Stereoselective Reduction of 'Capsanthol-3′-ones' (= 3,6′-Dihydroxy-β,κ-caroten-3′-ones) by Complex Hydrides

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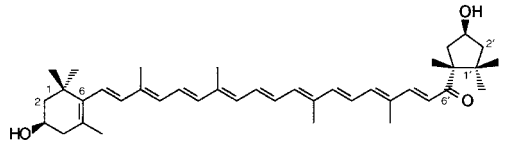
The (3*R*,5′*R*,6′*R*)- and (3*R*,5′*R*,6′*S*)-capsanthol-3′-one (= 3,6′-dihydroxy-β,κ-caroten-3′-one; **4** and **5**, resp.) were reduced by different complex metal hydrides containing organic ligands. The ratio of the thus obtained diastereoisomeric (3′*S*)-capsanthols **2** and **3** or (3′*R*)-capsanthols **6** and **7**, respectively, was investigated. Four complex hydrides showed remarkable stereoselectivity and produced the (3′*R*,6′*S*)-capsanthol (**6**) in 80–100% (see *Table 1*). The starting materials and the products were characterized by UV/VIS, CD, ^{1}H- and ^{13}C-NMR, and mass spectra.

Introduction. – For the reduction of the carbonyl function of carotenoids, metal hydrides are commonly used, either $LiAlH_4$ in Et_2O or in tetrahydrofuran, or $NaBH_4$ in EtOH or in EtOH/benzene. With the former reagent, the reaction is complete within a few minutes at room temperature. If the carbonyl functions are conjugated with the polyene chain, a hypsochromic shift (to shorter wavelengths) and increased spectral fine structure will be seen in the UV/VIS spectrum. Reduction products are usually readily separated from the starting compound because the carotenol product is more polar than the initial aldehyde or ketone. However, the reduction of keto groups of carotenoids produces two stereoisomers, which are very difficult to separate.

Matsuno and co-workers have reported on the reduction of carotenoids containing 2-, 3-, and 4-oxo-β- and 3-oxo-ε-end groups by $NaBH_4$. The diastereoisomer separation of the carotenoids obtained with a 3-hydroxy-β-end group (zeaxanthin) [1], a 3-hydroxy-4-oxo-β-end group (astaxanthin and phoenicoxanthin) [2], a 3-hydroxy-ε-end group (tunaxanthin) [3], a 2-hydroxy-β-end group (β,β-caroten-2-ol and β,β-carotene-2,2′-diol) [4], a 4-hydroxy-β-end group (isozeaxanthin, β-isocryptoxanthin) [5] was achieved by HPLC on a *Chiralcel OD* column after conversion to the corresponding benzoate or 4-bromobenzoates. Earlier in our laboratory, the reduction of capsanthin (**1**; (3*R*,3′*S*,5′*R*)) was studied [6]. The reduction of **1** with both $LiAlH_4$ or $NaBH_4$ gave the two stereoisomers **2** and **3** of capsanthol in a 4:1 and 2.5–3:1 molar ratio, respectively. The separation of **2** and **3** was achieved by column chromatography on $CaCO_3$.

Later, we reduced capsanthin (**1**) with different complex metal hydrides containing organic ligands [7]. The ratio of the (6′*R*)- and (6′*S*)-capsanthol epimers and the by-products were investigated. Besides the formation of the corresponding capsanthols **2** and **3**, some hydrides containing different organic ligands reacted with **1** in such a way that reduction of the C(7′)=C(8′) bond occurred yielding 7′,8′-dihydrocapsanthol



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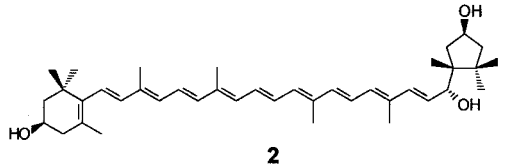

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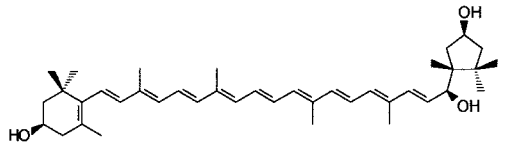

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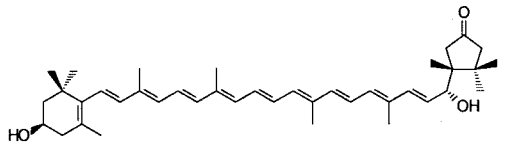

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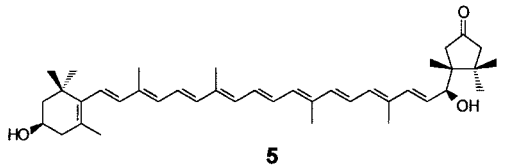

