Partial Synthesis and Characterization of Karpoxanthins and Cucurbitaxanthin A Epimers

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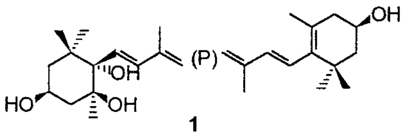
Karpoxanthin (=(all-*E*,3*S*,5*R*,6*R*,3′*R*)-5,6-dihydro-β,β-carotene-3,5,6,3′-tetrol; **7**), 6-epikarpoxanthin (=(all-*E*,3*S*,5*R*,6*S*,3′*R*)-5,6-dihydro-β,β-carotene-3,5,6,3′-tetrol; **4**), 5-epikarpoxanthin (=(all-*E*,3*S*,5*S*,6*R*,3′-*R*)-5,6-dihydro-β,β-carotene-3,5,6,3′-tetrol; **11**), cucurbitaxanthin A (=(all-*E*,3*S*,5*R*,6*R*,3′*R*)-3,6-epoxy-5,6-dihydro-β,β-carotene-5,3′-diol; **10**), epicucurbitaxanthin A (=(all-*E*-3*S*,5*S*,6*R*,3′*R*)-3,6-epoxy-5,6-dihydro-β,β-carotene-5,3′-diol; **14**), and the corresponding mutatoxanthin epimers **8**, **9**, **12**, and **13** were prepared in crystalline state by the acid-catalyzed hydrolysis of (3*S*,5*R*,6*S*,3′*R*)- and (3*S*,5*S*,6*R*,3′*R*)-antheraxanthin (**5** and **6**, resp.) and characterized by their UV/VIS, CD, ^{1}H- and ^{13}C-NMR, and mass spectra.

Introduction. – Recently, we described the isolation of 5,6-diepikarpoxanthin (**1**), 5,6-diepilatoxanthin (**2**), and 5,6-diepicapsokarpoxanthin (**3**), all of which contain the (3*S*,5*S*,6*S*)-5,6-dihydro-3,5,6-trihydroxy-β-end group, and of 6-epikarpoxanthin (**4**) containing the (3*S*,5*R*,6*S*)-5,6-dihydro-3,5,6-trihydroxy-β-end group, from red paprika [1]. We described the isolation of **1**, **3**, and **4** also from the petals of *Lilium tigrinum* [2]. For the structure elucidation of the 5,6-dihydro-3,5,6-trihydroxy-β-end groups, the partial synthesis by acid-catalyzed hydrolysis of 5,6-epoxy-3-hydroxy carotenoids has been used successfully before. By application of this method, heteroxanthin [4], karpoxanthin and 6-epikarpoxanthin [5], neoflor and 6-epineoflor [6], and 5,6-diepicapsokarpoxanthin [7] have been identified, and it was demonstrated that during the hydrolysis of 5,6-epoxy carotenoids, the configuration at C(5) is retained, whereas at C(6) both configurations are formed. In view of the unambiguous structure elucidation of the natural 5,6-diepikarpoxanthin (**1**) which was isolated for the first time in our laboratories [1–3], we report in the present paper the partial synthesis of several stereoisomers of **1** by acid-catalyzed hydrolysis of (3*S*,5*R*,6*S*,3′*R*)- and (3*S*,5*S*,6*R*,3′*R*)-antheraxanthin (**5** and **6**, resp.).

Results. – *Preparation and Characterization of Antheraxanthins.* (3*S*,5*R*,6*S*,3′*R*)- and (3*S*,5*S*,6*R*,3′*R*)-antheraxanthin (**5** and **6**, resp.) were prepared by the epoxidation of zeaxanthin diacetate with monoperphthalic acid according to [8]. The stereoisomeric **5** and **6** were characterized by their UV/VIS, mass, and ^{1}H- and ^{13}C-NMR spectra and by their chemical properties [9]. The spectral data correspond to the stereoisomers **5** and **6** and to the data from [10][11]. The CD spectra of **5** and **6** are opposite in sign [12], demonstrating the different configurations of the 5,6-epoxy group, which is mainly responsible for the sign of the *Cotton* effect, and are in agreement with the data reported before [10].



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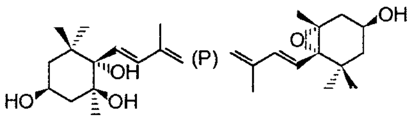

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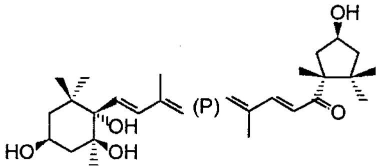

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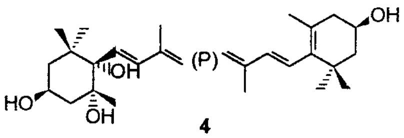

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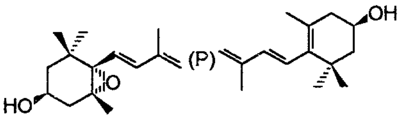

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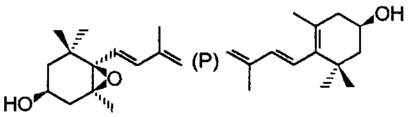

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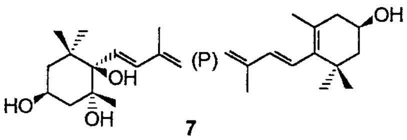

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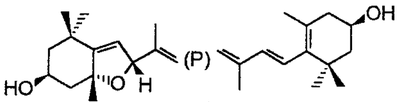

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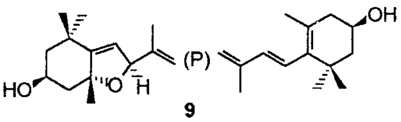

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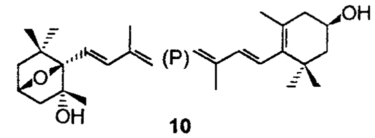

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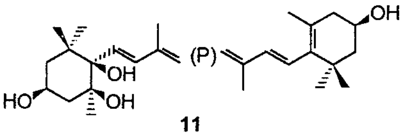

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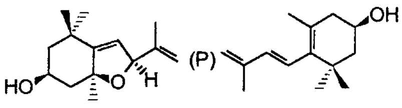

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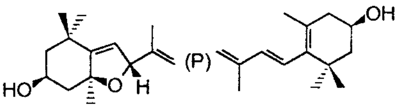

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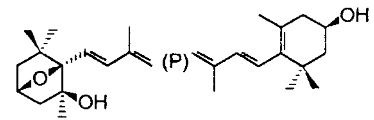

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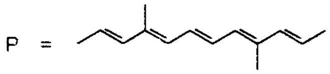

Hydrolysis of Antheraxanthins **5** *and* **6**. The antheraxanthins **5** and **6** were hydrolyzed according to the method of *Märki-Fischer* and *Eugster* [5] in THF/H_2O in the presence of $7.5 \cdot 10^{-4}$ N H_2SO_4. The reactions were monitored by UV/VIS spectroscopy and HPLC. The product mixtures were separated by repeated column chromatography, and then the products were crystallized.

Thus, hydrolysis of **5** gave two compounds having a 5,6-dihydro-3,5,6-trihydroxy-β-end group, namely (3*S*,5*R*,6*R*,3′*R*)-karpoxanthin (**7**), identical with the natural karpoxanthin, and (3*S*,5*R*,6*S*,3′*R*)-karpoxanthin (**4**), identical with the natural 6-epikarpoxanthin. In addition, (3*S*,5*R*,8*R*,3′*R*)- and (3*S*,5*R*,8*S*,3′*R*)-mutatoxanthin (**8** and **9**, resp.) and also (3*S*,5*R*,6*S*,3′*R*)-cucurbitaxanthin A (**10**) were obtained.

