Preparation of Partially Acetylated Carotenoids

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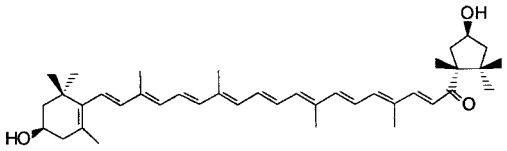
Partially acetylated carotenoids were prepared from fully acetylated carotenoids by reaction with $NaBH_4$, and were characterized by UV/VIS, CD, ^{1}H-NMR and mass spectra. The 3,6′-diacetate, 3′,6′-diacetate, and 6′-acetate **10**–**12**, respectively, of (6′*R*)-capsanthol (= (3*R*,3′*S*,5′*R*,6′*R*)-β,κ-carotene-3,3′,6′-triol; **4**) were obtained from (6′*R*)-capsanthol-3,3′,6′-triacetate (**9**), and the 3- and 3′-acetates **13** and **14**, respectively, of **4** from (6′*R*)-capsanthol 3,3′-diacetate (**8**). The utility of this method was also demonstrated by the preparation of zeaxanthin and lutein monoacetates **16**, **19**, and **20**.

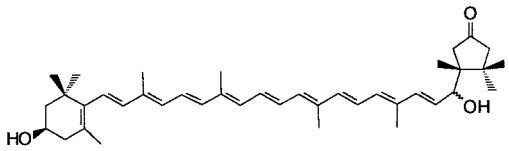
Introduction. – Complex metal hydrides (*e.g.*, $LiAlH_4$ or $NaBH_4$) are reagents commonly used for the reduction of carbonyl functions of carotenoids [1]. The reaction is complete in a few minutes at room temperature. When the carbonyl groups are conjugated with the polyene chain, a hypsochromic shift and increased spectral fine structure will be seen in the UV/VIS spectrum of the reaction products. Reduction products are usually readily separated from the parent compound, because the resulting carotenol product is more polar than either the initial aldehyde or ketone. However, the reduction of keto groups of carotenoids produces two stereoisomers, whose separation is difficult [2][3].

The reduction of capsanthin (**1**) and 'capsanthol-3′-ones' (= 3,6′-dihydroxy-β,κ-caroten-3′-ones) **2** and **3** was studied earlier in our laboratory. The reduction of capsanthin with either $LiAlH_4$ or $NaBH_4$ gave the (3′*S*,6′*R*)- and (3′*S*,6′*S*)-stereoisomers **4** and **5** of capsanthol [4]. The reduction of (6′*R*)- and (6′*S*)-'capsanthol-3′-ones' **2** and **3** produced the (3′*R*)- and (3′*S*)-stereoisomers **4**–**7** of the appropriate capsanthols [5]. These carotenoids were used as model compounds for circular-dichroism (CD) studies of supramolecular carotenoid self-assembly [6–9].

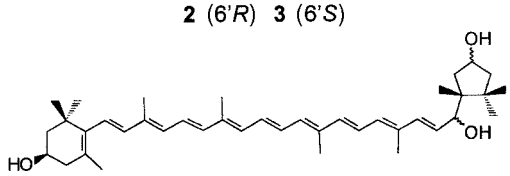
In previous studies on the reduction of oxo-carotenoids by $NaBH_4$, the transformation of carotenoid esters to free hydroxy-carotenoids was observed. Thus, the reduction of capsanthin 3,3′-diacetate resulted in the appropriate capsanthol 3,3′-diacetates, as well as free capsanthol epimers. Although the reduction of esters is a known method [10], systematic studies in the carotenoid chemistry have not been published. This observation led us to develop a method for the preparation of partially acetylated carotenoids. In the present work, we report the reduction of (6′*R*)-capsanthol 3,3′,6′-triacetate (**9**) and (6′*R*)-capsanthol 3,3′-diacetate (**8**) by $NaBH_4$. This method was extended to the preparation of other partially acetylated carotenoids. Zeaxanthin and lutein monoacetates were also prepared this way.