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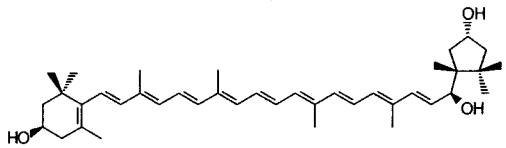

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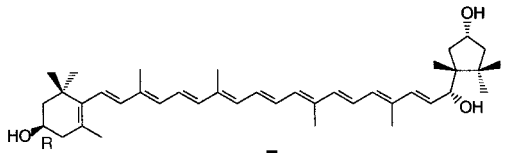

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epimers and 7′,8′-dihydrocapsanthin. The dihydrocarotenoids have been isolated and identified by their UV/VIS, CD, ^{1}H- and ^{13}C-NMR, and mass spectra [7].

In continuation of our work on the reduction of capsanthin derivatives, we aimed at studying the reduction of the 3′-oxo compounds that contain the keto function at the five-membered ring. Thus, the (6′*R*)- and (6′*S*)-'capsanthol-3′-ones' **4** and **5**, respec-

tively, were reduced with different complex hydrides and the structures of the formed products elucidated.

Results and Discussion. – The 'capsanthol-3′-ones' **4** and **5** were prepared in 1965 by *Oppenauer* oxidation of the corresponding capsanthols **2** and **3** [8]. We have now characterized the former by modern spectroscopic methods. The reduction of (6′*S*)-'capsanthol-3′-one' **5** yielded the stereoisomeric (3′*R*,6′*S*)- and (3′*S*,6′*S*)-capsanthols (**6** and **3** resp.), and that of (6′*R*)-'capsanthol-3′-one' **4** produced the stereoisomeric (3′*S*,6′*R*)- and (3′*R*,6′*R*)-capsanthols (**2** and **7**, resp.). While the separation of the diastereoisomers **2** and **7** was successfully achieved by reversed-phase HPLC, **6** and **3** were separated by HPLC on a (*S*,*S*)-*WHELK-O1* column.

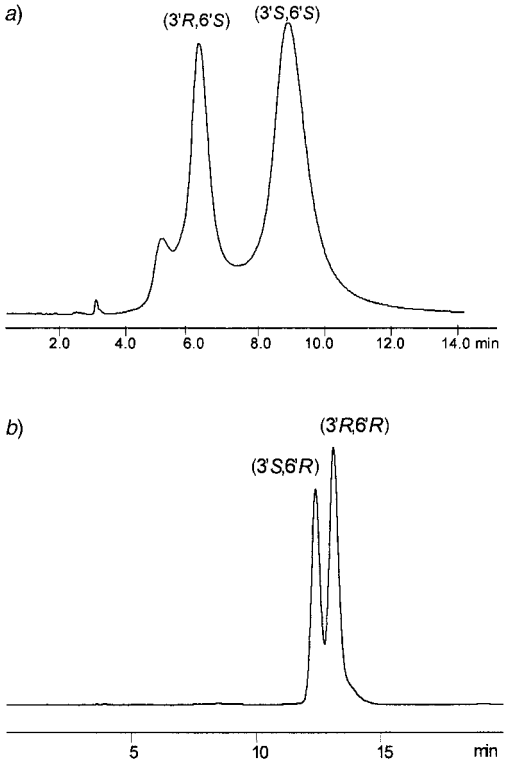

Fig. 1. *HPLC Separation of* a) *(3′*S*,6′*S*)- and (3′*R*,6′*S*)-capsanthols* (**3** and **6**, resp.) (column: (*S*,*S*)-*WHELK-O1* 250-4, 5 μm *and of* b) *the diastereoisomeric (3′*S*,6′*R*)- and (3′*R*,6′*R*)-capsanthols* (**2** and **7**, resp.) (column: *Chromsyl* C_{18}, 6 μm, not end-capped)

The reduction of the 'capsanthol-3′-ones' **4** and **5** was performed with eight different complex hydrides in abs. Et_2O (EtOH in the case of $NaBH_4$) and monitored by TLC. After removal of the starting material by column chromatography ($CaCO_3$, benzene), the ratio of the two stereoisomers produced was determined by HPLC. DIBAH, sodium diethyldihydroaluminate, sodium dihydrobis(2-methoxyethoxy)aluminate, and

L-Selectride® showed remarkable stereoselectivity and produced (3′*R*,6′*S*)-capsanthol (**6**) in 80–100% (see *Table 1*). The results establish that the molar ratio of the stereoisomeric capsanthols depends on the configuration at C(6′) of the starting 'capsanthol-3′-one'.

