Structure of Minor Carotenoids from the Crown-of-Thorns Starfish, *Acanthaster planci*

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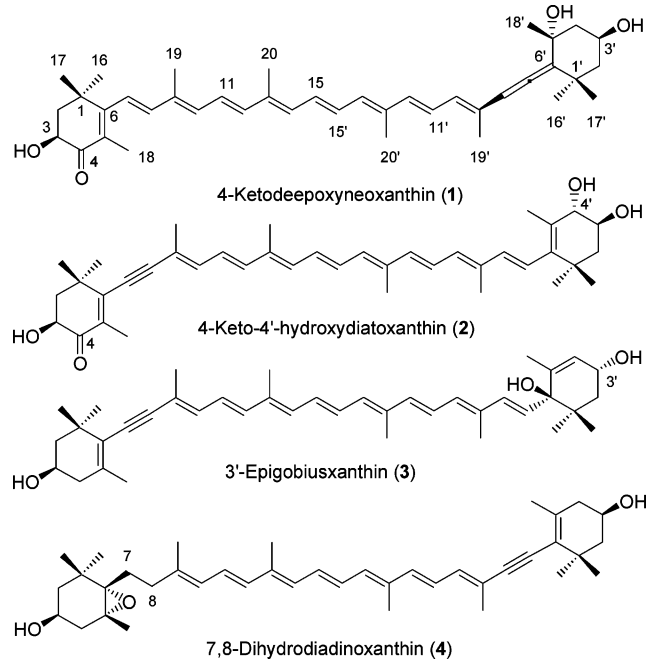
Four new carotenoids, named 4-ketodeepoxyneoxanthin (**1**), 4-keto-4′-hydroxydiatoxanthin (**2**), 3′-epigobiusxanthin (**3**), and 7,8-dihydrodiadinoxanthin (**4**), were isolated from the crown-of-thorns starfish, *Acanthaster planci.* Their structures were determined on the basis of chemical and spectroscopic data.

Marine animals, especially invertebrates, contain various carotenoids with structural diversity.[1,2] The crown-of-thorns starfish (*Acanthaster planci*) is a large, nocturnal sea star that preys upon coral polyps. The crown-of-thorns receives its name from the venomous thorn-like spines covering its body. In 1976, 7,8-didehydroastaxanthin was reported to be a major carotenoid in *A. planci*.[3] However, the detailed carotenoid composition in *A. planci* was uncertain. In the course of our studies on carotenoids in marine animals,[4–7] four new carotenoids (**1**−**4**) were isolated from *A. planci* as minor components along with the major carotenoids 7,8-didehydroastaxanthin, peridininol, and astaxanthin and several other minor carotenoids including 7,8,7′,8′-tetrahydroastaxanthin, diadinoxanthin, diatoxanthin, and alloxanthin. This paper reports the isolation and structure elucidation of these new carotenoids.

An acetone (Me_2CO) extract of *A. planci* (1870 g) was chromatographed on silica gel using an increasing percentage of Me_2CO in hexane. The fraction eluted with Me_2CO−hexane (6:4) was subjected to HPLC on silica gel with Me_2CO−hexane (4:6) and then on ODS silica with $CHCl_3$−MeCN (2:8) to yield **1** (0.14 mg), **2** (0.40 mg), **3** (0.10 mg), and **4** (0.20 mg).

The structures of these new carotenoids were elucidated on the basis of spectroscopic data and chemical derivatization. Due to the small amount of available samples, direct ^{13}C NMR measurement could not be performed. Thus, ^{13}C chemical shifts were derived from $^1H-^{13}C$ HSQC and $^1H-^{13}C$ HMBC spectra.

