Neodictyoprolenol and Dictyoprolenol, the Possible Biosynthetic Intermediates of Dictyopterenes, in the Japanese Brown Algae *Dictyopteris*

Yuuko Yamamoto, Yoshihiko Akakabe, Kenji Matsui, Hiroshi Shimizu and Tadahiko Kajiwara*

Department of Biological Chemistry, Faculty of Agriculture, Yamaguchi University, Yamaguchi 753–8515, Japan. Fax: +81–839–33–5849.
E-mail: kajiwara@agr.yamaguchi-u.ac.jp

* Author for correspondence and reprint requests

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Dictyopteris, Volatile Compounds, Pheromones

Neodictyoprolenol [(–)-(3*S*)-(1,5*Z*,8*Z*)-undecatrien-3-ol] and dictyoprolenol [(–)-(3*S*)-(1,5*Z*,8*Z*)-undecadien-3-ol]), which had been proposed as possible biosynthetic intermediates of the sex pheromones of marine brown algae such as dictyopterene B [(–)-*trans*-1-((1′*E*,3′*Z*)-hexadienyl)-2-vinylcyclopropane], D′ [(+)-6-((1′*Z*)-butenyl)-1,4-cycloheptadiene] and C′ [(+)-6-butyl-1,4-cycloheptadiene], were again identified in the essential oils from *Dictyopteris prolifera*, *D. latiscula*, and in *D. undulata*, together with the C11-related volatile compounds such as neodictyoprolene, dictyoprolene and dictyopterenes. Incubation of *D. prolifela* preparation with racemic neodictyoprolenol and dictyoprolenol as substrates showed (*S*)-enantioselective decreases of the added substrates and increases in dictyopterenes. From these results, a possible pathway to form dictyopterenes is discussed.

Introduction

As sex pheromones of brown algae, characteristic odoriferous C_{11}-hydrocarbons such as dictyopterenes (B, C′ and D′ in Fig. 1) have been identified from some genera of marine brown algae (Jaenicke, 1977; Boland *et al.*, 1987). They are thought to be key constituents of ocean smell and attractive stuffs for perfume or flavor (Moore *et al.*, 1974).

(+)-(3*S*)-Acetoxy-(1,5*Z*)-undecadiene [dictyoprolene **(+)-1a**] (Yamada *et al.*, 1979) and (+)-(3*S*)-acetoxy-(1,5*Z*,8*Z*)-undecatriene [neodictyoprolene **(+)-2a**] (Yamada *et al.*, 1986) and (3*S*)-(1,5*Z*)-undecadien-3-ol [dictyoprolenol **1**] (Kajiwara *et al.*, 1982), which is proposed as the possible biosynthetic intermediates of dictyopterene A and C′ (Moore *et al.*, 1974), have been identified from two species of marine brown algae, belonging to the genus of *Dictyopteris*. However, neodictyoprolenol [(3*S*)-(1,5*Z*,8*Z*)-undecatrien-3-ol **(–)-2**], the proposed intermediate of dictyopterene B and D′, has not been identified so far.

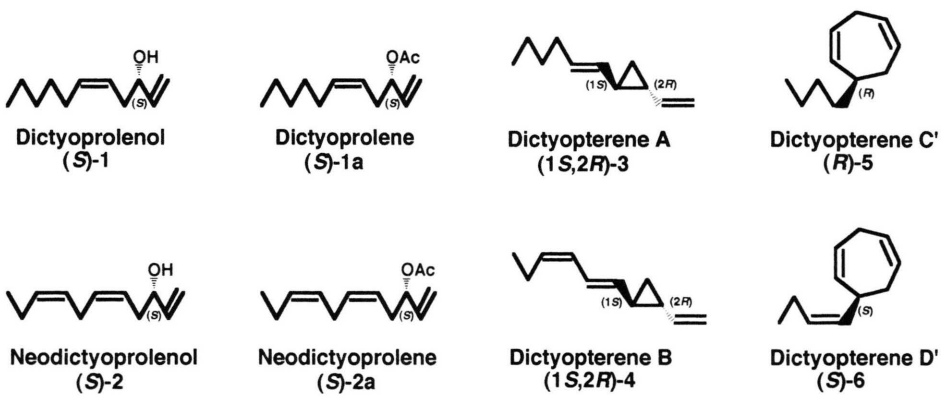

Fig. 1. Chemical structures of C_{11}-compounds identified in *Dictyopteris* oils.

