Structures of Five New Carotenoids from the Oyster *Crassostrea gigas*

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Received October 5, 2000

Five new minor carotenoids, **1**−**5**, were isolated from the oyster *Crassostrea gigas*. The structure of **1** was determined to be (3*S*,5*R*,6*R*,6′*S*)-3,5,6′-trihydroxy-3′-oxo-6,7-didehydro-5,6-dihydro-10,11,20-trinor-*β*,*ϵ*-caroten-19′,11′-olide 3-acetate by detailed analyses of NMR and CD data. The structures of the other carotenoids, **2**−**5**, were also determined in a similar manner. In the FAB-MS/MS of **2**−**4**, having the 5-hydroxy-3,6-epoxy-5,6-dihydro-*β*-carotene moiety, the characteristic product ions resulting from the sequential cleavage of C−C bonds in the polyene chain were observed.

In the course of the studies on new carotenoids in natural products, we reported the isolation and structure elucidation of the *retro*-carotenoid anhydroeschscholtzxanthin,[1a] the di-*Z*-carotenoid cucumariaxanthins,[1b] the purple carotenoid rhodobacterioxanthin,[1c] the C_{69} carotenoids pittosporumxanthins,[1d] and carotenoids possessing the unique end group of the crassostreaxanthins.[2] In the previous paper, we reported the isolation and structure elucidation of crassostreaxanthins A and B from the oyster *Crassostrea gigas* Thunberg (Ostreidae).[2]

Recently, we have isolated five new minor carotenoids, **1**−**5**, from the same species.

This paper deals with the isolation and structural elucidation of these five carotenoids and with the observed characteristic ions in FAB-MS/MS of **2**, **3**, and **4**.

Results and Discussion

Acetone extraction of the oyster *C. gigas* (10 kg), followed by treatment with Et_2O−*n*-hexane (1:1), gave a crude mixture of carotenoids. Repeated separations of the crude mixture of carotenoids by silica gel column chromatography and by HPLC on silica gel and on ODS furnished the new carotenoids **1** (0.5 mg), **2** (1 mg), **3** (0.5 mg), **4** (1 mg), and **5** (0.5 mg).

Carotenoid **1** was obtained as a red, amorphous solid exhibiting a molecular ion peak (HREIMS) at *m*/*z* 628.3395 corresponding to $C_{39}H_{48}O_7$. The UV−vis spectrum of **1** in Et_2O showed an absorption maximum at 457 nm. The ^{13}C NMR and HSQC spectra of **1** in $CDCl_3$ confirmed the presence of 39 carbons and 46 carbon-bonded protons. In the ^1H and ^{13}C NMR spectra of **1** the noticeable signals due to three carbonyl carbons and allene groups were observed at δ_C 170.4, 168.7, and 197.7 and at δ_C 202.7 and δ_H 6.06. The NMR and the UV−vis data suggested that **1** was an analogue of peridinin.[3,4] Thus, the NMR data of **1** were compared with those of peridinin.[4]

The ^1H and ^{13}C NMR signal assignments of **1** in $CDCl_3$ were made by ^1H−^1H COSY, HSQC, HMBC, and NOESY experiments. The ^1H assigned data of **1** are given in Table 1, together with those of the other carotenoids (**2**−**5**). The ^{13}C data of **1** and **4** are presented in the Experimental Section. The ^1H and ^{13}C data of **1** were almost identical with those of peridinin[4] except for the signals of the end group (C1′ to C6′). The connections of the unassigned end group in **1** were determined by the HMBC experiment. The HMBC data are summarized in Figure 1. The ^1H and ^{13}C signals for the unassigned end group of **1** showed cross-peaks in the HMBC spectrum between the following proton−carbon pairs: H16′, H17′−C1′, C2′, C6′, H2′−C3′, H18′−C5′, C6′, H4′−C18′, and H7′−C6′. On the basis of the HMBC connectivities, the partial structure of the end group (C1′ to C6′) was deduced (Figure 1). Thus, the whole chemical structure of **1** was determined. The structure of **1** was also supported by the data of ^1H−^1H COSY.