Compound **1** showed a broad UV−vis absorption maximum from 445−476 nm without fine structure, indicating the presence of a conjugated carbonyl group.[8] The molecular formula of **1** was determined to be $C_{40}H_{54}O_4$ by high-resolution FABMS. Regarding the four oxygen atoms, one was presented in a carbonyl group (δ_C 200.4), one was presented in a tertiary hydroxy group (δ_C 73.5), and the remaining two were presented in secondary hydroxy groups (δ_C 69.3, δ_H 4.30 and δ_C 64.3, δ_H 4.32) on the basis of NMR and acetylation. ^1H and ^{13}C NMR data of **1** (Table 1) showed the presence of a 3-hydroxy-4-keto-β-end group, a 3,5-dihydroxy-5,6-dihydro-β-end group, and a polyene chain containing an allenic group.[9] This structure was confirmed by COSY, HSQC, HMBC, and NOESY experiments. The chemical shifts and coupling constants of the new compound were fully in accordance with the presented constitution and configuration. Thus, the structure of **1** was determined to be 3,3′,5′-trihydroxy-6′,7′-didehydro-5′,6′-dihydro-β,β-caroten-4-one. The chemical shift of the allenic proton (H-8′) occurred at δ 6.04. On the basis of the diagnostic ^1H NMR data of allenic carotenoids,[10,11] the relative configuration of the allenic end group of **1** was compatible with a 3*S*,5*R*,6*R* structure. Furthermore, all allenic carotenoids that have been isolated from nature show the 3*S*,5*R*,6*R* absolute configuration.[12,13] The CD spectrum of **1** showed a similar curve to that of deepoxyneoxanthin,[14] except that the wavelength shift was about 15 nm longer than that of **1**, which is attributed to the presence of a carbonyl group at C-4 in **1**. This indicated that **1** had the same absolute configuration as deepoxyneoxanthin. Therefore, the 3*S*,3′*S*,5′*R*,6′*R* configuration was assigned to this compound. This structure corresponds to the 4-keto derivative of deepoxyneoxanthin. Therefore, **1** was named 4-ketodeepoxyneoxanthin.



Compound **2** showed a broad UV−vis absorption maximum of 450−471 nm without a fine structure, indicating the presence of a conjugated carbonyl group.[8] The molecular formula of **2** was determined as $C_{40}H_{52}O_4$ by high-resolution FABMS. Regarding the four oxygen atoms, one was present in a carbonyl group (δ_C 199.8) and three were present in secondary hydroxy groups (δ_C 69.2, δ_H 4.33; δ_C 71.6, δ_H 3.80; and δ_C 78.5, δ_H 3.95) on the basis of NMR data and acetylation. ^1H and ^{13}C NMR spectra of **2** (Table 1) showed the presence of a 7,8-didehydro-3-hydroxy-4-keto-β-end group, a 3,4-*trans*-3,4-dihydroxy-β-end group, and an all-*trans* polyene chain.[9] This was also confirmed by 2D NMR experiments. The

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Table 1. ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) Data of **1**−**4** ($CDCl_3$)