Hydrolysis of **6** gave (3*S*,5*S*,6*R*,3′*R*)-karpoxanthin (= 5-epikarpoxanthin; **11**), (3*S*,5*S*,8*S*,3′*R*)- and (3*S*,5*S*,8*R*,3′*R*)-mutatoxanthin (**12** and **13**, resp.), as well as (3*S*,5*S*,6*R*,3′*R*)-epicucurbitaxanthin A (**14**). The formation of the two stereoisomeric karpoxanthins **4** and **7** from antheraxanthin **5**, but of only one stereoisomeric karpoxanthin **11** from antheraxanthin **6**, is in agreement with previous observations of *Eugster* and co-workers [13].

On acid treatment, 5-epikarpoxanthin (**11**) and epicucurbitaxanthin A (**14**) underwent a furanoid-oxide reaction, and for both reactions the products were identical with the corresponding mutatoxanthin epimers **12** and **13** (by HPLC and by ^{1}H-NMR; **12**/**13** $\approx 1:2.5$).

Spectroscopic Characterization of the Stereoisomeric Karpoxanthins **4**, **7**, *and* **11**. The MS of **4**, **7**, and **11** all exhibited the corresponding molecular-ion peak at *m/z* 602. In addition to the signals typical for hydroxy carotenoids ($[M - H_2O]^+$, $[M - \text{toluene}]^+$), strong peaks at *m/z* 221 and 181, characteristic for the 5,6-dihydro-3,5,6-trihydroxy-β-end group, were observed. Based on the diagnostically relevant ^{1}H-NMR data which have been reported by *Eugster* and co-workers [5][13] and on our own NMR results, obtained by the partial synthesis of stereoisomeric capsokarpoxanthins [7], the configuration of the 5,6-dihydro-3,5,6-trihydroxy-β-end group of the semisynthetic karpoxanthins were confirmed as (3*S*,5*R*,6*R*) for **7** (= karpoxanthin), as (3*S*,5*R*,6*S*) for **4** (= 6-epikarpoxanthin), and as (3*S*,5*S*,6*R*) for **11** (= 5-epikarpoxanthin). In contrast, the natural 5,6-diepikarpoxanthin (**1**) isolated from paprika and lilium possesses the (3*S*,5*S*,6*S*)-configuration [1][2].

Whereas karpoxanthin (**7**) and 6-epikarpoxanthin (**4**) have previously been isolated from natural sources [1][2][5] and prepared by partial synthesis, 5-epikarpoxanthin (**11**) has not yet been found in Nature and is a new carotenoid prepared by partial synthesis. The CD spectrum of **11** with positive maxima at 287 and 454 nm and negative maxima at 217, 280, and 322 nm is very similar to those of **4** and **7** [15] (*Fig. 1*).

Spectroscopic Characterization of Cucurbitaxanthin A (**10**) *and 5-Epicucurbitaxanthin A* (**14**). Both the MS of **10** and **14** exhibited the corresponding molecular-ion peak at *m/z* 584. In addition to the signals typical for hydroxy carotenoids ($[M - H_2O]^+$, $[M - \text{toluene}]^+$), strong peaks at *m/z* 286, 221, 160, 155, and 43, characteristic for the 3,6-epoxy-end group, were observed. The NMR data of semisynthetic **10** and **14** fully confirmed the proposed constitutions and their different configuration at C(5). The inversion at this C-atom influences the chemical shifts of the 3,6-epoxy end group nuclei, mainly those of C(5) and H−C(8). Cucurbitaxanthin A (**10**) is a naturally occurring carotenoid [3][14] that has now been prepared for the first time by partial

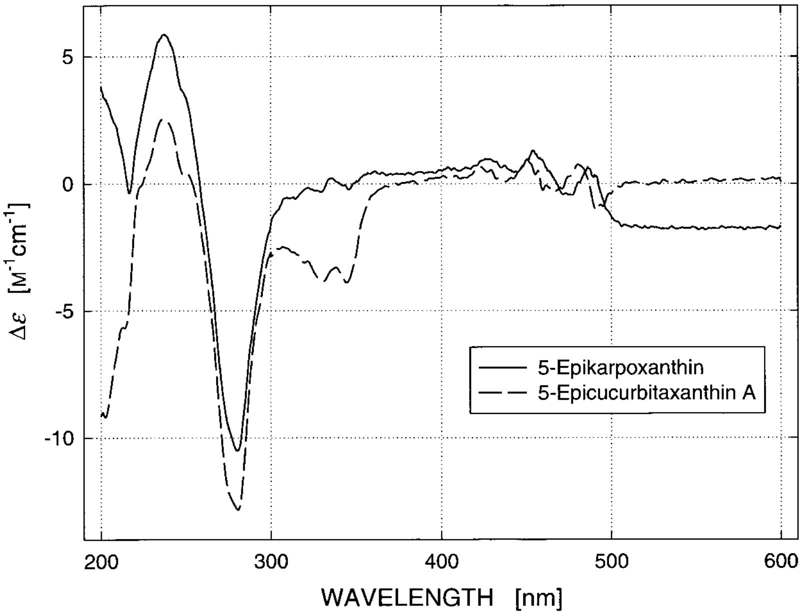

Fig. 1. *CD Spectra of 5-epikarpoxanthin* (**11**) *and 5-epicucurbitaxanthin A* (**14**) *in Et_2O/isopentane/EtOH 5 :5 :2 (*EPA*) at −180°*

synthesis. In contrast, its epimer **14** has not yet been isolated from natural sources and represents a new semisynthetic carotenoid. The CD spectrum of **14** is similar to that of **10**, exhibiting positive maxima at 237 and 249 nm and negative maxima at 203, 281, and 300 nm (*Fig. 1*).

Spectroscopic Characterization of the Stereoisomeric Mutatoxanthins **8**, **9**, **12**, *and* **13**. The MS of **8**, **9**, **12**, and **13** all showed the corresponding molecular-ion peaks at *m/z* 584. In addition to the signals typical for hydroxy carotenoids ($[M - H_2O]^+$, $[M - \text{toluene}]^+$, strong peaks at *m/z* 221 and 181 were observed, indicating the presence of the 5,8-epoxy-3-hydroxy end group. The ^1H- and ^{13}C-NMR data were found to be identical with published data [10][11][15][16] and allowed the identification of the configurational relationships. Whereas **8** and **9** have previously been isolated from natural sources and also prepared by acid-catalyzed rearrangement of antheraxanthin **5**, the corresponding 5-epimers (3*S*,5*S*,8*S*,3′*R*)- and (3*S*,5*S*,8*R*,3′*R*)-mutatoxanthin (**12** and **13**, resp.) have not yet been found in Nature. The existence of these compounds as products of the acid-catalyzed rearrangement of antheraxanthin **6** has been postulated previously. The CD spectra of **12** and **13** are very similar to each other (*Fig. 2*) and to those of **8** and **9** [10].

