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New C_{37} Skeletal Carotenoid from the Clam, *Paphia amabillis*

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Carotenoids in the muscle of *Paphia amabillis* (Veneridae) were investigated. Amarouciaxanthin 3-ester (**1a**) was found to be a major carotenoid along with amarouciaxanthin A (**1b**), fucoxanthinol 3-ester (**2**), peridininol 3′-ester (**3**), and a new C_{37} skeletal carotenoid, named hydratopyrrhoxanthinol 3′-ester. This structure was determined to be 3′-acyloxy-3,5,6-trihydroxy-7′,8′-didehydro-5,6-dihydro-12′,13′,20′-trinor-β,β-caroten-19,11-olide (**4**) by UV−vis, NMR, and FAB-MS spectral data. The absolute configuration of **4** was postulated to be (3*S*,5*R*,6*R*,3′*R*) on the bases of CD and ROESY data. The fatty acids esterified with hydratopyrrhoxanthinol were assigned as C22:6, C20:1, C20:4, C20:5, C18:0, C18:1, C17:0, C16:0, C16:1, and C14:0 on the basis of FAB-MS data.

KEYWORDS: Carotenoids; clam; *Paphia amabillis*; amarouciaxanthin A ester; hydratopyrrhoxanthinol 3′-ester; NMR; MS

INTRODUCTION

Marine shellfish, especially bivalves (oysters, clams, scallops, ark shells, etc.), contain various carotenoids, which show structural diversity (*1*−*3*). Bivalves accumulate carotenoids derived from their dietary algae and modify them through metabolic reactions (*1*−*3*). Many of the carotenoids present in bivalves are metabolites of fucoxanthin, peridinin, and diatoxanthin (*1*−*3*). Marine clams belonging to the genus *Paphia* are important edible shellfish in southern Japan, and their muscle has a bright red color due to the presence of carotenoids. However, there are few reports on the carotenoids of *Paphia* clams. Only amarouciaxanthin A ester was reported in *Paphia euglypta* (Veneridae, Sudaregai in Japanese) (*4*). In the course of carotenoid studies in shellfish (*4*−*9*), carotenoids in *Paphia amabillis* (Veneridae, Satsuma Akagai in Japanese) were investigated. Recently, amarouciaxnthin A 3′-ester (**1a**), amarouciaxnthin A (**1b**), fucoxanthinol 3-ester (**2**), peridininol 3′-ester (**3**), and a new C_{37} skeletal carotenoid, named hydratopyrrhoxanthinol 3′-ester (**4**), were isolated from the muscle of *P. amabillis*. In the present paper, we describe the carotenoids in *P. amabillis*, including the structural elucidation of a new carotenoid, **4**.

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MATERIALS AND METHODS

Apparatus. The UV−vis spectra were recorded with a Shimadzu UV-240 spectrophotometer in diethyl ether (Et_2O). The CD spectra were recorded in Et_2O at room temperature with a JASCO J-720 WI spectropolarimeter. The positive ion FAB-MS spectra were recorded using a JEOL JMS-HX 110A mass spectrometer with *m*-nitrobenzyl alcohol as a matrix. The ^1H 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. Preparative HPLC was performed on a Shimadzu LC-6AD with a Shimadzu SPD-6AV spectrophotometer set at 450 nm. The column used was a 300 × 10 mm i.d., 6 μm Chemcosorb 5Si (Chemco Co., Ltd., Osaka, Japan). Analytical HPLC was performed on a Cosmosil 5SL-II column (250 × 4.6 mm i.d., 5 μm, Nacalai Tesque Co., Ltd., Kyoto, Japan) with acetone (Me_2CO)/hexane (3:7) at a flow rate of 1.0 mL/min with the same instrument. Preparative gel permeation chromatography (GPC) was performed on an LC-908 HPLC system using a 600 × 20 mm i.d., 16 μm JAIGEL 2H column (Japan Analytical Industry Co., Ltd., Tokyo, Japan) with an RI-5 detector (Japan Analytical Industry Co., Ltd.) and $CHCl_3$ as an eluting solvent at a flow rate of 3.8 mL/min (*9*).

