

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

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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- $\beta,\epsilon$ -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- $\beta$ -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 anhydroeschscholtzianthin,<sup>1a</sup> the di-*Z*-carotenoid cucumariaxanthins,<sup>1b</sup> the purple carotenoid rhodobacterioxanthin,<sup>1c</sup> the C<sub>69</sub> carotenoids pittedoxanthins,<sup>1d</sup> and carotenoids possessing the unique end group of the crassostreaxanthins.<sup>2</sup> In the previous paper, we reported the isolation and structure elucidation of crassostreaxanthins A and B from the oyster *Crassostrea gigas* Thunberg (Ostreidae).<sup>2</sup>

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

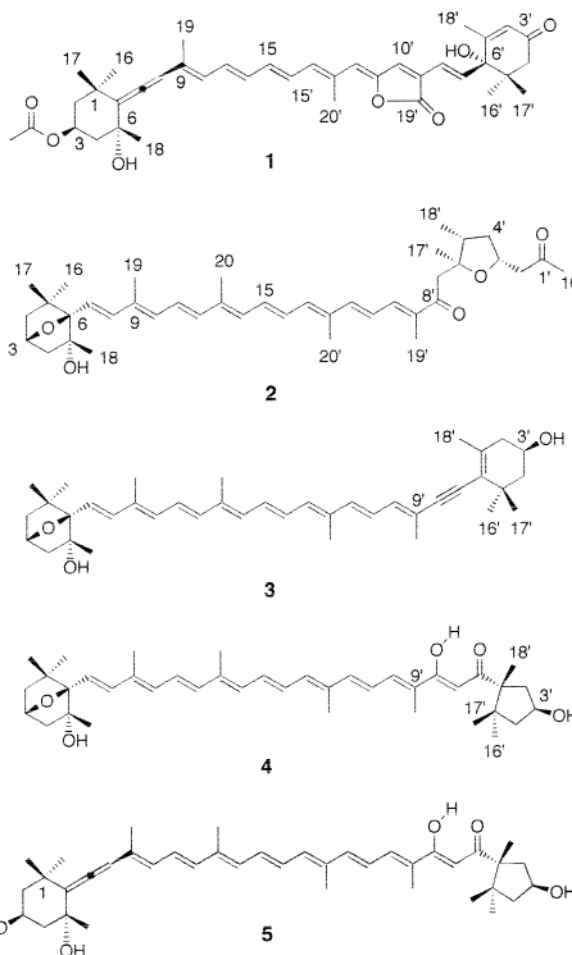
This paper deals with the isolation and structural elucidation of these five carotenoids and with the observed characteristic ions in FAB-MS/MS of **2**, **3**, and **4**.

### Results and Discussion

Acetone extraction of the oyster *C. gigas* (10 kg), followed by treatment with Et<sub>2</sub>O–*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<sub>39</sub>H<sub>48</sub>O<sub>7</sub>. The UV–vis spectrum of **1** in Et<sub>2</sub>O showed an absorption maximum at 457 nm. The <sup>13</sup>C NMR and HSQC spectra of **1** in CDCl<sub>3</sub> confirmed the presence of 39 carbons and 46 carbon-bonded protons. In the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1** the noticeable signals due to three carbonyl carbons and allene groups were observed at  $\delta_C$  170.4, 168.7, and 197.7 and at  $\delta_C$  202.7 and  $\delta_H$  6.06. The NMR and the UV–vis data suggested that **1** was an analogue of peridinin.<sup>3,4</sup> Thus, the NMR data of **1** were compared with those of peridinin.<sup>4</sup>

The <sup>1</sup>H and <sup>13</sup>C NMR signal assignments of **1** in CDCl<sub>3</sub> were made by <sup>1</sup>H–<sup>1</sup>H COSY, HSQC, HMBC, and NOESY experiments. The <sup>1</sup>H assigned data of **1** are given in Table 1, together with those of the other carotenoids (**2–5**). The <sup>13</sup>C data of **1** and **4** are presented in the Experimental Section. The <sup>1</sup>H and <sup>13</sup>C data of **1** were almost identical with those of peridinin<sup>4</sup> 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 <sup>1</sup>H and <sup>13</sup>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 <sup>1</sup>H–<sup>1</sup>H 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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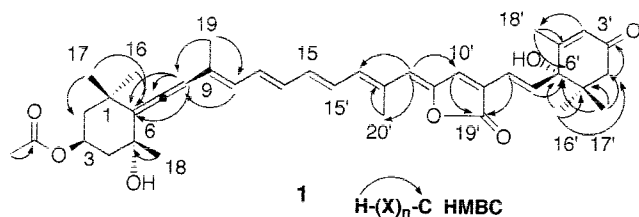
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**Table 1.**  $^1\text{H}$  NMR (500 MHz) Data of Carotenoids **1**–**5** in  $\text{CDCl}_3^{a,b}$ 