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Here we report identification of **2** and **2a**, and document the complete analyses of contents and optical purities of both dictyopterenes (**3**, **4**, **5** and **6**), the possible intermediates (**1**, **2**) and their acetates (**1a**, **2a**) in essential oils from *D. prolifera*, *D. latiscula*, *D. undulata* and *D. sp.* (unidentified species in *Dictyopteris*). A possible biosynthetic pathway of dictyopterenes via dictyoprolenols (**1**, **2**) is discussed.

Materials and Methods

Plant material

The fresh algae of *Dictyopteris* were washed with filtered sea water and frozen under −20 °C immediately after collection at different growth-locations. (*D. prolifera* (*DP*) and *D. undulata* (*DU*) were collected at Yoshimo Beach, *D. latiscula* (*DL*) at a beach on the west side of Hikoshima Island, and *D. sp.* at a beach around Susa in Yamaguchi prefecture, Japan).

Preparation of essential oil by SDE and examination of the seasonal variation in dictyopterenes and the C_{11}-related compounds

To find the best season for analyses of contents and compositions of all the pheromone-related C_{11}-compounds, the contents of dictyopterenes (**3** and **4**) and dictyoprolenes (**1a** and **2a**) in the essential oil from fronds of *DP* were analyzed every month throughout a year. The essential oil was prepared according to SDE (simultaneous distillation extraction) (Schultz *et al.*, 1977). Frozen *DP* fronds (100 g fr.wt.) were homogenized with distilled water (200 ml), and the homogenate containing the internal standard (I. S., 50 μmol of tridecane and *n*-heptanol, respectively) was immediately subjected to SDE for two hrs with *n*-pentane-dichloromethane (2:1 v/v, 50 ml) as an extraction solvent. The extract was dried over Na_2SO_4 and concentrated at 40 °C. The essential oils thus obtained were analyzed by GC performed with a Shimadzu GC-14B (Japan) on a capillary column of DB-WAX (J & W Scientific, U. S. A.) (column 0.25 mm × 60 m ; flow rate of He 33.5~32.0 cm/min; column temp. 80 °C (10 min) to 200 °C at the rate of 3 °C/min).

Preparation of essential oils by solvent extraction

For analyses of compositions and optical purities of dictyopterenes and the proposed biosynthetic intermediates such as dictyoprolenols and their acetates (dictyoprolenes), essential oils were prepared by solvent extraction as well; 300 g of frozen marine algae fronds were homogenized in 1 liter of *n*-pentane solution containing 30% of methanol, and digested for two weeks in the dark at 15 °C . The pentane layer was separated, and the methanol layer was extracted with *n*-pentane twice and combined with the pentane layer. The combined pentane extract containing I. S. (100 μmol of tridecane and *n*-heptanol, respectively) was washed with brine, dried over Na_2SO_4, concentrated at 40 °C and passed through a florisil column (50 g) with *n*-pentane and ether (200 ml and 100 ml, respectively). The eluate was again concentrated to give an essential oil. The % yields (g/g fresh weight) from *DP*, *DL*, *DU* and *D. sp.* were 4.77×10^{-3}, 4.01×10^{-3}, 3.65×10^{-3} and 3.13×10^{-3}, respectively.

