Isolation of (*S*)-1, *cis*-5-Undecadien-3-ol, a Possible Precursor of Male-Gamete Attractants from *Dictyopteris undulata*

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Dictyoprolenol, properly named (*S*)-1, *cis*-5-undecadien-3-ol, which was postulated as a possible precursor of male-gamete attractants by MOORE *et al.*, was isolated from *Dictyopteris undulata*. Dictyoprolene was not detected in *D. undulata* and (*S*)-1, *cis*-5-undecadien-3-ol was not detected in *D. prolifera*. This discrepancy is probably due to a difference in the acylesterase activities of *D. undulata* and *D. prolifera*.

Non-isoprenoids C_{11} -hydrocarbons such as dictyopterene A (1), B (2), C' (3) and D' (4) have been isolated from Hawaiian¹⁻⁶⁾ and Japanese *Dictyopteris*.⁷⁻⁹⁾ On the other hand, C_{11} -olefins, dictyopterene D' or ectocarpene (4), multifidene (5) and C_8 -olefin, fucoserratene (6), have been identified as male-gamete attractants of brown marine algae, *Ectocarpus*,⁴⁾ *Cutleria*,⁶⁾ *Fucus*¹⁰⁾ and *Sargassum*,^{11,12)} respectively. MOORE¹³⁾ and JAENICKE¹⁴⁾ have proposed an attractive hypothesis that these hydrocarbons (1-6) are biosynthesized via (*S*)-1, *cis*-5-undecadien-3-ol (7) and (*S*)-1, *cis*-5, *cis*-8-undecatrien-3-ol (8), from linoleic and linolenic acids, respectively as shown in Fig. 1. Recently, YAMADA *et al.*^{7,8)} have reported isolation of the acetates of 7 and 8, dictyoprolene and neodictyoprolene, from *Dictyopteris prolifera*.

This paper describes the isolation and structure determination of 7 from *D. undulata*.

Materials and Methods

IR spectra were taken by a Hitachi EPI-G2 spectrometer using a potassium bromide disk. PMR spectra were obtained with a Hitachi Perkin-Elmer R-24 spectrometer in *d*-chloroform or CCl_4 containing TMS as an internal reference. ¹³C-NMR spectra were measured with *d*-chloroform on a JEOL JNM-FX 100 spectrometer. Mass spectra were afforded with a Shimadzu LKB-9000 at 70 eV. Optical rotations were measured on a JASCO DPI-SL automatic polarimeter. Analytical and preparative GLC were performed on a Shimadzu GC-6A and a Varian 920 gas chroma-

tography, respectively: 5% PEG 20M 1 m × 5 mm, column temp. 170°C, flow rate 40 ml/min. (condition-a); 15% DEGS 3 m × 5 mm, column temp. 80°C, flow rate 50 ml/min. (condition-b); 20% PEG 20M glass capillary column 20 m × 0.25 mm, column temp. 130°C, flow rate 50 ml/min. (condition-c); FFAP glass capillary column 40 m × 0.3 mm, column temp. 150°C, flow rate 60 ml/min. (condition-d); 5% PEG 20M 3 m × 3 mm, column temp. 150°C, flow rate 60 ml/min (condition-e).

Dictyopteris undulata and *Dictyopteris prolifera* were collected along Usa coast, Kochi, Japan in August, 1980 and at Shimonoseki, Yamaguchi, Japan in June 1980, respectively.

Isolation and Identification of (*S*)-1, *cis*-5-Undecadien-3-ol

The freshly collected, wet *D. undulata* (2.1 kg) was digested in acetone (4 l) for 4 days and the solvent of the extract was evaporated *in vacuo*. The residual oil (3 g) was introduced onto a 2 × 30 cm column of silica gel and the chromatogram was developed with a mixed solvent of benzene and hexane: 50 ml of 10% benzene-hexane, 50 ml of 20% benzene-hexane, 50 ml of 30% benzene-hexane and 50 ml of 40% benzene-hexane (1 g of essential oil). The essential oil in hexane was silica gel column (1.7 × 16 cm) chromatographed using 25 ml of hexane, 25 ml of 35% benzene-hexane (sesquiterpens), 25 ml of 65% benzene-hexane, 25 ml of benzene and 35% ether-benzene (60 mg of alcohol). The crude alcohol was florisil column (1 × 14 cm) chromatographed using 18 ml of hexane, 12 ml of 25% ether-hexane

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Fig. 1. Hypothesis of biogenetic pathway of male-gamete attractants of marine brown algae.