$^1\text{H}$ no.	<b>1</b> $\delta$ mult. (J, Hz)	<b>2</b> $\delta$ mult. (J, Hz)	<b>3</b> $\delta$ mult. (J, Hz)	<b>4</b> $\delta$ mult. (J, Hz)	<b>5</b> $\delta$ mult. (J, Hz)
H-2 $\alpha$	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 $\beta$	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-4 $\alpha$	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 $\beta$	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
$\text{CH}_3\text{CO}$	2.04 s				
H-2' $\alpha$	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' $\beta$	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' $\alpha$	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' $\beta$		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

<sup>a</sup>  $^1\text{H}$  chemical shifts are reported downfield from internal TMS (=0.00). <sup>b</sup>  $^1\text{H}$  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**.

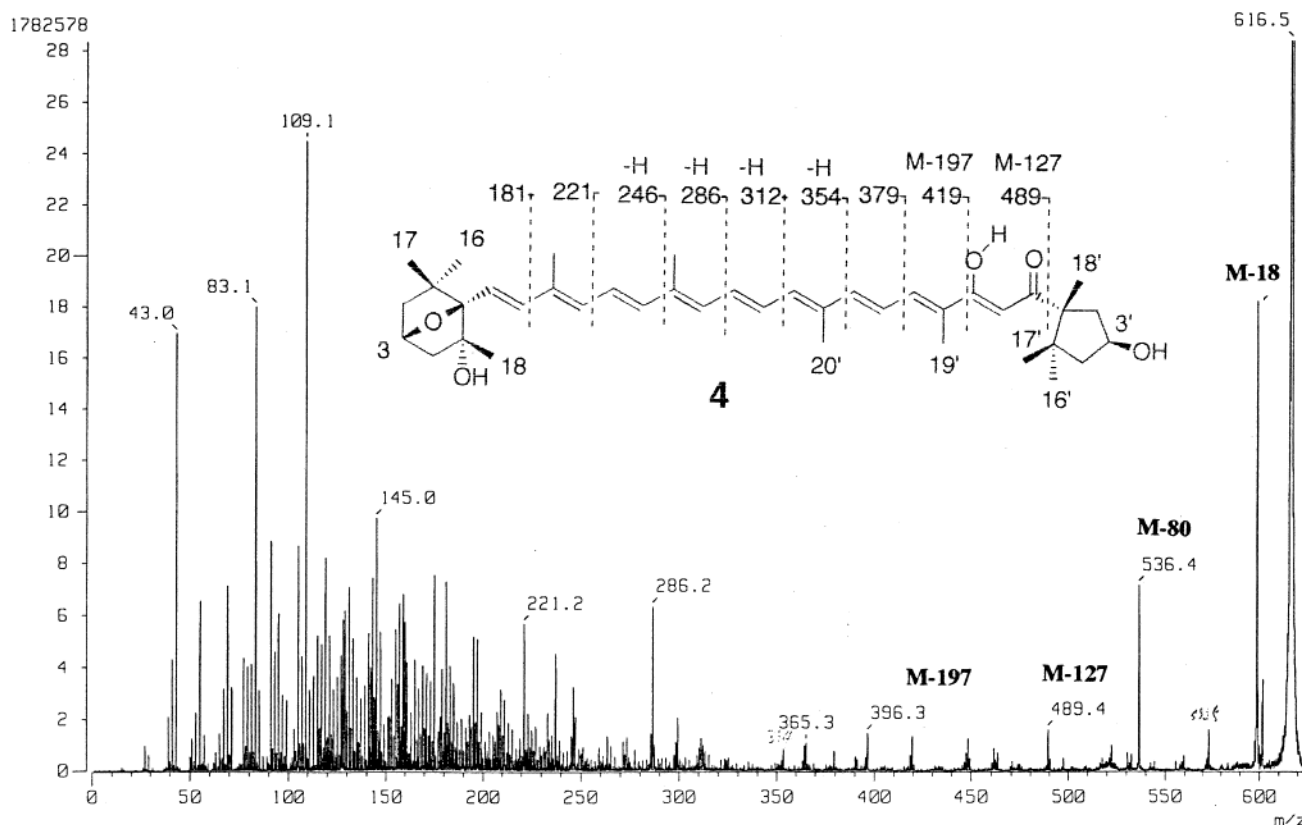
proton(s). The other observed NOE cross-peaks between the remaining protons in **1** were almost identical with those in peridinin.<sup>4</sup> Thus, the relative stereochemistry of **1** was assigned as shown in Figure 1. The CD spectrum of **1** showed characteristic Cotton effects similar to those of amarouciaxanthin A,<sup>5</sup> 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- $\beta$ , $\epsilon$ -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  $\text{Et}_2\text{O}$  showed absorption maxima at 443 and 468 and at 446 and 476 nm, respectively. The molecular formulas of **2** and **3** were determined as  $\text{C}_{40}\text{H}_{56}\text{O}_5$  and  $\text{C}_{40}\text{H}_{54}\text{O}_3$  by HREIMS, respectively.