	1		**2**		**3**		**4**	
	δ_C[a]	δ_H (J in Hz)	δ_C[a]	δ_H (J in Hz)	δ_C[a]	δ_H (J in Hz)	δ_C[a]	δ_H (J in Hz)
1	36.9		37.0		36.6		36.6	
2	45.8	α 2.16, dd (13, 6) β 1.82, dd (13, 13)	45.6	α 2.22, dd (13, 6) β 1.82, dd (13, 13)	46.7	α 1.84, ddd (12,3,1.5) β 1.45, dd (12, 12)	48.4	α 1.45, dd (12, 12) β 1.23, overlapped
3	69.3	4.30, overlapped	69.2	4.33, ddd (13, 6, 1.5)	65.0	3.39, m	64.5	3.84, m
4	200.4		199.8		41.7	α 2.43, ddd (18,5, 1.5) β 2.07, dd (18, 10)	41.7	α 2.32, ddd (14, 5, 1.5) β 1.63, dd (14, 9)
5	127.0		133.1		137.6		65.6	
6	162.2		147.8		124.5		69.0	
7	123.3	6.22, d (15.5)	88.1		89.7		36.5[b]	∼2.28
8	142.0	6.43, d (15.5)	111.7		98.6		37.4[b]	∼2.25
9	134.0		117.8		119.3		140.0	
10	135.1	6.30, d (11)	n.a.[c]	6.62, d (11)	135.1	6.46, d (11)	125.5	5.94, d (11)
11	125.0	6.62, dd (15, 11)	n.a.	6.52, dd (14, 11)	124.3	6.51, dd (15, 11)	ca. 124.7	6.51, dd (15, 11)
12	n.a.	6.45, d (15)	n.a.	6.45, d (14)	138.0	6.37, d (15)	135.1	6.24, d (15)
13	136.2		137.0		136.6		n.a.	
14	133.8	6.30, d (11)	135.3	6.34, d (11)	133.5	6.29, m	131.1	6.20, d (11)
15	130.4	6.66, m	130.6	6.66, m	ca. 130.7	6.64, m	ca. 130.7	6.64, m
16	26.2	1.32, s	31.1	1.35, s	29.0	1.15, s	25.7	1.07, s
17	30.8	1.23, s	26.5	1.31, s	30.0	1.20, s	29.1	1.20, s
18	14.0	1.95, s	14.5	2.03, s	22.9	1.92, s	21.4	1.37, s
19	13.0[b]	2.00, s	17.8	2.05, s	13.0	2.03, s	17.6	1.81, s
20	12.9[b]	1.97, s	13.0	1.99, s	18.6	1.97, s	13.0	1.95, s
1′	36.5		37.6		39.7		36.6	
2′	49.6	α 1.95, overlapped β 1.34, overlapped	44.9	α 1.75, dd (13, 3.5) β 1.59, dd (13, 13)	44.4	α 1.79, dd (13, 6) β 1.58, overlapped	46.7	α 1.84, ddd (12, 3, 1.5) β 1.45, dd (12, 12)
3′	64.3	4.32, overlapped	71.6	3.80, ddd (13, 7, 3.5)	66.4	4.30, m	65.0	3.39, m
4′	49.0	α2.27,ddd (13, 5, 15) β 1.51, overlapped	78.5	3.95, d (7.5)	127.5	5.57, br s	41.7	α 2.43, ddd (18, 5, 1.5) β 2.07, dd (18, 10)
5′	73.5		128.5		139.0		137.6	
6′	118.2		141.0		79.2		124.5	
7′	n.a.		125.5	6.07, d (15.5)	131.3	5.73, d (15.5)	89.7	
8′	103.3	6.04, s	139.0	6.16, d (15.5)	134.3	6.30, d (15.5)	98.6	
9′	132.9		136.5		135.0		119.3	
10′	128.4	6.12, d (11)	132.0	6.17, d (11)	132.3	6.22, d (11)	135.1	6.46, d (11)
11′	125.6	6.57, dd (15, 11)	125.7	6.62, dd (15, 11)	ca. 130.0	6.62, dd (15, 11)	124.3	6.51, dd (15, 11)
12′	n.a.	6.35, d (15)	n.a.	6.38, d (15)	137.8	6.35, d (15)	138.0	6.37, d (15)
13′	136.2		136.5		136.5		136.6	
14′	132.3	6.26, d (11)	132.8	6.28, d (11)	132.8	6.26, m	133.5	6.29, m
15′	130.4	6.66, m	130.6	6.66, m	130.7	6.66, m	ca. 130.7	6.64, m
16′	29.4	1.34, s	28.5	1.10, s	22.9	1.04, s	29.0	1.15, s
17′	32.2	1.07, s	30.4	1.08, s	25.3	0.93, s	30.0	1.20, s
18′	31.4	1.35, s	16.9	1.81, s	18.2	1.67, s	22.9	1.92, s
19′	14.1	1.81, s	13.0	1.97, s	13.9	1.93, s	13.0	2.03, s
20′	12.9[b]	1.98, s	13.0	1.97, s	13.0	1.96, s	18.6	1.97, s
OH		3.69, d (1.5)		3.69, d (1.5)				