Identification of volatile compounds

The essential oils were analyzed by GC and GC-MS. GC analysis performed with a Shimadzu GC-14B on a capillary column of DB-WAX (column 0.25 mm × 60 m ; flow rate of He 33.5 cm/min; column temp. 80 °C (10 min) to 220 °C at a rate of 3 °C/min). GC-MS analysis was carried out under the same condition on a Shimadzu GC-MS QP5050A (Japan) equipped with DB-WAX. The ionization energy was 70 eV. Most peaks were identified by comparison of retention times and their mass spectra with those of authentic compounds. Dictyoprolenol (**1**), neodictyoprolenol (**2**), dictyoprolene (**1a**), neodictyoprolene (**2a**) and dictyopterenes (**3~6**) were prepared as reported previously (Yamamoto *et al.*, 1999; Kajiwara *et al.*, 1980). The retention times and mass spectra (*m/z* (relative intensity, %)) of dictyopterenes (**3~6**) and the proposed intermediates (**1**, **2**) and their acetates (**1a**, **2a**) were coincided with those of the authentic samples. **5**: 10.48 min; 150 (M^+, 10), 135 (1), 121 (3), 107 (10), 93 (53), 91 (45), 79 (100), 67 (15), 41 (43), 39 (20). **3**: 12.23 min; 150 (M^+, 5), 121 (3), 107 (5), 93 (31), 91 (5), 79 (100), 77(26), 67 (20), 66 (20), 55 (4), 41 (25), 39 (19), 27 (14). **6**: 15.68 min; 148 (M^+, 5), 133 (6), 119 (31), 117 (8),

105 (35), 91 (97), 79(100), 77 (43), 67 (31), 66 (30), 55 (18), 41 (65), 39 (44), 27 (23). **4**: 16.85 min; 15.68 min; 148 (M^+, 5), 133 (6), 119 (31), 105 (35), 91 (94), 79(100), 66 (49), 41 (65), 39 (49), 27 (27). **1a**: 33.98 min; 210 (M^+, 1), 150 (M^+-AcOH, 31), 139 (1), 121 (5), 111 (6), 99 (100), 80 (74), 79 (92), 69 (25), 67 (28), 57 (28), 55 (36). **2a**: 36.94 min; 148 (M^+-AcOH, 6), 133 (3), 119 (28), 105 (25), 91 (52), 79 (100), 67 (71), 55 (48). **1**: 38.02 min; 150 (M^+-H_2O, 2), 141 (1), 126 (3), 112 (11), 95 (2), 83 (25), 69 (29), 57 (100). **2**: 41.01 min; 148 (M^+-H_2O, 5), 119 (1), 112 (3), 88 (4), 79(15), 67 (13), 55 (2), 42 (100).

Examination of optical purities of dictyopterenes, the proposed intermediates and their acetates

The essential oil was fractionated on silica gel 60 N (Merck) with *n*-pentane and 50% diethyl ether solution to afford a dictyopterenes fraction (containing **3**~**6**), an intermediates and their acetates fraction (containing **1**, **2**, **1a** and **2a**), respectively. The dictyopterene fraction was concentrated *in vacuo* and chromatographed on 17% $AgNO_3$-silica gel 60 N (5 g) with 50 ml of *n*-pentane containing 5% ether to give fractions containing **3**, **5**, **4** and **6**, in order of elution. Except for the fraction containing **6**, each one was concentrated appropriately and subjected directly to a chiral GC analysis using Lipodex (Macherey-Nagel, Germany) 0.25 μm (column 0.25 mm × 50 m ; flow rate of He 33.5~32.0 cm/min; column temp. 120 °C hold). The fraction containing **6** was concentrated in a microtube and 0.05 ml (0.5 μmol) of 10 mM tridecane (methanol soln.) was added as a standard. After estimation of the actual amount of **6**, an equivalent amount of hydrazine monohydrate was added to the tube slowly at 0 °C and stood for 10 min. Then the mixture was poured into 0.1 ml of cooled brine in an ice bath, extracted with 0.2 ml of diethyl ether, concentrated to give **3**, which was subjected directly to the chiral GC as described above (see Fig. 2). On the other hand, the intermediates and their acetates fraction was concentrated *in vacuo* and applied to preparative TLC (Merck, Germany). It was developed with *n*-pentane containing 20% diethyl ether to separate an acetate fraction containing **1a** and **2a**, and an alcohol fraction containing **1** and **2**. GC analyses of their optical purities were performed with CP-