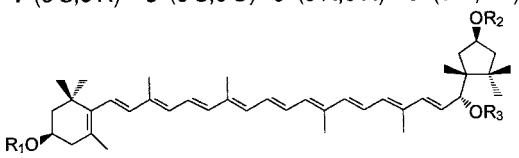
1



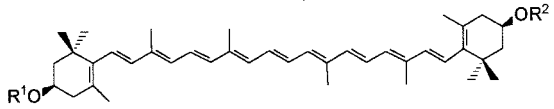
2 (6′*R*) **3** (6′*S*)



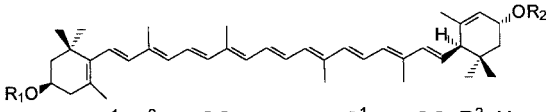
4 (3′*S*,6′*R*) **5** (3′*S*,6′*S*) **6** (3′*R*,6′*R*) **7** (3′*R*,6′*S*)



4 $R^1 = R^2 = R^3 = H$
8 $R^1 = R^2 = MeCO$; $R_3 = H$
9 $R^1 = R^2 = R^3 = MeCO$
10 $R^1 = R^3 = MeCO$, $R^2 = H$
11 $R^1 = H$, $R^2 = R^3 = MeCO$
12 $R^1 = R^2 = H$, $R^3 = MeCO$
13 $R^1 = MeCO$, $R^2 = R^3 = H$
14 $R^1 = R^3 = H$, $R^2 = MeCO$



15 $R^1=R^2=MeCO$, **16** $R^1=MeCO, R_2=H$ **17** $R^1=R^2=H$



18 $R^1=R^2=MeCO$ **19** $R^1=MeCO$, $R^2=H$
20 $R^1=H$, $R^2=MeCO$ **21** $R^1=R^2=H$

Results and Discussions. – *Preparation of (6′*R*)-Capsanthol Acetates.* Capsanthin 3,3′-diacetate was prepared by acetylation of capsanthin (**1**) (ex. *Capsicum annuum*) in accordance with [1]. Capsanthin 3,3′-diacetate was reduced with $NaBH_4$ in EtOH/benzene. The resulting (6′*R*)- and (6′*S*)-stereoisomers **8** and 3,3′-di-*O*-acetyl-**5**, respectively, of capsanthol 3,3′-diacetate were separated by prep. column chromatog-

raphy ($CaCO_3$, benzene/hexane). (6′*R*)-Capsanthol 3,3′,6′-triacetate (**9**) was obtained by acetylation of (6′*R*)-capsanthol 3,3′-diacetate (**8**).

The reductions of (6′*R*)-capsanthol 3,3′,6′-triacetate (**9**) and (6′*R*)-capsanthol 3,3′-diacetate (**8**) were performed in EtOH with $NaBH_4$ for 18 h. The reactions were monitored by HPLC (*Figs. 1* and *2*). The reduction of **9** gave 3,6′-diacetate **10** and 3′,6′-diacetate **11** as main products, whereas the 3,3′-diacetate **8** and 6′-acetate **12** were minor products. This result showed that both the 3- and 3′-*O*-acetyl groups were better leaving groups than the 6′-*O*-acetyl. After repeated column chromatography and crystallization, the carotenoids **10**–**12** were isolated.

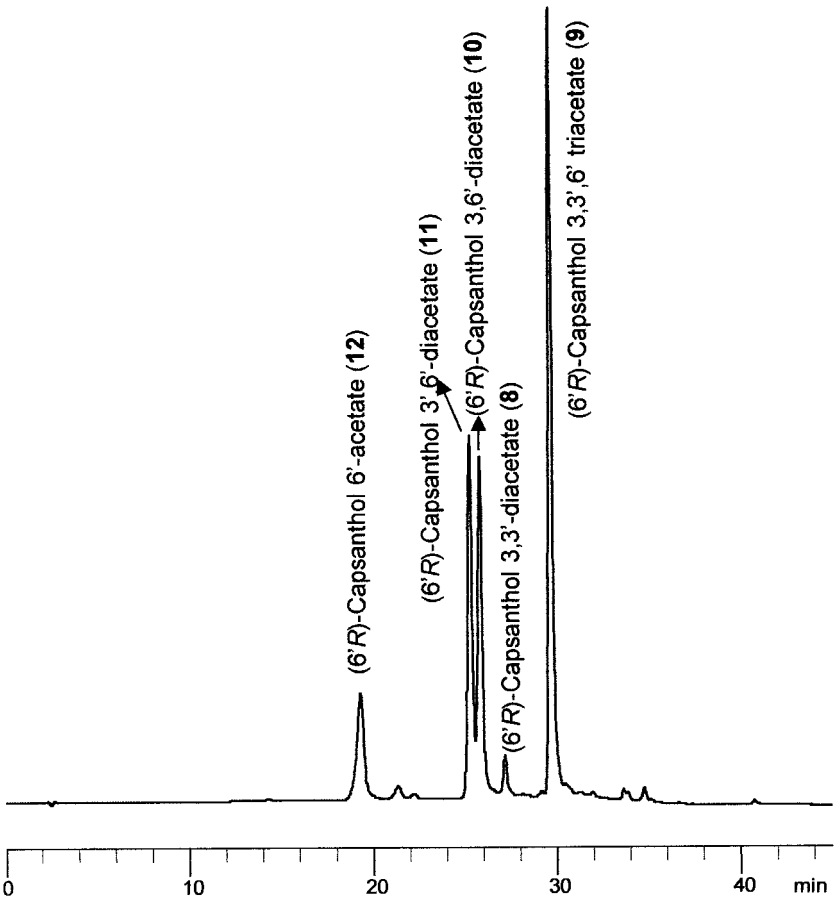


Fig. 1. *HPLC Separation of reaction mixture from (6′*R*)-capsanthol 3,3′,6′-triacetate* (**9**) *after 18 h*. For standard procedure, see text.