The stereochemistry of **1** was confirmed by NOESY and CD data. The NOESY spectrum showed NOE cross-peaks between H17′ and H7′ and between H16′ and hydroxy

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10.1021/np000476w CCC: $20.00
Published on Web 04/19/2001

Table 1. ^{1}H NMR (500 MHz) Data of Carotenoids **1**−**5** in $CDCl_3$[a,b]

^{1}H no.	**1** δ mult. (*J*, Hz)	**2** δ mult. (*J*, Hz)	**3** δ mult. (*J*, Hz)	**4** δ mult. (*J*, Hz)	**5** δ mult. (*J*, Hz)
H-2α	2.00 ddd (12, 4, 2)	1.61 d (11.5)	1.61 d (11.5)	1.61 d (11.5)	1.95 ddd (12, 4, 2)
H-2*β*	1.41 dd (12, 12)	1.84 ddd (11.5, 6, 2)	1.84 dm(11.5)	1.84 ddd(11.5, 6, 2)	1.34 dd (12, 12)
H-3	5.37 m	4.39 t (6)	4.39 t (6)	4.39 t (6)	4.32 m
H-4α	2.29 ddd (13, 4, 2)	1.67 d (12)	1.67 d (12)	1.67 d (12)	2.26 ddd (13, 4, 2)
H-4*β*	1.51 dd (13, 13)	2.06 ddd (12, 6, 2)	2.06 ddd (12, 6, 2)	2.06 ddd (12, 6, 2)	1.41 dd (13, 13)
H-7		5.75 d (16)	5.75 d (16)	5.75 d (16)	
H-8	6.06 s	6.38 d (16)	6.38 d (16)	6.38 d (16)	6.04 s
H-10		6.21 d (11.5)	6.20 d (11.5)	6.21 d (11.5)	6.12 d (11.5)
H-11		6.66 dd (15. 11.5)	6.63 dd (15, 11.5)	6.64 dd (15, 11.5)	6.59 dd (15, 11.5)
H-12	6.12 d (11.5)	6.37 d (15)	6.36 d (15)	6.37 d (15)	6.35 d (15)
H-13	6.62 dd (14.5, 11.5)				
H-14	6.36 dd (14.5, 11.5)	6.27 d (11.5)	6.26 d (10)	6.28 d (11)	6.26 d (11.5)
H-15	6.53 dd (14.5, 11.5)	6.74 dd (14.5, 11.5)	6.63 m	6.72dd (14.5, 11.5)	6.72dd(14.5,11.5)
H-16	1.39 s	1.44 s	1.44 s	1.44 s	1.34 s
H-17	1.07 s	0.89 s	0.89 s	0.89 s	1.07 s
H-18	1.35 s	1.22 s	1.22 s	1.22 s	1.35 s
H-19	1.80 s	1.96 s	1.96 s	1.96 s	1.81 s
H-20		1.99 s	1.97 s	1.98 s	1.98 s
CH_{3CO}	2.04 s				
H-2′α	2.55 d (18)	2.52 dd (15, 5)	1.84 ddd(12.5,4,2)	2.19 dd (13.5, 8)	2.19 dd (13.5, 8)
H-2′*β*	2.30 d (18)	2.69 dd (15, 7)	1.46 dd (12.5, 12.5)	1.72 dd (13.5, 4.5)	1.72 dd (13.5, 4.5)
H-3′		4.21 m	4.00 m	4.53 m	4.53 m
H-4′α	5.95 br s	1.31 ddd (12, 11, 10)	2.43 ddd (18, 5.5, 2)	2.88 dd (14.5, 8.5)	2.88 dd (14.5, 8.5)
H-4′*β*		2.17 ddd (12, 7, 5)	2.09 dd (18, 9)	1.55 dd (14.5, 2.5)	1.55 dd (14.5, 2.5)
H-5′		2.32 ddq (11, 7, 7)			
H-7′	6.97 d (15)	2.86 d (13.5)		5.86 s	5.86 s
		2.93 d (13.5)			
H-8′	6.55 d (15)				
H-10′	7.10 s	7.26 d (11)	6.46 d (11)	7.24 d (11)	7.24 d (11)
H-11′		6.59 dd (15, 11)	6.51 dd (14.5, 11.5)	6.60 dd (15, 11)	6.59 dd (15, 11)
H-12′	5.72 s	6.68 d (15)	6.36 d (14.5)	6.66 d (15)	6.65 d (15)
H-14′	6.48 d (11.5)	6.42 d (11.5)	6.27 d (10)	6.38 d (11.5)	6.37 d (11.5)
H-15′	6.61 dd (14.5, 11.5)	6.66 dd (14.5, 11.5)	6.63 m	6.63 dd (14.5, 11.5)	6.63 dd (14.5, 11.5)
H-16′	1.11 s	2.14 s	1.15 s	0.85 s	0.85 s
H-17′	1.04 s	1.10 s	1.20 s	1.19 s	1.19 s
H-18′	1.91 d (1.2)	0.99 d (7)	1.92 s	1.35 s	1.35 s
H-19′		1.93 s	1.95 s	1.99 s	1.98 s
H-20′	2.23 s	1.99 s	2.01 s	1.99s	1.99 s
OH-8′				16.30 s	16.30 s