[a] ^{13}C chemical shifts were measured from HSQC and HMBC experiment. [b] Assignments may be exchangeable. [c] n.a.: not assigned.

coupling constant of $J_{3'-4'} = 7.5$ Hz at H-4′ (δ 3.95) indicated that the 3′, 4′ glycol had a *trans* configuration.[9] The CD spectrum of **2** was similar to that of pectenolone,[15] having the same chromophore system. Therefore, a 3*S*,3′*S*,4′*S* configuration was assigned to this compound. Thus, the structure of **2** was determined as (3*S*,3′*S*,4′*S*′)-3,3′,4′-trihydroxy-7,8-didehydro-β,β-caroten-4-one, and the compound was named 4-keto-4′-hydroxydiatoxanthin. This compound was assumed to be an oxidized metabolite of diatoxanthin. Compound **2** is an acetylenic bond positional isomer of a very similar carotenoid, (3*S*,3′*S*,4′*S*′)-3,3′,4′-trihydroxy-7′,8′-didehydro-β,β-caroten-4-one, which was isolated from the starfish *Asterina pectinifera* and *Asterias amurensis*.[15]

Compound **3** showed UV−vis absorption maxima at 420, 445, and 475 nm. The molecular formula of **3** was determined as $C_{40}H_{54}O_3$ by high-resolution FABMS. The presence of two secondary hydroxy groups (δ_C 65.0, δ_H 3.99 and δ_C 66.4, δ_H 4.30) and one tertiary hydroxy group (δ_C 79.2) in **3** was revealed by NMR, MS data, and acetylation. The presence of two secondary hydroxy groups at C-3 and C-3′ and one tertiary hydroxy group at C-6′ was revealed by COSY and HMBC data. ^{1}H and ^{13}C NMR data of **3** (Table 1) showed the presence of a 7,8-didehydro-3-hydroxy-β-end group and an all-*trans* polyene chain. The remaining structural part was assigned to a 3′,6′-dihydroxy-ε-end group on the basis of COSY, HSQC, and HMBC data. Therefore, the planar structure of **3** was determined as 7,8-didehydro-β,ε-carotene-3,3′,6′-triol, which showed the same constitution as gobiusxanthin isolated from the common freshwater goby *Rhinogobius brunneus*.[16] However, ^{1}H chemical shifts of the 3′,6′-dihydroxy-ε-end group in **3** were slightly different from those of gobiusxanthin,[16] exhibiting a 3*R*,3′*S*,6′*R* configuration. This suggested that **3** might be an epimer of gobiusxanthin. The relative configuration of the 3′,6′-dihydroxy-ε-end group in **3** was elucidated by performing a NOESY experiment. In the cases of gobiusxanthin,[16] salmoxanthin,[17] and deepoxysalmoxanthin,[17] which have a 3′,6′-*cis*-dihydroxy-ε-end group, NOESY correlations for H-16′/H-3′ and H-16′/H-7′ were observed.[17] However, the NOESY correlation for H-16′/H-3′ was not noted in **3**, as shown in Figure 1. This clearly indicated that **3** was a 3′-epimer of gobiusxanthin. These stereostructures were also confirmed using the *ab initio* molecular orbital method employing the Gaussian 03 program (see Supporting Information). It has been

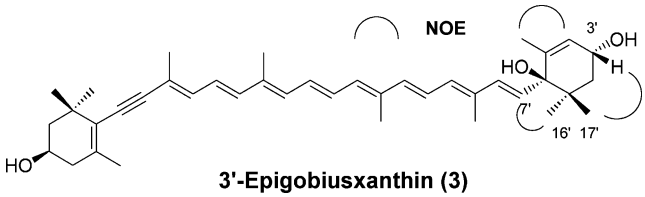

Figure 1. Key NOESY correlations of 3′-epigobiusxanthin (**3**).