The 3- and 3′-acetates **13** and **14**, respectively, could be prepared by the reaction of (6′*R*)-capsanthol 3,3′-diacetate (**8**) with $NaBH_4$. After column chromatography, crystalline **13** and **14** were isolated.

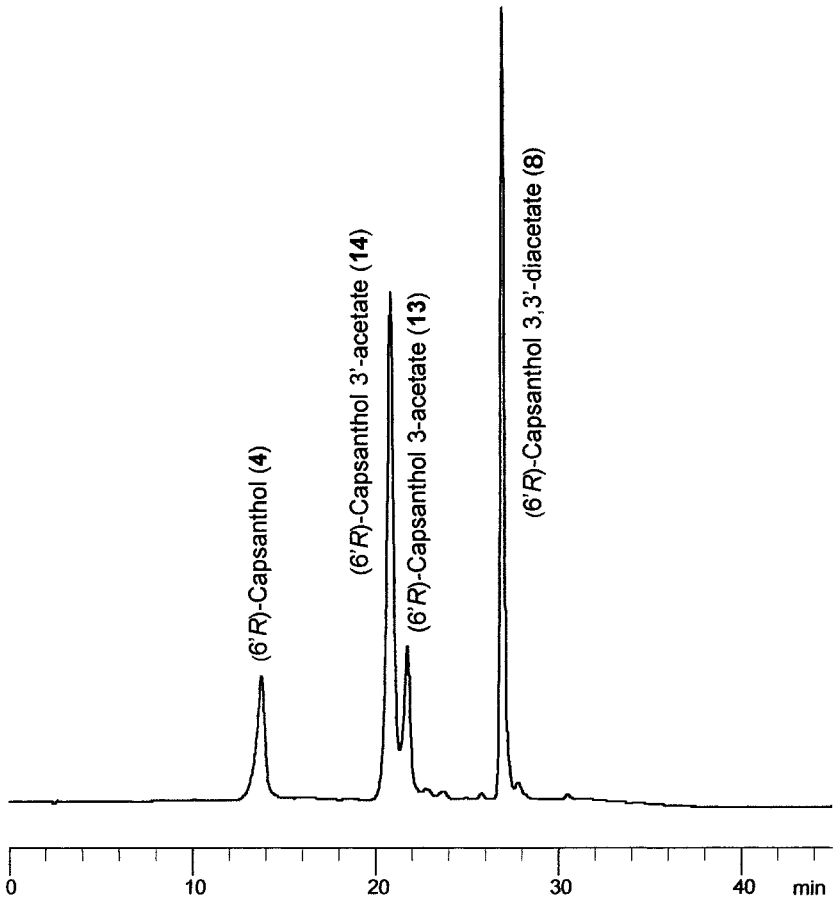


Fig. 2. *HPLC Separation of reaction mixture from (6'*R*)-capsanthol 3,3'-diacetate* (**8**) *after 18 h*. For standard procedure, see text.

Preparation of Zeaxanthin and Lutein Acetates. Zeaxanthin 3,3′-diacetate (**15**) and lutein 3,3′-diacetate (**18**) were prepared by acetylation of zeaxanthin (**17**; ex. *Lycium halimifolium*) and lutein (**21**; ex. *Caltha palustris*). The reductions of the diacetates were performed in EtOH with $NaBH_4$ for 18 h. After column chromatography and crystallization, zeaxanthin 3-acetate (**16**) and lutein 3- and 3′-acetate (**19** and **20**, resp.) were isolated.

Spectroscopic Characterization. All isolated compounds and starting acetates were characterized on the basis of their UV/VIS, CD, NMR, and mass spectra. In each case, the mass spectra showed the corresponding molecular-ion peaks. In addition, the ions typical for hydroxy- ($[M-H_2O]^+$, $[M-92]^+$) and (acetyloxy)-carotenoids ($[M-60]^+$, $[M-60-92]^+$) were observed [11].