[a] ^{1}H chemical shifts are reported downfield from internal TMS (=0.00). [b] ^{1}H NMR signals were assigned by gmq-COSY and NOESY experiments and by comparison with those of related compounds (ref 4).

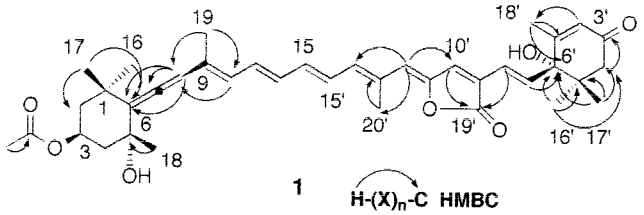

Figure 1. Structure and HMBC correlations for carotenoid **1**.

proton(s). The other observed NOE cross-peaks between the remaining protons in **1** were almost identical with those in peridinin.[4] Thus, the relative stereochemistry of **1** was assigned as shown in Figure 1. The CD spectrum of **1** showed characteristic Cotton effects similar to those of amarouciaxanthin A,[5] which possesses 3*S*,5*R*,6*R*,6′*S* chiralities. Consequently, the absolute structure of **1** was determined to be (3*S*,5*R*,6*R*,6′*S*)-3,5,6′-trihydroxy-3′-oxo-6,7-didehydro-5,6-dihydro-10,11,20-trinor-*β*,*ϵ*-caroten-19′,11′-olide 3-acetate.

Carotenoids **2** and **3** were obtained as orange amorphous solids. The UV−vis spectra of **2** and **3** in Et_2O showed absorption maxima at 443 and 468 and at 446 and 476 nm, respectively. The molecular formulas of **2** and **3** were determined as $C_{40}H_{56}O_5$ and $C_{40}H_{54}O_3$ by HREIMS, respectively.

As can be seen from Table 1, the ^{1}H chemical shifts and the spin-couplings of H2 to H20 in **2** and **3** were almost identical with those in cycloviolaxanthin.[6] That is, the data indicated the presence of a cycloviolaxanthin partial structure in **2** and **3**. The NMR signals of the remaining unassigned protons (H2′ to H20′) of **2** and **3** were similar to those of a partial structure in crassostreaxanthin A[2] and alloxanthin,[4] respectively. Consequently, the structures of **2** and **3**, each of which was made up of the corresponding partial structures in cycloviolaxanthin and crassostreaxanthin A and in cycloviolaxanthin and alloxanthin, respectively, were determined to be that shown. The relative stereochemistries of **2** and **3** were also supported by the results of NOESY and ^{1}H−^{1}H COSY experiments. The NOESY data summary is given in Figure S1 of the Supporting Information.

Carotenoid **4** was obtained as a red, amorphous solid, with the molecular formula $C_{40}H_{56}O_5$, as established by HREIMS. The UV−vis spectrum of **4** in Et_2O showed an absorption maximum at 464 nm. As shown in Table 1, the ^{1}H chemical shifts and the spin-couplings of H2 to H20 in **4** were almost identical with those in cycloviolaxanthin.[6] The ^{1}H NMR signals of the remaining protons in **4** were similar to those in mytiloxanthin.[7] Thus, the structure of **4** was determined to be made up of the corresponding partial structures in cycloviolaxanthin and mytiloxanthin. The relative stereochemisty of **4** was also supported by the results of the NOESY (Figure S1) and ^{1}H−^{1}H COSY experiments and the ^{13}C chemical shifts listed in the Experimental Section.