Discussion. – The present and our previous results [1][7] confirm the observations of *Eugster* and co-workers [5][6][13] and show that the configuration of 3,5,6-trihydroxy carotenoids originating from 5,6-epoxy-3-hydroxy carotenoids by acid-catalyzed hydrolysis does not depend on the remote end group. In the acid-catalyzed hydrolysis, the configuration of the 5,6-epoxy-5,6-dihydro-3-hydroxy-*β*-end group is

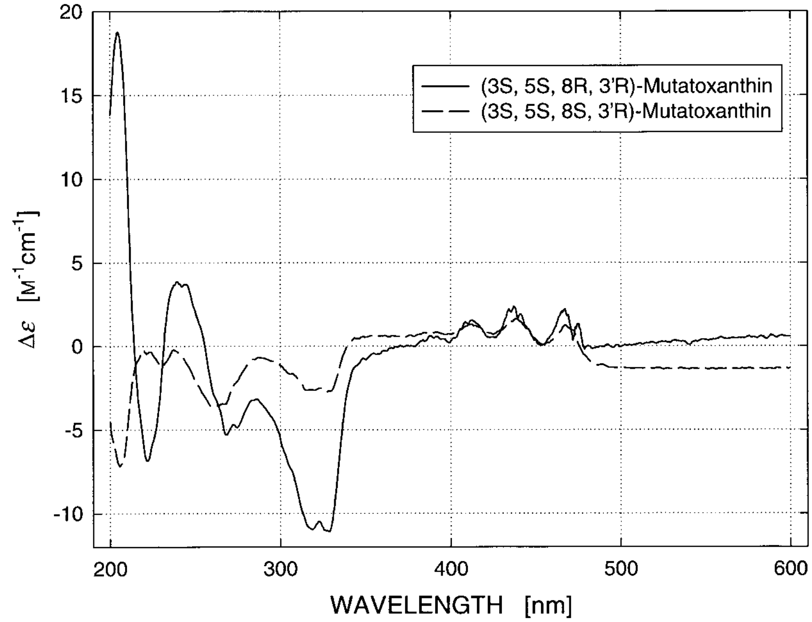

Fig. 2. *CD Spectra of (3*S*,5*S*,8*S*,3'*R*)- and (3*S*,5*S*,8*R*,3'*R*)-Mutatoxanthin* (**12** and **13**, resp.) *in Et_2O/isopentane/EtOH 5:5:2 (*EPA*) at –180°*

decisive for the configuration of the 5,6-dihydro-3,5,6-trihydroxy-β-end group, and the mechanism has been discussed in [7]. The formation of 3,6-epoxycarotenoids in the acid-catalyzed hydrolysis [7] was confirmed, and further investigations of the mechanism of this new reaction are in progress.

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Experimental Part

1. *General.* See [1][2].

2. *(3*S*,5*R*,6*S*,3'*R*)- and (3*S*,5*S*,6*R*,3'*R*)-Antheraxanthin* (**5** and **6**, resp.) were prepared and characterized previously [8][9][12].

3. *Hydrolysis of* **5**. To a soln. of **5** (85 mg) in THF (350 ml; free of peroxide) and H_2O (150 ml), $7.5 \cdot 10^{-4}$ N H_2SO_4 (200 ml) was added at r.t. The mixture was kept under N_2 in the dark (UV/VIS and HPLC monitoring). After 4 h, the mixture was diluted with Et_2O (600 ml) and washed with 5% aq. $NaHCO_3$ soln., the Et_2O phase dried (Na_2SO_4) and evaporated, and the residue dissolved in benzene/hexane 1:1 and submitted to CC (5 columns, benzene/hexane 1:1). Picture after development: 20 mm of pale yellow and 15 mm of yellow *Zone 1* (mixture of **4** and **7**, of the (*Z*)-isomers of these compounds, and of unidentified carotenoids); 10 mm of an intermediate zone; 30 mm of yellow *Zone 2* (**8**); 5 mm of a pale yellow zone (unidentified); 30 mm of an intermediate zone; 30 mm of yellow *Zone 3* (**9**); 10 mm of an intermediate zone; 50 mm of pale diffuse ochre *Zone 4* (**5**/**10**). *Zone 1* was submitted to a second CC (2 columns, 5–8% acetone in hexane). Picture after

development: 25 mm of pale yellow *Zone 1.1* (mixture of unidentified components); 6 mm of an intermediate zone; 20 mm of pale yellow *Zone 1.2* (mixture of (*Z*)-isomers of **4** and **7** and unidentified components); 5 mm of an intermediate zone; 40 mm of yellow *Zone 1.3* (**4**/**7**); 5 mm of an intermediate zone; 10 mm of pale yellow *Zone 1.4* (mixture of unidentified components). *Zone 1.3* was submitted to a third CC (1 column, 8% acetone/hexane). Picture after development: 3 mm of a pale yellow zone (unidentified); 120 mm of an intermediate zone; 40 mm of yellow *Zone 1.3.1* (**7**); 2 mm of an intermediate zone; 20 mm of yellow *Zone 1.3.2* (**4**). The material of *Zone 4* underwent a furanoid-oxide reaction, and the reaction mixture was submitted to repeated CC (1 column, benzene/hexane 1 : 1). Picture after development: 2 mm of a pale yellow zone (unidentified); 10 mm of yellow *Zone 4.1* (**8**); 10 mm of an intermediate zone; 8 mm of pale yellow *Zone 4.2* (**9**); 30 mm of an intermediate zone; 20 mm of ochre *Zone 4.3* (**10**). After CC separation, the pigments were crystallized (benzene/hexane) to give 2.0 mg of **7**, 0.8 mg of **4**, 11.9 mg of **8**, 11.7 mg of **9**, and 0.8 mg of **10**.

4. *Hydrolysis of* **6**. As described in *Exper. 3*, with 80 mg of **6**. After evaporation, the residue was dissolved in benzene/hexane 1:1 and submitted to CC (5 columns, benzene/hexane 1:1). Picture after development: 2 mm of a pale yellow zone (unidentified); 6 mm of ochre *Zone 1* (mixture of (*Z*)-isomers of **11** and unidentified components); 2 mm of a pale zone (unidentified); 10 mm of ochre *Zone 2* (mixture of **11** and unidentified components); 3 mm of a pale yellow zone (unidentified); 20 mm of yellow *Zone 3* (**12**); 12 mm of an intermediate zone; 25 mm of yellow *Zone 4* (**13**); 20 mm of an intermediate zone; 16 mm of ochre *Zone 5* (mixture of (*Z*)-isomers of **6** and **14**); 25 mm of pale ochre *Zone 6* (**6**/**14**). *Zone 2* was submitted to a second CC (3 columns, 1.5% acetone in benzene). Picture after development: 50 mm of a diffuse pale yellow zone (unidentified); 2 mm of an intermediate zone; 15 mm of ochre *Zone 2.1* (**11**); 20 mm of an intermediate zone; 10 mm of pale yellow *Zone 2.2* (**12**). *Zone 6* was submitted to a second CC (3 columns, 30–40% benzene in hexane). Picture after development: 1 mm of a yellow zone (unidentified); 20 mm of an intermediate zone; 15 mm of yellow *Zone 6.1* (**14**); 3 mm of a yellow zone ((*Z*)-isomer of **6** or **14**); 10 mm of yellow *Zone 6.2* (**6**). After CC separation the pigments were crystallized (benzene/hexane) to give 1.8 mg of **11**, 14.5 mg of **12**, 7.3 mg of **13**, and 1.3 mg of **14**.