The structure elucidation of the isolated compounds was performed by ^{1}H-NMR measurements. The ^{1}H assignments were based on simple ^{1}H- as well as ^{1}H,^{1}H-COSY

experiments analyzed with standard *Varian* software. The positions of the Ac groups in the mono- or di-*O*-acetylated compounds could be easily established from the presence of the characteristic ^{1}H resonances (*e.g.*, H–C(3), H–C(3′) and H–C(6′)) in their NMR spectra in comparison with the respective ^{1}H signals of the di- and tri-*O*-acetylated or free carotenoids and corroborated by ^{1}H,^{1}H correlations in the COSY spectra. The δ(H) (see *Tables 1* and *2*) and *J*(H,H) values were identical to the corresponding data from previous works [4][5][12].

The esterification of the free OH groups in the 3-, 3′- and 6′-positions does not alter the VIS absorption and CD spectra significantly.

Acylation of carotenoids with acyl chloride or acid anhydride usually produces fully *O*-acylated carotenoids, while the hydrolysis (saponification) of the carotenoid esters

Table 1. *Chemical Shifts of (6′*R*)-Capsanthol Derivatives*

	4	**13**	**14**	**12**	**8**	**10**	**11**	**9**
H_{ax}–C(2)	1.47	1.57	1.48	1.47	1.58	1.58	1.47	1.58
H_{eq}–C(2)	1.76	1.78	1.77	1.76	1.78	1.77	1.77	1.78
H–C(3)	4.01	5.06	4.00	4.00	5.05	5.06	4.00	5.06
MeCO	–	2.05	–	–	2.05	2.06	–	2.05
H_{ax}–C(4)	2.04	2.11	2.04	2.04	2.10	2.12	2.03	2.11
H_{eq}–C(4)	2.39	2.44	2.39	2.38	2.45	2.44	2.38	2.45
H–C(7)	6.10	6.09	6.10	6.09	6.10	6.09	6.10	6.10
H–C(8)	6.16	6.13	6.14	6.13	6.15	6.13	6.13	6.16
H–C(10)	6.15	6.16	6.15	6.15	6.16	6.16	6.15	6.16
H–C(11)	6.65	6.64	6.64	6.64	6.64	6.64	6.64	6.65
H–C(12)	6.36	6.36	6.36	6.35	6.36	6.36	6.36	6.36
H–C(14)	6.25	6.25	6.25	6.25	6.26	6.25	6.25	6.25
H–C(15)	6.64	6.63	6.63	6.63	6.63	6.62	6.64	6.64
Me(16)	1.07	1.12	1.07	1.07	1.13	1.10	1.07	1.11
Me(17)	1.07	1.07	1.07	1.07	1.06	1.07	1.07	1.08
Me(18)	1.73	1.72	1.73	1.73	1.72	1.73	1.73	1.72
Me(19)	1.97	1.97	1.97	1.97	1.97	1.97	1.97	1.97
Me(20)	1.97	1.97	1.96	1.96	1.96	1.96	1.96	1.99
H_{ax}–C(2′)	1.75	1.75	1.83	1.76	1.83	1.76	1.83	1.83
H_{eq}–C(2′)	1.96	1.96	2.00	1.96	1.98	1.96	2.01	2.01
H–C(3′)	4.35	4.35	5.09	4.36	5.08	4.36	5.09	5.09
MeCO	–	–	1.99	–	2.00	–	2.06	2.07
H_{ax}–C(4′)	1.27	1.27	1.31	1.31	1.31	1.32	1.36	1.37
H_{eq}–C(4′)	2.08	2.08	2.13	2.13	2.13	2.12	2.19	2.19
H–C(6′)	4.20	4.21	4.22	5.28	4.22	5.28	5.30	5.29
MeCO	–	–	–	2.06	–	2.05	2.00	2.00
H–C(7′)	5.74	5.75	5.72	5.58	5.72	5.58	5.56	5.56
H–C(8′)	6.29	6.29	6.29	6.27	6.29	6.27	6.27	6.27
H–C(10′)	6.17	6.17	6.17	6.17	6.17	6.17	6.17	6.17
H–C(11′)	6.60	6.60	6.59	6.57	6.62	6.57	6.56	6.56
H–C(12′)	6.36	6.36	6.36	6.35	6.36	6.36	6.36	6.36
H–C(14′)	6.27	6.27	6.27	6.26	6.26	6.26	6.26	6.26
H–C(15′)	6.64	6.63	6.63	6.63	6.63	6.63	6.63	6.64
Me(16′)	1.03	1.03	1.05	0.89	1.05	0.89	0.92	0.92
Me(17′)	1.13	1.13	1.13	1.03	1.16	1.04	1.04	1.04
Me(18′)	1.11	1.11	1.07	1.20	1.07	1.26	1.15	1.16
Me(19′)	1.91	1.91	1.90	1.87	1.90	1.88	1.87	1.87
Me(20′)	1.97	1.97	1.96	1.95	1.96	1.95	1.95	1.95