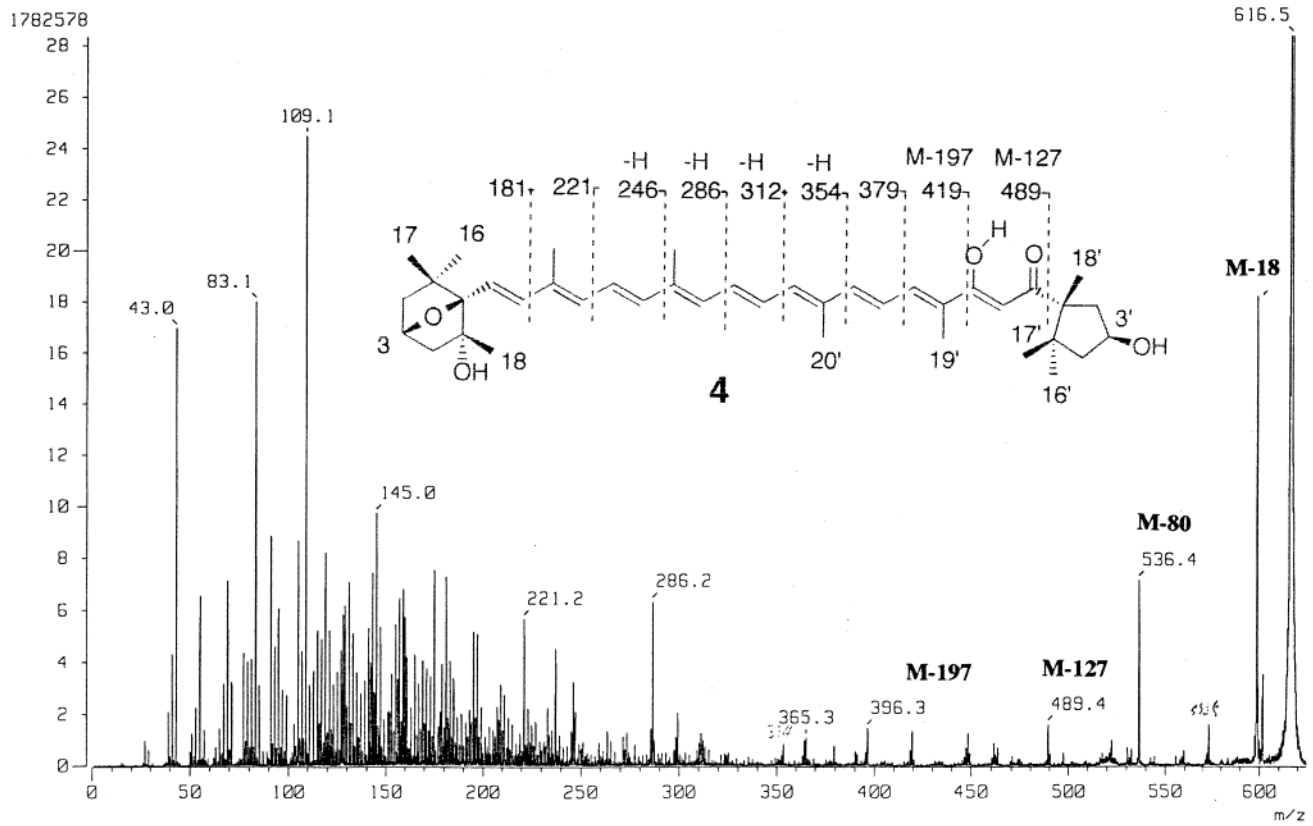

Figure 2. Structure and FAB MS/MS spectrum of carotenoid **4**.

The absolute structures of **2**, **3**, and **4** were tentatively postulated on the basis of the NOESY and the CD data. The CD spectrum of **3** showed characteristic Cotton effects similar to the combined CD spectra of cycloviolaxanthin (3*S*,5*R*,6*R*)[6b] and alloxanthin (3*R*),[8] by the use of the additivity rules of CD spectra of dichiral carotenoids.[8] In carotenoid **2**, the 3*S*,5*R*,6*R* chiralities were postulated on the basis of the fact that the CD spectrum of **2** exhibits the same Cotton effects as that of cycloviolaxanthin.

