(10',11') = 11.2, H–C(10')); 6.62 (*dd*, J(11',10') = 11.2, J(11',12') = 14.6, H–C(11')); 6.62 (*dd*, J(15',14') ≈ 12, J(15',15) = 14.3, H–C(15')); 6.65 (*dd*, J(11,10) = 11.3, J(11,12) = 15.4, H–C(11)); 6.70 (*d*, J(15,14) = 11.0, J(15,15') = 14.3, H–C(15)); 7.33 (*d*, J(8',7') = 15.0, H–C(8')). ^{13}C-NMR ($CDCl_3$)[4]: 12.73 (C(19')); 12.86 (C(19,20,20')); 21.29 (C(18')); 25.09 (C(17')); 25.72 (C(16)); 25.86 (C(16')); 31.58 (C(18)); 32.15 (C(17)); 43.97 (C(1')); 44.00 (C(1)); 45.32 (C(4')); 47.71 (C(4)); 48.51 (C(2)); 50.87 (C(2')); 58.94 (C(5')); 70.38 (C(3)); 75.38 (C(3)); 82.48 (C(5)); 91.63 (C(6)); 120.89 (C(7')); 123.0* (C(7)); 124.09 (C(11')); 125.2* (C(11));

[4]) *: Chemical shift extracted from the inverse HMQC spectrum due to decomposition during the ^{13}C-NMR experiments; signals of C(9) and C(13) not observed.

130.0* (C(15)); 129.73 (C(15')); 131.6* (C(10)); 132.4* (C(14)); 133.64 (C(9')); 134.8* (C(8)); 135.22 (C(14')); 137.51 (C(13')); 137.6* (C(12)); 140.68 (C(10')); 141.95 (C(12')); 146.84 (C(8')); 202.89 (C(6)). EI-MS: 600 (12, M^+), 582, (3, $[M - H_2O]^+$), 494 (38), 299 (22), 286 (29), 221 (64), 181 (36), 160 (44), 155 (29), 145 (33), 119 (17), 109 (64), 105 (55), 91 (100), 83 (33), 43 (86).