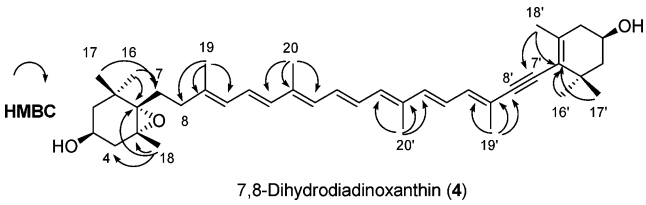

Figure 2. Key HMBC correlations of 7,8-dihydrodiadinoxanthin (**4**).

reported that CD spectra of carotenoids with an ε-end group mainly reflect the chirality at C-6.[18] As with gobiusxanthin, **3** showed a negative Cotton effect around 280 nm in the CD spectrum, indicating a 6′*R* configuration.[16–18] Therefore, the structure of **3** was determined to be (3*R*,3′*R*,6′*R*)-7,8-didehydro-β,ε-carotene-3,3′,6′-triol, and the compound was named 3′-epigobiusxanthin.

Compound **4** showed UV−vis absorption maxima at 405, 430, and 460 nm. The molecular formula of **4** was determined to be $C_{40}H_{56}O_3$ by HRFABMS data. The presence of two secondary hydroxy groups in **4** was consistent with the formation of a diacetate. The ^{1}H NMR spectrum of **4** showed 10 methyl signals, 12 methylene signals, two oxy methine signals, and 10 olefinic proton signals. ^{1}H and ^{13}C NMR data of **4** (Table 1) revealed the presence of an alloxanthin moiety (C-1′ to C-20′). The remaining structural part (C-1 to C-20) was elucidated by ^{1}H−^{1}H COSY, HSQC, HMBC, and NOESY experiments. The presence of a hydroxy group at C-3 (δ_H 3.84, δ_C 64.5) was revealed by COSY, HSQC, and HMBC data. HMBC correlations from δ_H 1.37 (H-18) to δ_C 65.6 and 69.0, from δ_H 1.07 (H-16) to δ_C 69.0, and from δ_H 1.20 (H-17) to δ_C 69.0 revealed that the two quaternary carbons at δ_C 65.6 and 69.0 were epoxy carbons at C-5 and C-6, respectively. Furthermore, characteristic HMBC correlations from δ_H 1.07 (H-16) and 1.20 (H-17) to a methylene carbon at δ_C 36.5 (C-7) and from δ_H 1.81 (H-19) to a methylene carbon at δ_C 37.4 (C-8) were observed. This clearly indicated the presence of a $-CH_2-CH_2-$ single bond at C-7/C-8 in **4**, as shown in Figure 2. The structure of **4** was thus determined to be 5,6-epoxy-7,8-dihydro-7′,8′-didehydro-β,β-carotene-3,3′-diol. This structure corresponds to a 7,8-dihydro derivative of diadinoxanthin. Therefore, compound **4** was named 7,8-dihydrodiadinoxanthin. The chirality of this compound could not be determined from CD spectroscopic data because it showed a very weak CD spectrum. Diadinoxanthin, having (3*S*,5*R*,6*S*,3′*R*) chirality, is assumed to be the precursor of this compound. Therefore, the (3*S*,5*R*,6*S*,3′*R*) configuration is tentatively proposed for **4**.