The CD spectrum of **4** showed characteristic Cotton effects similar to those of capsanthin 3,6-epoxide (3*S*,5*R*,6*R*,3′*S*,5′*R*), which possesses the same asymmetric carbons and the same chromophore.[6b]

Taking the results of their CD and relative stereochemistries into account, the structures of **2**, **3**, and **4** were determined to be (3*S*,5*R*,6*R*)-5-hydroxy-3,6:3′,6′-diepoxy-5,6,1′,2′,5′,6′,7′,8′-octahydro-6′-methyl-16′-nor-*β*,*φ*-carotene-1′,8′-dione, (3*S*,5*R*,6*R*,3′*R*)-3,6-epoxy-7′,8′-didehydro-5,6-dihydro-*β*,*β*-carotene-5,3′-diol, and (3*S*,5*R*,6*R*,3′*S*,5′*R*)-5,3′,8′-trihydroxy-3,6-epoxy-5,6-dihydro-*β*,*κ*-caroten-6′-one, respectively.

Carotenoid **5** was obtained as a red, amorphous solid exhibiting a molecular ion peak (HREIMS) at *m*/*z* 616.4119 corresponding to $C_{40}H_{56}O_5$. The UV−vis spectrum of **5** in Et_2O showed an absorption maximum at 457 nm. The chemical structure of **5** was deduced to be that shown by comparing the ^{1}H NMR data of **5** with those of the corresponding partial structures in fucoxanthinol[4] and mytiloxanthin.[7] The relative stereochemistries in the end groups of **5** were supported by the NOESY correlations and the magnitudes of ^{1}H−^{1}H spin-couplings in Table 1. The CD spectrum of **5** was similar to that of fucoxanthinol,[8] and the absolute stereochemistry of the other end group (C1′ to C6′) was deduced to be the same as in **4**. Thus, the absolute structure of **5** was determined to be (3*S*,5*R*,6*R*,3′*S*,5′*R*)-3,5,3′,8′-tertahydroxy-6,7-didehydro-5,6-dihydro-*β*,*κ*-caroten-6′-one.

Finally, the FAB-MS/MS spectrum of **4** is shown in Figure 2. As can be seen from Figure 2, the CID (collision-induced dissociation) MS spectra of the $M^{\bullet+}$ (616) showed the characteristic product ions resulting from the sequential cleavage of C−C bonds in the polyene chain in addition to the $[M - 18]^{\bullet+}$ and $[M - 80]^{\bullet+}$.[9] The characteristic product ions were also observed for the CID MS spectra of the $M^{\bullet+}$ of **2** and **3**.

In addition to the new carotenois **1**−**5**, 17 known carotenoids (see Experimental Section) were isolated and identified by UV−vis, EIMS, CD, and ^{1}H NMR. Their structures are presented in the Supporting Information data, Figure S2.

Experimental Section

General Experimental Procedures. The UV−visible (vis) spectra were recorded on a Shimadzu UV-240 spectrophotometer in Et_2O. The EIMS, FABMS, and FAB-MS/MS spectra were recorded using a JEOL JMS-HX/HX 110A mass spectrometer. The EIMS spectra were recorded with a direct inlet system with ionization energy of 70 eV. The positive ion FAB MS/MS measurement conditions were as follows: matrix, 3-nitrobenzyl alcohol; accelerating voltage, 10 kV; emitter current, 5 mV; collision gas, argon; collision cell voltage, 3 kV. The ^{13}C (125 MHz) and ^{1}H NMR (500 MHz) spectra were recorded on a Varian UNITY INOVA 500 spectrometer in $CDCl_3$ with TMS as an internal standard. The ^{13}C NMR spectra of **1** (0.5 mg) and **4** (1 mg) were measured in 40 μL of $CDCl_3$ solution using a Nanoprobe (Varian). All two-dimensional experiments were carried out without sample spinning. The gmq (pulsed field gradient multi-quantum) COSY, NOESY (mixing time 1.3 s), gHSQC ($^1J_{CH}$ optimized for 142 Hz), and gHMBC ($^nJ_{CH}$ optimized for 8 Hz) spectra were acquired using

the standard Varian pulse programs. and the software used to obtain 2D spectra was from Varian, version 6.1A. CD spectra were recorded in Et_2O at room temperature with a JASCO J-500 spectropolarimeter. HPLC was performed on a Shimadzu LC-6AD instrument with a Shimadzu SPD-6AV spectrophotometer set at 450 nm. The columns used were a Shim-Pack PREP-SIL (Shimadzu, 20 mm × 250 mm, 5 μm) and a Lichrospher 100 RP-18 (Cica Merck, 20 × 250 mm, 10 μm).

