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DICTYOPROLENE AND NEODICTYOPROLENE, TWO NEW ODORIFEROUS COMPOUNDS FROM THE BROWN ALGA *DICTYOPTERIS PROLIFERA*: STRUCTURES AND SYNTHESIS

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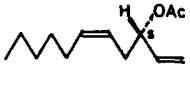
Abstract - Two new odoriferous compounds, dictyoprolene 1 and neodictyoprolene 2 have been isolated from the brown alga *Dictyopteris prolifera* and their structures determined by chemical and spectral means. Synthesis of optically active 1 and racemic 2 has been made. Dictyoprolene 1 and neodictyoprolene 2 have been shown to be the acetates of the 1-undecen-3-ols, the postulated biosynthetic precursors of various C_{11} hydrocarbons and the related compounds obtained from brown algae, *Dictyopteris*, *Ectocarpus*, and *Cutleria*.

The brown algae belonging to the genus *Dictyopteris* are known to possess a characteristic odor.[1-3] We have investigated the odor of the brown alga *Dictyopteris prolifera* collected in July off the coast of Wagu, Mie Prefecture, Japan, and isolated two new odoriferous compounds, dictyoprolene 1[4] and neodictyoprolene 2[5] together with the known odoriferous compounds, dictyopterene A 3[6,8] and B 4.[7,8] This paper describes isolation, structures, and synthesis of 1 and 2, and their biogenetic significance.

ISOLATION AND CHARACTERIZATION

The hexane soluble portion from the acetone extract of fresh *D. prolifera* was passed through a column of alumina with EtOAc to afford the oily material almost free from fatty acids, which was subsequently chromatographed over silica gel with $CHCl_3$: the early fraction gave a mixture of 3 and 4 and the later fraction provided a mixture of 1 and 2. Repetition of the chromatography of the mixture of 3 and 4 over silica gel and silica gel impregnated with $AgNO_3$ provided dictyopterene A 3 (2.1 x 10^{-3}%) and dictyopterene B 4 (1.9 x 10^{-3}%), respectively (yields based on fresh alga). After being passed through a column of alumina, the mixture of 1 and 2 was repeatedly chromatographed on silica gel and silica gel impregnated with $AgNO_3$ to give dictyoprolene 1 (2.4 x 10^{-3}%) and neodictyoprolene 2 (1.1 x 10^{-4}%), respectively. They were finally purified by preparative GLC: dictyoprolene 1, $C_{13}H_{22}O_2$, colorless liquid, $[\alpha]_D^{27}$ +13° (*c* 1.30, $CHCl_3$); neodictyoprolene 2, $C_{13}H_{20}O_2$, colorless liquid, $[\alpha]_D^{22}$ +20° (*c* 1.00, $CHCl_3$).



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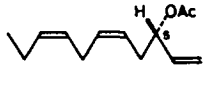

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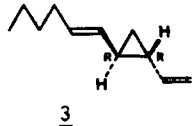

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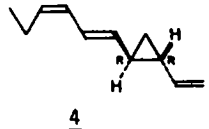

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The spectral data of 1 indicated the presence of an acetate group [IR 1740, 1238, and 1103 cm^{-1}; ^1H NMR δ 2.06 (3H, s); ^{13}C NMR δ 21.0(q) and 169.7(s)], a monosubstituted double bond, and a 1,2-disubstituted double bond [^{13}C NMR δ 116.4(t), 123.8(d), 133.0(d), and 136.5(d)]. Catalytic hydrogenation of 1 followed by methanolysis with NaOMe in MeOH afforded (3*R*)-(-)-undecan-3-ol,[9] $[\alpha]_D^{22}$ -7.1° (*c* 0.57, EtOH), establishing the carbon skeleton and absolute stereochemistry (3*S*) of 1. The detailed double resonance measurements of the ^1H NMR spectrum of 1 (Table) revealed that the two double bonds were located at C-1 and at C-5 in the undecan-3-ol skeleton of 1 and that the stereochemistry of the double bond at C-5 was *cis* ($J_{5,6}$ = 10.9 Hz). The structure including the absolute stereochemistry of dictyoprolene 1 was thus established.