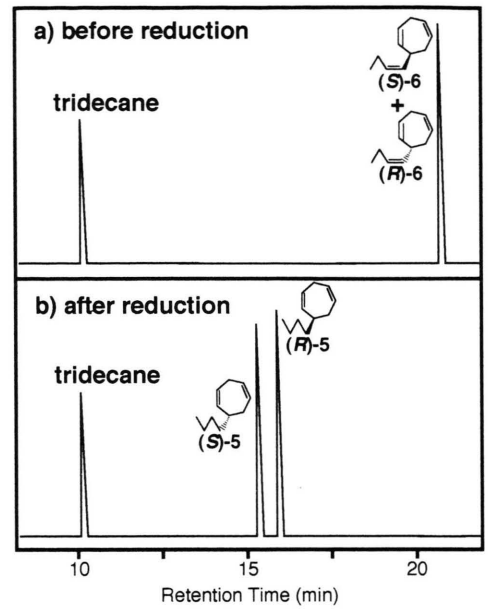

Fig. 2. Determination of enantiomeric composition of **6** derived from **5** after side-chain reduction of **6** with hydrazine on chiral phase (Lipodex, see Material and Methods).

Cyclodex 236M (Gasukuro Kogyo, Japan) (col. 0.25 mm × 50 m ; flow rate of He 33.5~32.0 cm/min; col. temp. 110 °C hold). **1** and **2** were analyzed as their acetate form (**1a** and **2a**) according to the method reported previously (Yamamoto *et al.*, 1999).

Examination of enzymatic conversion of dictyoprolenols to dictyopterenes in D. prolifera

Fresh fronds of *DP* was homogenized with 90 ml of phosphate buffer (pH 7.0) containing 0.5% (w/v) Triton X-100 (Aldrich, U. S. A.) and filtered through 4 layers of gauze. The crude enzyme solution (15 ml) thus obtained was incubated with dictyoprolenols (50 μmol of **(±)-1** and 50 μmol of **(±)-2**) as substrates at 15 °C for two hrs. After I. S. (50 μmol of tridecane and 50 μmol of *n*-heptanol) in 20 ml of ether were added to the reaction mixture, it was centrifuged at 2000 rpm for 10 min. The ether layer was separated, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* at 0 °C. The residue was passed through a florisil column (Wako, Japan) with *n*-pentane. Contents and enantiomeric compositions of products in the eluate were analyzed as described above by chiral GC

analysis of dictyopterenes and the possible intermediates.

Results and Discussion

Identification of volatile compounds including neodictyoprolenol and neodictyoprolene in D. latiscula and D. sp.

Volatile components in the essential oils prepared by an apparatus for SDE from *D. latiscula* and *D. sp.* were analyzed for the first time (Table I). With *DL*, 30 volatiles including **3**, **4** and **1**, and in *D. sp.*, 32 volatiles including **3**, zonarene and α-cadinene as major compounds were identified, respectively. The oil yield of *D. sp.* (3.1×10^{-3}%, g/g fresh weight) is lowest among the other three species of *Dictyopteris* such as *DP*, *DU* and *DL*. However, the oil odor is somewhat analogous to that of *DP* probably due to the composition of dictyopterenes **(1*S*,2*R*)-3** and **(1*S*,2*R*)-4**, which contribute to the characteristic aroma of *Dictyopteris* oil. On the other hand, the constituent composition of *DL* is relatively analogous to that of *DP* although the fresh and floral smell is not so strong as *DP*. A significant difference in the composition of **(1*S*,2*R*)-4** between *DL* and *DP* was observed. Thus, the characteristic aromas of *Dictyopteris* oils are thought to depend on the concentration of **(1*S*,2*R*)-4** rather than that of **(1*S*,2*R*)-3**. To identify the proposed intermediates in *Dictyopteris.*, an alternative solvent extraction method using *n*-pentane containing methanol was adopted, which is more efficient for detection of smaller amount of components. All dictyopterenes (**3**~**5**) were eluted in the pentane fraction, whereas the acetates (**(*S*)-1a**, **(*S*)-2a**) and the alcohols (**(*S*)-1**, **(*S*)-2**) were found in ether fraction. The volatile compounds were identified by comparison of GC retention times and GC-MS data with those of synthesized standards (Table II). The intermediate of dictyopterene B (**4**), neodictyoprolenol (**(*S*)-2**) as proposed by Moore *et. al.* (1974), was identified for the first time in *D. prolifera*, *D. latiscula* and *D. undulata*.