Table 1. *Ratio of the Capsanthol Diastereoisomers*

Hydride	Time	(3′*R*,6′*S*)/(3′*S*,6′*S*) (= **6**/**3**; from **5**)	(3′*R*,6′*R*)/(3′*S*,6′*R*) (= **7**/**2**; from **4**)
Lithium aluminium hydride	50 min	50 : 50	40 : 60
Sodium borohydride	50 min	40 : 60	50 : 50
Sodium diethyldihydridoaluminate	3 min	90 : 10	40 : 60
Super Hydride® (lithium triethylborohydride)	3 min	50 : 50	50 : 50
DIBAH (diisobutylaluminium hydride)	3 min	90 : 10	50 : 50
Sodium dihydridobis(2-methoxy-ethoxy)aluminate	5 min	100 : 0	30 : 70
L-Selectride® (lithium tri-*sec*-butylborohydride)	2 h	80 : 20	50 : 50
Sodium trimethoxyborohydride	30 min	50 : 50	60 : 40

For structure elucidation, samples of **6** and **3** as well as of **7** and **2** were synthesized by preparative $NaBH_4$ reduction of **5** and **4**, respectively. The separation of **6** and **3** was successful by prep. TLC (silica-gel plate, benzene/AcOEt/MeOH) yielding the pure compounds after crystallization, whereas the separation and purification of **7** and **2** was performed by CC ($CaCO_3$, benzene) followed by crystallization.

The UV/VIS, CD, mass, and NMR spectra of **4**–**7** are consistent with their structures. In particular, all the MS show the corresponding molecular-ion peak and signals typical for carotenoids [9]. The shape of the CD spectra of **2**–**7** at wavelengths below 300 nm is similar, while it is uncharacteristic in the VIS range. Thus, the spacial orientation of the OH group at the (6′*R*)-, (6′*S*)-, (3′*R*)-, and (3′*S*)-configured stereogenic centers cannot be distinguished in the CD spectra (*Figs. 2–4*).

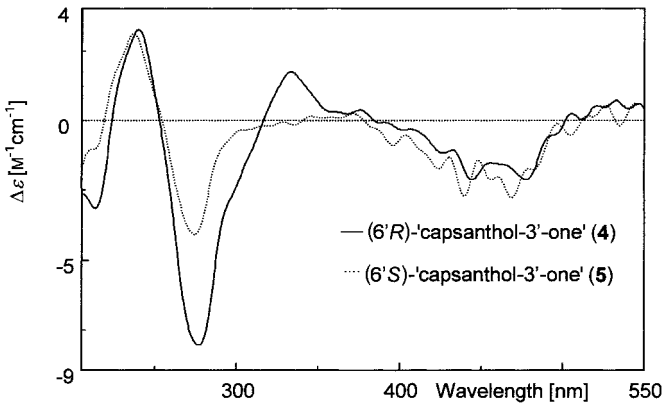

Fig. 2. *CD Spectra of the (6′*R*)- and (6′*S*)-'capsanthol-3′-ones'* (**4** and **5**, resp.) *in EtOH at room temperature*

All ^{1}H-NMR resonances of **2**–**7** could be assigned by ^{1}H and ^{1}H,^{1}H-COSY experiments. ^{13}C-Line assignments were successfully achieved by means of APT,

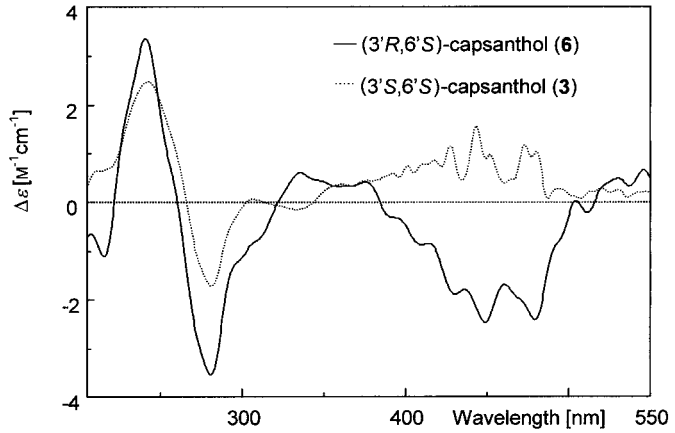

Fig. 3. *CD Spectra of the (3′*S*,6′*S*)- and (3′*R*,6′*S*)-capsanthols* (**3** and **6**, resp.) *in EtOH at room temperature*