Animal Material. *C. gigas* was purchased at the fish market in Kyoto City in February. Voucher specimens[2] have been deposited at Kyoto Pharmaceutical University.

Extraction and Isolation of Carotenoids. The Me_2CO extract of the edible parts of *C. gigas* (10 kg) was partitioned between *n*-hexanes−Et_2O (1:1) and aqueous NaCl. The organic layer was dried over Na_2SO_4 and then concentrated to dryness. The residue was subjected to column chromatography (CC) on Si gel using an increasing percentage of Me_2CO in *n*-hexane. The fraction eluted with *n*-hexane−Me_2CO (1:1) from a Si gel column was purified by HPLC on silica with *n*-hexane−Me_2-CO (7:3) and further purified by HPLC on ODS with $CHCl_3$−MeCN (1:9) to yield **1** (0.5 mg), **2** (1 mg), **3** (0.5 mg), and **4** (1 mg). The fraction eluted with Me_2CO from a Si gel column was further purified by HPLC on silica with *n*-hexane−Me_2-CO (6:4) and on ODS with $CHCl_3$−MeCN (1:9) to yield **5** (0.5 mg).

In the present isolation, the following additional known carotenoids[3,4,8,9] were isolated and identified by UV−vis, EIMS, ^{1}H NMR, and CD spectral data: alloxanthin (5 mg) and its 3-acetate (3 mg), 8′-apo-alloxanthinal (5 mg), crassostreaxanthin A (10 mg) and its 3-acetate (4 mg), crassostreaxanthin B (6 mg) and its 3-acetate (4 mg), diatoxanthin (4 mg), fucoxanthin (4 mg), fucoxanthinol (2 mg), halocynthiaxanthin (20 mg)and its 3′-acetate (5 mg), mytiloxanthin (12 mg), pectenol A (2 mg), peridinin (5 mg), peridininol (1 mg), pyrrhoxanthinol (2 mg).

Carotenoid 1: red, amorphous solid; UV−vis (Et_2O) λ_{max} 457 nm; CD (Et_2O) $\lambda_{ext}(\Delta\epsilon)$ 225 (−6.8), 255 (+10.2), 352 (−6.1); ^{1}H NMR ($CDCl_3$), Table 1; ^{13}C NMR ($CDCl_3$) δ 14.0 (q, C-19), 15.4 (q, C-20′), 18.9 (q, C-18′), 21.4 (q, CH_3CO), 23.0 (q, C-16′), 24.3 (q, C-17′), 29.1 (q, C-16), 31.2 (q, C-18), 32.0 (q, C-17), 35.8 (s, C-1), 41.6 (s, C-1′), 45.2 (t, C-4), 45.4 (t, C-2), 49.7 (t, C-2′), 67.9 (d, C-3), 72.6 (s, C-5), 79.7 (s, C-6′), 103.3 (d, C-8), 117.6 (s, C-6), 119.9 (d, C-12′), 122.6(d, C-8′),124.4(s, C-9′), 127.3 (d, C-4′), 128.1 (d, C-12), 128.8 (d, C-15′), 131.7 (d, C-13), 132.9 (s, C-9), 133.8 (d, C-14), 134.1 (s, C-13′), 136.2 (d, C-7′), 136.9 (d, C-10′), 137.6 (d, C-15), 138.6 (d, C-14′), 146.6(s, C-11′), 161.4 (s, C-5′), 168.7 (s, C-19′), 170.4 (s, CH_3CO), 197.7 (s, C-3′), 202.7 (s, C-7); EIMS *m*/*z* 628 $[M]^+$ (18), 610 (100), 550 (74), 536 (12), 416 (20), 397 (20), 297 (20), 223 (42), 197 (34), 152 (34), 43 (34); HREIMS *m*/*z* 628.3395 (calcd for $C_{39}H_{48}O_7$, 628.3394).