Animal Materials. The clam, *P. amabillis*, was collected on the coast of Mimase in Kochi prefecture, Japan, in May 2008.

Quantification of Carotenoids. The total carotenoid content extracted from *P. amabillis* was calculated using the extinction coefficient of $E_{cm}^{1\%} = 1600$ at λ_{max} (460 nm) in Et_2O. The amount of carotenoids eluted from chromatography was calculated using the extinction coefficient of $E_{cm}^{1\%} = 1600$ at λ_{max} (460 nm) in eluting solvent for fractions 1 and 3 and using the extinction coefficient of $E_{cm}^{1\%} = 1300$ at λ_{max} (455 nm) in eluting solvent for fraction 2 (*10*). On HPLC analysis, the relative amounts of individual carotenoids were calculated from the peak area detected at 450 nm.

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

	amarouciaxanthin A 3-ester (**1a**)			hydratopyrrhoxanthinol 3′-ester (**4**)		
position	δ ^{13}C	δ ^{1}H	mult (*J*, Hz)	δ ^{13}C	δ ^{1}H	mult (*J*, Hz)
1	35.8			40.3		
2	45.4	(eq) 1.99	ddd (12, 4, 2)	45.7	∼1.61	m
		(ax) 1.41	dd (12, 12)			
3	68.0	5.37	m	64.4	4.21	m
4	45.2	(eq) 2.28	ddd (13, 4, 2)	45.2	(eq) 1.90	ddd (13, 4, 2)
		(ax) 1.51	dd (13, 13)		(ax) 1.78	dd (13, 11)
5	72.7			77.5		
6	117.5			79.1		
7	202.4			138.3	7.26	d (16)
8	103.3	6.06	s	119.9	6.52	d (16)
9	132.9			125.3		
10	128.3	6.12	d (11)	135.7	7.09	s
11	126.0	6.63	dd (15, 11)	147.0		
12	138.1	6.35	d (15)	119.0	5.74	s
13	138.7			134.4		
14	132.0	6.27	d (11)	137.8	6.41	d (11)
15	133.3	6.78	dd (14, 11)	129.8	6.64	dd (14, 11)
16	29.2	1.39	s	25.6	1.30	s
17	32.1	1.07	s	26.7	0.87	s
18	31.3	1.35	s	27.4	1.18	s
19	14.0	1.81	s	169.0		
20	12.9	2.00	s	15.4	2.34	s
1′	42.0			36.1		
2′	49.7	2.33	d (18)	42.4	(eq) 1.84	ddd (12, 4, 1.5)
		2.47	d (18)		(ax) 1.57	dd (12, 11)
3′	197.7			67.6	5.04	m
4′	126.0	5.84	s	37.6	(eq) 2.49	ddd (18, 6, 1.5)
					(ax) 2.13	dd (18, 10)
5′	168.0			137.3		
6′	78.5			124.3		
7′	38.6	2.93		90.1		
		3.05	d (17)			
8′	203.4			98.5		
9′	134.8			121.0		
10′	147.1	7.10	d (11)	134.6	6.44	d (11)
11′	123.0	6.54	dd (15, 11)	130.7	6.58	dd (14, 11)
12′	142.3	6.71	d (15)			
13′	135.1					
14′	136.9	6.46	d (11)	133.7	6.41	dd (14, 11)
15′	129.2	6.63	dd (14, 11)	136.9	6.50	dd (14, 11)
16′	24.8	1.06	s	28.7	1.18	s
17′	23.2	1.04	s	30.2	1.20	s
18′	20.8	1.90	s	22.4	1.91	s
19′	11.6	1.96	s	18.1	2.00	s
20′	12.7	2.01	s			
fatty acid part						
CH_2COO-	173.5			173.5		
$CH=CH-$	130.0	5.37	m	130.0	5.37	m
CH_2COO-	34.3	2.28	t (7.5)	34.3	2.28	t (7.5)
$-CH_2-$	25−34	1.25	s	25−34	1.25	s
CH_3	14.1	0.88	t (6.5)	14.1	0.88	t (6.5)