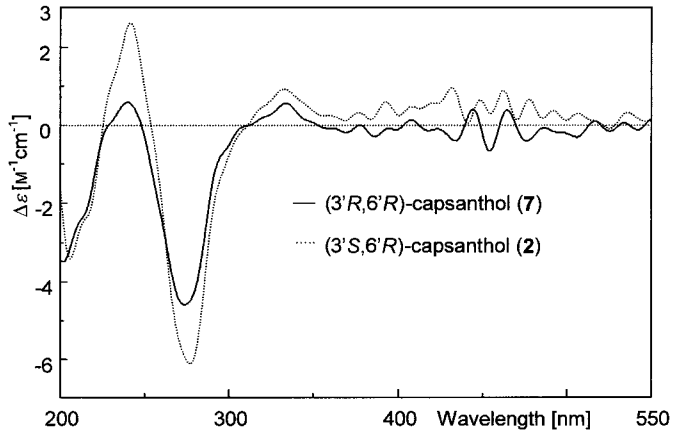

Fig. 4. *CD Spectra of (3′*S*,6′*R*)- and (3′*R*,6′*R*)-capsanthols* (**2** and **7**, resp.) *in EtOH at room temperature*

HSQC, and HMBC experiments. The ^{1}H- and ^{13}C-NMR data were identical with published data [10–12] and allowed the identification of the configurational relationships. The configurations at all the C(3′) atoms were confirmed by TROESY experiments, *i.e.*, they were established as (3′*S*) for **2** and **3** and as (3′*R*) for **6** and **7**. The ^{1}H-NMR data typical for the κ-end group are shown in *Table 2*.

The compounds **4**–**7** represent new semisynthetic carotenoids that have not yet been found in nature. The isolated compounds may serve as reference compounds for further investigations of the chemical and physical properties of carotenoids containing the κ-end group.

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Table 2. *Characteristic ^{1}H-NMR Data of the κ-End Groups of* **2**–**7**

	2	**3**	**4**	**5**	**6**	**7**
H_α–C(2′)	1.73	1.75	2.35	2.14	2.07	2.12
H_β–C(2′)	1.99	1.96	2.07	2.46	1.79	1.51
H–C(3′)	4.42	4.35	–	–	4.32	4.36
H_α–C(4′)	1.64	1.27	1.84	2.15	2.00	1.77
H_β–C(4′)	2.41	2.08	2.27	2.53	1.90	1.66
H–C(6′)	4.11	4.20	4.38	4.31	4.20	4.37
H–C(7′)	5.80	5.74	5.69	5.77	5.83	5.76
H–C(8′)	6.31	6.29	6.30	6.34	6.31	6.30
Me(16′)	0.93	1.03	1.18	1.17	1.12	1.24
Me(17′)	0.93	1.13	1.24	1.04	0.85	1.05
Me(18′)	1.09	1.11	1.08	0.97	0.77	0.90

Experimental Part

1. *General*. HPLC: *a*) *JASCO* instrument, pump *PU 980*, UV/VIS detector *UV 975* at 450 nm; eluent hexane/^{i}PrOH 80:20, flow rate 0.9 ml/min; column (*S,S*)-*WHELK-O1 250-4*, 5 μm, *Merck*; *b*) *Gynkotek* pump model *480*, UV/VIS detector *HP 1050* at 450 nm; eluent MeOH/H_2O 90:10, flow rate 1.25 ml/min; column *Chromsyl* C_{18}, 6 μm, not end-capped. UV/VIS Spectra: *Beckman DU-65* spectrometer; λ_{max} in nm. CD Spectra: *Jasco J-715/150S* spectrometer, λ ($\Delta\varepsilon$) in nm. NMR Spectra: *Varian Unity-Inova-400-WB* spectrometer; ^{1}H at 400 MHz, ^{13}C at 100 MHz; $CDCl_3$ solns. at 25° probe temp.; chemical shifts δ in ppm rel. to Me_4Si (^{1}H) or to the residual solvent signals (^{13}C). MS: *ThermoQuest Automass III* quadrupole spectrometer with a data acquisition system; *m*/*z* (rel. %).

2. *General Procedure of Reduction.* 'Capsanthol-3′-one' (0.5 mg) was dissolved in dry freshly distilled Et_2O under N_2. Then the appropriate complex hydride (0.1 ml) was added. The mixture was kept at r.t. Then solid NaOH and EtOH were added to the soln. to decompose the complex. The mixture was diluted with Et_2O, washed with 10% NaOH soln. (4–5 ×) and then with H_2O (10 ×), the soln. dried (Na_2SO_4) and evaporated, and the residue dissolved in benzene. In the case of $NaBH_4$, the reduction was performed in 4–5% H_2O/EtOH.

3. *Column Chromatography (CC)*. The reduction mixture was subjected to CC (3 × 30 cm column, $CaCO_3$ (*Biogal*), benzene). Typical picture after development: 1 mm of yellow zone (*cis*-isomers), 10 mm of intermediate zone, 15 mm of yellow zone (mixture of capsanthols), 10 mm of intermediate zone, 2 mm of yellow zone (starting material). After the usual workup (cutting and extracting) the zone containing the capsanthol stereoisomers was submitted to HPLC analysis.