Comparison of the molecular formulas and the spectral properties between 1 and 2 showed that neodictyoprolene 2 was a dehydro analogue of dictyoprolene 1. Catalytic hydrogenation of 2 and subsequent methanolysis with NaOMe in MeOH afforded (3*R*)-(-)-undecan-3-ol,[9] $[\alpha]_D^{28}$ -7.0° (*c* 0.57, EtOH), disclosing the carbon skeleton and absolute stereochemistry of 2. The double resonance experiments of the ^1H NMR spectrum of 2 (Table) clearly indicated that the three double bonds were located at C-1, C-5, and C-8 in the undecan-3-ol skeleton of 2 and that the stereochemistry of the double bonds at C-5 and C-8 were *cis* ($J_{5,6}$ = $J_{8,9}$ = 10.6 Hz). The structure including absolute stereochemistry of neodictyoprolene was therefore shown to be 2.

Table ^1H NMR spectral data*

	1	2
H-1a	5.25 (1H, ddd, 17.5, 1.3, 1.3)	5.26 (1H, ddd, 17.2, 1.3, 1.3)
H-1b	5.17 (1H, ddd, 10.6, 1.3, 1.3)	5.18 (1H, ddd, 10.6, 1.3, 1.3)
H-2	5.81 (1H, ddd, 17.5, 10.6, 5.9)	5.80 (1H, ddd, 17.2, 10.6, 6.3)
H-3	5.26 (1H, br dt, 5.9, 7.6)	5.28 (1H, br dt, 6.3, 7.0)
H-4a	2.42 (1H, ddd, 14.8, 7.6, 7.1)	2.45 (1H, ddd, 14.5, 7.0, 6.6)
H-4b	2.34 (1H, ddd, 14.8, 7.6, 7.1)	2.38 (1H, ddd, 14.5, 7.0, 6.6)
H-5	5.32 (1H, dtt, 10.9, 7.1, 1.5)	5.36 (1H, dtt, 10.6, 6.6, 1.3)
H-6	5.51 (1H, dtt, 10.9, 7.3, 1.5)	5.49 (1H, dtt, 10.6, 7.0, 1.3)
H-7	2.02 (2H, dt, 7.3, 7.0)	2.79 (2H, br t, 7.0)
H-8		5.29 (1H, dtt, 10.6, 7.0, 1.3)
H-9	1.2 - 1.4 (6H, m)	5.41 (1H, dtt, 10.6, 7.2, 1.3)
H-10		2.07 (2H, dq, 7.2, 7.4)
H-11	0.89 (3H, br t, 6.9)	0.98 (3H, t, 7.4)
AcO	2.06 (3H, s)	2.06 (3H, s)

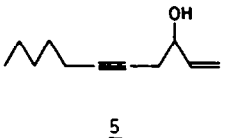
* Chemical shifts (δ in ppm) relative to internal TMS. Multiplicities and coupling constants (Hz) are given in parentheses. Spectra were measured in $CDCl_3$ at 270 MHz.

SYNTHESIS

In order to confirm the structures of 1 and 2 described above, the synthesis of 1 and 2 was carried out.

Acrolein was condensed with 1-bromo-2-octyne[10] in the presence of activated zinc in THF to afford 1-undecen-5-yn-3-ol 5 (17%). For optical resolution, the alcohol 5 was esterified with 3β-acetoxy-5-androstene-17β-carboxylic acid chloride[11,12] in toluene to give a diastereomeric mixture of the ester 6, which was separated by preparative TLC on silica gel impregnated with $AgNO_3$ providing the two diastereomers, 6a (38%) and 6b (39%). Both isomers were differentiated by ^1H NMR spectral analysis [δ 0.70 (3H, s, H-18 of the steroid moiety) for 6a and δ 0.72 for 6b]. Hydrogenation of the diastereomer 6a in the presence of Lindlar catalyst in benzene yielded the *cis*-olefinic ester 7a (91%). Reduction of 7a with $LiAlH_4$ in THF followed by acetylation with Ac_2O in pyridine provided (+)-dictyoprolene 1, $[\alpha]_D^{25}$ +11° (*c* 1.17, $CHCl_3$) (77% overall yield), which was proved to be identical with natural 1 by spectral (IR, ^1H NMR, and MS) and chromatographic comparison.