5. *Karpoxanthin (=(all-*E*,3*S*,5*R*,6*R*,3′*R*)-5,6-Dihydro-β,β-carotene-3,5,6,3′-tetrol*; **7**). M.p. 168–170°. UV/VIS (benzene): 487, 457, 435. CD (EPA, r.t.): 200 (– 1.91), 210 (– 2.10), 243 (+ 0.05), 276 (– 1.69), 333 (– 0.13), 446 (– 0.36), 477 (– 0.39). CD (EPA, – 180°): 201 (– 1.22), 216 (– 2.69), 237 (+ 1.92), 280 (– 5.00), 320 (– 0.31), 420 (– 0.70), 467 (– 1.08), 494 (– 1.32). ^{1}H-NMR (CDCl$_3$): 0.87 (*s*, Me(16)); 1.07 (*s*, Me(16′)); 1.07 (*s*, Me(17′)); 1.18 (*s*, Me(18)); 1.25 (*s*, Me(17)); 1.48 ('*t*', $J_{\text{gem}} \approx J(2'\text{ax},3') = 11.3$, H$_{\text{ax}}$–C(2′)); 1.59 (*m*, H$_{\text{eq}}$–C(2)); 1.63 (*m*, H$_{\text{ax}}$–C(2)); 1.74 (*s*, Me(18′)); 1.77 (*ddd*, $J_{\text{gem}} = 11.3$, $J(2'\text{eq},3') = 3.7$, $J(2'\text{eq},4'\text{eq}) = 2.2$, H$_{\text{eq}}$–C(2′)); 1.81 ('*t*', $J_{\text{gem}} \approx J(4\text{ax},3) = 11.1$, H$_{\text{ax}}$–C(4)); 1.88 (*ddd*, $J_{\text{gem}} = 11.1$, $J(4\text{eq},3) = 4.8$, $J(4\text{eq},2\text{eq}) = 1.2$, H$_{\text{eq}}$–C(4)); 1.97 (*s*, Me(19), Me(19′), Me(20), Me(20′)); 2.04 (*dd*, $J_{\text{gem}} = 16.3$, $J(4'\text{ax},3') = 9.4$, H$_{\text{ax}}$–C(4′)); 2.39 (*ddd*, $J_{\text{gem}} = 16.3$, $J(4'\text{eq},3') = 5.3$, $J(4'\text{eq},2'\text{eq}) = 2.2$, H$_{\text{eq}}$–C(4′)); 4.00 (*m*, H–C(3′)); 4.16 (*m*, H–C(3)); 6.10 (*d*, $J(7',8') = 16.6$, H–C(7′)); 6.14 (*d*, $J(7,8) = 16.1$, H–C(7)); 6.14 (*d*, $J(10',11') = 10.4$, H–C(10′)); 6.15 (*d*, $J(8',7') = 16.6$, H–C(8′)); 6.23 (*d*, $J(10,11) = 11.0$, H–C(10)); 6.26 (*m*, H–C(14′)); 6.28 (*m*, H–C(14)); 6.36 (*d*, $J(12',11')) = 15.2$, H–C(12′)); 6.38 (*d*, $J(12,11) = 15.1$, H–C(12)); 6.40 (*d*, $J(8,7) = 16.1$, H–C(8)); 6.63 (*dd*, $J(11,10) = 11.0$, $J(11,12) = 15.1$, H–C(11)); 6.63 (*m*, H–C(15)); 6.64 (*dd*, $J(11',10') = 10.4$, $J(11',12') = 15.2$, H–C(11′)); 6.64 (*m*, H–C(15′)). ^{13}C-NMR (CDCl$_3$)1)): 12.8 (C(20)); 12.8 (C(19′), C(20′)); 13.4 (C(19)); 21.6 (C(18′)); 25.5 (C(17)); 26.8 (C(16)); 27.5 (C(18)); 28.8 (C(16′)); 30.4 (C(17′)); 42.5 (C(4′)); 45.4 (C(4)); 45.8 (C(2)); 48.5 (C(2′)); 64.5 (C(3)); 65.1 (C(3′)); 124.5 (C(11)); 124.9 (C(11′)); 125.6 (C(7′)); 128.6 (C(7)); 130.1 (C(15), C(15′)); 131.3 (C(10′)); 132.0 (C(10)); 132.6 (C(14)); 132.9 (C(14′)); 135.3 (C(8)); 137.6 (C(12′)); 138.2 (C(12)); 138.6 (C(8′)). EI-MS: 602 (100, M^+), 584 (14, $[M - H_2O]^+$), 566 (4, $[M - 2\,H_2O]^+$), 526 (48), 510 (11, $[M - \text{toluene}]^+$), 221 (15), 181 (16), 145 (23), 119 (25), 91 (26), 58 (27), 43 (65).

6. *6-Epikarpoxanthin (=(all-*E*,3*S*,5*R*,6*S*,3′*R*)-5,6-Dihydro-β,β-carotene-3,5,6,3′-tetrol*; **4**). M.p. 158–160°. UV/VIS (benzene): 487, 457, 435. CD (EPA, r.t.): 200 (– 0.68), 220 (– 0.24), 243 (+ 0.32), 278 (– 0.67), 334 (+ 0.05). CD (EPA, – 180°): 200 (– 0.60), 208 (+ 0.22), 217 (0.71), 244 (+ 1.59), 281 (– 3.63), 428 (+ 0.27), 450 (+ 0.27), 482 (+ 0.25), 490 (– 0.50). ^{1}H-NMR (CDCl$_3$): see data in [1]. ^{13}C-NMR (CDCl$_3$)1)): 12.8 (C(20)); 12.8 (C(19′), C(20′)); 13.0 (C(19)); 21.6 (C(18′)); 24.6 (C(17)); 27.8 (C(18)); 28.6 (C(16)); 28.7 (C(16′)); 30.2 (C(17′)); 42.7 (C(4′)); 45.9 (C(4))2)); 48.3 (C(2))2)), C(2′)); 124.5 (C(11′)); 125.4 (C(11)); 125.6 (C(7′)); 129.4 (C(7))2)); 130.1 (C(15), C(15′)); 131.4 (C(10′)); 132.7 (C(14), C(14′)); 137.6 (C(8))2)); 138.1 (C(12′)); 138.2

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1) Data extracted from inverse HMQC traces. Quaternary C-atoms not identified.

2) Assignment uncertain.

(C(12)); 138.6 (C(8′))[3]. EI-MS: 602 (77, M^+), 584 (57, $[M-H_2O]^+$), 566 (9, $[M-2\,H_2O]^+$), 510 (11, $[M-\text{toluene}]^+$), 504 (38), 352 (30), 221 (67), 181 (49), 157 (67), 145 (78), 119 (87), 105 (65), 55 (48).