Table I. Volatile compounds identified in essential oils from *D. latiscula* and *D. spec.*

Compounds	Composition (%)	
	D. latiscula	*D. spec.*
Hydrocabone		
cis-3-Butyl-4-vinylcyclopentene	0.56	0.48
trans-2[(1*Z*)-Hexenyl]-2-vinylcyclopropane	0.08	0.06
Dictyopterene A (**3**)	40.1	10.9
4-[(1*E*)-Hexenyl]-cyclopentene	t	t
Dictyopterne D′ (**6**)	0.1	t
6-[(1*E*)-Butenyl]-cycloheptа-1,4-diene	2.8	1.1
Dictyopterene C′ (**5**)	2.2	0.9
Dictyopterene B′ (**4**)	3.0	0.6
(1,3*E*,5*Z*,8*Z*)-Undecatetraene	0.12	0.08
Undecane	t	t
(1,3*E*,5*E*)-Undecatriene	0.02	0.04
Aldehydes		
2-Pentenal	0.2	0.3
Hexanal	0.4	0.4
(2*E*)-Hexenal	0.5	0.6
(2*E*,4*E*)-Heptadienal	0.3	0.2
Nonanal	0.2	0.3
(2*E*,6*Z*)-Nonadienal	0.1	0.2
β-Cyclocitral	0.2	0.1
Tridecanal	0.8	0.6
Pentadecanal	1.1	1.0
Acetates		
Dictyoprolene (**1a**)	1.7	0.8
Neodictyoprolene (**2a**)	0.4	t
Alcohols		
Dictyoprolenol (**1**)	5.2	0.6
Neodictyoprolenol (**2**)	0.1	–
1-Penten-3-ol	0.2	0.2
2-Pentenol	1.1	0.9
(3*Z*)-Hexenol	0.4	0.6
Hexanol	0.3	0.5
1-Octen-3-ol	0.2	0.4
Isoprenoids		
Zonarene	0.8	18.1
Cubenol	nd	1.2
Epicubenol	nd	t
α-Cadinene	nd	12.0
β-Elemene	nd	0.8
δ-Elemene	t	0.02
Germacrene D	nd	0.13
γ-Selinene	nd	0.02
β-Caryophyllene	nd	t
α-Cubebene	nd	t
α-Copaene	nd	t

DL; D. latiscula (1998, Jun, Hikoshima in Yamaguchi pref.).
D. spec.; unidentified species of *Dictyopteris* (2000, Jul, Susa in Yamaguchi pref.).
t = less than 0.01%.
nd = not detected.

Composition and optical purities of dictyopterenes and the possible intermediates

If the ability to form algal sex pheromones, dictyopterenes, varies developmentally, the contents of dictyoprolenes (**1a**, **2a**) and dictyopterenes (**1**, **2**) should change through the seasons. Thus, each amount of **3**, **4**, **1**, **2**, **1a** and **2a** was traced in the essential oil prepared from fronds of *D. prolifera* by SDE through a year (Fig. 3). Although **1** and

Table II. Compositions and optical purities of dictyopterenes and the related C_{11}-compounds in *Dictyopteris* essential oils-

Compounds	*Dictyopteria*			
	*DP**	*DL*	*DU*	*D.sp.*
Hydrocarbon				
(1*S*,2*R*)-Dictyopterne A (**3**)	48.9[1] (97.7)[2]	40.1 (95.1)	21.1 (96.6)	10.9 (84.2)
(1*S*,2*R*)-Dictyopterne B (**4**)	15.6 (98.9)	3.0 (98.7)	2.3 (90.1)	0.6 (78.8)
(*R*)-Dictyopterene C′ (**5**)	5.8 (97.1)	2.2 (92.3)	2.0 (94.2)	0.9 (82.7)
(*S*)-Dictyopterne D′ (**6**)	2.2 (99.9)	0.1 (99.1)	0.2 (99.1)	–
Alcohol				
(*S*)-Dictyoprolenol (**1**)	4.4 (98.2)	5.2 (97.1)	1.1 (96.5)	0.6 (89.9)
(*S*)-Neodictyoprolenol (**2**)	0.5 (98.8)	0.1 (96.9)	0.1 (97.0)	–
Acetate				
(*S*)-Dictyoprolene (**1a**)	11.2 (98.9)	1.7 (97.3)	1.5 (96.9)	0.6 (88.4)
(*S*)-Neodictyoprolene (**2a**)	1.2 (98.9)	0.4 (95.1)	0.2 (97.1)	–

[1] Composition (%) in the essential oil. [2] *e.e.* %.
DP; D. prolifera (1998), Jun, Yoshimo beach in Yamaguchi pref.).
DL; D. latiscula (1998), Jun, Hikoshima in Yamaguchi pref.).
DU; D. undulata (1998), Jun, Yoshimo beach in Yamaguchi pref.).
D. spec.; unidentifield species of *Dictyopteris* (2000, Jul, Susa in Yamaguchi pref.).

