Reduction of Capsorubin and Cryptocapsin

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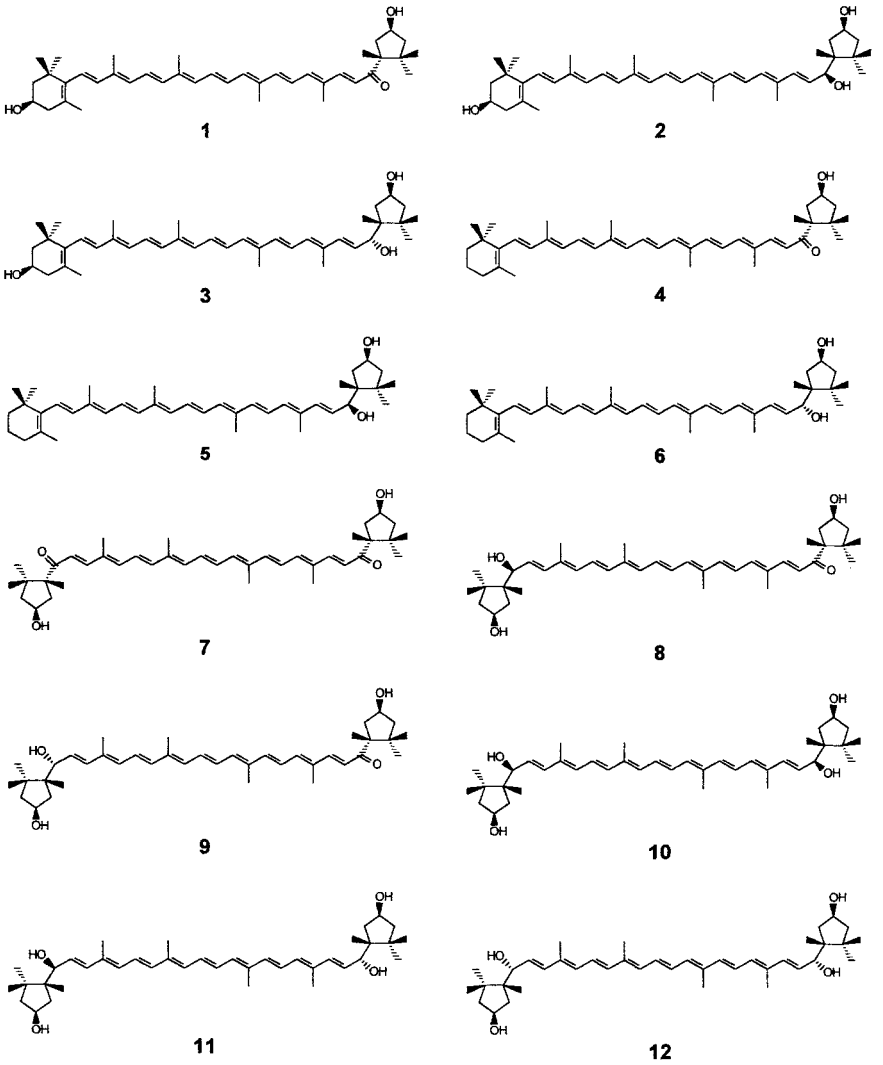
(6′*S*)- and (6′*R*)-'Capsorubol-6-one' (=(3*S*,3′*S*,5*R*,5′*R*,6′*S*)- and (3*S*,3′*S*,5*R*,5′*R*,6′*R*)-3,3′,6′-trihydroxy-κ,κ-caroten-6-one; **8** and **9**, resp.), (6*S*,6′*R*)- and (6*R*,6′*R*)-capsorubol (=3*S*,3′*S*,5*R*,5′*R*,6*S*,6′*R*)- and (3*S*,3′*S*,5*R*,5′*R*,6*R*,6′*R*)-κ,κ-carotene-3,3′,6,6′-tetrol; **11** and **12**, resp.) and (6′*S*)- and (6′*R*)-cryptocapsol (=(3′*S*,5′*R*,6′*S*)- and (3′*S*,5′*R*,6′*R*)-β,κ-carotene-3′,6′-diol; **5** and **6**, resp.) were prepared in crystalline from by the reduction of capsorubin (=(3*S*,3′*S*,5*R*,5′*R*)-3,3′-dihydroxy-κ,κ-carotene-6,6′-dione; **7**) and cryptocapsin (=(3′*S*,5′*R*)-3′-hydroxy-β,κ-caroten-6′-one; **4**) and characterized by their UV/VIS, CD, ^{1}H-NMR, and mass spectra.

Introduction. – For the reduction of keto carotenoids, $NaBH_4$ is commonly used in EtOH or EtOH/benzene [1]. The reaction is complete within 1 h at room temperature. The reduction of a keto group of carotenoids produces two stereoisomeric alcohols, which are very difficult to separate. Reduction products are usually readily separated from the starting ketone because the carotenols are more polar than the ketone.