7. *5-Epikarpoxanthin (=(all-*E*,3*S*,5*S*,6*R*,3′*R*)-5,6-Dihydro-β,β-carotene-3,5,6,3′-tetrol*; **11**). M.p. 183–185°. UV/VIS (benzene): 487, 458, 436; after acid treatment: 466, 438, 415. CD (EPA, r.t.): 213 (– 0.13), 217 (+ 0.05), 238 (+ 2.13), 275 (– 1.03), 299 (+ 1.04), 464.5 (+ 1.15). CD (EPA, – 180°): 217 (– 0.34), 237 (+ 5.85), 280 (– 10.52), 322 (– 0.15), 454 (1.31). ^{1}H-NMR ($CDCl_3$): 1.03 (*s*, Me(16)); 1.06 (*s*, Me(17)); 1.07 (*s*, Me(16′), Me(17′)); 1.35 (*s*, Me(18)); 1.48 (‘*t*’, $J_{gem} \approx J(2'ax,3') = 12.0$, H_{ax}–C(2′)); 1.61 (*dd*, $J_{gem} = 13.3$, $J(2eq,3) = 2.9$, H_{eq}–C(2)); 1.74 (*s*, Me(18′)); 1.77 (*ddd*, $J_{gem} = 12.0$, $J(2'eq,3') = 3.4$, $J(2'eq,4'eq) = 2.1$, H_{eq}–C(2′)); 1.82 (*dd*, $J_{gem} = 13.2$, $J(2ax,3) = 9.4$, H_{ax}–C(2)); 1.88 (*dd*, $J_{gem} \approx 12.7$, $J(4ax,3) \approx 1.3$, H_{ax}–C(4)); 1.93 (*dd*, $J_{gem} \approx 12.7$, $J(4eq,3) \approx 1.7$, H_{eq}–C(4)); 1.94 (*s*, Me(19)); 1.97 (*s*, Me(20), Me(19′), Me(20′)); 2.04 (*dd*, $J_{gem} = 16.8$, $J(4'ax,3') = 9.3$, H_{ax}–C(4′)); 2.39 (*ddd*, $J_{gem} = 16.8$, $J(4'eq,3') = 5.4$, $J(4'eq,2'eq) = 2.1$, H_{eq}–C(4′)); 3.97 (*m*, H–C(3)); 4.00 (*m*, H–C(3′)); 5.83 (*d*, $J(7,8) = 15.4$, H–C(7)); 6.10 (*AB*, $J(7',8') \approx 17$, H–C(7′)); 6.15 (*AB*, $J(8',7') \approx 17$, H–C(8′)); 6.15 (*d*, $J(10',11') = 11.7$, H–C(10′)); 6.24 (*m*, H–C(14′)); 6.25 (*d*, $J(10,11) = 11.8$, H–C(10)); 6.28 (*m*, H–C(14)); 6.36 (*d*, $J(12',11') = 15.0$, H–C(12′)); 6.38 (*d*, $J(12,11) = 15.0$, H–C(12)); 6.55 (*d*, $J(8,7) = 15.4$, H–C(8)); 6.62 (*dd*, $J(11,10) = 11.8$, $J(11,12) = 15.0$, H–C(11)); 6.64 (*m*, H–C(15)); 6.65 (*dd*, $J(11',10') = 11.7$, $J(11',12') = 15.0$, H–C(11′)); 6.65 (*m*, H–C(15′)). ^{13}C-NMR ($CDCl_3$): 12.77 (C(20′)); 12.80 (C(19′)); 12.82 (C(20)); 13.24 (C(19)); 21.62 (C(18′)); 26.95 (C(17)); 27.09 (C(16)); 27.18 (C(18)); 28.75 (C(16′)); 30.26 (C(17′)); 37.12 (C(1′)); 38.71 (C(1)); 42.56 (C(4′)); 43.56 (C(4)); 45.19 (C(2)); 48.44 (C(2′)); 65.10 (C(3′)); 66.30 (C(3)); 76.30 (C(5)); 79.40 (C(6)); 124.57 (C(11)); 125.01 (C(11′)); 125.56 (C(7′)); 126.17 (C(5′)); 127.55 (C(7)); 129.96 (C(15′)); 130.33 (C(15)); 131.28 (C(10′)); 132.47 (C(10)); 132.74 (C(14′)); 132.98 (C(14)); 134.08 (C(9)); 135.75 (C(9′)); 136.12 (C(8)); 136.24 (C(13)); 136.66 (C(13′)); 137.53 (C(12′)); 137.76 (C(6′)); 138.31 (C(12)); 138.49 (C(8′)). EI-MS: 602 (100, M^+), 584 (32, $[M-H_2O]^+$), 542 (7), 525 (4), 430 (7).

8. *Cucurbitaxanthin A (=(all-*E*,3*S*,5*R*,6*R*,3′*R*)-3,6-Epoxy-5,6-dihydro-β,β-carotene-5,3′-diol*; **10**). M.p. 148–150°. UV/VIS (benzene): 487, 457, 435. CD (EPA, r.t.): 204 (– 0.37), 245 (+ 0.29), 280 (– 0.07), 300 (+ 0.17), 363 (+ 0.09), 470 (– 0.08). CD (EPA, – 180°): 204 (+ 0.15), 216 (– 0.04), 237 (+ 0.95), 281 (– 1.11), 338 (+ 0.15), 470 (– 0.20), 495 (– 0.30). ^{1}H- and ^{13}C-NMR: see data in [14]. EI-MS: 584 (100, M^+), 566 (4, $[M-H_2O]^+$), 504 (12), 492 (6, $[M-\text{toluene}]^+$), 286 (20), 221 (11), 197 (16), 181 (14), 160 (24), 155 (10), 91 (32).

9. *5-Epicucurbitaxanthin A (=(all-*E*,3*S*,5*S*,6*R*,3′*R*)-3,6-Epoxy-5,6-dihydro-β,β-carotene-5,3′-diol*; **14**). M.p. 139–141°. UV/VIS (benzene): 487, 458, 437; after acid treatment: 465, 437, 417. CD (EPA, r.t.): 200 (– 7.27), 243 (– 0.12), 273 (– 4.56), 299 (– 0.98). CD (EPA, – 180°): 203 (– 9.20), 237 (+ 2.58), 249 (+ 0.35), 281 (– 12.84), 300 (– 2.79). ^{1}H-NMR ($CDCl_3$): 0.91 (*s*, Me(16)); 1.07 (*s*, Me(16′), Me(17′)); 1.25 (*s*, Me(17)); 1.40 (*d*, $J_{gem} = 11.5$, H_{ax}–C(2)); 1.48 (‘*t*’, $J_{gem} \approx J(2'ax,3') = 11.8$, H_{ax}–C(2′)); 1.49 (*s*, Me(18)); 1.70 (*d*, $J_{gem} = 12.9$, H_{ax}–C(4)); 1.73 (*s*, Me(18′)); 1.77 (*ddd*, $J_{gem} = 11.8$, $J(2'eq,3') = 3.6$, $J(2'eq,4'eq) = 1.4$, H_{eq}–C(2′)); 1.79 (*ddd*, $J_{gem} = 11.5$, $J(2eq,3) = 5.7$, $J(2eq,4eq) = 2.3$, H_{eq}–C(2)); 1.95 (*s*, Me(19)); 1.96 (*s*, Me(20), Me(19′), Me(20′)); 2.04 (*dd*, $J_{gem} = 17.9$, $J(4'ax,3') = 7.2$, H_{ax}–C(4′)); 2.10 (*ddd*, $J_{gem} = 12.9$, $J(4eq,3) = 6.4$, $J(4eq,2eq) = 2.3$, H_{eq}–C(4)); 2.39 (*ddd*, $J_{gem} = 17.0$, $J(4'eq,3') = 5.4$, $J(4'eq,2'eq) = 1.4$, H_{eq}–C(4′)); 4.00 (*m*, H–C(3′)); 4.48 (‘*t*’, $J(3,2eq) = J(3,4eq) = 5.9$, H–C(3)); 5.72 (*d*, $J(7,8) = 15.8$, H–C(7)); 6.10 (*AB*, $J(7',8') = 16.6$, H–C(7′)); 6.15 (*AB*, $J(8',7') = 16.6$, H–C(8′)); 6.15 (*d*, $J(10',11') = 11.3$, H–C(10′)); 6.21 (*d*, $J(10,11) = 11.2$, H–C(10)); 6.25 (*m*, H–C(14′)); 6.27 (*m*, H–C(14)); 6.36 (*d*, $J(12,11) = 15.0$, H–C(12)); 6.36 (*d*, $J(12',11') = 15.0$, H–C(12′)); 6.46 (*d*, $J(8,7) = 15.8$, H–C(8)); 6.61 (*dd*, $J(11,10) = 11.2$, $J(11,12) = 15.0$, H–C(11)); 6.63 (*m*, H–C(15)); 6.63 (*m*, H–C(15′)); 6.64 (*dd*, $J(11',10') = 11.3$, $J(11',12') = 15.0$, H–C(11′)). ^{13}C-NMR ($CDCl_3$): 12.75 (C(19′)); 12.80 (C(19))[4]; 12.81 (C(20))[4]; 12.86 (C(20′))[4]; 21.62 (C(18′)); 22.69 (C(18)); 26.35 (C(17)); 28.72 (C(16′)); 30.25 (C(17′)); 31.91 (C(16)); 37.12 (C(1′)); 41.49 (C(1)); 42.55 (C(4′)); 48.49 (C(2)); 48.51 (C(2′)); 49.13 (C(4)); 65.10 (C(3′)); 74.41 (C(3)); 80.12 (C(5)); 95.77 (C(6)); 120.80 (C(7)); 124.80 (C(11)); 124.92 (C(11′)); 125.56 (C(7′)); 126.15 (C(5′)); 130.05 (C(15′)); 130.15 (C(15)); 131.31 (C(10′)); 132.15 (C(10)); 132.59 (C(14)); 132.77 (C(14′)); 134.48 (C(9)); 135.67 (C(9′)); 136.39 (C(13)); 136.52 (C(13′)); 137.57 (C(6′)); 136.79 (C(8)); 137.76 (C(12′)); 138.01 (C(12)); 138.50 (C(8′)). EI-MS: 584 (100, M^+), 566 (10, $[M-H_2O]^+$), 504 (14), 492 (17, $[M-\text{toluene}]^+$), 221 (209, 181 (23), 155 (24), 91 (28), 43 (39).