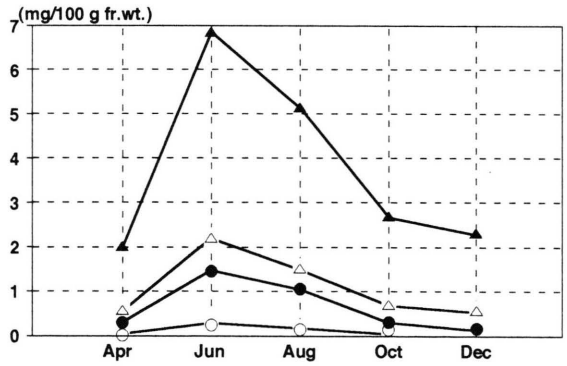

Fig. 3. Seasonal variation of C_{11}-compounds in *Dictyopteris prolifera.*
–▲– Dictyopterene A (**3**).
–△– Dictyopterene B (**4**).
–●– Dictyoprolene (**1a**).
–○– Neodictyoprolene (**2a**).

2, the most prominent intermediates, showed no marked change in the amount due to their low contents, the pheromones **3** and **4** fluctuated significantly having a maximum amount at June, which corresponds to the period of spore formation. Referring to this trace of C_{11}-compounds, fronds of four species of *Dictyopteris* were collected in June, and compositions and optical purities of constituents their essential oils were analyzed (Table II). All samples were analyzed by GC and the results summarized in Table II. Significant differences were observed both in composition and in optical purities among the oils of the four species. The configurations of the intermediates (**1**, **2**) and their acetates (**1a**, **2a**) were found to be (*S*)-form with greater than 95% *e.e.* (enantiomeric excess), and the corresponding dictyopterenes (**3**~**6**) have high *e.e.* values (over 90% *e.e.*). However, with *D. sp.* the both compositions were low (**1** and **1a** around 89% *e.e.*, and dictyopterenes 78~84% *e.e.*). On the other hand, enantiomeric compositions of dictyopterene D′ (**6**), which cannot be separated by commercially available chiral GC or LC columns, were successfully determined as a form of hydrogenated dictyopterene D′, dictyopterene C′ (**5**) after side chain reduction of **6** with hydrazine (Fig. 2).

Examination of enzymatic conversion of dictyoprolenols to dictyopterenes in D. prolifera

Although a possible biogenesis of dictyopterenes in female gametes of brown algae (Stratmann *et. al.*, 1993; Kajiwara *et. al.*, 1993 a; Kodama *et. al.*, 1993 b) and in a fresh water diatom (Pohnert *et. al.*, 1996) have been reported, an alternative biosynthetic pathway for **(1*S*,2*R*)-3** and **(1*S*,2*R*)-4** via the proposed intermediates (*S*)-dictyoprolenols (**(*S*)-1**, **(*S*)-2**) has not been investigated in detail as yet. The preparation from fresh fronds of *DP* was incubated with synthetic **(±)-1** and **(±)-2** as substrates, which were prepared according to the method previously reported (Yamamoto *et. al.*, 1999). The contents and enantiomeric compositions of products were analyzed by GC (Table II). As seen in Table III, (*S*)-enantiomers in racemic substrates added (**1** and **2**) were selectively consumed. With the heat-treated preparation, an enantioselective decrease of the added substrates were not observed. Thus, the decrease of **1** and **2** are thought to be attributable to an enzymatic reaction. On the other hand, significant increase of dictyopterenes **(1*S*,2*R*)-3** and **(*S*)-6** were ob-

Table III. Enzymatic conversion of dictyoprolenols to dictyopterenes in *D. prolifela.*