In conclusion, four new carotenoids with either an allenic group (**1**) or an acetylenic group (**2**−**4**) were isolated from the starfish *A. planci.*

Experimental Section

General Experimental Procedures. The UV−vis spectra were recorded with a Hitachi U-2001 spectrophotometer in Et_2O. The CD spectra were recorded in Et_2O at room temperature with a JASCO J-720 WI spectropolarimeter. The ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were measured with a Varian UNITY INOVA 500 spectrometer in $CDCl_3$ with TMS as an internal standard. The ^{13}C chemical shifts were recorded from ^{1}H−^{13}C HSQC and ^{1}H−^{13}C HMBC spectra. The positive ion FABMS spectra were recorded using a JEOL JMS-HX 110A mass spectrometer with *m*-nitrobenzyl alcohol as a matrix. Preparative HPLC was performed on a Shimadzu LC-6AD with a Shimadzu SPD-6AV spectrophotometer set at 450 nm. The column used was a 250 × 10 mm i.d., 10 μm LiChrospher RP-18 (e) (Cica-Merck, Darmstadt, Germany) and a 300 × 10 mm i.d., 5 μm Chemcosorb 5 Si (Chemco Co., Ltd., Osaka, Japan).

Animal Material. The crown-of-thorns starfish, *Acanthaster planci*, was collected at the Ootsuki coast, Kochi Prefecture, Japan, in August 2009. Voucher specimens (2009-1) have been deposited at the Research Institute for Production Development.

Extraction and Isolation of Carotenoids. The starfish (10 specimens, 1870 g) were extracted with Me_2CO. The Me_2CO extract was partitioned between Et_2O−hexane (1:1) and H_2O. The organic layer was dried over Na_2SO_4 and then evaporated under reduced pressure. The residual red-colored oil was chromatographed on silica gel using an increasing percentage of Me_2CO in hexane. The fraction eluted with Me_2CO−hexane (6:4) was subjected to HPLC on silica gel with Me_2CO−hexane (4:6) and then on ODS silica with $CHCl_3$−MeCN (2:8) to yield **1** (0.14 mg), **2** (0.40 mg), **3** (0.10 mg), and **4** (0.20 mg). In the present investigation, the following carotenoids were also isolated and identified: β-carotene (0.09 mg), echinenone (0.12 mg), canthaxanthin (0.13 mg), 7,8,7′,8′-tetradehydroastaxanthin (0.16 mg), 7,8-didehydroastaxanthin (2.9 mg), astaxanthin (0.82 mg), pectenolone (0.26 mg), alloxanthin (0.20 mg), diatoxanthin (0.26 mg), diadinoxanthin (0.24 mg), 7,8-dihydrodiadinoxanthin (0.20 mg), 3′-epigobiusxanthin (0.16 mg), pectenol A (0.16 mg), pectenol B (0.33 mg), 4-keto-4′-hydroxydiatoxanthin (0.40 mg), 4-ketodeepoxyneoxanthin (0.14 mg), deepoxyneoxanthin (0.08 mg), heteroxanthin (0.09 mg), and peridininol (1.17 mg).

Quantification of Carotenoids. The amounts of carotenoids were calculated using the extinction coefficient of $E = 2100$ at lambda max.[8] In the HPLC analysis, the relative amounts of individual carotenoids were calculated from the peak area detected at 450 nm.

4-Ketodeepoxyneoxanthin (1): yellow solid; UV−vis (Et_2O) λ_{max} 445−476 nm; CD (20 μg/mL, Et_2O) λ ($\Delta\varepsilon$) 220 (+2.0), 235 (0), 250 (−2.1), 270 (−1,0), 295 (−2.0), 318 (−0.8), 350 (−1.5), and 380 (0) nm; ^{1}H NMR and ^{13}C NMR, Table 1; NOESY correlations, H-16/H-3 and H-7, H-17/H-7, H-18/H-8, H-19/H-7 and H-11, H-20/H-11 and H-15, H-16′/H-3′, H-19′/H-11′, and H-20′/H-11′ and H-15′; HRFABMS *m*/*z* 598.4026 [M$^+$] (calcd for $C_{40}H_{54}O_4$, 598.4022). Acetylation of **1** with acetic anhydride in pyridine at room temperature for 1 h gave a diacetate of **1**: FABMS *m*/*z* 682 [M$^+$].