10. *(3*S*,5*R*,8*R*,3′*R*)-Mutatoxanthin (=(all-*E*,3*S*,5*R*,8*R*,3′*R*)-5,8-Epoxy-5,8-dihydro-β,β-carotene-3,3′-diol*; **8**). M.p. 90–91°. UV/VIS (benzene): 465, 438, 416. CD (EPA, r.t.): 200 (+ 4.29), 206.5 (+ 8.17), 222.5 (– 0.77), 250 (+ 3.57), 316 (– 4.00), 420 (+ 1.20). CD (EPA, – 180°): 200 (+ 13.94), 204 (+ 17.69), 223 (– 5.17), 245 (+ 3.43), 268 (– 3.60), 275 (– 3.80), 318 (– 8.02), 328 (– 8.02), 406 (+ 1.40), 435 (+ 1.70), 467 (+ 2.23).

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[3] Atoms C(3′), C(10), and C(10′) not identified.

[4] Assignment may be interchanged.

^{1}H-NMR (CDCl$_3$): 1.07 (*s*, Me(16′)); 1.07 (*s*, Me(17′)); 1.17 (*s*, Me(16)); 1.33 (*s*, Me(17)); 1.48 (‘*t*’, $J_{\text{gem}} \approx J(2'\text{ax},3') \approx 11.9$, H$_{\text{ax}}$−C(2′)); 1.51 (*dd*, $J_{\text{gem}} = 14.3$, $J(2\text{eq},3) = 3.6$, H$_{\text{eq}}$−C(2)); 1.61 (*s*, Me(18)); 1.71 (*d*, $J(19.8) = 0.8$, Me(19)); 1.73 (*s*, Me(18′)); 1.76 (*ddd*, $J_{\text{gem}} = 14.3$, $J(2\text{ax},3)$[5], $J(2\text{ax},4\text{ax}) \approx 1$, H$_{\text{ax}}$−C(2)); 1.77 (*ddd*, $J_{\text{gem}} = 11.9$, $J(2'\text{eq},3')$[5], $J(2'\text{eq},4'\text{eq})$[5], H$_{\text{eq}}$−C(2′)); 1.94 (*s*, Me(20)); 1.96 (*s*, Me(19′), Me(20′)); 1.98 (*dd*, $J_{\text{gem}} = 12.6$, $J(4\text{eq},3) = 4.1$, H$_{\text{eq}}$−C(4)); 2.05 (*dd*, $J_{\text{gem}} = 17.7$, $J(4'\text{ax},3') = 9.8$, H$_{\text{ax}}$−C(4′)); 2.12 (*ddd*, $J_{\text{gem}} = 12.6$, $J(4\text{ax},3) = 4.0$, $J(4\text{ax},2\text{ax}) \approx 1$, H$_{\text{ax}}$−C(4)); 2.38 (*ddd*, $J_{\text{gem}} = 17.7$, $J(4'\text{eq},3') = 4.9$, $J(4'\text{eq},2'\text{eq})$[5], H$_{\text{eq}}$−C(4′)); 4.00 (*m*, H−C(3′)); 4.24 (*m*, H−C(3)); 5.16 (br. *s*, H−C(8)); 5.25 (*d*, $J(7,8) = 1.0$, H−C(7)); 6.10 (*AB*, $J(7',8') = 16.9$, H−C(7′)); 6.14 (*AB*, $J(8',7') = 16.9$, H−C(8′)); 6.15 (*d*, $J(10',11') = 11.5$, H−C(10′)); 6.19 (*d*, $J(10,11) = 11.2$, H−C(10)); 6.22 (*m*, H−C(14)); 6.24 (*m*, H−C(14′)); 6.32 (*d*, $J(12,11) = 15.2$, H−C(12)); 6.35 (*d*, $J(12',11') = 14.7$, H−C(12′)); 6.49 (*dd*, $J(11,10) = 11.2$, $J(11,12) = 15.2$, H−C(11)); 6.61 (*m*, H−C(15)); 6.62 (*m*, H−C(15′)); 6.63 (*dd*, $J(11',10') = 11.5$, $J(11',12') = 14.7$, H−C(11′)). ^{13}C-NMR (CDCl$_3$): 12.64 (C(19)); 12.74 (C(19′)); 12.80 (C(20), C(20′)); 21.61 (C(18′)); 28.71 (C(16′)); 28.87 (C(17)); 29.01 (C(18)); 30.25 (C(17′)); 31.37 (C(16)); 33.67 (C(1)); 37.11 (C(1′)); 42.54 (C(4′)); 46.66 (C(2)); 47.35 (C(4)); 48.41 (C(2′)); 65.08 (C(3′)); 67.71 (C(3)); 86.81 (C(5)); 87.71 (C(8)); 119.85 (C(7)); 124.31 (C(11)); 124.86 (C(11′)); 125.53 (C(7′)); 126.13 (C(5′)); 127.24 (C(10)); 129.95 (C(15))[4]; 129.98 (C(15′))[4]; 131.28 (C(10′)); 132.30 (C(14)); 132.52 (C(14′)); 135.63 (C(9′)); 136.23 (C(13)); 136.38 (C(13′)); 137.56 (C(12)); 137.56 (C(12′)); 137.74 (C(6′)); 137.89 (C(9)); 138.49 (C(8′)); 154.04 (C(6)). EI-MS: 584 (46, M^+), 566 (5, $[M - \text{H}_2\text{O}]^+$), 504 (56, $[M - 80]^+$), 492 (23, $[M - \text{toluene}]^+$), 352 (47), 221 (54), 181 (31), 91 (100), 43 (33).