(methyl ester of fatty acid) and 12 ml of 65% ether-hexane (18 mg of C_{11} -alcohol). The C_{11} -alcohol fraction was rechromatographed: 3 ml of 35% dichloromethane-hexane, 3 ml of 50% dichloromethane-hexane and 8 ml of 65% dichloromethane-hexane (9.4 mg of pure C_{11} -alcohol).

Isolation of Dictyoprolene

The freshly collected, wet *Dictyopteris prolifera* (10.5 kg) was digested in acetone (18 l) twice and the extract was concentrated under reduced pressure. The concentrate (90 g) was introduced on silica gel (for dry column chromatography: 1 kg) column. Elution with 3 l of 20% benzene-pentane gave 8.2 g of odoriferous oil. The oil was florisil (50 g) column chromatographed: 180 ml of pet. ether (5.5 g, fraction-1); 400 ml of 10–80% benzene-pet. ether (0.1 g); 200 ml of 90–100% benzene-pet. ether (1.2 g, fraction-2); 150 ml of 10–30% ether-benzene (58 mg of triglyceride). Fraction-2 was rechromatographed on florisil: elution with 85 ml of 30% ether-hexane gave 400 mg of crude acetate which was separated to three fractions by preparative GLC (condition-a): fraction-a (3.5 min, dictyoprolene 45 mg), fraction-b (8.5 min methyl ester of fatty acids) and fraction-c (15 min, unknown 5.3 g).

Fraction 1 was distilled to afford C_{11} -hydrocarbons (bp. 78–80°C/15 mmHg) which was chromatographed on 25% silver nitrate-silica gel: 100 ml of 5% ether-hexane (fraction 3 700 mg) and 100 ml of 10% ether-hexane (dictyopterene B 80 mg). Fraction 3 was separated into dictyopterene C' (20 mg), dictyopterene D' (20 mg) and dictyopterene A (300 mg) by preparative GLC (condition-b).

Conversion of 1, 5-cis-Undecadien-3-ol to Dictyoprolene

Fresh *D. prolifera* (10 g) were blended with H_2O (10 ml) for 3 min and the homogenate thus obtained was incubated with 1, 5-cis-undecadien-3-ol (10 μl) at 35°C for 10 min. The reaction mixture was extracted with ether (50 ml $\times$ 3) and the solvent was evaporated *in vacuo*. The concentrate was analyzed by GLC (condition-e) using authentic dictyoprolene (8.6 min) and 1, cis-5-undecadien-3-ol (10.3 min).

Results and Discussions

The fresh wet *D. undulata* (2.1 kg) were soaked in acetone and the acetone soluble extract was concentrated *in vacuo* to yield a brown oil, which was chromatographed on silica with 40% benzene-

Table 1. ^1H -NMR and ^{13}C -NMR data of dictyoprolenol from *D. undulata*

Carbon No.	^{13}C -NMR	^1H -NMR	
	δ (ppm)	δ (ppm), Multiplicity, J (Hz)	
1	114.7	4.95 dt	10, 2
		5.26 dt	17, 2
2	140.5	5.81 ddd	17, 10, 6
3	72.5	4.01 q	6
4	35.0	2.19 t	6
5	124.2*	5.30 m	
6	133.8*		
7	27.4	2.01 q	6
8	29.3	1.26 m	
9	31.5		
10	22.5	0.88 t	6
11	14.0		
-OH	—	1.50 s	

* Assignments for values marked with the symbols may be interchanged.