Earlier in our laboratory, the reduction of capsanthin (=(3*R*,3′*S*,5′*R*)-3,3′-dihydroxy-β,κ-caroten-6′-one; **1**) was studied. The reduction of **1** with $NaBH_4$ gave the two steroisomeric capsanthols **2** and **3** ((3*R*,3′*S*,5′*R*,6′*S*)- and (3*R*,3′*S*,5′*R*,6′*R*)-β-κ-carotene-3,3′,6′-triol, resp.) [2]. In another work, the (3*R*,5′*R*,6′*S*)- and (3*R*,5′*R*,6′*R*)-'capsanthol-3′-ones' (= 3,6-dihydroxy-β,κ-carotene-3′,6′-diones) were reduced by different complex metal hydrides. The diastereoisomeric (3′*S*)- and (3′*R*)-capsanthols were characterized by their UV/VIS, CD, ^{1}H- and ^{13}C-NMR, and mass spectra [3]. These semisynthetic compounds were used for the study of the chirality of supramolecular carotenoid self-assemblies by CD spectroscopy [4][5].

In continuation of our work on the reduction of keto carotenoids, we aimed to study the reduction of other paprika carotenoids containing κ-end group(s). Thus, capsorubin (=(3*S*,3′*S*,5*R*,5′*R*)-3,3′-dihydroxy-κ,κ-carotene-6,6′-dione; **7**) and cryptocapsin (=(3′*S*,5′*R*)-3′-hydroxy-β,κ-caroten-6′-one; **4**) were reduced with $NaBH_4$, and the structures of the reaction products were elucidated.

Results and Discussion. – *Reduction of Capsorubin and Cryptocapsin.* Capsorubin (**7**) and cryptocapsin (**4**) were reduced by $NaBH_4$ in EtOH solution for 50 min, and the product mixtures were analyzed by HPLC (*Fig. 1*). The reduction of capsorubin (**7**) gave the two stereoisomers **8** and **9** of 'capsorubol-6′-one' and the three stereoisomers **10**–**12** of capsorubol, while the reduction of cryptocapsin (**4**) resulted in the two stereoisomeric cryptocapsols **5** and **6**. After repeated column chromatography and crystallization, the carotenoids **5**, **6**, and **8**–**12** were isolated.



Spectroscopic Characterization. In the UV/VIS spectra, the maxima for **5** and **6** (436, 457, and 487 nm in benzene) as well as for **10**–**12** (425, 451, and 481 nm in benzene) and also the increased fine structure were in accordance with the reduction of the C=O groups. The UV/VIS spectra of **8** and **9** (477 and 507 (shoulder) nm in benzene) was in agreement with a decaene chromophore including a conjugated C=O group.

With the exception of **10**, isolated in an insufficient amount for ^{1}H,^{1}H-COSY analysis, the ^{1}H assignments were successfully achieved by means of ^{1}H-NMR and ^{1}H,^{1}H-COSY experiments for the compounds **5**, **6**, and **8**–**12**, and the δ(H) and J(H,H) values (see *Exper. Part*) were identical to the corresponding data from both our previous works [2][3] and from [6]. Based on these results, the configurations at C(6)

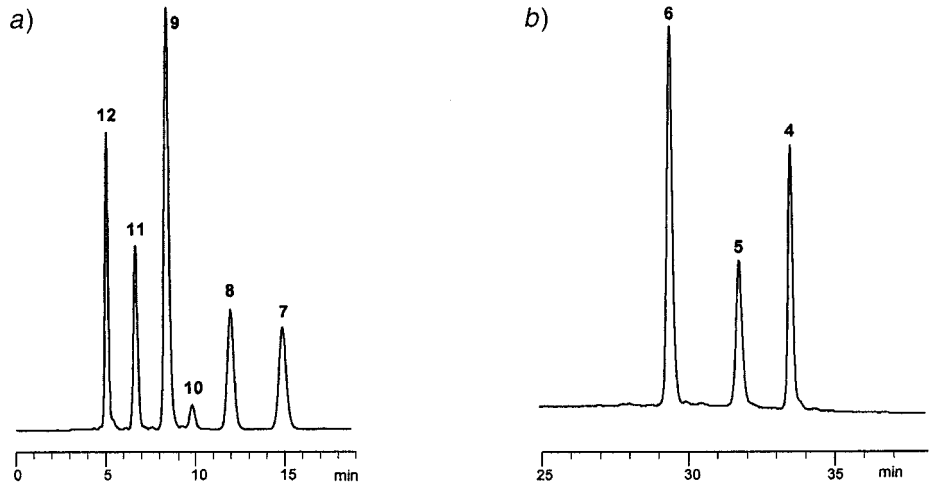


Fig. 1. *HPLC Separation* a) *of capsorubin* (**7**), *'capsorubol-6-ones'* **8** *and* **9**, *and capsorubol epimers* **10**–**12** *in eluent I and* b) *of cryptocapsin* (**4**) *and cryptocapsol epimers* **5** *and* **6** *in eluent II*

and C(6′) were established as (6′*S*) for **8**, (6′*R*) for **9**, (6′*S*) for **5**, (6′*R*) for **6**, as well as (6*S*,6′*S*) for **10**, (6*S*,6′*R*) for **11** and (6*R*,6′*R*) for **12**.