4. *Thin Layer Chromatography.* TLC (silica gel *60* F_{254} on Al foil (*Merck*), benzene/AcOEt/MeOH 7:2:1): R_f 0.25 (for **2** and **7**), 0.19 (for **3**), 0.44 (for **4**), 0.55 (for **5**), and 0.29 (for **6**).

5. *Preparative Reduction of* **4** *or* **5**. The 'capsanthol-3′-one' **4** or **5** (10 mg) was reduced with $NaBH_4$ in EtOH: **3**/**6** and **2**/**7**, resp.

Prep. TLC (silica gel *60* F_{254} on Al foil (*Merck*), AcOEt/MeOH 7:2:1) of **3**/**6** yielded, after crystallization from benzene/hexane, 3.1 mg of **6** and 4.0 mg of **3**.

CC (4 6 × 30 cm columns $CaCO_3$ (*Biogal*), benzene of **2**/**7** gave the following picture after development: 15 mm of yellow *Zone 1* (**2**), 2 mm of intermediate zone, 12 mm of yellow *Zone 2* (**7**). The carotenoids were crystallized from benzene/hexane: 4.0 mg of **2** and 3.5 mg of **7**.

6. *Data of* **2**–**7**. *(3′S,6′R)-Capsanthol* (= *(all*-E,*3*R,*3′*S,*5′*R,*6′*R*)-β,κ-Carotene-3,3′,6′-triol*; **2**): M.p. 163–165°. UV/VIS (benzene): 487, 458, 433. CD (EtOH, r.t.): 242 (+2.60), 277 (−6.14), 332.5 (+0.90). NMR and MS: *Table 2* and [7].

(3′S,6′S)-Capsanthol (= *(all*-E,*3*R,*3′*S,*5′*R,*6′*S*)-β,κ-Carotene-3,3′,6′-triol*; **3**): M.p. 172–174°. UV/VIS (benzene): 487, 458, 433. CD (EtOH, r.t.): 242.5 (+2.46), 281 (−1.73), 306.5 (+0.04), 335.5 (−0.16), 427.5 (+1.15), 443.5 (+1.6), 473.5 (+1.17). NMR and MS: *Table 2* and [7].

(6′R)-'Capsanthol-3′-one' (= *(all*-E,*3*R,*5′*R,*6′*R*)-3,6′-Dihydroxy-β,κ-caroten-3′-one*; **4**): Red crystals. M.p. 164–165°. UV/VIS (benzene): 487, 457, 433. CD (EtOH, r.t.): 240 (+3.14), 276.5 (−8.19), 334 (+1.63), 445.5 (−2.25), 477 (−2.23). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.06 (*s*, Me(16), Me(17)); 1.08 (*s*, Me(18′)); 1.18 (*s*, Me(17′)); 1.24 (*s*, Me(16′)); 1.47 ('*t*', J(2ax,3) = J_{gem} = 12.1, H_{ax}–C(2)); 1.50 (*s*, OH–C(3)); 1.56 (*d*, ^3J(6′,OH) = 3.5, OH–C(6′)); 1.72 (*s*, Me(18)); 1.76 (*ddd*, J_{gem} = 12.1, J(2eq,3) = 3.5, J(2eq,4q) = 2.2,