The reaction of vinylmagnesium bromide with (3Z,6Z)-3,6-nonadienal 8[13] in THF gave (5Z,8Z)-(±)-1,5,8-undecatrien-3-ol (10%), acetylation of which with Ac_2O in pyridine afforded (±)-neodictyoprolene 2 (98%). The spectral (IR, ^1H NMR, and MS) and chromatographic properties of synthetic 2 were identical with those of natural 2.



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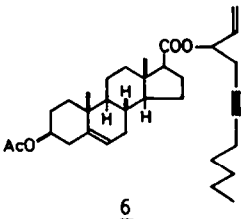

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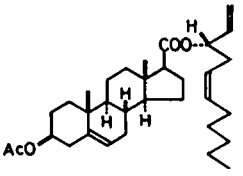

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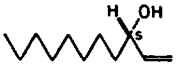
DISCUSSION

The brown algae such as *Dictyopteris*, *Ectocarpus*, and *Cutleria* are known to contain a variety of novel C_{11} hydrocarbons and the related compounds.[1-3,14] Some of the representative examples are dictyopterene A 3, dictyopterene B 4, and ectocarpene (= dictyopterene D') 12,[8,15,16] the last one being the male-attracting substance excreted by the female gametes of the brown alga *Ectocarpus siliculosus*.



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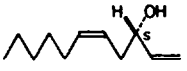

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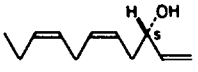

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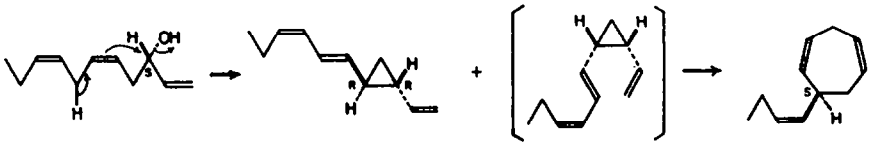
Examination of the structures including absolute stereochemistry of these compounds led Moore to propose a hypothesis that the three kinds of 1-undecen-3-ols (9, 10, and 11) derived from oleic, linoleic, and linolenic acids, respectively were precursors in the biosynthesis of these C_{11} compounds.[1-3,17] For example, dictyopterene B 4 and ectocarpene 12 were postulated to be biosynthesized from (3*S*,5Z,8Z)-1,5,8-undecatrien-3-ol 11 as depicted in Scheme 1.[1,2] In spite of the efforts searching for these 1-undecen-3-ols, 10 and 11, they could not be detected in mature plants of Hawaiian *Dictyopteris*.[3]

Isolation of dictyoprolene 1 and neodictyoprolene 2 from *D. prolifera* in the present study is biogenetically significant: these two compounds, 1 and 2, have been found to be the acetates of two postulated biosynthetic intermediates among the three ones (9, 10, and 11). Further, the absolute stereochemistry at C-3 of dictyoprolene 1 and neodictyoprolene 2 was established to be *S*, proving the validity of the Moore's assumption[1-3] that the 1-undecen-3-ols, hypothetical precursors of various C_{11} hydrocarbons would possess *S* absolute stereochemistry at C-3.
Synthesis of racemic (5Z)-1,5-undecadien-3-ol 10 and racemic (5Z,8Z)-1,5,8-undecatrien-3-ol 11 was carried out by the Moore's group and by the Jaenicke's group, respectively, in connection with the work on the biogenesis and the biomimetic reactions of these C_{11} hydrocarbons.[3]