Molecules of **5**, **6**, and **8**–**12** have chiral five-membered-ring end groups connecting to the polyene chain *via* single stereogenic centers. In the case of cryptocapsols **5** and **6**, the β-end groups are achiral and, therefore, do not contribute to molecular chirality. It can be expected that the chiral perturbation of the planar polyene chromophore will mainly be caused by the centers C(6) and C(6′) attached directly to the conjugated π-system, and the cyclic end groups play only a secondary role. Furthermore, the relatively high degree of conformational mobility decreases the CD band intensities measured at room temperature. CD Spectra of **5** and **6** clearly demonstrate the decisive role of the absolute configuration at C(6′). Below 350 nm, the two spectra are in mirror image relation, although the compounds themselves are diastereoisomeric (*Fig. 2*). Because stereogenic centers can be found at only one end of the polyene chains, the CD bands are weak. The role of the stereogenic centers C(6) and C(6′) is confirmed by the CD curves of (6*S*,6′*S*)- and (6*R*,6′*R*)-capsorubols (**10** and **12**, resp.), which exhibit a phenomenon similar to that found for the cryptocapsols (*Fig. 3*). They are very similar, but opposite in sign, and show enhanced *Cotton* effects at *ca.* 265 nm, suggesting the effects of C(6) and C(6′) to be independent and roughly additive (*cf. Fig. 2*). Obviously, opposite configurations at C(6) and C(6′) show up in weaker CD bands, as found for **11** (*Fig. 3*). It should be noted, however, that these two centers do not exert the same degree of chiral perturbation, as revealed in the spectrum of **11** by the reduced CD but definitely of (*S*) character. It seems that the (*S*) configuration at C(6) by interactions of this center with the chiral cyclic end group, induces a conformational equilibrium in which the chiral conformer responsible for the measured spectrum is more populated than in the case of (*R*) configuration.

According to the longer conjugation, absorption and CD bands of 'capsorubol-6-ones' **8** and **9** are red-shifted (*Fig. 4*). These molecules have distinct chiral moieties at

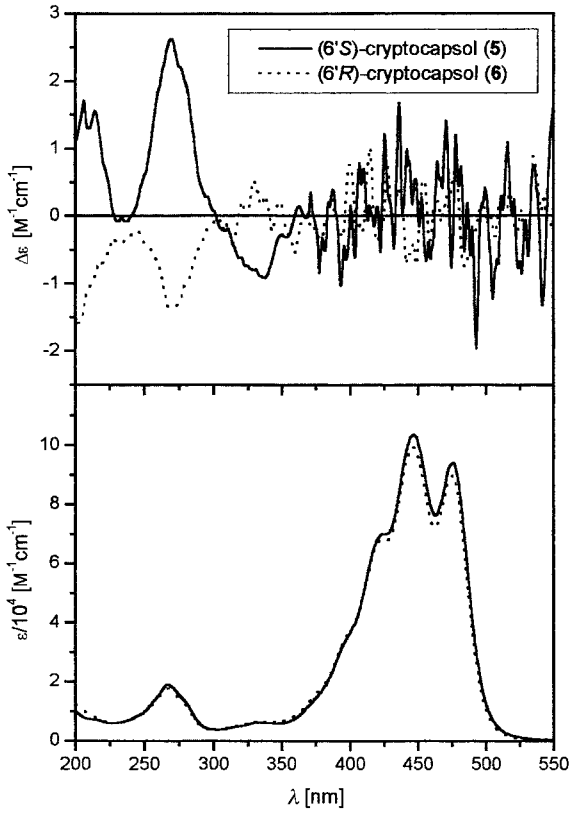


Fig. 2. *CD and UV Spectra of (6′*S*)- and (6′*R*)-cryptocapsols* (**5** and **6**, resp.) *in EtOH at room temperature*

their end groups. It is known that in capsorubin (**7**), C(5) and C(5′) exclusively influence the CD spectrum causing a strong positive band at *ca.* 310 nm [7]. It seems from the spectra of **8** and **9** that the effects of the configurations (6′*S*) and (5*R*) reinforce each other, making an intense *Cotton* effect at 282 nm, while (6′*R*) configuration reduces almost to zero the intensity of this band.

The mass spectra of **5**, **6**, and **8**–**12** showed the corresponding molecular-ion peaks. In addition, signals typical for carotenoids were observed [8].

Although the reduction of cryptocapsin and capsorubin is a routine method for the identification of these carotenoids, as yet the reaction products had not been isolated and characterized exactly. Thus, the compounds **5**, **6**, and **8**–**12** represent new semisynthetic carotenoids. These carotenoids are used as model compounds for the CD study of supramolecular carotenoid self-assemblies.

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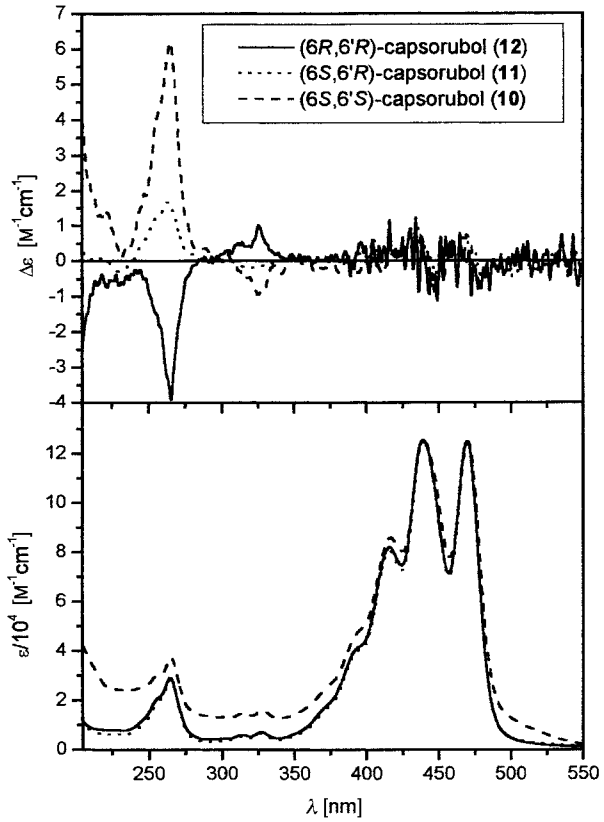