Table 2. Carotenoid Content and Composition of Muscle of *Paphia amabilis*

carotenoid content (mg/100 g of muscle)	2.2
carotenoid composition (%)	
amarouciaxanthin A 3-ester (**1a**)	76.1
amarouciaxanthin A (**1b**)	8.2
fucoxanthinol 3-ester (**2**)	4.2
peridininol 3′-ester (**3**)	4.8
hydratopyrrhoxanthinol 3′-ester (**4**)	5.4
others	1.3

Isolation of Carotenoids. Procedures to isolate carotenoids from the muscle of *P. amabillis* were as follows: The muscle (300 g) was extracted with 1000 mL of Me_2CO twice at room temperature. The Me_2CO extract was partitioned between 1000 mL of Et_2O and 1000 mL of aqueous NaCl, with shaking twice. The organic layer was dried over Na_2SO_4 and then concentrated to dryness. The residue was dissolved in 20 mL of $CHCl_3$ and subjected to silica gel column chromatography (300 × 20 mm). The fraction eluted with 300 mL of Me_2CO/hexane (3:7) (fraction 1) was concentrated to dryness and dissolved in 2 mL of $CHCl_3$. Then, it was subjected to GPC on JAIGEL 2H with $CHCl_3$ as an eluting solvent to yield amarouciaxanthin A esters (**1a**) [retention time (t_R) of 44 min]. The fraction eluted with 400 mL of Me_2CO/hexane (5:5) (fraction 2) was concentrated to dryness and was dissolved 2 mL of $CHCl_3$. Then it was subjected to GPC on JAIGEL 2H with $CHCl_3$ as an eluting solvent. The orange fraction eluted at 44 min was collected and was further purified by preparative HPLC on silica gel with Me_2CO/hexane (4:6) at a flow rate of 2.0 mL/min to yield peridininol 3′-ester (**3**) (t_R of 13−15 min), fucoxanthinol 3-ester (**2**) (t_R of 17−20 min), and a new carotenoid, hydratopyrrhoxanthinol 3′-ester (**4**) (t_R of 24−28 min). The fraction eluted with 200 mL of Me_2CO/hexane (7:3) (fraction 3) was concentrated to dryness and was dissolved in 2 mL of $CHCl_3$. Then it was subjected to preparative HPLC on silica gel with Me_2CO/hexane (4:6) at a flow rate of 2.0 mL/min to yield amarouciaxanthin A (**1b**) (t_R of 29 min).