Table 2. Formation of dictyoprolene from dictyoprolenol by the homogenate of *D. prolifera*

Substrate (10 μl)	Dictyoprolene* produced (mm ²)
None	trace
1, 5- <i>cis</i> -undecadien-3-ol	60
1, 5- <i>cis</i> -undecadien-3-ol + AcOH (6 μl)	320

* 10 μl of concentrate (1 ml) of reaction mixture was analyzed by GLC as given in Materials and Methods. Chirotopical data of the product, dictyoprolene, have not been obtained.

hexane, to give an odoriferous oil (1 g). The oil was found to be a mixture of sesquiterpenes⁹⁾ (α -copaene: 2% 15.5 min, β -cubebene; 7% 16.7 min, δ -cadinene 60% 21.7 min and unknown 20%) and C_{11} -hydrocarbons⁹⁾ (1; 6% 7.3 min, 3; 2% 8.1 min, 4; 0.3% 8.3 min, 2; 2% 9.3 min and unknown 0.7%) accompanied by a small amount of alcohol by capillary GLC (condition-c) and MS analyses. Chromatography of the crude alcohol on florisil (hexane and increasing amount of diethyl ether) gave fairly pure alcohol (18 mg), which was rechromatographed on florisil to give 9.4 mg of (S)-1, cis-5-undecadien-3-ol (7); $[\alpha]_D^{25} + 3.7^\circ$ (c, 0.16); MS m/z (70 eV): 168 (M^+ , 0.08%), 150 ($\text{M}^+ - 18$, 0.8%), 84 (13%), 83 (24%), 70 (37%), 69 (35%), 67 (8%), 57 (base peak), 56 (31%), 55 (48%), 54 (12%), 43 (12%), 42 (11%), 41 (47%), 29 (17%), 19 (39%), 18 (12%), 17 (19%); IR (neat) 3400, 3080, 3000, 1840, 1640 (cm^{-1}). The

structure of 7 was fully substantiated by comparison of ^1H -NMR and ^{13}C -NMR data with those of authentic ($\pm$)-7*⁸ and its acetate as indicated in Table 1. Acetylation (Ac_2O -pyridine, room temp. 12 hr) gave an acetate $[\alpha]_D^{25} + 13.0^\circ$ (c, 0.11); ^1H -NMR (CDCl_3) δ 0.87 (t, 3H, J=6), 1.28 (m, 6H), 2.06 (q, 2H, J=6), 2.30 (t, 2H, J=6), 4.92–5.33 (m, 5H), 5.72 (ddd, 1H, J=17, 10, 6) COMe 1.98 (s, 3H); ^{13}C -NMR δ 14.1, 22.6, 27.2, 29.2, 31.4, 32.2, 74.2, 116.7, 123.5, 133.1, 136.2, COMe 21.1, C=O 170.1; MS m/z (70 eV): 150 ($\text{M}^+ - \text{AcOH}$, 3%), 99 (19%), 79 (10%), 43 (base peak); IR (neat) 3080, 3000, 1740, 1640 (cm^{-1}); GLC data (condition-d): undecadien-3-ol 31.5 min; its acetate 26.0 min, which was identified with natural dictyoprolene. Thus the absolute configuration of dictyoprolenol (7) should be (S).

On the other hand, an odoriferous oil from fresh wet *D. prolifera* was chromatographed on florisil with benzene-petroleum ether to give an essential oil (fraction-2). Fraction 2 was rechromatographed on florisil (hexane and increasing amount of diethyl ether) to afford an odoriferous oil which was separated into three fractions by preparative GLC (condition-a); dictyoprolene (3.5 min, 45 mg), methyl ester of fatty acids and unknown compounds.

In *D. undulata*, dictyoprolene, the acetate of dictyoprolenol (7), was not detected and 7 not detected in *D. prolifera*. This discrepancy is probably due to acylesterase activities producing dictyoprolene from the corresponding alcohol in *D. prolifera*, as shown in Table 2. The increase of dictyoprolene was observed in addition of synthetic 1, cis-5-undecadien-3-ol to homogenates of *D. prolifera*. When the substrates were added to the heat-denatured homogenate, the alcohol was not converted to the corresponding acetate, dictyoprolene. Experiments on seasonal changes of the acylesterase activities and isolation of 1, cis-5, cis-8-undecatrien-3-ol (8) are in progress.

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*⁸ The tetrahydropyran derivative of hex-1-en-5-yn-3-ol was converted into the sodium salt and then alkylated with amyl bromide.¹⁰⁾ Hydrolysis of the resulting THP derivative of undeca-1-en-5-yn-3-ol with methanolic TsOH followed by catalytic hydrogenation afforded racemic 7.

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