Table 2. *Chemical Shifts of Zeaxanthin* (**17**), *Lutein* (**21**), *and Their Derivatives* **15**, **16**, *and* **18**–**20**

	17	**15**	**16**	**21**	**18**	**19**	**20**
H_{ax}–C(2)	1.47	1.58	1.58	1.47	1.58	1.58	1.47
H_{eq}–C(2)	1.76	1.78	1.77	1.76	1.78	1.77	1.77
H–C(3)	3.99	5.06	5.06	3.99	5.06	5.05	4.00
MeCO	–	2.05	2.05	–	2.05	2.04	–
H_{ax}–C(4)	2.04	2.10	2.11	2.04	2.10	2.10	2.04
H_{eq}–C(4)	2.39	2.44	2.44	2.38	2.44	2.44	2.38
H–C(7)	6.10	6.09	6.09	6.10	6.09	6.09	6.10
H–C(8)	6.13	6.12	6.12	6.13	6.12	6.12	6.13
H–C(10)	6.15	6.16	6.16	6.15	6.16	6.16	6.15
H–C(11)	6.64	6.64	6.64	6.64	6.64	6.64	6.64
H–C(12)	6.36	6.36	6.36	6.35	6.36	6.36	6.35
H–C(14)	6.25	6.25	6.25	6.26	6.26	6.26	6.26
H–C(15)	6.62	6.62	6.62	6.62	6.62	6.62	6.62
Me(16)	1.07	1.10	1.10	1.07	1.10	1.10	1.07
Me(17)	1.07	1.07	1.07	1.07	1.07	1.07	1.07
Me(18)	1.73	1.72	1.73	1.73	1.72	1.72	1.73
Me(19)	1.97	1.97	1.97	1.97	1.97	1.97	1.96
Me(20)	1.97	1.96	1.96	1.96	1.96	1.96	1.96
H_{ax}–C(2′)	1.47	1.58	1.48	1.36	1.45	1.36	1.45
H_{eq}–C(2′)	1.76	1.77	1.77	1.83	1.84	1.84	1.84
H–C(3′)	3.99	5.06	4.00	4.36	5.32	4.25	5.32
MeCO	–	2.05	–	–	2.04	–	2.04
H_{ax}–C(4′)	2.04	2.10	2.04	5.54	5.48	5.54	5.48
H_{eq}–C(4′)	2.39	2.44	2.39				
H–C(6′)	–	–	–	2.40	2.40	2.40	2.40
H–C(7′)	6.10	6.09	6.09	5.42	5.43	5.42	5.42
H–C(8′)	6.13	6.12	6.12	6.13	6.13	6.13	6.14
H–C(10′)	6.15	6.16	6.16	6.14	6.16	6.15	6.15
H–C(11′)	6.64	6.64	6.64	6.60	6.60	6.61	6.60
H–C(12′)	6.36	6.36	6.36	6.35	6.35	6.35	6.35
H–C(14′)	6.25	6.25	6.25	6.24	6.24	6.24	6.24
H–C(15′)	6.62	6.62	6.62	6.62	6.62	6.63	6.62
Me(16′)	1.07	1.10	1.07	0.84	0.87	0.84	0.87
Me(17′)	1.07	1.07	1.07	0.99	1.00	0.99	1.00
Me(18′)	1.73	1.72	1.72	1.61	1.64	1.62	1.64
Me(19′)	1.97	1.97	1.97	1.90	1.90	1.90	1.90
Me(20′)	1.97	1.96	1.96	1.96	1.96	1.96	1.96

with NaOH or KOH results in the formation of the free hydroxy-carotenoids. With our methods, the partially *O*-acetylated carotenoids can be easily prepared in 30–40% yields. The prepared carotenoid acetates were used as model compounds for the CD study of supramolecular carotenoid self-assembly [9].

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Experimental Part

1. *General.* HPLC: *Gynkotek* pump model *480*; UV/VIS detector *HP 1050* at 450 nm; eluent *A* 12% H_2O/MeOH, eluent *B* MeOH, eluent *C* 30% CH_2Cl_2/MeOH; gradient program: 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 min → 100% *C*, 34–41 min 100% *C* (linear steps); flow rate 1.25 ml/min; column *Chromsyl* C_{18}, 6 μm, end-capped. UV/VIS Spectra: *Beckman DU-65* spectrometer for benzene solns., λ_{max} in nm; *Jasco J-715* spectropolarimeter for EtOH solns., λ_{max} in nm, ε values in $M^{-1}\,cm^{-1}$. CD Spectra: *Jasco J-715* spectropolarimeter at r.t. in EtOH solns.; optical pathlength 0.5 cm, λ_{max} in nm, $\Delta\varepsilon$ values in $M^{-1}\,cm^{-1}$. NMR Spectra: *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_4Si. MS: *Varian MA-CH-7A* spectrometer; *m/z* (rel. %).