11. *3,6-Epoxyepicapsanthin* (*(all-*E*,3*S*,5*S*,6*R*,3'*S*,5'*R*)-3,6-Epoxy-5,6-dihydro-5,3'-dihydroxy-β,κ-caroten-6'-one*; **15**): 4.1 mg. M.p. 152–154°; UV/VIS (benzene): 507, 479; after treatment: 487, 462; after $NaBH_4$ reduction (benzene): 482, 452, 426. CD (EPA, r.t.): 205 (+ 3.57), 237 (−0.30), 258 (+ 0.63), 280 (+ 1.51), 302 (−0.20), 326 (0.00), 368 (−0.97), 391 (−0.76), 455 (−1.08). CD (EPA, −180°): 217 (+ 2.72), 248 (−0.71), 275 (+ 2.00), 285 (+ 4.61), 310 (−0.41), 328 (+ 1.00), 343 (+ 1.71), 352 (−0.26), 359 (+ 1.17), 374 (−2.50), 453 (−2.00), 485 (−2.25), 520 (−1.50). ^{1}H-NMR ($CDCl_3$): 0.84 (*s*, Me(16')); 0.91 (*s*, Me(16)); 1.20 (*s*, Me(17')); 1.25 (*s*, Me(17)); 1.36 (*s*, Me(18')); 1.40 (*d*, J_{gem} = 11.5, H_{ax}–C(2)); 1.48 (*dd*, J_{gem} = 14.3, J(4'ax,3') = 3.2, H_{ax}–C(4')); 1.49 (*s*, Me(18)); 1.71 (*d*, J_{gem} = 12.7, H_{ax}–C(4)); 1.71 (*dd*, J_{gem} = 13.7, J(2'ax,3') ≈ 4, H_{ax}–C(2')); 1.79 (*ddd*, J_{gem} = 11.5, J(2eq,3) = 5.8, J(2eq,4eq) = 2.2, H_{eq}–C(2)); 1.952 (*s*, Me(19')); 1.958 (*s*, Me(19)); 1.972 (*s*, Me(20')); 1.975 (*s*, Me(20)); 2.00 (*dd*, J_{gem} = 13.7, J(2'eq,3') = 7.8, H_{eq}–C(2')); 2.10 (*ddd*, J_{gem} = 12.7, J(4eq,3) = 6.0, J(4eq,2eq) = 2.2, H_{eq}–C(4)); 2.96 (*dd*, J_{gem} = 14.3, J(4'eq,3') = 8.5, H_{eq}–C(4')); 4.48 (Ψ*t*, J(3,2eq) = 5.8, J(3,4eq) = 6.0, H–C(3)); 4.51 (*m*, H–C(3')); 5.74 (*d*, J(7,8) = 15.9, H–C(7)); 6.21 (*dd*, J(10,11) = 11.7, H–C(10)); 6.27 (*d*, J(14,15) = 11.1, H–C(14)); 6.35 (*d*, J(14',15') = 11.5, H–C(14')); 6.36 (*d*, J(12,11) = 15.1, H–C(12)); 6.44 (*d*, J(7',8') = 15.0, H–C(7')); 6.46 (*d*, J(8,7) = 15.9, H–C(8)); 6.51 (*d*, J(12',11') = 14.4, H–C(12')); 6.55 (*d*, J(10',11') = 11.1, H–C(10')); 6.61 (*dd*, J(11',10') = 11.1, J(11',12') = 14.4, H–C(11')); 6.62 (*dd*, J(15',14') = 11.5, J(15',15) = 14.4, H–C(15')); 6.64 (*dd*, J(11,10) = 11.7, J(11,12) = 15.1, H–C(11)); 6.70 (*dd*, J(15,14) = 11.1, J(15,15') = 14.4, H–C(15)); 7.32 (*d*, J(8',7') = 15.0, H–C(8')). ^{13}C-NMR ($CDCl_3$)[1]: 12.73 (C(19')); 12.84 (C(20))*; 12.86 (C(20'))*; 12.89 (C(20))*; 21.28 (C(18')); 22.67 (C(18)); 25.08 (C(17')); 25.85 (C(16')); 26.34 (C(17)); 31.90 (C(16)); 41.48 (C(1)); 43.96 (C(1')); 45.30 (C(4')); 48.48 (C(2)); 49.13 (C(4)); 50.85 (C(2')); 58.93 (C(5')); 70.37 (C(3')); 74.41 (C(3)); 80.12 (C(5)); 95.76 (C(6)); 120.88 (C(7')); 121.08 (C(7)); 124.10 (C(11')); 125.38 (C(11)); 129.77 (C(15')); 131.60 (C(15)); 132.06 (C(10)); 132.54 (C(14)); 133.64 (C(9')); 134.91 (C(9)); 135.22 (C(14')); 135.94 (C(13)); 136.73 (C(8)); 137.49 (C(13')); 137.83 (C(12)); 140.68 (C(10')); 141.95 (C(12')); 146.85 (C(8')); 202.89 (C(6')). EI-MS: 600 (18, M^+), 582, (5, $[M - H_2O]^+$), 494 (20), 299 (11), 286 (15), 221 (42), 181 (29), 160 (27), 155 (18), 145 (31), 119 (24), 109 (100), 105 (30), 91 (60), 83 (58), 43 (100).