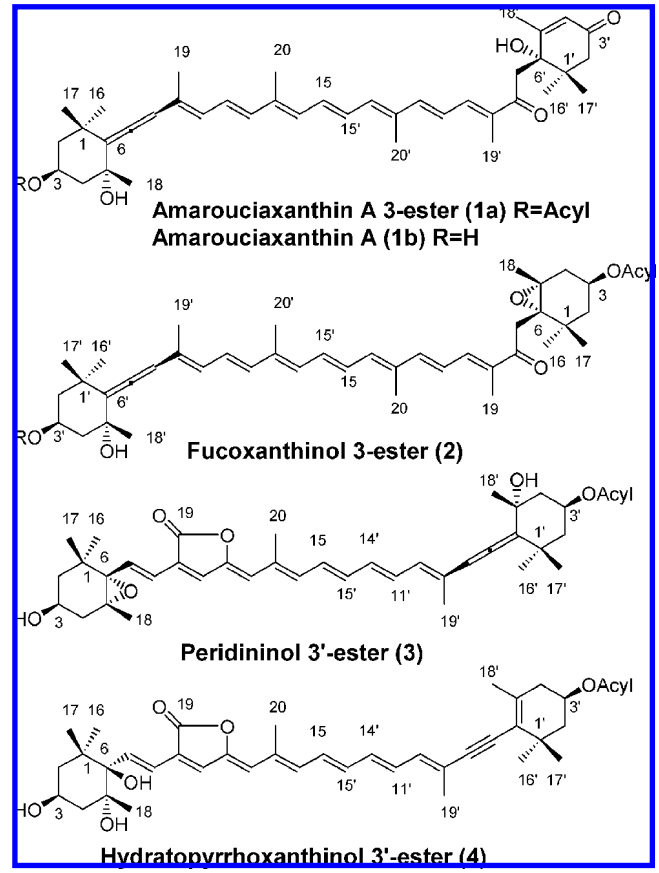

Figure 1. Structures of carotenoids in *Paphia amabilis*.

Hydrolysis of Hydratopyrrhoxanthinol 3′-Ester (4) with Lipase. A 5 mL ethanol solution of hydratopyrrhoxanthinol 3′-ester (0.2 mg/5 mL in EtOH) was added to a 200 mL solution of Lipase-OF (Meito Sangyo Co., Ltd., Tokyo, Japan) (0.9 g/100 mL in ion exchange water). The solution was stirred at 37 °C for 16 h. After this, deacylated carotenoid was extracted with Et_2O from reaction mixtures and purified by preparative HPLC on silica gel with acetone/hexane (4:6) at a flow rate of 2.0 mL/min.

*Amarouciaxanthin 3-ester (**1a**):* UV−vis λ_{max} (Et_2O) 460 nm; CD (Et_2O) λ ($\Delta\varepsilon$) 210 (+3.0), 220 (0), 245 (−45.0), 260 (0), 270 (+17.0), 330 (0), 370 (−5.0), 390 (0); ^{1}H NMR and ^{13}C NMR spectral data (**Table 1**); FAB-MS *m/z* 924 $[M]^+$ amarouciaxanthin A docosahexaenate (C22:6), *m/z* 906 eicosenoate (C20:1), *m/z* 900 eicosatetraenate (C20:4), *m/z* 898 eicosapentaenate (C20:5), *m/z* 880 octadecanoate (C18:0), *m/z* 878 octadecenoate (C18:1), *m/z* 866 heptadecanoate (C17:0), *m/z* 852 hexadecanoate (C16:0), *m/z* 850 hexadecenoate (C16:1), *m/z* 824 tetradecanoate (C14:0).

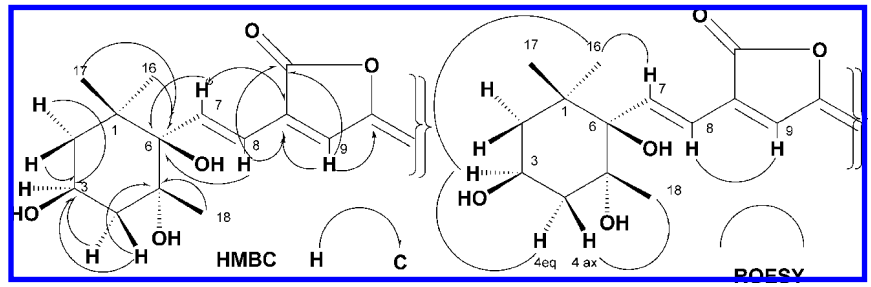

Figure 2. Key HMBC and ROESY correlations in the partial structure of a new carotenoid, **4**.

*Fucoxanthinol 3-ester (**2**):* UV−vis, ^{1}H NMR, and FAB-MS data were agreement with previously published values (*9*).