Compounds	Configuration	Control [μmol]	+Substrates [μmol]	Fluctuation [μmol]
Dictyoprolenol (**1**)	**(*S*)-1**	t	4.87	−20.13*
	(*R*)-1	nd	23.89	−1.11*
Dictyoprolene (**1a**)	**(*S*)-1a**	4.69	8.30	+3.61
	(*R*)-1a	nd	nd	–
Dictyopterene A (**3**)	**(1*S*,2*R*)-3**	0.41	0.61	+10.18
	(1*R*,2*S*)-3	0.41	0.61	+0.20
Dictyopterene C′ (**5**)	**(*R*)-5**	29.45	31.18	+1.73
	(*S*)-5	nd	nd	–
Neodictyoprolenol (**2**)	**(*S*)-2**	t	1.89	−23.11*
	(*R*)-2	nd	23.70	−1.30*
Neodictyoprolene (**2a**)	**(*S*)-2a**	1.10	2.55	+1.45
	(*R*)-2a	nd	nd	–
Dictyopterene B (**4**)	**(1*S*,2*R*)-4**	21.17	22.27	+1.10
	(1*R*,2*S*)-4	0.13	0.22	+0.09
Dictyopterene D′ (**6**)	**(*S*)-6**	13.09	22.49	+9.4
	(*R*)-6	0.04	0.12	−0.08

Substrate concentration: whole reaction mixture contained substrates (50 μmol of **(±)-1** and 50 μmol of **(±)-2**) and crude enzyme (15 ml, see Material and Method).
* fluctuation (μmol); 25 μmol − residual enantiomer of **1** or **2** (μmol).
nd; not detected.
t; less than 0.01%.

served. In all cases, the enantiomers in natural form remarkably increased. A sum of increase was 5.52 μmol (**(*S*)-1a**; 3.61, **(1*S*,2*R*)-3**; 10.18, **(*R*)-5**; 1.73) while that of decrease in **(*S*)-1** was 20.13 μmol. On the other hand, a sum of increase was 11.95 μmol (**(*S*)-2a**; 1.45, **(1*S*,2*R*)-4**; 1.10, **(*S*)-6**; 9.4) and a decrease of 23.11 μmol of **(*S*)-2** was observed. This could be explained by formation of other compounds such as oxidized or oxygenized ones. In practice, during the incubation, an increase of 4.2~6.3 μmol of (1,5*Z*,8*Z*)-undecatrien-3-one, which is thought to be formed from **2**, was observed. Based on this result, **(*S*)-1** and **(*S*)-2** are assumed to be the possible biosynthetic intermediates for dictyopterenes.

Recently, Hombeck *et. al.* (1998) reported a possible biosynthetic pathway of dictyopterene A in the diatom *Gomphonema parvulum*, in which is formed by oxidative cleavage of (9*S*)-hydroperoxyicosatetraenoic acid [(9S)-HPITE]. From the (9*S*)-hydroperoxides such as (9*S*)-HPITE and (9*S*)-hydroperoxyicosapentaenoic acid [(9*S*)-HPIPE], dictyopterenes via dictyoprolenols (**(*S*)-1**, **(*S*)-2**) and dictyoprolenes (**(*S*)-1a**, **(*S*)-2a**) might be formed by stereo-specific shifting of the hydroxy group at C-9 to C-12 via a six-membered ring as shown in Fig. 4. Further experiments are under way to elucidate the hypothesis.