12. *(3*S*,5*R*,8*R*,3'*S*,5'*R*)-Capsochrome* (*(all-*E*,3*S*,5*R*,8*R*,3'*S*,5'*R*)-5,8-Epoxy-5,6-dihydro-3,3'-dihydroxy-β,κ-caroten-6'-one*; **9**): 16.3 mg. M.p. 163–165°. UV/VIS (benzene): 489, 462. CD (EPA, r.t.): 203 (+ 16.84), 227 (+ 2.86), 2.66 (+ 5.54), 340 (−0.54), 471 (−1.00). CD (EPA, −180°): 204 (+ 18.80), 221 (+ 1.82), 234 (+ 4.55), 244 (+ 2.54), 261 (+ 3.50), 269 (+ 5.01), 297 (+ 0.64), 327 (+ 2.50), 342 (+ 2.32), 368 (−1.18), 467 (−3.03), 480 (−1.75), 497 (−2.67). ^{1}H-NMR ($CDCl_3$): 0.83 (*s*, Me(16')); 1.17 (*s*, Me(16)); 1.20 (*s*, Me(17')); 1.33 (*s*, Me(17)); 1.36 (*s*, Me(18')); 1.48 (*dd*, J_{gem} = 14.3, J(4'ax,3') = 3.2, H_{ax}–C(4')); 1.51 (*dd*, J_{gem} = 13.8, J(2eq,3) = 3.6, H_{eq}–C(2)); 1.62 (*s*, Me(18)); 1.71 (*dd*, J_{gem} ≈ 14, J(2'ax,3') = 4.7, H_{ax}–C(2')); 1.72 (*s*, Me(19)); 1.75 (*ddd*, J_{gem} = 13.8, J(2ax,3) = 4.5, J(2ax,4ax) ≈ 1.1, H_{ax}–C(2)); 1.948 (*s*, Me(19')); 1.953 (*s*, Me(20)); 1.966 (*s*, Me(20')); 1.99 (*m*, J_{gem} = 13.6, H_{eq}–C(4)); 2.00 (*m*, J_{gem} ≈ 14, H_{eq}–C(2')); 2.13 (*ddd*, J_{gem} = 13.6, J(4ax,3) = 4.0, J(4ax,2ax) ≈ 1.1, H_{ax}–C(4)); 2.95 (*dd*, J_{gem} = 14.3, J(4'eq,3') = 8.3, H_{eq}–C(4')); 4.24 (*m*, H–C(3)); 4.51 (*m*, H–C(3')); 5.17 (*s*, Me(8)); 5.25 (*d*, J(7,8) = 0.9, H–C(7)); 6.19 (*dd*, J(10,11) = 11.0, J(10,8) = 0.9, H–C(10)); 6.23 (*d*, J(14,15) = 11.1, H–C(14)); 6.32 (*d*, J(12,11) = 15.1, H–C(12)); 6.34 (*d*, J(14',15') = 10.9, H–C(14')); 6.44 (*d*, J(7',8') = 15.1, H–C(7')); 6.51 (*d*, J(12',11') = 14.4, H–C(12')); 6.52 (*dd*, J(11,10) = 11.0, J(11,12) = 15.1, H–C(11)); 6.54 (*d*, J(10',11') = 11.5, H–C(10')); 6.61 (*dd*, J(11',12') = 11.5, J(11',12') = 14.4, H–C(11')); 6.61 (*dd*, J(15',14') = 10.9, J(15',15) = 14.3, H–C(15')); 6.68 (*dd*, J(15,14) = 11.1, J(15,15') = 14.3, H–C(15)); 7.32 (*d*, J(8',7') = 15.1, H–C(8')). ^{13}C-NMR ($CDCl_3$): 12.64 (C(19)); 12.72 (C(19')); 12.82 (C(20)); 12.86 (C(20')); 21.28 (C(18')); 25.07 (C(17')); 25.85 (C(16')); 28.86 (C(17)); 29.01 (C(18)); 31.37 (C(16)); 33.68 (C(1)); 43.95 (C(1')); 45.28 (C(4')); 46.66 (C(2)); 47.34 (C(4)); 50.84 (C(2')); 58.93 (C(5')); 67.70 (C(3)); 70.34 (C(3')); 86.86 (C(5)); 87.67 (C(8)); 119.78 (C(7)); 120.87 (C(7')); 124.05 (C(11')); 124.90 (C(11)); 127.14 (C(10)); 129.58 (C(15')); 131.55 (C(15)); 132.08 (C(14)); 133.60 (C(9')); 135.17 (C(14')); 135.82 (C(13)); 137.35 (C(13')); 137.41 (C(12)); 138.40 (C(9)); 140.68 (C(10')); 141.96 (C(12')); 146.86 (C(8')); 154.11 (C(6)); 202.82 (C(6')). EI-MS: 600 (28, M^+), 582 (2, $[M - H_2O]^+$), 520 (9), 508 (13), 494 (26), 287 (43), 221 (100), 181 (18), 109 (45), 91 (57).

Derivatization. Reduction of **9** with $NaBH_4$ yielded a mixture of the epimers of 5,8-epoxy-5,6-dihydro-β,κ-carotene-3,3',6'-triol. UV/VIS (benzene): 460, 432, 408. EI-MS: 602 (40, M^+), 584 (9, $[M - H_2O]^+$), 522 (32), 510 (21), 496 (28), 289 (100), 221 (77), 181 (35), 109 (25), 91 (48).