*Peridininol 3′-ester (**3**):* UV−vis λ_{max} (Et_2O) 455 and 475 nm; ^{1}H NMR was almost identical with that of peridiin (*11, 12*) except for the acetyl signal δ 2.04 instead of the presence of signals of the fatty acid moieties; δ 0.88 (3H, t, J = 7.5 Hz, CH_3), 1.25 (s, CH_2) 2.28 (2H, t, J = 7.5 Hz, $-CH_2-COO$), and 5.37 (1H, m, $-CH=CH-$); FAB-MS *m/z* 882 $[M]^+$ peridininol eicosanoate (C20:0), *m/z* 880 eicosenoate (C20:1), *m/z* 854 octadecanoate (C18:0), *m/z* 852 octadecenoate (C18:1), *m/z* 840 heptadecanoate (C17:0), *m/z* 826 hexadecanoate (C16:0), *m/z* 824 hexadecenoate (C16:1), *m/z* 798 tetradecanoate (C14:0).

*Hydratopyrrhoxanthinol 3′-ester (**4**):* UV−vis λ_{max} (Et_2O) 455 and 475 nm; CD (Et_2O) λ ($\Delta\varepsilon$) 215 (−5.0), 250 (−0.5), 300 (0); ^{1}H NMR and ^{13}C NMR spectral data (**Table 1**); FAB-MS *m/z* 898 $[M]^+$ hydratopyrrhoxanthinol docosahexaenate (C22:6), *m/z* 880 eicosenoate (C20:1), *m/z* 874 eicosatetraenate (C20:4), *m/z* 872 eicosapentaenate (C20:5), *m/z* 854 octadecanoate (C18:0), *m/z* 852 octadecenoate (C18:1), *m/z* 840 heptadecanoate (C17:0), *m/z* 826 hexadecanoate (C16:0), *m/z* 824 hexadecenoate (C16:1), *m/z* 798 tetradecanoate (C14:0).

Hydratopyrrhoxanthinol: UV−vis λ_{max} (Et_2O) 455 and 475 nm; HR FAB-MS *m/z* 588.3453 (calcd for $C_{37}H_{48}O_6$, 588.3451).

*Amarouciaxanthin A (**1b**):* UV−vis, ^{1}H NMR, and FAB-MS data were agreement with previously published values (*13*).

RESULTS AND DISCUSSION

The carotenoid content and composition of the muscle of *P. amabillis* are shown in **Table 2**. Amarouciaxanthin A 3-ester was identified as a major component (76.1% of total carotenoids) along with free amarouciaxanthin A (8.2%), fucoxanthinol 3-ester (4.2%), peridininol 3′-ester (4.8%), and a new C_{37} skeletal carotenoid ester (5.4%), as shown in **Figure 1**.

The structure of amarouciaxanthin A ester (**1a**) was fully characterized on the basis of ^{1}H and ^{13}C NMR (**Table 1**) and FAB-MS spectral data. The ^{1}H NMR signal of H-3 (δ 5.37), which showed a 1.09 ppm downfield shift relative to the corresponding signal in amarouciaxanthin A (*13*), indicated that the hydroxy group at C-3 was acylated. Fatty acids esterified with amarouciaxanthin A were assigned as C24:6, C20:1, C20:4, C20:5, C18:0, C18:1, C17:0, C16:0, C16:1, and C14:0 on the basis of FAB-MS data. There have been no reports on the complete ^{1}H and ^{13}C NMR assignments of amarouciaxanthin A 3-ester (**1a**). Therefore, in the present study, complete ^{1}H and ^{13}C NMR assignments of **1a** (**Table 1**) were made by two-dimensional NMR analysis.

Fucoxanthinol 3-ester (**2**) and peridininol 3′-ester (**3**) were also isolated as minor components. They were characterized from ^{1}H NMR and FAB-MS data. This is the first report of the complete characterization of peridininol 3′-ester (**3**).