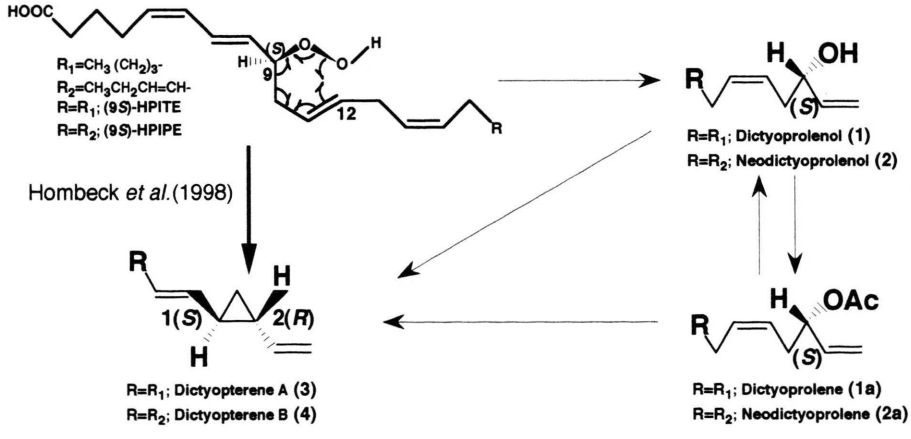

Fig. 4. Part of the hypothetic biosynthetic pathway of dictyopterenes, dictyoprolenols (**1, 2**) and dictyoprolenes (**1a, 2a**).
HPITE; hydroperoxyicosatetraenoic acid.
HPIPE; hydroperoxyicosapentaenoic acid.

Boland W., Flegel U., Jordt G. and Müller D. G. (1987), Absolute configuration and enantiomer composition of hormosirene. Naturwissenschaften **74**, 448–449.

Hombeck M., Pohnert G. and Boland W. (1998), Biosynthesis of dictyopterene A: stereoselectivity of a lipoxygenase/hydroperoxide lyase from *Gomphonema parvulum* (Bacillariophyceae). Chem. Commun., 243–244.

Jaenicke L. (1977), Sex pheromones of brown algae. Naturwissenschaften **64**, 69–75.

Kajiwara T., Nakatomi T., Sasaki Y. and Hatanaka A. (1980), Stereoselective synthesis of optically active dictyopterenes A and B and their geometrical isomers. Agric. Biol. Chem. **44**, 2099–2104.

Kajiwara T., Kodama K. and Hatanaka A. (1982), Isolation of (3*S*)-1, *cis*-5-undecadien-3-ol, a possible precursor of male-gamete attractants from *Dictyopteris undulata*. Bull. Japan. Soc. Sci. Fish. **48**, 211–214.

Kajiwara T., Kodama K., Hatanaka A and Matsui K. (1993a), Volatile compounds from Japanese marine brown algae. In: Bioactive Volatile Attractants from Plants. ed. by R. Teranishi and H. Sugisawa. Am. Chem. Soc. Symp. Ser. **525**, Washington D.C. p. 103–120.

Kodama K., Matsui K., Hatanaka A., Ishihara M. and Kajiwara T. (1993 b), A female gamete-characteristic (3*Z*,6*Z*,9*Z*)-dodecatrienoic acid from *Analipus japonicus*. Phytochemistry **32**, 1039–1042.

Moore R. E., Pettus J. A. and Mistysyn J. (1974), Odoriferous C11 hydrocarbons from Hawaiian *Dictyopteris*. J. Org. Chem. **39**, 2201–2207.

Pohnert G. and Boland W. (1996), Biosynthesis of the algal pheromone hormosirene by the fresh water diatom *Gomphonema parvulum* (Bacillariopthyceae). Tetrahedron **52**, 10073–10082.

Schlutz T. H., Flath R. A., Mon T. R., Eggling S. B. and Teranishi R. (1977), Isolation of volatile compounds from a model system. J. Agric. Food Chem. **25**, 446–449.

Stratmann K., Boland W. and Müller D. G. (1993), Biosynthesis of pheromones in female gametes of marine brown algae (Phaeophyceae). Tetrahedron **49**, 3755–3766.

Yamada K., Tan H. and Tatematsu H. (1979), Isolation and structure of dictyoprolene, a possible precursor of various undecanes in brown algae from *Dictyopteris prolifera*. J. Chem. Soc. Chem. Comm. 572–573.

Yamada K., Tan H., Tatematsu H. and Ojika M. (1986), Dictyoprolene and neodictyoprolene, two new odoriferous compounds from the brown alga *Dictyopteris prolifera* : structures and synthesis. Tetrahedron **42**, 3775–3780.

Yamamoto Y., Akakabe Y., Matsui K., Shimidzu H. and Kajiwara T. (1999), Chemo-enzymatic syntheses of both enantiomers of neodictyoprolenol and neodictyoprolene; possible biosynthetic intermediates of sex pheromones in brown algae. Z. Naturforsch. **54c**, 1027–1032.