Fig. 3. *CD and UV Spectra of (6*S,*6′*S*)-, (6*S,*6′*R*)- and (6*R,*6′*R*)-capsorubols* (**10**, **11**, and **12**, resp.) *in EtOH at room temperature*

Experimental Part

1. *General*. HPLC: *Gynkotek* pump, model *480*, UV/VIS detector *HP 1050* at 450 nm: eluent *I:* MeOH/H_2O 90:10; eluent *II* (*A* = 12% H_2O/MeOH, *B* = MeOH, C = 30% CH_2Cl_2/MeOH): 0–2 min 100% *A*; 2–10 min → 80% *A*/20% *B*, 10–18 min → 50% *A*/50% *B*, 18–25 min → 100% *B*, 25–27 min 100% *B*, 27–34 → 100% *C*, 34–41 min 100% *C* (linear steps); flow rate 1.25 ml/min; column *Chromsyl C18*, 6 μm, end-capped. UV/VIS Spectra: *Beckman DU-65* spectrometer; λ_{max} (ε) in nm. CD and UV/VIS Spectra: *Jasco J-715* spectropolarimeter; at 25 ± 0.2°, rectangular cuvette of 0.5-cm path length. Temp. control: *Peltier* thermostat. NMR: *Varian Unity-Inova-440-WB* spectrometer, ^1H at 400 MHz; $CDCl_3$ solns. at 25° probe temp.; chemical shifts δ in ppm rel. to Me_3Si. MS: *ThermoQuest Automass-III* quadrupole spectrometer with a data acquisition system; *m*/*z* (rel. %).

2. *General Procedure of Reduction*. Capsorubin (**7**) or cryptocapsin (**4**) (20 mg) was dissolved in 4–5% H_2O/EtOH, and then $NaBH_4$ was added. The mixture was kept at r.t. for 50 min. Then solid NaOH was added to the soln. to decompose the complex. The mixture was diluted with benzene, the org. phase washed with H_2O (10 ×), dried (Na_2SO_4), and evaporated, and the residue dissolved in benzene.

3. *Column Chromatography of the Mixture from* **7**. The reduction mixture from **7** was subjected to CC (2 6 × 30-cm columns, $CaCO_3$ (*Biogal*), 2% acetone/benzene). Picture after development: 1 mm of yellow *Zone 1* (**10**), 1 mm of intermediate zone, 10 mm of yellow *Zone 2* (**11**), 15 mm of ochre *Zone 3* (**8**), 60 mm of intermediate zone, 40 mm of red *Zone 4* (**7** and **9**), 15 mm of yellow *Zone 5* (**12**). After usual workup (cutting and extracting), the extract of *Zone 3* was crystallized from benzene/hexane to yield 1.5 mg of **8**. The extract of *Zone 2* was submitted to CC (6 × 30-cm column, $CaCO_3$ (*Biogal*), 4% acetone/benzene). Picture after

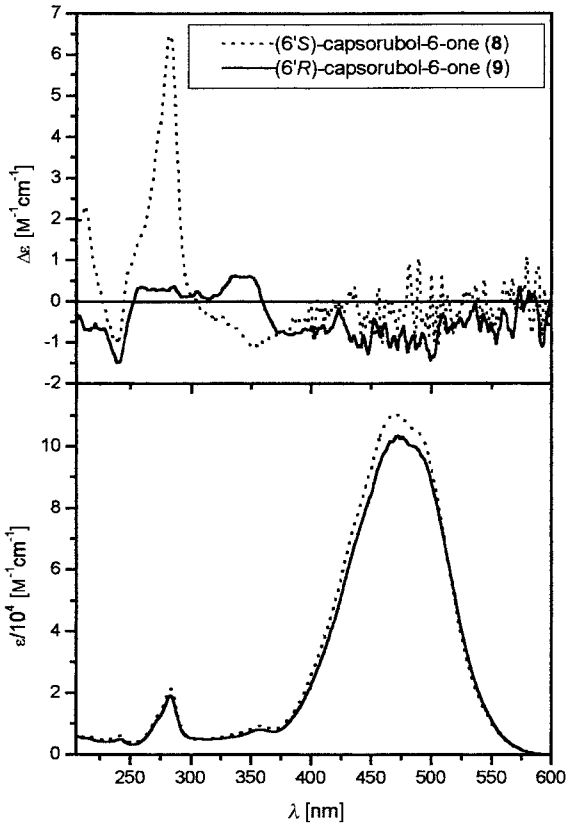

Fig. 4. *CD and UV Spectra of (6′*S*)- and (6′*R*)-'capsorubol-6-ones'* (**8** and **9**, resp.) *in EtOH at room temperature*

development: 50 mm of intermediate zone, 60 mm of yellow *Zone 2.1* (**11**), 10 mm of intermediate zone, 1 mm of pink zone. The crystallization of the extract of *Zone 2.1* from benzene/hexane yielded 0.9 mg of **11**. After CC of the extract of *Zone 4* (6 × 30-cm column, $CaCO_3$ (*Biogal*), benzene, 15 mm of ochre *Zone 4.1* (**9**), 10 mm of purple *Zone 4.2* (**7**)), the carotenoids were crystallized from benzene/hexane, yielding 0.8 mg of **9** and 0.3 mg of **7**. *Zone 5* was subjected to CC (6 × 30-cm column, $CaCO_3$ (*Biogal*), 6% acetone/benzene). Picture after development: 50 mm of red *Zone 5.1*, 25 mm of yellow *Zone 5.2* (**12**). After workup and crystallization from benzene/hexane, the extract of *Zone 5.2* yielded 0.5 mg of **12**.