Furthermore, a new C_{37} skeletal carotenoid ester (**4**) was isolated. After lipase hydrolysis, the molecular formula of free C_{37} skeletal carotenoid was determined to be $C_{37}H_{48}O_6$ by HR FAB-MS. This carotenoid ester showed absorption maxima at 455 and 475 nm, similar to that of pyrroxanthinol (*10, 12*). ^{1}H and ^{13}C NMR data on this carotenoid ester are shown in **Table 1**. They were assigned on the basis of COSY, ROESY, HSQC, and HMBC spectra and compared with ^{1}H and ^{13}C NMR data on pyrroxanthin and pyrroxanthinol (*11, 12*). ^{1}H and ^{13}C NMR of **4** were almost similar to those of pyrroxanthin (*11, 12*) except for one end group. The acyloxy position was determined to be at C-3′ from the ^{1}H NMR (δ 5.04) and ^{13}C NMR (δ 67.6) signals. The structure of the remaining end group was determined to be a 3,5,6-trihydroxy-5,6-dihydro-β-end group from the two-dimensional NMR data. The positions of two tertiary hydroxy groups at C-5 (δ 77.5) and C-6 (δ 79.1) were confirmed by HMBC experiment, as shown in **Figure 2**. Therefore, the planer structure was determined to be 3′-acyloxy-3,5,6-trihydroxy-7′,8′-didehydro-5,6-dihydro-12′,13′,20′-trinor-β,β-caroten-19,11-olide and named hydratopyrrhoxanthinol 3′-ester (**4**), as shown in **Figure 1**. CD of **4** showed a weak negative Cotton effect, which resembled that of pyrroxanthin (*14*), indicating 3*S*,3′*R* chirality. Key ROESY correlations between CH_3-16 and H-3, between CH_3-16 and H-7, between H-3 and H-4_{eq}, and between CH_3-18 and H-4_{ax} were observed. These data indicated that CH_3-16, H-3, H-4_{eq}, and H-7 are located on the same side of the 3,5,6-trihydroxy-5,6-dihydro-β-end group and that CH_3-18 and H-4_{ax} are located on another side of the end group, as shown in **Figure 2**. Therefore, from the CD and ROESY correlations described above, the (3*S*,5*R*,6*R*,3′*R*) configuration of **4** can be proposed. The fatty acids esterified with hydratopyrrhoxanthinol were assigned as C22:6, C20:1, C20:4, C20:5, C18:0, C18:1, C17:0, C16:0, C16:1, and C14:0 from FAB-MS data.

Hydratopyrrhoxanthinol (3,5,6,3′-tetrahydroxy-7′,8′-didehydro-5,6-dihydro-12′,13′,20′-trinor-β,β-caroten-19,11-olide) was first reported from the edible muscle, *Mytilus edulis*, by Hertzberg et al. (*15*). However, the stereostructure of hydratopyrrhoxanthinol from *M. edulis* was not reported (*15*). The chemical shift values of methyl groups at CH_3-16, -17, and -18 of hydratopyrrhoxanthinol isolated from *M. edulis* (*15*) were slightly different from those of hydratopyrrhoxanthinol 3′-ester (**4**) from *P. amabillis*. Therefore, hydratopyrrhoxanthinol isolated from *M. edulis* is assumed to be a stereoisomer of **4**.

The constitution and compositions, which were estimated by the intensity of molecular ion peaks of FAB-MS (data not shown) of fatty acids esterified with amarouciaxanthin A, peridininol, fucoxanthinol, and hydratopyrrhoxanthinol were almost similar to each other. An odd-numbered fatty acid, heptadecanoic acid (C17:0), was identified as one of the esterified fatty acids in amarouciaxanthin A, peridininol, fucoxanthinol, and hydratopyrrhoxanthinol. Although odd-numbered fatty acids are rare in nature, heptadecanoic acid is sometimes found in marine shellfish (*16*−*18*).

In general, animals do not synthesize carotenoids de novo, and those found in animals are either directly accumulated from food or partly modified through metabolic reactions. The major food sources of marine clams are phytoplankton, such as diatoms

and dinoflagellates (*2*). Fucoxanthin and peridinin are characteristic carotenoids in diatoms and dinoflagellates, respectively (*2*). From the structure of carotenoids isolated from *P. amabillis* and in their food algae, it might be concluded that fucoxanthin and peridinin were metabolized to amarouciaxanthin A and hydratopyrrhoxanthinol, respectively, in *P. amabillis*, and most of these metabolites were accumulated as esterified forms in their muscle.

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