2. *General Reaction Procedure.* The appropriate di- or tri-*O*-acetyl-carotenoid (40 mg) was dissolved in 4–5% H_2O/EtOH (400 ml), and then $NaBH_4$ (5 mg) was added. The mixture was kept at r.t. for 18 h. Then, solid NaOH was added to the soln. to decompose the complex. The mixture was diluted with benzene, the soln. washed with H_2O (10 ×), dried (Na_2SO_4), and evaporated, and the residue dissolved in benzene.

3. *Column Chromatography* (CC) *of the Reaction Mixture from (6′*R*)-Capsanthol 3,3′,6′-Triacetate* (**9**). The reduction mixture from **9** was subjected to CC (6 columns, 6 × 30 cm, $CaCO_3$ (*Biogal*), benzene/hexane 1:1). Picture after development: 15 mm of yellow *Zone 1*, 30 mm of intermediate zone, 40 mm of yellow *Zone 2* (**11**), 10 mm of intermediate zone, 30 mm of yellow *Zone 3* (**10**), 20 mm of intermediate zone, 50 mm of yellow *Zone 4* (**9**). After the usual workup (cutting and extracting), the carotenoids from *Zones 2–4* were crystallized from benzene/hexane: 9 mg of **11**, 6 mg of **10**, and 10 mg of **9**. The carotenoids of *Zone 1* were submitted to CC (3 columns, 6 × 30 cm, $CaCO_3$ (*Biogal*), 70% benzene/hexane). Picture after development: 20 mm yellow *Zone 11* (**12**), 5 mm of intermediate zone, 5 mm of pale yellow *Zone 12* (unidentified). Crystallization of the carotenoid from *Zone 11* from benzene/hexane yielded 5 mg of **12**.

4. *CC of the Reaction Mixture from (6′*R*)-capsanthol 3,3′-Diacetate* (**8**). The reduction mixture from **8** was subjected to CC (4 columns, 6 × 30 cm, $CaCO_3$ (*Biogal*), 30% benzene/hexane). Picture after development: 30 mm of yellow *Zone 1*, 10 mm of intermediate zone, 80 mm of yellow *Zone 2*, 20 mm of intermediate zone, 60 mm of yellow *Zone 3* (**8**). *Zone 2* was submitted to CC (3 columns, 6 × 30 cm, $CaCO_3$ (*Biogal*), 2% acetone in hexane). Picture after development: 60 mm of yellow *Zone 21* (**14**), 2 mm of intermediate zone, 10 mm of yellow *Zone 22* (**13**). After the usual workup, the carotenoids from *Zones 21* and *22* were crystallized from benzene/hexane: 6 mg of **14** and 4 mg of **13**.

5. *CC of the Reaction Mixture from Zeaxanthin 3,3′-Diacetate* (**15**). The reduction mixture from **15** was subjected to CC (6 columns, 6 × 30 cm, $CaCO_3$ (*Biogal*), 30% benzene/hexane). Picture after development: 30 mm of yellow *Zone 1* (**16**), 10 mm of intermediate zone, 70 mm of yellow *Zone 2* (**15**). Crystallization of the carotenoid from *Zone 1* from benzene/hexane yielded 9 mg of **16**.

6. *CC of the Reaction Mixture from Lutein 3,3′-Diacetate* (**18**). The reduction mixture from **18** was subjected to CC (5 columns, 6 × 30 cm, $CaCO_3$ (*Biogal*), 30% benzene/hexane). Picture after development: 20 mm of yellow *Zone 1* (**20**), 10 mm of intermediate zone, 20 mm yellow *Zone 2* (**19**), 20 mm of intermediate zone, 60 mm of yellow *Zone 3* (**18**). Crystallization of the carotenoids from *Zones 1* and *2* from benzene/hexane yielded 3 mg of **19** and 3 mg of **20**.

7. *Data of* **8**–**16** *and* **18**–**20**. *(6′*R*)-Capsanthol 3,3′,6′-Triacetate* (=(*all*-E,*3*R,*3′*S,*5′*R,*6′*R*)-β,κ-Carotene-3,3′,6′-triol 3,3′6′-Triacetate;* **9**). M.p. 112–114°. UV/VIS (benzene): 487, 458, 433. UV/VIS (EtOH): 474.5 (115000), 445.5 (126000), 423 (sh, 85000), 331 (7300), 267.5 (21000). CD (EtOH, r.t.): 221.5 (0), 241.5 (+2.75), 257.5 (0), 279.5 (−4.76), 311 (0), 332 (+0.77). ^1H-NMR: *Table 1*. EI-MS: 712 (4, M^+), 652 (12, $[M - AcOH]^+$), 592 (3, $[M - 2\ AcOH]^+$), 119 (23), 109 (100), 91 (64).