11. *(3*S*,5*R*,8*S*,3′*R*)-Mutatoxanthin (=(all-*E*,3*S*,5*R*,8*S*,3′*R*)-5,8-Epoxy-5,8-dihydro-β,β-carotene-3,3′-diol*; **9**). M.p. 148–150°. UV/VIS (benzene): 465, 438, 416. CD (EPA, r.t.): 200 (−10.89), 208 (−15.17), 228 (−1.27), 258 (−6.44), 308 (+0.11), 429 (−1.01), 442 (−0.59), 458 (−1.24). CD (EPA, −180°): 200 (−7.57), 208 (−26.74), 227 (+0.15), 231 (−1.44), 239 (+0.90), 267 (−14.25), 292 (−3.01), 320 (−7.24), 329 (−7.57), 408 (+0.95), 437 (+2.11), 466 (+1.26). ^{1}H-NMR (CDCl$_3$): 1.07 (*s*, Me(16′)); 1.07 (*s*, Me(17′)); 1.19 (*s*, Me(16)); 1.34 (*s*, Me(17)); 1.48 (*dd*, $J_{\text{gem}} \approx 14.5$, $J(2\text{eq},3) \approx 4$, H$_{\text{eq}}$−C(2)); 1.48 (‘*t*’, ‘$J$’$_{\text{gem}} \approx J(2'\text{ax},3') \approx 12$, H$_{\text{ax}}$−C(2′)); 1.68 (*s*, Me(18)); 1.73 (*s*, Me(18′)); 1.77 (*ddd*, $J_{\text{gem}} \approx 12$, $J(2'\text{eq},3') \approx 4$, $J(2'\text{eq},4'\text{eq})$ not resolved, H$_{\text{eq}}$−C(2′)); 1.80 (*ddd*, $J_{\text{gem}} \approx 14.5$, $J(2\text{ax},3) \approx 4$, $J(2\text{ax},4\text{ax}) \approx 1$, H$_{\text{ax}}$−C(2)); 1.80 (*s*, Me(19)); 1.90 (*dd*, $J_{\text{gem}} = 13.6$, $J(4\text{eq},3) = 4.3$, H$_{\text{eq}}$−C(4)); 1.95 (*s*, Me(20)); 1.96 (*s*, Me(19′), Me(20′)); 2.04 (*dd*, $J_{\text{gem}} = 17.3$, $J(4'\text{ax},3') = 9.6$, H$_{\text{ax}}$−C(4′)); 2.11 (*ddd*, $J(4\text{ax},4\text{eq}) = 13.6$, $J(4\text{ax},3) = 2.0$, $J(4\text{ax},2\text{ax}) \approx 1$, H$_{\text{ax}}$−C(4)); 2.39 (*ddd*, $J_{\text{gem}} = 17.3$, $J(4'\text{eq},3') = 4.2$, $J(4'\text{eq},2'\text{eq})$ not resolved, H$_{\text{eq}}$−C(4′)); 4.00 (*m*, H−C(3′)); 4.24 (*m*, H−C(3)); 5.07 (br. *s*, H−C(8)); 5.30 (*d*, $J(7,8) = 11.6$, H−C(7)); 6.10 (*AB*, $J(7',8') = 16.6$, H−C(7′)); 6.14 (*AB*, $J(8',7') = 16.6$, H−C(8′)); 6.15 (*d*, $J(10',11') = 10.6$, H−C(10′)); 6.18 (*d*, $J(10,11) = 11.1$, H−C(10)); 6.23 (*m*, H−C(14)); 6.25 (*m*, H−C(14′)); 6.32 (*d*, $J(12,11) = 15.1$, H−C(12)); 6.36 (*d*, $J(12',11') = 14.5$, H−C(12′)); 6.50 (*dd*, $J(11,10) = 11.1$, $J(11,12) = 15.1$, H−C(11)); 6.62 (*m*, H−C(15)); 6.63 (*m*, H−C(15′)); 6.64 (*dd*, $J(11',10') = 10.6$, $J(11',12') = 14.5$, H−C(11′)). ^{13}C-NMR (CDCl$_3$): 12.75 (C(20)); 12.81 (C(19′), C(20′)); 13.40 (C(19)); 21.62 (C(18′)); 28.4 (C(17)); 28.73 (C(16′)); 30.26 (C(17′)); 30.57 (C(18)); 31.26 (C(16)); 34.22 (C(1)); 37.12 (C(1′)); 42.56 (C(4′)); 47.38 (C(2)); 47.40 (C(4)); 48.44 (C(2′)); 65.10 (C(3′)); 67.93 (C(3)); 87.18 (C(5)); 88.38 (C(8)); 118.74 (C(7)); 124.50 (C(11)); 124.83 (C(11′)); 125.53 (C(7′)); 126.14 (C(5′)); 126.19 (C(10)); 129.86 (C(15)); 130.05 (C(15′)); 131.30 (C(10′)); 132.16 (C(14)); 132.56 (C(14′)); 135.61 (C(9′)); 136.32 (C(13), C(13′)); 137.35 (C(12)); 137.59 (C(12′)); 137.76 (C(6′)); 138.51 (C(8′)); 138.65 (C(9)); 153.19 (C(6)). EI-MS: 584 (69, M^+), 566 (5, $[M - \text{H}_2\text{O}]^+$), 504 (100, $[M - 80]^+$), 492 (25, $[M - \text{toluene}]^+$), 352 (65), 221 (80), 181 (33), 145 (31), 105 (25), 91 (31).

12. *(3*S*,5*S*,8*S*,3′*R*)-Mutatoxanthin (=(all-*E*,3*S*,5*S*,8*S*,3′*R*)-5,8-Epoxy-5,8-dihydro-β,β-carotene-3,3′-diol*; **12**). M.p. 101–103°. UV/VIS (benzene): 466, 438, 418. CD (EPA, r.t.): 200 (−5.67), 204 (−8.08), 227 (−0.47), 254 (−2.29), 264 (−1.66), 298 (−0.86). CD (EPA, −180°): 200 (−4.52), 206 (−7.19), 220 (−0.22), 222 (−0.48), 230 (−1.26), 238 (−0.22), 261 (−3.65), 268 (−3.46), 287 (−0.66), 318 (−2.27), 327 (−2.75), 346 (+0.42), 354 (+0.64), 385 (+0.85), 412 (+1.30), 438 (+1.64), 467 (+1.24). ^{1}H-NMR (CDCl$_3$): 1.07 (*s*, Me(16′)); 1.07 (*s*, Me(17′)); 1.14 (*s*, Me(16)); 1.20 (*s*, Me(17)); 1.26 (*m*, overlapped, H$_{\text{ax}}$−C(2)); 1.44 (*s*, Me(18)); 1.48 (*ddd*, overlapped, H$_{\text{ax}}$−C(2′)); 1.60 (*dd*, $J_{\text{gem}} = 12.1$, $J(4\text{ax},3) = 11.2$, H$_{\text{ax}}$−C(4)); 1.73 (*s*, Me(18′)); 1.74 (*s*, Me(19)); 1.77 (*dd*, overlapped, H$_{\text{eq}}$−C(2′)); 1.87 (*ddd*, $J_{\text{gem}} = 11.9$, $J(2\text{eq},3)$ and $J(2\text{eq},4\text{eq})$ not resolved, H$_{\text{eq}}$−C(2)); 1.94 (*s*, Me(20)); 1.96 (*s*, Me(19′), Me(20′)); 2.04 (*dd*, $J(4'\text{ax},4'\text{eq}) = 16.6$, $J(4'\text{ax},3') = 10.2$, H$_{\text{ax}}$−C(4′)); 2.31 (*ddd*, $J_{\text{gem}} = 12.1$, $J(4\text{eq},3)$ and $J(4\text{eq},2\text{eq})$ not resolved, H$_{\text{eq}}$−C(4)); 2.38 (*dd*, $J_{\text{gem}} = 16.6$, $J(4'\text{eq},3') = 4.5$, H$_{\text{eq}}$−C(4′)); 3.99 (*m*, H−C(3′)); 4.02 (*m*, H−C(3)); 5.18 (br. *s*, $J(8,7) < 1$, H−C(8)); 5.26 (br. *s*, $J(7,8) < 1$, H−C(7)); 6.11 (*AB*, $J(7',8) \approx 16$, H−C(7′)); 6.15 (*AB*, $J(8',7') \approx 16$, H−C(8′)); 6.15 (*d*, $J(10',11') = 10.5$, H−C(10′)); 6.19 (*d*, $J(10,11) = 10.8$, H−C(10)); 6.23 (*m*, H−C(14)); 6.25 (*m*, H−C(14′)); 6.32 (*d*, $J(12,11) =$

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[5] *J* Values are not determined due to signal overlap.