13. *(3*S*,5*R*,8*S*,3'*S*,5'*R*)-Capsochrome* (*(all-*E*,3*S*,5*R*,8*S*,3'*S*,5'*R*)-5,8-Epoxy-5,6-dihydro-3,3'-dihydroxy-β,κ-caroten-6'-one*; **10**): 11.0 mg. M.p. 196–198°. UV/VIS (benzene): 490, 463. CD (EPA, r.t.): 202 (+ 2.20), 206

(−9.91), 227 (−1.30), 244 (−0.50), 268 (−3.73), 328 (+3.80), 462 (−3.30). CD (EPA, −180°): 197 (−7.20), 205 (−23.47), 226 (+1.86), 235 (−0.97), 260 (−5.79), 270 (−9.63), 314 (+4.34), 328 (+9.41), 335 (+4.76), 343 (+11.35), 364 (−1.57), 438 (−3.14), 4.67 (−5.55), 494 (−4.95). ^{1}H-NMR ($CDCl_3$): 0.83 (*s*, Me(16′)); 1.19 (*s*, Me(16)); 1.20 (*s*, Me(17′)); 1.34 (*s*, Me(17)); 1.36 (*s*, Me(18′)); 1.47 (*dd*, J_{gem} = 14.4, J(2eq,3) = 3.9, H_{eq}–C(2)); 1.48 (*dd*, J_{gem} = 14.4, J(4′ax,3′) = 3.3, H_{ax}–C(4′)); 1.68 (*s*, Me(18)); 1.71 (*dd*, J_{gem} = 13.7, J(2′ax,3′) = 4.6, H_{ax}–C(2′)); 1.80 (*ddd*, J_{gem} = 14.4, J(2ax,3) = 3.8, J(2ax,4ax) = 1.4, H_{ax}–C(2)); 1.81 (*s*, Me(19)); 1.90 (*dd*, J_{gem} = 13.6, J(4eq,3) = 4.4, H_{eq}–C(4)); 1.951 (*s*, Me(19′)); 1.961 (*s*, Me(20)); 1.967 (*s*, Me(20′)); 2.00 (*dd*, J_{gem} = 13.7, J(2′eq,3′) = 7.8, H_{eq}–C(2′)); 2.11 (*ddd*, J_{gem} = 13.6, J(4ax,3) = 3.5, J(4ax,3ax) ≈ 1.4, H_{ax}–C(4)); 2.95 (*dd*, J_{gem} = 14.4, J(4′eq,3′) = 8.5, H_{eq}–C(4′)); 4.24 (*m*, H–C(3)); 4.51 (*m*, H–C(3′)); 5.07 (*s*, Me(8)); 5.30 (*d*, J(7,8) = 1.8, H–C(7)); 6.19 (*dd*, J(10,11) = 11.5, J(10,8) < 0.5, H–C(10)); 6.23 (*d*, J(14,15) = 11.3, H–C(14)); 6.32 (*d*, J(12,11) = 15.1, H–C(12)); 6.34 (*d*, J(14′,15′) = 11.1, H–C(14′)); 6.44 (*d*, J(7′,8′) = 15.0, H–C(7′)); 6.51 (*d*, J(12′,11′) = 14.1, H–C(12′)); 6.53 (*dd*, J(11,10) = 11.5, J(11,12) = 15.1, H–C(11)); 6.55 (*d*, J(10′,11′) = 11.7, H–C(10′)); 6.60 (*dd*, J(15′,14′) = 11.1, J(15′,15) = 14.1, H–C(15′)); 6.61 (*dd*, J(11′,12′) = 11.7, J(11′,12′) = 14.1, H–C(11′)); 6.69 (*dd*, J(15,14) = 11.3, J(15,15′) = 14.1, H–C(15)); 7.32 (*d*, J(8′,7′) = 15.0, H–C(8′)). ^{13}C-NMR ($CDCl_3$): 12.71 (C(19′)); 12.83 (C(20)); 12.86 (C(20′)); 13.42 (C(19)); 21.28 (C(18′)); 25.07 (C(17′)); 25.85 (C(16′)); 28.12 (C(17)); 30.55 (C(18)); 31.25 (C(16)); 34.21 (C(1)); 43.95 (C(1′)); 45.29 (C(4′)); 47.36 (C(2)); 47.38 (C(4)); 50.84 (C(2′)); 58.92 (C(5′)); 67.89 (C(3)); 70.34 (C(3′)); 87.22 (C(5)); 88.32 (C(8)); 118.65 (C(7)); 120.86 (C(7′)); 124.01 (C(11′)); 125.07 (C(11)); 126.05 (C(10)); 129.48 (C(15′)); 131.60 (C(15)); 131.93 (C(14)); 133.57 (C(9′)); 135.20 (C(14′)); 135.75 (C(13)); 137.11 (C(12)); 137.43 (C(13′)); 139.15 (C(9)); 140.69 (C(10′)); 141.98 (C(12′)); 146.86 (C(8′)); 153.23 (C(6)); 202.91 (C(6′)). EI-MS: 600 (22, M^+), 494 (15), 287 (30), 221 (100), 181 (29), 109 (78), 91 (50).