*(6′*R*)-Capsanthol 3,3′-Diacetate* (=(*all*-E,*3*R,*3′*S,*5′*R,*6′*R*)-β,κ-Carotene-3,3′,6′-triol 3,3′-Diacetate;* **8**). M.p. 84°. UV/VIS (benzene): 487, 458, 433. UV/VIS (EtOH): 473 (90000), 445.5 (100000), 422.5 (sh, 71000), 332 (10000), 267.5 (20000). CD (EtOH, r.t.): 223 (0), 240 (+2.90), 252 (0), 273.5 (−7.10), 307 (0), 328.5 (+1.74). ^1H-NMR: *Table 1*. EI-MS: 670 (41, M^+), 395 (43), 335 (62), 119 (17), 109 (100), 91 (18).

*(6′*R*)-Capsanthol 3,6′-Diacetate* (=(*all*-E,*3*R,*3′*S,*5′*R,*6′*R*)-β,κ-Carotene-3,3′,6′-triol 3,6′-Diacetate,* **10**). M.p. 131–133°. UV/VIS (benzene): 487, 458, 433. UV/VIS (EtOH): 475.5 (116000), 446.5 (127000), 423.5 (sh, 87000), 332.5 (7100), 267.5 (22000). CD (EtOH, r.t.): 221.5 (0), 243 (+2.85), 261.5 (0), 280.5 (−3.88). ^1H-NMR: *Table 1*. EI-MS: 670 (5, M^+), 610 (18, $[M - AcOH]^+$), 518 (8), 458 (10), 119 (62), 91 (58), 43 (100).

*(6′*R*)-Capsanthol 3′,6′-Diacetate* (=(*all-E,3*R,*3′*S,*5′*R,*6′*R*)-β,κ-Carotene-3,3′,6′-triol 3′,6′-Diacetate;* **11**). M.p. 103–105°. UV/VIS (benzene): 487, 458, 433. UV/VIS (EtOH): 476.5 (10800), 446.5 (118000), 424 (sh, 80000), 333 (7000), 267.5 (21100). CD (EtOH, r.t.): 221 (0), 242.5 (+2.94), 258.5 (0), 278 (−4.95), 332.5

(+0.80). ^{1}H-NMR: *Table 1*. EI-MS: 670 (4, M^+), 610 (18, $[M-\text{AcOH}]^+$), 550 (12, $[M-2\text{AcOH}]^+$), 518 (5), 458 (19), 119 (53), 91 (77), 43 (100).

*(6′*R*)-Capsanthol 3-Acetate* (=(*all*-E,*3*R,*3′*S,*5′*R,*6′*R*)-β,κ-Carotene-3,3′,6′-triol 3-Acetate;* **13**). M.p. 131–134°. UV/VIS (benzene): 487, 458, 433. UV/VIS (EtOH): 474 (105000), 446 (115000), 423.5 (sh, 78000), 335.5 (6000), 267 (20000). CD (EtOH, r.t.): 225 (0), 243 (+2.88), 254 (0), 275.5 (−7.24), 319 (0), 332 (+0.86). ^{1}H-NMR: *Table 1*. EI-MS: 628 (20, M^+), 353 (5), 313 (6), 119 (73), 109 (100), 91 (53).

*(6′*R*)-Capsanthol 3′-Acetate* (=(*all*-E,*3*R,*3′*S,*5′*R,*6′*R*)-β,κ-Carotene-3,3′,6′-triol 3′-Acetate;* **14**). M.p. 161–163°. UV/VIS (benzene): 487, 458, 433. UV/VIS (EtOH): 475 (95000), 446 (105000), 423.5 (sh, 70000), 331.5 (8500), 267.5 (20000). CD (EtOH, r.t.): 224.5 (0), 240 (+3.10), 253.5 (0), 276 (−7.83), 306.5 (0), 335 (+1.98). ^{1}H-NMR: *Table 1*. EI-MS: 628 (15, M^+), 353 (10), 313 (8), 119 (66), 109 (100), 91 (42).