$H_{eq}-C(2)$); 1.84 (d, $J_{gem}=18.5$, $H_{\beta}-C(4')$); 1.88 (s, Me(19′)); 1.95 (s, Me(20), Me(20′)); 1.96 (s, Me(19)); 2.03 (dd, $J_{gem}=16.9$, $J(4ax,3)=9.7$, $H_{ax}-C(4)$); 2.07 (d, $J_{gem}=18.7$, $H_{\alpha}-C(2')$); 2.27 (d, $J_{gem}=18.5$, $H_{\alpha}-C(4')$); 2.35 (d, $J_{gem}=18.7$, $H_{\beta}-C(2')$); 2.37 (dd, $J_{gem}=16.9$, $J(4eq,3)=5.8$, $H_{eq}-C(4)$); 3.99 (m, H−C(3)); 4.38 (dd, $J(6',7')=7.2$, $^3J(6',OH)=3.5$, H−C(6′)); 5.69 (dd, $J(7',8')=15.5$, $J(7',6')=7.2$, H−C(7′)); 6.08 (AB, $J(7,8)=16.2$, H−C(7)); 6.13 (AB, $J(8,7)=16.2$, H−C(8)); 6.14 (d, $J(10,11)=10.9$, H−C(10)); 6.17 (d, H−C(10′)); 6.24 (m, H−C(14)); 6.26 (m, H−C(14′)); 6.30 (d, $J(8',7')=15.5$, H−C(8′)); 6.35 (d, $J(12,11)=14.8$, H−C(12)); 6.36 (d, $J(12',11')=14.9$, H−C(12′)); 6.57 (dd, $J(11',12')=14.9$, $J(11',10')=11.3$, H−C(11′)); 6.62 (m, H−C(15′)); 6.64 (m, H−C(11), H−C(15)). ^{13}C-NMR (100 MHz, $CDCl_3$; starred signals may be interchanged): 12.73* (C(20)); 12.77 (C(19)); 12.81* (C(20′)); 13.01 (C(19′)); 16.62 (C(18′)); 21.59 (C(18)); 24.82 (C(17′)); 25.36 (C(16′)); 28.70** (C(16)); 30.24** (C(17)); 37.10 (C(1)); 41.15 (C(1′)); 42.52 (C(4)); 46.92 (C(5′)); 48.40 (C(2)); 50.04 (C(4′)); 53.81 (C(2′)); 65.05 (C(3)); 77.54 (C(6′)); 124.38 (C(11′)); 125.06 (C(11)); 125.64 (C(7)); 126.18 (C(5)); 128.20 (C(7′)); 129.90 (C(15′)); 130.45 (C(15)); 131.25 (C(10)); 132.48 (C(14)); 132.90 (C(10′)); 133.20 (C(14′)); 133.96 (C(9′)); 135.78*** (C(13′)); 136.15*** (C(9)); 136.58 (C(8′)); 136.74*** (C(13)); 137.48 (C(12)); 137.72 (C(6)); 138.45 (C(8)); 138.60 (C(12′)); 217.63 (C(3′)). EI-MS: 586 (10, M^+), 568 (6, $[M-H_2O]^+$), 494 (5, $[M-$toluene$]^+$), 480 (38), 119 (95), 109 (100).

*(6′*S*)-'Capsanthol-3′-one'* (= *(all-*E*,3*R*,5′*R*,6′*S*)-3,6′-Dihydroxy-β,κ-caroten-3′-one*; **5**): Red crystals. M.p. 148–150°. UV/VIS (benzene): 487, 457, 433. CD (EtOH, r.t.): 242 (+3.10), 279 (−4.12), 445.5 (−2.75), 473.5 (−2.80). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.97 (s, Me(18′)); 1.04 (s, Me(17′)); 1.06 (s, Me(16), Me(17)); 1.17 (s, Me(16′)); 1.40 (br. s, OH−C(6′)); 1.47 ('t', $J_{gem}=J(2ax,3)=12.0$, $H_{ax}-C(2)$); 1.73 (s, Me(18)); 1.76 (ddd, $J_{gem}=12.0$, $J(2eq,3)=3.6$, $J(2eq,4eq)=2.1$, $H_{eq}-C(2)$); 1.92 (s, Me(19′)); 1.96 (s, Me(19), Me(20′)); 1.97 (s, Me(20)); 2.04 (dd, $J_{gem}=16.8$, $J(4ax,3)=9.6$, $H_{ax}-C(4)$); 2.14 (d, $J_{gem}=18.8$, $H_{\alpha}-C(2')$); 2.15 (d, $J_{gem}=19.1$, $H_{\alpha}-C(4')$); 2.46 (d, $J_{gem}=18.8$, $H_{\beta}-C(2')$); 2.38 (dd, $J_{gem}=16.8$, $J(4eq,3)=5.6$, $H_{eq}-C(4)$); 2.53 (d, $J_{gem}=19.1$, $H_{\beta}-C(4')$); 3.99 (m, H−C(3)); 4.31 (d, $J(6',7')=8.0$, H−C(6′)); 5.77 (dd, $J(7',8')=15.6$, $J(7',6')=8.0$, H−C(7′)); 6.09 (AB, $J(7,8)=16.2$, H−C(7)); 6.13 (AB, $J(8,7)=16.2$, H−C(8)); 6.15 (d, $J(10,11)=11.6$, H−C(10)); 6.20 (d, $J(10',11')=11.4$, H−C(10′)); 6.25 (m, H−C(14)); 6.27 (m, H−C(14′)); 6.34 (d, $J(8',7')=15.6$, H−C(8′)); 6.35 (d, $J(12,11)=14.9$, H−C(12)); 6.38 (d, $J(12',11')=14.9$, H−C(12′)); 6.59 (dd, $J(11',12')=14.9$, $J(11',10')=11.4$, H−C(11′)); 6.63 (m, H−C(15), H−C(15′)); 6.64 (d, $J(11,12)=14.9$, $J(11,10)=11.6$, H−C(11)). ^{13}C-NMR (100 MHz, $CDCl_3$; starred signals may be interchanged): 12.75* (C(20)); 12.78* (C(19)); 12.82* (C(20′)); 13.03 (C(19′)); 17.88 (C(18′)); 21.60 (C(18)); 23.48 (C(16′)); 26.59 (C(17′)); 28.72** (C(16)); 30.25** (C(17)); 37.11 (C(1)); 40.82 (C(1′)); 42.55 (C(4)); 47.47 (C(4′)); 47.55 (C(5′)); 48.42 (C(2)); 54.31 (C(2′)); 65.08 (C(3)); 77.74 (C(6′)); 124.32 (C(11′)); 125.13 (C(11)); 125.69 (C(7)); 126.20 (C(5)); 127.95 (C(7′)); 129.88*** (C(15′)); 130.55*** (C(15)); 131.26 (C(10)); 132.46 (C(14)); 133.17 (C(10′)); 133.33 (C(14′)); 134.03**** (C(9′)); 135.84**** (C(13′)); 136.13**** (C(9)); 136.83**** (C(13)); 137.48 (C(6)); 137.75 (C(12)); 137.90 (C(8′)); 138.46 (C(8)); 138.81 (C(12′)); 214.72 (C(3′)). EI-MS: 586 (15, M^+), 568 (6, $[M-H_2O]^+$), 494 (4, $[M-$toluene$]^+$, 480 (15), 119 (90), 109 (100).