Derivatization. Reduction of **10** with $NaBH_4$ yielded a mixture of the epimers of 5,8-epoxy-5,6-dihydro-β,κ-carotene-3,3′,6′-triol. UV/VIS (benzene): 460, 432, 408. EI-MS: 602 (50, M^+), 584 (14, $[M - H_2O]^+$), 522 (32), 510 (15), 496 (26), 289 (100), 221 (89), 181 (40), 109 (32), 91 (36).

14. *(3S,5S,8S,3′S,5′R)-Capsochrome* (*(all-*E*,3S,5S,8S,3′S,5′R)-5,8-Epoxy-5,6-dihydro-3,3′-dihydroxy-β,κ-caroten-6′-one*; **13**): 21.5 mg. M.p. 166–168°. UV/VIS (benzene): 487, 463. CD (EPA, r.t.): 204 (−10.74), 226 (+0.76), 267 (−6.23), 320 (+4.08), 335 (+4.87), 459 (−2.79), 478 (−2.60). CD (EPA, −180°): 204 (−21.31), 228 (+1.52), 261 (−5.42), 270 (−8.35), 315 (+2.71), 329 (+6.58), 336 (+2.78), 344 (+8.39), 369 (−1.88), 470 (−2.98), 488 (−1.38), 499 (−2.52). ^{1}H-NMR ($CDCl_3$): 0.83 (*s*, Me(16′)); 1.14 (*s*, Me(16)); 1.20 (*s*, Me(17)); 1.20 (*s*, Me(17′)); 1.26 (*dd*, J_{gem} = 12.4, J(2ax,3) = 8.5, H_{ax}–C(2)); 1.36 (*s*, Me(18′)); 1.45 (*s*, Me(18)); 1.48 (*dd*, J_{gem} = 14.4, J(4′ax,3′) = 3.5, H_{ax}–C(4′)); 1.60 (*m*, J_{gem} = 11.2, H_{ax}–C(4)); 1.71 (*dd*, J_{gem} = 13.6, J(2′ax,3′) = 4.5, H_{ax}–C(2′)); 1.74 (*d*, J(19,8) = 0.93, H–C(19)); 1.88 (*ddd*, J_{gem} = 12.4, J(2eq,3) = 4.0, J(2eq,4eq) = 1.7, H_{eq}–C(2)); 1.95 (*s*, Me(19′)); 1.96 (*s*, Me(20)); 1.97 (*s*, Me(20′)); 1.99 (*dd*, J_{gem} = 13.6, J(2′eq,3′) = 7.7, H_{eq}–C(2′)); 2.32 (*ddd*, J_{gem} = 11.2, J(4eq,3) = 3.9, J(4eq,2eq) = 1.7, H_{eq}–C(4)); 2.95 (*dd*, J_{gem} = 14.4, J(4′eq,3′) = 8.4, H_{eq}–C(4′)); 4.02 (*m*, H–C(3)); 4.51 (*m*, H–C(3′)); 5.18 (*s*, Me(8)); 5.26 (*s*, Me(7)); 6.19 (*dd*, J(10,11) = 11.2, J(10,8) = 1.1, H–C(10)); 6.23 (*d*, J(14,15) = 10.8, H–C(14)); 6.32 (*d*, J(12,11) = 15.1, H–C(12)); 6.34 (*d*, J(14′,15′) = 11.8, H–C(14′)); 6.44 (*d*, J(7′,8′) = 15.0, H–C(7′)); 6.51 (*d*, J(12′,11′) = 14.4, H–C(12′)); 6.52 (*dd*, J(11,10) = 11.2, J(11,12) = 15.1, H–C(11)); 6.54 (*d*, J(10′,11′) = 11.1, H–C(10′)); 6.61 (*dd*, J(11′,10′) = 11.1, J(11′,12′) = 14.4, H–C(11′)); 6.62 (*dd*, J(15′,14′) = 11.8, J(15′,15) = 14.6, H–C(15′)); 6.69 (*dd*, J(15,14) = 10.8, J(15,15′) = 14.6, H–C(15)); 7.32 (*d*, J(8′,7′) = 15.0, H–C(8′)). ^{13}C-NMR ($CDCl_3$)[1]): 12.71 (C(19)); 12.73 (C(19′)); 12.84 (C(20′))*; 12.87 (C(20))*; 21.35 (C(18′)); 25.10 (C(17′)); 25.90 (C(16′)); 26.96 (C(16)); 27.13 (C(18)); 30.75 (C(17)); 33.30 (C(1)); 43.97 (C(1′)); 45.41 (C(4′)); 50.19 (C(4)); 50.31 (C(2)); 50.99 (C(2′)); 58.95 (C(5′)); 66.10 (C(3)); 70.39 (C(3′)); 87.63 (C(5)); 88.24 (C(8)); 120.29 (C(7)); 120.99 (C(7′)); 124.07 (C(11′)); 124.86 (C(11)); 127.28 (C(10)); 129.64 (C(15′)); 131.56 (C(15)); 132.13 (C(14)); 133.63 (C(9′)); 135.14 (C(14′)); 135.84 (C(13)); 137.33 (C(13′)); 137.57 (C(12)); 138.19 (C(9)); 140.59 (C(10′)); 141.94 (C(12′)); 146.83 (C(8′)); 153.01 (C(6)); 202.83 (C(6′)). EI-MS: 600 (34, M^+), 582 (9, $[M - H_2O]^+$), 520 (10), 508 (11), 494 (32), 287 (41), 221 (100), 181 (32), 109 (66), 91 (83).