*(6′*R*)-Capsanthol 6′-Acetate* (=(*all*-E,*3*R,*3′*S,*5′*R,*6′*R*)-β,κ-Carotene-3,3′,6′-triol 6′-Acetate;* **12**). M.p. 120–122°. UV/VIS (benzene): 487, 458, 433. UV/VIS (EtOH): 476 (120000), 446.5 (130000), 424 (sh, 95000), 331 (sh, 20000), 267 (25000). CD (EtOH, r.t.): 205 (−3.05), 226 (0), 242 (+2.21), 253 (0), 276 (−5.77), 312 (0), 332.5 (+0.83). ^{1}H-NMR: *Table 1*. EI-MS: 628 (4, M^+), 568 (3, $[M-\text{AcOH}]^+$), 476 (2), 119 (45), 109 (49), 91 (44), 43 (100).

Zeaxanthin 3,3′-Diacetate (=(*all*-E,*3*R,*3′*R*)-β,β-Carotene-3,3′-diol 3,3′-Diacetate;* **15**). M.p. 124–125°. UV/VIS (benzene): 492, 463. UV/VIS (EtOH): 478 (96000), 451 (110000), 422.5 (sh, 70000), 337 (sh, 5300), 276 (15000). CD (EtOH, r.t.): 206 (+5.31), 213 (0), 222.5 (−7.51), 232.5 (0), 247.5 (+7.51), 262 (0), 283 (−11.42), 314 (0), 338.5 (+2.38). ^{1}H-NMR: *Table 2*. EI-MS: 652 (70, M^+), 592 (12, $[M-\text{AcOH}]^+$), 532 (5, $[M-2\text{AcOH}]^+$), 119 (76), 105 (55).

Zeaxanthin 3-Acetate (=(*all*-E,*3*R,*3′*R*)-β,β-Carotene-3,3′-diol 3-Acetate;* **16**). M.p. 150–153°. UV/VIS (benzene): 493, 463. UV/VIS (EtOH): 480.5 (110000), 452.5 (124000), 423.5 (sh, 81000), 340 (sh, 6300), 275.5 (18500). CD (EtOH, r.t.) 206.5 (+6.43), 213.5 (0), 222.5 (−10.1), 233 (0), 246.5 (+9.63), 263 (0), 283.5 (−15.0), 314.5 (0), 340.5 (+3.37). ^{1}H-NMR: *Table 2*. EI-MS: 610 (90, M^+), 550 (4, $[M-\text{AcOH}]^+$), 518 (62, $[M-92]^+$), 458 (18), 145 (48), 119 (77), 105 (57).

Lutein 3,3′-Diacetate (=(*all*-E,*3*R,*3′*R,*6′*R*)-β,ε-Carotene-3,3′-diol 3,3′-Diacetate;* **18**). M.p. 158–160°. UV/VIS (benzene): 487, 457, 434. UV/VIS (EtOH): 476 (115000), 446.5 (125000), 423.5 (sh, 85000), 331.5 (7500), 268 (25000). CD (EtOH, r.t.): 208 (+10.70), 244 (+8.40), 268.5 (0), 282 (−4.39), 296.5 (0), 334.5 (+1.92). ^{1}H-NMR: *Table 2*. EI-MS: 652 (10, M^+), 592 (8, $[M-\text{AcOH}]^+$), 532 (6, $[M-2\text{AcOH}]^+$), 458 (4), 145 (75), 119 (100).

Lutein 3-Acetate (=(*all*-E,*3*R,*3′*R,*6′*R*)-β,ε-Carotene-3,3′-diol 3-Acetate;* **19**). M.p. 125–127°. UV/VIS (benzene): 487, 457, 437. UV/VIS (EtOH): 476 (91000), 446.5 (101000), 418.5 (sh, 65000). CD (EtOH, r.t.): 211(+6.68), 245.5 (+5.0), 276.5 (0), 284.5 (−1.73). ^{1}H-NMR: *Table 2*. EI-MS: 610 (100, M^+), 592 ([16, $M-H_2O]^+$), 550 (6, $[M-\text{AcOH}]^+$), 518 (3, $[M-92]^+$), 458 (4), 145 (67), 119 (73).

Lutein 3′-Acetate (=(*all*-E,*3*R,*3′*R,*6′*R*)-β,ε-Carotene-3,3′-diol 3′-Acetate;* **20**). M.p. 132–134°. UV/VIS (benzene): 487, 457, 433. UV/VIS (EtOH): 476 (125000), 446.5 (137000), 418.5 (sh, 90000), 333 (7000), 268.5 (23300). CD (EtOH, r.t.): 208 (+11.64), 244 (+9.16), 283.5 (−4.50), 303.5 (0), 334 (+1.97). ^{1}H-NMR: *Table 2*. EI-MS: 610 (52, M^+), 568 (12), 550 (67, $[M-\text{AcOH}]^+$), 518 (2, $[M-92]^+$), 458 (5), 145 (85), 119 (100), 105 (83).

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