*(3′*R*,6′*S*)-Capsanthol* (= *(all-*E*,3*R*,3′*R*,5′*R*,6′*S*)-β,κ-Carotene-3,3′,6′-triol*; **6**): Red crystals. M.p. 150–153°. UV/VIS (benzene): 487, 458, 433. CD (EtOH, r.t.): 241 (+3.34), 280 (−3.54), 333.5 (+0.60), 448.5 (−2.48), 479.5 (−2.43). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.77 (s, Me(18′)); 0.85 (s, Me(17′)); 1.07 (s, Me(16), Me(17)); 1.12 (s, Me(16′)); 1.47 ('t', $J_{gem}=J(2ax,3)=11.9$, $H_{ax}-C(2)$); 1.73 (s, Me(18)); 1.76 (ddd, $J_{gem}=11.9$, $J(2eq,3)=3.5$, $J(2eq,4eq)=2.1$, $H_{eq}-C(2)$); 1.79 (dd, $J_{gem}=14.1$, $J(2'\beta,3')=4.0$, $H_{\beta}-C(2')$); 1.90 (dd, $J_{gem}=14.8$, $J(4'\beta,3')=2.5$, $H_{\beta}-C(4')$); 1.92 (s, Me(19′)); 1.96 (s, Me(10), Me(20′)); 1.97 (s, Me(19)); 2.00 (d, not resolved, $H_{\alpha}-C(4')$); 2.04 (dd, $J_{gem}=16.9$, $H_{ax}-C(4)$); 2.07 (dd, $J_{gem}=14.1$, $J(2'\alpha,3')=8.5$, $H_{\alpha}-C(2')$); 2.38 (ddd, $J_{gem}=16.9$, $J(4ax,3)=5.7$, $J(4eq,2eq)=2.1$, $H_{eq}-C(4)$); 3.99 (m, H−C(3)); 4.20 (d, $J(6',7')=7.9$, H−C(6′)); 5.83 (dd, $J(7',8')=15.5$, $J(7',6')=7.9$, H−C(7′)); 6.09 (AB, $J(7,8)=16.1$, H−C(7)); 6.13 (AB, $J(8,7)=16.1$, H−C(8)); 6.15 (d, $J(10,11)=11.7$, H−C(10)); 6.19 (d, $J(10',11')=11.6$, H−C(10′)); 6.25 (m, H−C(14)); 6.26 (m, H−C(14′)); 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′)); 6.59 (d, $J(11',10')=11.6$, H−C(11′)); 6.64 (m, H−C(15), H−C(15′)); 6.65 (m, H−C(11)). ^{13}C-NMR (100 MHz, $CDCl_3$; starred signals may be interchanged): 12.75* (C(19′)); 12.79* (C(19)); 12.82* (C(20)); 13.07 (C(20′)); 19.07 (C(18′)); 21.61 (C(18)); 23.44 (C(16′)); 27.95 (C(17′)); 28.72** (C(16)); 30.26** (C(17)); 37.12 (C(1)); 42.56 (C(4)); 43.92 (C(1′)); 44.65 (C(4′)); 48.44 (C(2)); 49.90 (C(5′)); 52.79 (C(2′)); 65.09 (C(3)); 70.80 (C(3′)); 77.97 (C(6′)); 124.54 (C(11′)); 125.04 (C(11)); 125.64 (C(7)); 126.18 (C(5)); 129.11 (C(7′)); 129.95 (C(15)); 130.37 (C(15)); 131.28 (C(10)); 132.52 (C(14)); 132.58 (C(10′)); 133.06 (C(14′)); 134.47 (C(9′)); 135.77 (C(13′)); 136.25 (C(9)); 136.69 (C(13)); 137.15 (C(8′)); 137.52 (C(12)); 137.76 (C(6)); 138.38 (C(12′)); 138.48 (C(8)). EI-MS: 586 (19, M^+), 568 (5, $[M-H_2O]^+$), 492 (5, $[M-$toluene$]^+$), 478 (8), 119 (95), 109 (100), 91 (100).