4. *Column Chromatography of the Mixture from* **4**. The reduction mixture from **4** was subjected to CC (2 6 × 30-cm columns, $CaCO_3$ (*Biogal*), benzene/hexane 3:7). Picture after development: 5 mm of yellow *Zone 1* (**5**), 15 mm of intermediate zone, 20 mm of pink *Zone 2* (**4**), 30 mm of intermediate zone, 45 mm of yellow *Zone 3* (**6**). The crystallization of the extracts of *Zone 1* and *Zone 3* from benzene/hexane yielded 0.5 mg of **5** and 4 mg of **6**, resp.

5. *(6′*S*)-Cryptocapsol* (= (all-E,*3′*S,*5′*R,*6′*S*)-β,κ-Carotene-3′,6′-diol*; **5**). M.p. 103–105°. UV/VIS (benzene): 487, 457, 436. UV/VIS (EtOH): 475.5 (95000), 447 (104000), 333 (6100), 267 (19000). CD (EtOH, r.t.): 337.5 (−0.92), 269.5 (+2.62), 214 (+1.55). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.93 (*s*, Me(16′)); 0.93 (*s*, Me(17′)); 1.02 (*s*, Me(16)); 1.02 (*s*, Me(17)); 1.08 (*s*, Me(18′)); 1.46 (*m*, H−C(2)); 1.60 (*m*, H−C(3)); 1.64 (*dd*, J_{gem} = 14.6, J(4′ax,3′) = 2.9, H_{ax}−C(4′)); 1.71 (*s*, Me(18)); 1.73 (*dd*, J_{gem} = 13.2, J(2′ax,3′) = 6.1, H_{ax}−C(2′)); 1.93 (*s*, Me(19′)); 1.96 (*s*, Me(20)); 1.97 (*s*, Me(19)); 1.97 (*s*, Me(20′)); 1.99 (undefined, H_{eq}−C(2′)); 2.01 (*m*, H−C(4)); 2.40 (*dd*, J_{gem} = 14.6, J(4′eq,3′) = 8.8, H_{eq}−C(4′)); 4.10 (*d*, J(6′,7′) = 8.0, H−C(6′)); 4.42 (*m*, H−C(3′)); 5.79 (*dd*, J(7′,8′) = 15.6, J(7′,6′) = 8.0, H−C(7′)); *ca.* 6.13 (*AB*, H−C(8)); *ca.* 6.15 (*AB*, H−C(7)); *ca.* 6.17

(*m*, H–C(10)); 6.18 (*d*, *J*(10′,11′) = 11.2, H–C(10′)); 6.24 (*m*, H–C(14)); 6.26 (*m*, H–C(14′)); 6.31 (*d*, *J*(8′,7′) = 15.6, H–C(8′)); 6.34 (*d*, *J*(11,12) = 15.1, H–C(12)); 6.37 (*d*, *J*(12′,11′) = 15.0, H–C(12′)); 6.59 (*dd*, *J*(11′,10′) = 11.2, *J*(11′,12′) = 15.0, H–C(11′)); 6.62 (*m*, H–C(11)); 6.62 (*m*, H–C(15)); 6.64 (*m*, H–C(15′)). EI-MS: 570 (6, M^+), 464 (6, $[M-106]^+$), 119 (32), 109 (90), 91 (100).

6. *(6′*R*)-Cryptocapsol* (= *(*all-E,*3*′S,*5*′R,*6*′R*)-β,κ-Carotene-3′,6′-diol*; **6**). M.p. 154–155°. UV/VIS (benzene): 487, 457, 436. UV/VIS (EtOH): 475.5 (90000), 446.5 (100000), 423.5 (68000), 266.5 (19000). CD (EtOH, r.t.): 268.5 (−1.36). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.02 (*s*, Me(16)); 1.02 (*s*, Me(17)); 1.02 (*s*, Me(16′)); 1.11 (*s*, Me(18′)); 1.12 (*s*, Me(17′)); 1.28 (undefined, H_{ax}–C(4′)); 1.46 (*m*, H–C(2)); 1.61 (*m*, H–C(3)); 1.71 (*s*, Me(18)); 1.75 (*dd*, J_{gem} = 13.4, *J*(2′ax,3′) = 6.5, H_{ax}–C(2′)); 1.90 (*s*, Me(19′)); *ca.* 1.94 (undefined, H_{eq}–C(2′)); 1.96 (*s*, Me(20)); 1.97 (*s*, Me(19)); 1.97 (*s*, Me(20′)); 2.01 (*m*, H–C(4)); 2.08 (*dd*, J_{gem} = 14.5, *J*(4′eq,3′) = 8.9, H_{eq}–C(4′)); 4.20 (*dd*, *J*(6′,7′) = 6.7, *J*(6′,OH) = 4.7, H–C(6′)); 4.35 (*m*, H–C(3′)); 5.74 (*dd*, *J*(7′,8′) = 15.5, *J*(6′,7′) = 6.7, H–C(7′)); *ca.* 6.12 (*AB*, H–C(8)); *ca.* 6.15 (*AB*, H–C(7)); 6.17 (*d*, *J*(10′,11′) = 11.4, H–C(10′)); *ca.* 6.17 (*m*, H–C(10)); 6.24 (*m*, H–C(14)); 6.27 (*m*, H–C(14′)); 6.29 (*d*, *J*(8′,7′) = 15.5, H–C(8′)); 6.35 (*d*, *J*(11,12) = 15.0, H–C(12)); 6.36 (*d*, *J*(12′,11′) = 14.9, H–C(12′)); 6.59 (*dd*, *J*(11′,10′) = 11.4, *J*(11′,12′) = 14.9, H–C(11′)); 6.62 (*m*, H–C(11)); 6.62 (*m*, H–C(15)); 6.64 (*m*, H–C(15′)). EI-MS: 570 (15, M^+), 464 (45, $[M-106]^+$), 145 (85), 119 (100), 109 (80), 91 (85).