Derivatization. Reduction of **13** with $NaBH_4$ yielded a mixture of the epimers of 5,8-epoxy-5,6-dihydro-β,κ-carotene-3,3′,6′-triol. UV/VIS (benzene): 460, 432, 408. EI-MS: 602 (42, M^+), 584 (12, $[M - H_2O]^+$), 522 (33), 510 (10), 496 (10), 289 (61), 221 (100), 181 (42), 109 (39), 91 (78).

15. *(3S,5S,8R,3′S,5′R)-Capsochrome* (*(all-*E*,3S,5S,6R,3′S,5′R)-5,8-Epoxy-5,6-dihydro-3,3′-dihydroxy-β,κ-caroten-6′-one*; **14**): 11.2 mg. M.p. 160–162°. UV/VIS (benzene): 489, 461. CD (EPA, r.t.): 204 (+16.96), 225 (+0.91), 267 (+4.17), 292 (−0.78), 325 (−0.26), 352 (−1.63), 422 (−0.13), 476 (−0.91). CD (EPA, −180°): 205 (+24.2), 221 (−1.03), 234 (+4.84), 245 (+2.27), 262 (+4.53), 270 (+7.17), 294 (−0.34), 314 (+0.85), 327 (+2.27), 336 (−0.01), 342 (+2.06), 361 (−2.52), 421 (−0.38), 469 (−2.50), 490 (−1.23), 499 (−2.14). ^{1}H-NMR ($CDCl_3$): 0.83 (*s*, Me(16′)); 1.17 (*s*, Me(16)); 1.20 (*s*, Me(17′)); 1.21 (*dd*, J_{gem} = 12.4, J(2ax,3) ≈ 8.5, H_{ax}–C(2));