*(3′*R*,6′*R*)-Capsanthol* (= *(all-*E*,3*R*,3′*R*,5′*R*,6′*R*)-β,κ-Carotene-3,3′,6′-triol*; **7**): Red crystals. M.p. 142–145°. UV/VIS (benzene): 487, 458, 433. CD (EtOH, r.t.): 240 (+0.57), 273.5 (−4.61), 333.5 (+0.54). ^{1}H-NMR

(400 MHz, $CDCl_3$): 0.90 (*s*, Me(18′)); 1.05 (*s*, Me(17′)); 1.07 (*s*, Me(16), Me(17)); 1.24 (*s*, Me(16′)); 1.47 ('*t*', $J_{gem} = J(2ax,3) = 12.0$, $H_{ax}-C(2)$); 1.51 (*dd*, $J(2'\beta,3') = 2.3$, $H_\beta-C(2')$); 1.66 (*dd*, $J(4'\beta,3') = 5.9$, $H_\beta-C(4')$); 1.73 (*s*, Me(18)); 1.76 (*m*, not resolved, $H_{eq}-C(2)$); 1.77 (*dd*, $J_{gem} = 13.7$, $J(4'\alpha,3') = 8.0$, $H_\alpha-C(4')$); 1.91 (*s*, Me(19′)); 1.96 (*s*, Me(20), Me(20′)); 1.97 (*s*, Me(19)); 2.04 (*dd*, $J_{gem} = 17.0$, $J(4ax,3) = 9.6$, $H_{ax}-C(4)$); 2.12 (*dd*, $J_{gem} = 14.4$, $J(2'\alpha,3') = 8.5$, $H_\alpha-C(2')$); 2.38 (*ddd*, $J_{gem} = 17.0$, $J(4eq,3) = 5.7$, $J(4eq,2eq) = 1.7$, $H_{eq}-C(4)$); 4.00 (*m*, H–C(3)); 4.36 (*m*, H–C(3′)); 4.37 (*d*, $J(6',7') = 6.9$, H–C(6′)); 5.76 (*dd*, $J(7',8') = 15.6$, $J(7',6') = 6.9$, H–C(7′)); 6.09 (*AB*, $J(7,8) = 16.2$, H–C(7)); 6.13 (*AB*, $J(8,7) = 16.2$, H–C(8)); 6.15 (*d*, $J(10,11) = 11.3$, H–C(10)); 6.17 (*d*, $J(10',11') = 11.5$, H–C(10′)); 6.25 (*m*, H–C(14)); 6.26 (*m*, H–C(14′)); 6.30 (*d*, $J(8',7') =$ 15.6, 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′)); 6.59 (*dd*, $J(11',10') =$ 11.5, $J(11',12') = 14.9$, H–C(11′)); 6.63 (*m*, H–C(15′)); 6.64 (*m*, H–C(11), H–C(15)). ^{13}C-NMR (100 MHz, $CDCl_3$; starred signals may be interchanged): 12.75* (C(20′)); 12.79* (C(19)); 12.82* (C(20)); 13.04 (C(19′)); 16.84 (C(18′)); 21.61 (C(18)); 25.98 (C(17′)); 26.20 (C(16′)); 28.72** (C(16)); 30.26** (C(17)); 37.12 (C(1)); 42.57 (C(4)); 43.64 (C(1′)); 48.08 (C(4′)); 48.46 (C(2)); 50.02 (C(5′)); 51.59 (C(2′)); 65.10 (C(3)); 70.70 (C(3′)); 78.13 (C(6′)); 124.63 (C(11′)); 125.01 (C(11)); 125.62 (C(7)); 126.17 (C(5)); 129.57 (C(7′)); 129.99*** (C(15)); 130.29*** (C(15′)); 131.29 (C(10)); 132.25 (C(10′)); 132.54 (C(14)); 132.94 (C(14′)); 134.50 (C(9′)); 135.74 (C(13′)); 135.77 (C(8′)); 136.29 (C(9)); 136.64 (C(13)); 137.54 (C(12)); 137.77 (C(6)); 138.17 (C(12′)); 138.49 (C(8)). EI-MS: 586 (15, M^+), 568 (4, $[M - H_2O]^+$ 492 (4, $[M -$ toluene$]^+$), 478 (10), 119 (90), 109 (100), 91 (100).

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