As can be seen from Table 1, the  $^1\text{H}$  chemical shifts and the spin-couplings of H2 to H20 in **2** and **3** were almost

identical with those in cycloviolaxanthin.<sup>6</sup> 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<sup>2</sup> and alloxanthin,<sup>4</sup> 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  $^1\text{H}$ - $^1\text{H}$  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  $\text{C}_{40}\text{H}_{56}\text{O}_5$ , as established by HREIMS. The UV-vis spectrum of **4** in  $\text{Et}_2\text{O}$  showed an absorption maximum at 464 nm. As shown in Table 1, the  $^1\text{H}$  chemical shifts and the spin-couplings of H2 to H20 in **4** were almost identical with those in cycloviolaxanthin.<sup>6</sup> The  $^1\text{H}$  NMR signals of the remaining protons in **4** were similar to those in mytiloxanthin.<sup>7</sup> Thus, the structure of **4** was determined to be made up of the corresponding partial structures in cycloviolaxanthin and mytiloxanthin. The relative stereochemistry of **4** was also supported by the results of the NOESY (Figure S1) and  $^1\text{H}$ - $^1\text{H}$  COSY experiments and the  $^{13}\text{C}$  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*)<sup>6b</sup> and alloxanthin (3*R*),<sup>8</sup> by the use of the additivity rules of CD spectra of dichiral carotenoids.<sup>8</sup> 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.<sup>6b</sup>

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- $\beta$ , $\varphi$ -carotene-1',8'-dione, (3*S*,5*R*,6*R*,3'*R*)-3,6-epoxy-7',8'-didehydro-5,6-dihydro- $\beta$ , $\beta$ -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- $\beta$ , $\kappa$ -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<sub>40</sub>H<sub>56</sub>O<sub>5</sub>. The UV-vis spectrum of **5** in Et<sub>2</sub>O showed an absorption maximum at 457 nm. The chemical structure of **5** was deduced to be that shown by comparing the <sup>1</sup>H NMR data of **5** with those of the corresponding partial structures in fucoxanthinol<sup>4</sup> and mytiloxanthin.<sup>7</sup> The relative stereochemistries in the end groups of **5** were supported by the NOESY correlations and the magnitudes of <sup>1</sup>H-<sup>1</sup>H spin-couplings in Table 1. The CD spectrum of **5** was similar to that of fucoxanthinol,<sup>8</sup> 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'-tetrahydroxy-6,7-didehydro-5,6-dihydro- $\beta$ , $\kappa$ -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<sup>+</sup> (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]<sup>+</sup> and [M - 80]<sup>+</sup>.<sup>9</sup> The characteristic product ions were also observed for the CID MS spectra of the M<sup>+</sup> of **2** and **3**.

In addition to the new carotenoids **1-5**, 17 known carotenoids (see Experimental Section) were isolated and identified by UV-vis, EIMS, CD, and <sup>1</sup>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<sub>2</sub>O. 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 mA; collision gas, argon; collision cell voltage, 3 kV. The <sup>13</sup>C (125 MHz) and <sup>1</sup>H NMR (500 MHz) spectra were recorded on a Varian UNITY INOVA 500 spectrometer in CDCl<sub>3</sub> with TMS as an internal standard. The <sup>13</sup>C NMR spectra of **1** (0.5 mg) and **4** (1 mg) were measured in 40  $\mu$ L of CDCl<sub>3</sub> 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 (<sup>1</sup>J<sub>CH</sub> optimized for 142 Hz), and gHMBC (<sup>n</sup>J<sub>CH</sub> 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<sub>2</sub>O 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<sup>2</sup> have been deposited at Kyoto Pharmaceutical University.