1.23 (*s*, Me(17)); 1.36 (*s*, Me(18')); 1.48 (*s*, Me(18)); 1.48 (*ddd*, J_{gem} = 14.3, J(4'ax,3') = 3.3, H_{ax}–C(4')); *ca.* 1.51 (*dd*, J_{gem} = 11.4, J(4ax,3) = 11.0, H_{ax}–C(4)); 1.71 (*dd*, J_{gem} = 13.4, J(2'ax,3') = 4.7, H_{ax}–C(2')); 1.79 (*d*, J(19,8) = 1.0, H–C(19)); 1.90 (*ddd*, J_{gem} = 12.4, J(2eq,3) = 4.2, J(2eq,4eq) = 2.1, H_{eq}–C(2)); 1.952 (*s*, Me(19')); 1.96 (*s*, Me(20)); 1.97 (*s*, Me(20')); 2.00 (*dd*, J_{gem} = 13.4, J(2'eq,3') = 7.7, H_{eq}–C(2')); 2.28 (*ddd*, J_{gem} = 11.4, J(4eq,3) = 3.8, J(4eq,2eq) = 2.06, H_{eq}–C(4)); 2.95 (*dd*, J_{gem} = 14.3, J(4'eq,3') = 8.5, H_{eq}–C(4')); 4.02 (*m*, H–C(3)); 4.51 (*m*, H–C(3')); 5.11 (*s*, Me(8)); 5.34 (*d*, J(7,8) = 1.9, H–C(7)); 6.19 (*dd*, J(10,11) = 10.8, J(10,8) = 0.9, H–C(10)); 6.23 (*d*, J(14,15) = 11.0, H–C(14)); 6.32 (*dd*, J(12,11) = 15.1, H–C(12)); 6.34 (*d*, J(14',15') = 10.6, H–C(14')); 6.44 (*d*, J(7',8') = 15.1, H–C(7')); 6.52 (*dd*, J(11,10) = 10.8, J(11,12) = 15.1, H–C(11)); 6.52 (*d*, J(12',11') ≈ 15, H–C(12')); 6.54 (*d*, J(10',11') = 11.2, H–C(10')); 6.61 (*dd*, J(11',10') = 11.2, J(11',12') ≈ 15, H–C(11')); 6.62 (*dd*, J(15',14') = 10.6, J(15',15) = 14.3, H–C(15')); 6.68 (*dd*, J(15,14) = 11.0, J(15,15') = 14.3, H–C(15)); 7.3 (*d*, J(8',7') = 15.1, H–C(8')). ^{13}C-NMR ($CDCl_3$)[1]: 12.71 (C(19'))*; 12.81 (C(20'))*; 12.85 (C(20))*; 13.43 (C(19)); 21.35 (C(18')); 25.10 (C(17')); 25.90 (C(16')); 26.53 (C(16)); 28.72 (C(18)); 30.69 (C(17)); 33.50 (C(1)); 43.97 (C(1')); 45.41 (C(4')); 50.31 (C(4)); 50.83 (C(2)); 50.99 (C(2')); 58.95 (C(5')); 66.44 (C(3)); 70.38 (C(3')); 87.73 (C(5)); 88.67 (C(8)); 119.35 (C(7)); 120.99 (C(7')); 124.06 (C(11')); 124.98 (C(11)); 126.19 (C(10)); 129.58 (C(15')); 131.58 (C(15)); 132.02 (C(14)); 133.63 (C(9')); 135.15 (C(14')); 135.81 (C(13)); 137.34 (C(13')); 137.34 (C(12)); 138.78 (C(9)); 140.59 (C(10')); 141.94 (C(12')); 146.84 (C(8')); 152.26 (C(6)); 202.84 (C(6')). EI-MS: 600 (29, M^+), 582 (9, $[M - H_2O]^+$), 520 (7), 508 (10), 494 (31), 287 (41), 221 (100), 181 (31), 109 (72), 83 (92).

Derivatization. Reduction of **14** with $NaBH_4$ yielded a mixture of the epimers of 5,8-epoxy-5,6-dihydro-β,κ-carotene-3,3',6'-triol. UV/VIS (benzene): 460, 432, 408. EI-MS: 602 (40, M^+), 584 (8, $[M - H_2O]^+$), 522 (30), 510 (9), 496 (10), 289 (66), 221 (100), 181 (32), 109 (34), 91 (86).

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