7. *(6′*S*)-'Capsorubol-6-one'* (= *(*all-E,*3*S,*3*′S,*5*R,*5*′R,*6*′S*)-3,3′,6′-Trihydroxy-κ,κ-caroten-6-one*; **8**). M.p. 165–166°. UV/VIS (benzene): 507, 477. UV/VIS (EtOH): 471 (110000), 358.2 (9200), 283.4 (21400), 242 (6000), 214.6 (6000). CD (EtOH, r.t.): 351 (−1.14), 281.6 (+6.50), 240 (−1.05), 213 (+2.32). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.83 (*s*, Me(16)); 0.93 (*s*, Me(16′)); 0.93 (*s*, Me(17′)); 1.08 (*s*, Me(18′)); 1.20 (*s*, Me(17)); 1.36 (*s*, Me(18)); 1.48 (*dd*, J_{gem} = 14.2, *J*(4ax,3) ≈ 3, H_{ax}–C(4)); 1.64 (*dd*, J_{gem} = 14.5, *J*(4′ax,3′) = 2.9, H_{ax}–C(4′)); 1.70 (*dd*, J_{gem} = 13.6, *J*(2ax,3) = 4.7, H_{ax}–C(2)); 1.73 (*dd*, J_{gem} = 13.4, *J*(2′ax,3′) = 6.1, H_{ax}–C(2′)); 1.93 (*s*, Me(19′)); 1.95 (*s*, Me(19)); 1.97 (*s*, Me(20′)); 1.97 (*s*, Me(20)); 1.98 (*dd*, J_{gem} = 13.4, *J*(2′eq,3′) = 8.0, H_{eq}–C(2′)); 1.99 (*dd*, J_{gem} = 13.6, *J*(2eq,3) = 7.7, H_{eq}–C(2)); 2.40 (*dd*, J_{gem} = 14.5, *J*(4′eq,3′) = 8.9, H_{eq}–C(4′)); 2.95 (*dd*, J_{gem} = 14.2, *J*(4eq,3) = 8.5, H_{eq}–C(4)); 4.11 (*d*, *J*(6′,7′) = 8.0, H–C(6′)); 4.42 (*m*, H–C(3′)); 4.51 (*m*, H–C(3)); 5.81 (*dd*, *J*(7′,6′) = 8.0, *J*(7′,8′) = 15.6, H–C(7′)); 6.19 (*d*, *J*(10′,11′) = 11.4, H–C(10′)); 6.27 (*d*, *J*(14′,15′) = 11.0, H–C(14′)); 6.31 (*d*, *J*(8′,7′) = 15.6, H–C(8′)); 6.35 (*d*, *J*(14,15) = 10.7, H–C(14)); 6.37 (*d*, *J*(12′,11′) = 14.6, H–C(12′)); 6.44 (*d*, *J*(7,8) = 15.1, H–C(7)); 6.51 (*d*, *J*(12,11) = 14.6, H–C(12)); 6.56 (*m*, H–C(10)); 6.60 (*m*, H–C(11′)); 6.61 (*m*, H–C(11)); 6.63 (*m*, H–C(15′)); 6.69 (*m*, H–C(15)); 7.32 (*d*, *J*(8,7) = 15.1, H–C(8)). EI-MS: 602 (8, M^+), 584 (2, $[M-H_2O]^+$), 496 (3, $[M-106]^+$), 145 (4), 119 (6), 109 (28), 91 (32), 41 (100).