Carotenoid 2: orange, amorphous solid; UV−vis (Et_2O) λ_{max} 443, 468 nm (%III/II = 65); CD (Et_2O) $\lambda_{ext}(\Delta\epsilon)$ 235 (−1), 285 (+1), 325 (−1); ^{1}H NMR ($CDCl_3$), Table 1; EIMS *m*/*z* 616 $[M]^+$ (30), 598 (2), 558 (4), 524 (4), 462 (15), 221 (13), 155 (100), 113(20), 43(16); HREIMS *m*/*z*, 616.4137 (calcd for $C_{40}H_{56}O_5$, 616.4125).

Carotenoid 3: orange, amorphous solid; UV−vis (Et_2O) λ_{max} 446, 476 nm (%III/II = 65); CD (Et_2O) $\lambda_{ext}(\Delta\epsilon)$ 240 (−2), 275 (0), 320 (−1.7); ^{1}H NMR ($CDCl_3$), Table 1; EIMS *m*/*z* 582 $[M]^+$ (100), 564 (5), 502 (5), 490(10), 299 (12), 286 (21), 221 (37), 181(13), 160 (15), 43 (12); HREIMS *m*/*z*, 582.4080 (calcd for $C_{40}H_{54}O_3$, 582.4072).

Carotenoid 4: red, amorphous solid; UV−vis (Et_2O) λ_{max} 464 nm; CD (Et_2O) $\lambda_{ext}(\Delta\epsilon)$ 240 (−0.5), 280 (+1), 360 (−2); ^{1}H NMR ($CDCl_3$), Table 1; ^{13}C NMR ($CDCl_3$) δ 12.5 (q, C-20′),-12.8 (q, C-20), 12.9 (q, C-19), 12.9 (q, C-19′), 22.2 (q, C-18′), 25.0 (q, C-17′), 25.7 (q, C-16), 25.9 (q, C-16′), 31.6 (q, C-18), 32.2 (q, C-17), 44.0 (s, C-1), 44.7 (s, C-1′), 45.2 (t, C-4′), 47.7 (t, C-4), 48.5 (t, C-2), 50.8 (t, C-2′), 56.1 (s, C-5′), 70.5 (d, C-3′), 75.4 (d, C-3), 82.5 (s, C-5), 91.7 (s, C-6), 94.5 (d, C-7′), 123.2 (d, C-7), 123.3 (d, C-14), 123.6 (d, C-11′), 125.5 (d, C-11), 129.6 (d, C-15), 131.5 (d, C-10), 132.6 (d, C-15′), 134.8 (d, C-8), 135.3 (s, C-9), 135.7 (s, C-13), 135.8 (d, C-10′), 135.8 (d, C-14′), 136.4 (s, C-9′), 137.6 (d, C-12), 137.8 (s, C-13′), 144.0 (d, C-12′), 182.0 (s, C-8′), 202.3 (s, C-6′); EIMS *m*/*z* 616 $[M]^+$ (100), 598 (15), 580 (5), 536 (7), 524 (20), 506 (10), 419 (5), 313 (17), 287 (23), 221 (63), 179(35), 109 (43), 83 (25), 43 (22); HREIMS *m*/*z* 616.4133 (calcd for $C_{40}H_{56}O_5$, 616.4125).

Carotenoid 5: red, amorphous solid; UV−vis (Et_2O) λ_{max} 468 nm; CD (Et_2O) $\lambda_{ext}(\Delta\epsilon)$: 227 (−1.5), 290 (−3), 370 (−1); ^{1}H NMR ($CDCl_3$), Table 1; EIMS *m*/*z* 616 $[M]^+$ (32), 598 (33), 580 (10), 524 (5), 386 (10), 237 (23), 197 (42), 179 (25), 127 (35), 109 (100), 83 (40), 43 (32); HREIMS *m*/*z* 616.4119 (calcd for $C_{40}H_{56}O_5$, 616.4125).

Supporting Information Available: Figure S1 indicating NOESY data summary of **1**−**5**. Figure S2 indicating structures of 17 known carotenoids. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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NP000476W