14.9, H–C(12)); 6.35 (*d*, *J*(12′,11′) ≈ 14.5, H–C(12′)); 6.48 (*dd*, *J*(11,10) = 10.8, *J*(11,12) = 14.9, H–C(11)); 6.63 (*m*, H–C(15)); 6.63 (*m*, H–C(15′)); 6.64 (*dd*, *J*(11′,10′) = 10.5, *J*(11′12′) ≈ 14.5, H–C(11′)). ^{13}C-NMR (CDCl$_3$): 12.61 (C(19)); 12.73 (C(20)); 12.79 (C(19′)); 12.79 (C(20′)); 21.60 (C(18′)); 26.93 (C(16)); 27.14 (C(18)); 28.71 (C(16′)); 30.24 (C(17′)); 30.73 (C(17)); 33.22 (C(1)); 37.11 (C(1′)); 42.53 (C(4′)); 48.40 (C(2′)); 50.07 (C(2)); 50.18 (C(4)); 65.06 (C(3′)); 66.07 (C(3)); 87.57 (C(5)); 88.30 (C(8)); 120.29 (C(7)); 124.23 (C(11)); 124.87 (C(11′)); 125.54 (C(7′)); 126.14 (C(5′)); 127.46 (C(10)); 129.97 (C(15)); 130.00 (C(15′)); 131.28 (C(10′)); 132.38 (C(14)); 132.51 (C(14′)); 135.63 (C(9′)); 136.20 (C(13)); 136.41 (C(13′)); 137.55 (C(12′)); 137.59 (C(9)); 137.73 (C(12)); 137.73 (C(6′)); 138.48 (C(8′)); 152.88 (C(6)). EI-MS: 584 (82, M^+), 566 (6, $[M-H_2O]^+$), 504 (63, $[M-80]^+$), 492 (29, $[M-\text{toluene}]^+$), 352 (62), 221 (75), 181 (47), 145 (28), 105 (28), 91 (100), 43 (35).

13. *(3*S*,5*S*,8*R*,3′*R*)-Mutatoxanthin (=(all-*E*,3*S*,5*S*,8*R*,3′*R*)-5,8-Epoxy-5,8-dihydro-β,β-carotene-3,3′-diol*; **13**). M.p. 123–125°. UV/VIS (benzene): 465, 438, 417. CD (EPA, r.t.): 200 (+5.82), 206 (+8.49), 223 (+0.70), 241 (+3.36), 244 (+3.45), 271 (–1.00), 286 (–0.50), 314 (–2.70), 425 (+1.80), 450 (+1.90). CD (EPA, –180°): 200 (+13.81), 205 (+18.77), 222 (–6.86), 240 (+3.86), 269 (–5.32), 277 (–4.80), 286 (–3.16), 318 (–9.90), 329 (–11.09), 388 (+0.70), 412 (+0.50), 438 (+2.33), 465 (+2.20). ^{1}H-NMR (CDCl$_3$): 1.07 (*s*, Me(16′)); 1.07 (*s*, Me(17′)); 1.15 (*s*, Me(16)); 1.20 (*m*, overlapped, H$_{ax}$–C(2)); 1.23 (*s*, Me(17)); 1.48 (*s*, Me(18)); 1.48 (*ddd*, overlapped, H$_{ax}$–C(2′)); 1.50 ('*t*', J_{gem} = *J*(4ax,3) = 12.6, H$_{ax}$–C(4)); 1.73 (*s*, Me(18′)); 1.77 (*dd*, overlapped, H$_{eq}$–C(2′)); 1.79 (*s*, Me(19)); 1.90 (*ddd*, J_{gem} ≈ 13, *J*(2eq,3) and *J*(2eq,4eq) not resolved, H$_{eq}$–C(2)); 1.95 (*s*, Me(20)); 1.96 (*s*, Me(19′), Me(20′)); 2.04 (*dd*, J_{gem} = 16.7, *J*(4′ax,3′) = 9.8, H$_{ax}$–C(4′)); 2.28 (*ddd*, J_{gem} = 12.6, *J*(4eq,3) and *J*(4eq,2eq) not resolved, H$_{eq}$–C(4)); 2.38 (*dd*, *J*(4′eq,4′ax) = 16.7, *J*(4′eq,3′) = 4.1, H$_{eq}$–C(4′)); 4.00 (*m*, H–C(3′)); 4.02 (*m*, H–C(3)); 5.11 (br. *s*, H–C(8)); 5.34 (br. *s*, H–C(7)); 6.10 (*AB*, *J*(7′,8′) ≈ 16, H–C(7′)); 6.15 (*AB*, *J*(8′,7′) ≈ 16, H–C(8′)); 6.15 (*d*, *J*(10′,11′) ≈ 10.5, H–C(10′)); 6.18 (*d*, *J*(10,11) = 11.2, H–C(10)); 6.23 (*m*, H–C(14)); 6.25 (*m*, H–C(14′)); 6.32 (*d*, *J*(12,11) = 14.8, H–C(12)); 6.35 (*d*, *J*(12′,11′) ≈ 14.5, H–C(12′)); 6.49 (*dd*, *J*(10,10) = 11.2, *J*(11,12) = 14.8, H–C(11)); 6.63 (*m*, H–C(15)); 6.63 (*m*, H–C(15′)); 6.64 (*dd*, *J*(11′,10′) ≈ 10.5, *J*(11′,12′) ≈ 14.5, H–C(11′)). ^{13}C-NMR (CDCl$_3$): 12.74 (C(20)); 12.80 (C(19′)); 12.80 (C(20′)); 13.38 (C(19)); 21.61 (C(18′)); 26.50 (C(16)); 28.70 (C(18)); 28.70 (C(16′)); 30.24 (C(17′)); 30.67 (C(17)); 33.46 (C(1)); 37.11 (C(1′)); 42.53 (C(4′)); 48.41 (C(2′)); 50.21 (C(4)); 50.69 (C(2)); 65.08 (C(3′)); 66.43 (C(3)); 87.68 (C(5)); 88.71 (C(8)); 119.35 (C(7)); 124.35 (C(11)); 124.86 (C(11′)); 125.54 (C(7′)); 126.14 (C(5′)); 126.29 (C(10)); 129.93 (C(15)); 129.99 (C(15′)); 131.28 (C(10′)); 132.26 (C(14)); 132.52 (C(14′)); 135.63 (C(9′)); 136.23 (C(13)); 136.37 (C(13′)); 137.49 (C(12)); 137.55 (C(12′)); 137.74 (C(6′)); 138.20 (C(9)); 138.49 (C(8′)); 152.12 (C(6)). EI-MS: 584 (100, M^+), 566 (8, $[M-H_2O]^+$), 504 (79, $[M-80]^+$), 492 (29, $[M-\text{toluene}]^+$), 352 (27), 221 (24), 181 (47), 43 (79).

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