8. *(6′*-R*)-'Capsorubol-6-one'* (= *(*all-E,*3*S,*3*′S,*5*R,*5*′R,*6*R*)-3,3′,6′-Trihydroxy-κ,κ-caroten-6-one*; **9**). M.p. 174–177°. UV/VIS (benzene): 507, 477. UV/VIS (EtOH): 472 (106000), 358.4 (10500), 283 (22000), 242 (7500). CD (EtOH, r.t.): 384.6 (−0.82), 336.6 (+0.62), 239.4 (−1.50). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.83 (*s*, Me(16)); 1.03 (*s*, Me(16′)); 1.11 (*s*, Me(18′)); 1.12 (*s*, Me(17′)); 1.20 (*s*, Me(17)); 1.28 (*m*, H_{ax}–C(4′)); 1.36 (*s*, Me(18)); 1.48 (*dd*, J_{gem} = 14.5, *J*(4ax,3) = 3.2, H_{ax}–C(4)); 1.71 (*dd*, J_{gem} = 13.9, *J*(2ax,3) = 4.7, H_{ax}–C(2)); 1.75 (*dd*, J_{gem} = 13.6, *J*(2′ax,3′) = 6.5, H_{ax}–C(2′)); 1.91 (*s*, Me(19′)); 1.95 (*s*, Me(19)); 1.96 (undefined, H_{eq}–C(2′)); 1.97 (*s*, Me(20′)); 1.97 (*s*, Me(20)); 1.99 (*dd*, J_{gem} = 13.9, *J*(2eq,3) = 7.9, H_{eq}–C(2)); 2.08 (*dd*, J_{gem} = 14.5, *J*(4′eq,3′) = 8.8, H_{eq}–C(4′)); 2.95 (*dd*, J_{gem} = 14.5, *J*(4eq,3) = 8.5, H_{eq}–C(4)); 4.21 (*m*, H–C(6′)); 4.35 (*m*, H–C(3′)); 4.51 (*m*, H–C(3)); 5.76 (*dd*, *J*(7′,6′) = 6.6, *J*(7′,8′) = 15.6, H–C(7′)); 6.17 (*d*, *J*(10′,11′) = 11.3, H–C(10′)); 6.27 (*d*, *J*(14′,15′) = 10.7, H–C(14′)); 6.29 (*d*, *J*(8′,7′) = 15.6, H–C(8′)); 6.35 (*d*, *J*(14,15) = 10.7, H–C(14)); 6.36 (*d*, *J*(14′,15′) = 15.1, H–C(12′)); 6.44 (*d*, *J*(7,8) = 15.1, H–C(7)); 6.51 (*d*, *J*(12,11) = 14.4, H–C(12)); 6.56 (*m*, H–C(10)); 6.60 (*m*, H–C(11′)); 6.61 (*m*, H–C(11)); 6.63 (*m*, H–C(15′)); 6.69 (*m*, H–C(15)); 7.32 (*d*, *J*(8,7) = 15.1, H–C(8)). EI-MS: 602 (10, M^+), 584 (1, $[M-H_2O]^+$), 496 (4, $[M-106]^+$), 145 (8), 119 (16), 109 (34), 91 (42), 41 (100).

9. (6S,*6′*S*)-Capsorubol* (= *(*all-E,*3*S,*3*′S,*5*R,*5*′R,*6*S,*6*′S*)-κ,κ-Carotene-3,3′,6,6′-tetrol*; **10**). UV/VIS (benzene): 481, 451, 425. UV/VIS (EtOH): 470 (125000), 439.8 (125000), 417 (86000), 327.8 (16000), 313.8 (14000), 265.2 (37000). CD (EtOH, r.t.): 325.2 (−0.96), 265.2 (+6.20). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.94 (*s*, Me(16), Me(16′), Me(17), Me(17′)); 1.08 (*s*, Me(18), Me(18′)); 1.64 (*dd*, J_{gem} = 14.6, *J*(4ax,3) = *J*(4′eq,3′) ≈ 2.6, H_{ax}–C(4), H_{ax}–C(4′)); 1.73 (*dd*, J_{gem} = 13.6, *J*(2ax,3) = *J*(2′ax,3′) = 6.3, H_{ax}–C(2), H_{ax}–C(2′)); 1.93 (*s*, Me(19), Me(19′)); 1.97 (*s*, Me(20), Me(20′)); 2.00 (undefined, H_{eq}–C(2), H_{eq}–C(2′)); 2.41 (*dd*, J_{gem} = 14.5, *J*(4eq,3) = *J*(4′eq,3′) = 8.7, H_{eq}–C(4), H_{eq}–C(4′)); 4.11 (*m*, H–C(6), H–C(6′)); 4.42 (*m*, H–C(3), H–C(3′)); 5.81 (*dd*, *J*(6,7) = *J*(6′,7′) = 8.1, *J*(7,8) = *J*(7′,8′) = 15.7, H–C(7), H–C(7′)); 6.19 (*d*, *J*(10,11) = *J*(10′,11′) = 11.3, H–C(10), H–C(10′)); 6.27 (*m*, H–C(14), H–C(14′)); 6.31 (*d*, *J*(8,7) = *J*(8′,7′) = 15.7, H–C(8), H–C(8′)); 6.37 (*d*, *J*(12,11) = *J*(12′,11′) = 15.0, H–C(12), H–C(12′)); 6.60 (*dd*, *J*(11,10) = *J*(11′,10′) = 11.3, *J*(11,12) =

$J(11',12') = 15.0$, H–C(11), H–C(11')); 6.64 (*m*, H–C(15), H–C(15')). MS: 604 (1, M^+), 588 (1, $[M - H_2O]^+$), 498 (3, $[M - 106]^+$), 145 (90), 109 (98), 109 (100), 91 (100).