**Extraction and Isolation of Carotenoids.** The Me<sub>2</sub>CO extract of the edible parts of *C. gigas* (10 kg) was partitioned between *n*-hexanes–Et<sub>2</sub>O (1:1) and aqueous NaCl. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and then concentrated to dryness. The residue was subjected to column chromatography (CC) on Si gel using an increasing percentage of Me<sub>2</sub>CO in *n*-hexane. The fraction eluted with *n*-hexane–Me<sub>2</sub>CO (1:1) from a Si gel column was purified by HPLC on silica with *n*-hexane–Me<sub>2</sub>CO (7:3) and further purified by HPLC on ODS with CHCl<sub>3</sub>–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<sub>2</sub>CO from a Si gel column was further purified by HPLC on silica with *n*-hexane–Me<sub>2</sub>CO (6:4) and on ODS with CHCl<sub>3</sub>–MeCN (1:9) to yield **5** (0.5 mg).

In the present isolation, the following additional known carotenoids<sup>3,4,8,9</sup> were isolated and identified by UV–vis, EIMS, <sup>1</sup>H NMR, and CD spectral data: alloxanthin (5 mg) and its 3-acetate (3 mg), 8'-apo-alloxanthin (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<sub>2</sub>O) λ<sub>max</sub> 457 nm; CD (Et<sub>2</sub>O) λ<sub>ext</sub>(Δε) 225 (–6.8), 255 (+10.2), 352 (–6.1); <sup>1</sup>H NMR (CDCl<sub>3</sub>), Table 1; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 14.0 (q, C-19), 15.4 (q, C-20'), 18.9 (q, C-18'), 21.4 (q, CH<sub>3</sub>CO), 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<sub>3</sub>CO), 197.7 (s, C-3'), 202.7 (s, C-7); EIMS *m/z* 628 [M]<sup>+</sup> (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<sub>39</sub>H<sub>48</sub>O<sub>7</sub>, 628.3394).

**Carotenoid 2:** orange, amorphous solid; UV–vis (Et<sub>2</sub>O) λ<sub>max</sub> 443, 468 nm (%III/II = 65); CD (Et<sub>2</sub>O) λ<sub>ext</sub>(Δε) 235 (–1), 285 (+1), 325 (–1); <sup>1</sup>H NMR (CDCl<sub>3</sub>), Table 1; EIMS *m/z* 616 [M]<sup>+</sup> (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<sub>40</sub>H<sub>56</sub>O<sub>5</sub>, 616.4125).

**Carotenoid 3:** orange, amorphous solid; UV–vis (Et<sub>2</sub>O) λ<sub>max</sub> 446, 476 nm (%III/II = 65); CD (Et<sub>2</sub>O) λ<sub>ext</sub>(Δε) 240 (–2),

275 (0), 320 (–1.7); <sup>1</sup>H NMR (CDCl<sub>3</sub>), Table 1; EIMS *m/z* 582 [M]<sup>+</sup> (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<sub>40</sub>H<sub>54</sub>O<sub>3</sub>, 582.4072).

**Carotenoid 4:** red, amorphous solid; UV–vis (Et<sub>2</sub>O) λ<sub>max</sub> 464 nm; CD (Et<sub>2</sub>O) λ<sub>ext</sub>(Δε) 240 (–0.5), 280 (+1), 360 (–2); <sup>1</sup>H NMR (CDCl<sub>3</sub>), Table 1; <sup>13</sup>C NMR (CDCl<sub>3</sub>) 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]<sup>+</sup> (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<sub>40</sub>H<sub>56</sub>O<sub>5</sub>, 616.4125).

**Carotenoid 5:** red, amorphous solid; UV–vis (Et<sub>2</sub>O) λ<sub>max</sub> 468 nm; CD (Et<sub>2</sub>O) λ<sub>ext</sub>(Δε) 227 (–1.5), 290 (–3), 370 (–1); <sup>1</sup>H NMR (CDCl<sub>3</sub>), Table 1; EIMS *m/z* 616 [M]<sup>+</sup> (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<sub>40</sub>H<sub>56</sub>O<sub>5</sub>, 616.4125).

**Supporting Information Available:** Figure S1 indicating NOE-SY 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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