4-Keto-4′-hydroxydiatoxanthin (2): orange solid; UV−vis (Et_2O) λ_{max} 450−471 nm; CD (20 μg/mL, Et_2O) λ ($\Delta\varepsilon$) 210 (0), 220 (+4.5), 250 (0), 258 (+1.8), 298 (−11.5), 329 (0), 3650 (+2.5), and 390 (0) nm; ^{1}H NMR and ^{13}C NMR, Table 1; NOESY correlations, H-16/H-3 and H-2α, H-17/H-2β, H-19/H-11, H-20/H-11 and H-15, H-16′/H-3′, H-2′α, and H-7′, H-17′/H-2′β and H-7′, H-18′/H-4′ and H-8′, H-19′/H-8′ and H-11′, and H-20′/H-11′ and H-15′; HRFABMS *m*/*z* 596.3870 [M$^+$] (calcd for $C_{40}H_{52}O_4$, 596.3865); Acetylation of **2** with acetic anhydride in pyridine at room temperature for 1 h gave a triacetate of **2**: FABMS *m*/*z* 722 [M$^+$].

3′-Epigobiusxanthin (3): yellow solid; UV−vis (Et_2O) λ_{max} 420, 445, and 475 nm; CD (20 μg/mL, Et_2O) λ ($\Delta\varepsilon$) 228 (0), 234 (+2.0), 250 (0), 278 (−6.5), 325 (0), 334 (+2.2), 345 (0), and 365 (0) nm; ^{1}H NMR and ^{13}C NMR, Table 1; NOESY correlations, H-16/H-3 and H-2α, H-17/H-2β, H-19/H-11, H-20/H-11 and H-15, H-16′/H-3′, H-2′α/H-3′, H-17′/H-2′β and H-7′, H-18′/H-4′ and H-8′, H-19′/H-8′ and H-11′, and H-20′/H-11′ and H-15′; HRFABMS *m*/*z* 582.4076 [M$^+$] (calcd for $C_{40}H_{54}O_3$, 582.4073). Acetylation of **3** with acetic anhydride in pyridine at room temperature for 1 h gave a diacetate of **3**: FABMS *m*/*z* 666 [M$^+$].

7,8-Dihydrodiadinoxanthin (4): yellow solid; UV−vis (Et_2O) λ_{max} 405, 430, and 460 nm; CD (20 μg/mL, Et_2O) λ ($\Delta\varepsilon$) 250 (−0.5), 260 (0), 267 (+0.1), 315 (−0.2), and 350 (0) nm; ^{1}H NMR and ^{13}C NMR, Table 1; NOESY correlations, H-16/H-3 and H-2α, H-17/H-2β and H-7, H-18/H-4 and H-8, H-19/H-7 and H-11, H-20/H-11 and H-15, H-16′/H-3′, H-2′α/H-3′, H-17′/H-2′β, H-18′/H-4′, H-19′/H-11′, and H-20′/H-11′ and H-15′; HRFABMS *m*/*z* 584.4226 [M$^+$] (calcd for $C_{40}H_{56}O_3$, 584.4229). Acetylation of **4** with acetic anhydride in pyridine at room temperature for 1 h gave a diacetate of **4**: FABMS *m*/*z* 668 [M$^+$].

Deepoxyneoxanthin: CD (20 μg/mL, Et_2O) λ ($\Delta\varepsilon$) 210 (+2.0), 220 (0), 235 (−2.0), 255 (−0.5), 280 (−2.5), 305 (−0.5), 330 (−1.0), and 370 (0) nm.

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Supporting Information Available: ^{1}H NMR, HSQC, HMBC, and CD spectra of new carotenoids (**1**−**4**) and molecular orbital calculation models of 3′-epigobiusxanthin (**3**) and gobiusxanthin. These materials are available free charges via the Internet at http://pubs.acs.org.

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