10. *(6S,6'R)-Capsorubol* (= *(*all-E,*3S,3'S,5R,5'R,6'R,6S)-κ,κ-Carotene-3,3',6,6'-tetrol*; **11**). M.p. 184–187°. UV/VIS (benzene): 481, 451, 425. UV/VIS (EtOH): 470 (125000), 439.6 (124000), 416.6 (80000), 327.6 (6700), 314 (5200), 265 (29000). CD (EtOH, r.t.): 321.4 (−0.19), 263.8 (+1.67), 231.4 (−0.32). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.93 (*s*, Me(16), Me(17)); 1.03 (*s*, Me(16')); 1.08 (*s*, Me(18)); 1.11 (*s*, Me(18')); 1.12 (*s*, Me(17')); 1.27 (*m*, H_{axv}–C(4')); 1.64 (*dd*, $J_{gem} = 14.6$, $J(2ax,3) = 2.8$, H_{ax}–C(4)); 1.72 (*dd*, $J_{gem} = 13.3$, $J(2ax,3) = 6.1$, H_{ax}–C(2)); 1.76 (*dd*, $J_{gem} = 13.6$, $J(2'ax,3') = 6.8$, H_{ax}–C(2')); 1.90 (*s*, Me(19')); 1.93 (*s*, Me(19)); 1.96 (undefined, H_{eq}–C(2')); 1.96 (*s*, Me(20), Me(20')); 1.99 (*m*, H_{eq}–C(2)); 2.08 (*dd*, $J_{gem} = 14.5$, $J(4'eq,3') = 9.0$, H_{eq}–C(4')); 2.41 (*dd*, $J_{gem} = 14.6$, $J(4eq,3) = 8.7$, H_{eq}–C(4)); 4.11 (*m*, H–C(6)); 4.20 (*m*, H–C(6')); 4.35 (*m*, H–C(3')); 4.42 (*m*, H–C(3)); 5.75 (*dd*, $J(6',7') = 6.8$, $J(7',8') = 15.6$, H–C(7')); 5.80 (*dd*, $J(6,7) = 8.1$, $J(7,8) = 15.5$, H–C(7)); 6.17 (*d*, $J(10',11') = 11.3$, H–C(10')); 6.19 (*d*, $J(10,11) = 11.3$, H–C(10)); 6.26 (*m*, H–C(14)); 6.26 (*m*, H–C(14')); 6.29 (*d*, $J(8',7') = 15.6$, H–C(8')); 6.31 (*d*, $J(8,7) = 15.5$, H–C(8)); 6.36 (*d*, $J(12',11') = 14.9$, H–C(12')); 6.37 (*d*, $J(12,11) = 14.9$, H–C(12)); 6.60 (*dd*, $J(11,10) = 11.3$, $J(11,12) = 14.9$, H–C(11')); 6.60 (*dd*, $J(11',10') = 11.3$, J (11',12') = 14.9, H–C(11')); 6.63 (*m*, H–C(15)); 6.63 (*m*, H–C(15')). EI-MS: 604 (8, M^+), 588 (1, $[M - H_2O]^+$), 498 (22, $[M - 106]$), 145 (95), 119 (85), 109 (100), 91 (100).

11. *(6R,6'R)-Capsorubol* (= *(*all-E,*3S,3'S,5R,5'R,6R,6'R)-κ,κ-Carotene-3,3',6,6'-tetrol*; **12**). M.p. 167–168°. UV/VIS (benzene): 481, 451, 425. UV/VIS (EtOH): 469.6 (125000), 439.4 (125000), 415.8 (82000), 327 (7100), 264.8 (29100). CD (EtOH, r.t.): 325.8 (+0.99), 265.4 (−3.92). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.03 (*s*, Me(16), Me(16')); 1.11 (*s*, Me(18), Me(18')); 1.12 (*s*, Me(17), Me(17')); 1.27 (undefined, H_{ax}–C(4), H_{ax}–C(4')); 1.75 (*dd*, $J_{gem} = 13.6$, $J(2ax,3) = J(2'ax,3') = 6.4$, H_{ax}–C(2), H_{ax}–C(2')); 1.90 (*s*, Me(19), Me(19')); 1.95 (*dd*, $J_{gem} = 13.6$, $J(2eq,3) \approx J(2'eq,3') \approx 8$, H_{eq}–C(2), H_{eq}–C(2')); 1.96 (*s*, Me(20), Me(20')); 2.08 (*dd*, $J_{gem} = 14.7$, $J(4eq,3) = J(4'eq,3') = 8.9$, H_{eq}–C(4), H_{eq}–C(4')); 4.20 (*m*, H–C(6), H–C(6')); 4.35 (*m*, H–C(3), H–C(3')); 5.74 (*dd*, $J(6,7) = J(6',7') = 6.7$, $J(7,8) = J(7',8') = 15.5$, H–C(7), H–C(7')); 6.17 (*d*, $J(10,11) = J(10',11') = 11.3$, H–C(10), H–C(10')); 6.26 (*m*, H–C(14), H–C(14')); 6.29 (*d*, $J(8,7) = J(8',7') = 15.5$, H–C(8), H–C(8')); 6.36 (*d*, $J(12,11) = J(12',11') = 14.9$, H–C(12), H–C(12')); 6.60 (*dd*, $J(11,10) = J(11',10') = 11.3$, $J(11,12) = J(11',12') = 14.9$, H–C(11), H–C(11')); 6.63 (*m*, H–C(15), H–C(15')). EI-MS: 604 (5, M^+), 588 (1, $[M - H_2O]^+$), 498 (4, $[M - 106]^+$), 145 (82), 109 (100), 109 (100), 91 (100).

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