Scheme 1[1,2]



11 4 12

EXPERIMENTAL

IR spectra were recorded on a JASCO Model IRS spectrophotometer in $CHCl_3$ solution, unless otherwise stated. ^1H NMR spectra were obtained on JEOL FX-90QE (90 MHz), Varian HA-100 (100 MHz), and JEOL JNM-GX270 (270 MHz) instruments in $CDCl_3$: chemical shifts (δ) are reported in ppm downfield from internal TMS and coupling constants in Hz. ^{13}C NMR spectra were measured using JEOL FX-90QE (22.5 MHz) spectrometer in $CDCl_3$: chemical shifts (δ) are reported in ppm downfield from internal TMS. Mass spectra were recorded on Hitachi RMU-6C and JEOL JMS-DX303 instruments. Optical rotations were measured on JASCO DIP-4 and DIP-181 polarimeters. Fuji-Davison silica gel BW-80 and Merck aluminium oxide 90 (activity II-III) were used for column chromatography. Merck precoated silica gel $60F_{254}$ plates were used for TLC and Merck silica gel PF_{254} for preparative TLC. A Varian 1828-4 gas chromatograph was used for GLC. Organic solutions in the synthetic operations were dried over anhydrous Na_2SO_4 and concentrated by vacuum rotary evaporator.

Isolation of dictyoprolene 1, neodictyoprolene 2, dictyopterene A 3, and dictyopterene B 4. The fresh alga (*D. prolifera*, 82 kg) collected in July, at Wagu, Mie Prefecture, Japan, was extracted with acetone (80 ℓ) at room temperature. After filtration the solvent was removed under reduced pressure to afford an aqueous suspension (34 ℓ), which was extracted with hexane (2 x 17 ℓ). The combined extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give an oily material (197 g), which was passed through a column of alumina (1 kg) with EtOAc to yield an oil (110 g) almost free from fatty acids. The oil was chromatographed on silica gel with $CHCl_3$: from the early fraction (1 ℓ) a mixture containing 3 and 4 (9.1 g) was obtained and from the later fraction (6 ℓ) a mixture containing 1 and 2 (30 g) was secured. A portion of the mixture containing 3 and 4 (3.03 g) was chromatographed twice on silica gel (60 g and 40 g) with hexane to give the fraction A containing mainly 3 (837 mg) and the fraction B containing mainly 4 (759 mg). A portion of the fraction A (83.7 mg) was further separated by chromatography on 15% $AgNO_3$ impregnated silica gel (4 g) with EtOAc-hexane (2:98 → 5:95) to afford 3 (57 mg, 2.1 x 10^{-3}%), $[\alpha]_D^{22}$ +70° (*c* 2.33, $CHCl_3$) [lit.[8] $[\alpha]_D^{22}$ +72° (*c* 6.74, $CHCl_3$)] as a colorless oil. A portion of the fraction B (75.9 mg) was separated by chromatography on 15% $AgNO_3$ impregnated silica gel (4 g) with EtOAc-hexane (10:90 → 20:80) to provide 4 (51 mg, 1.9 x 10^{-3}%), $[\alpha]_D^{22}$ -40° (*c* 2.05, $CHCl_3$) [lit.[8] $[\alpha]_D^{24}$ -43° (*c* 10.1, $CHCl_3$)] as a colorless oil. The spectral (UV, IR, ^1H NMR, and MS) properties of 3 and 4 were identical with those of dictyopterene A[8] and B,[8] respectively.

The mixture containing 1 and 2 (30 g) was passed through a column of alumina (100 g) with CH_2Cl_2 for complete removal of fatty acids present in the mixture to afford an oily material (26 g), which was chromatographed on silica gel (520 g) with EtOAc-hexane (5:95). The fractions containing 1 and 2 were collected and concentrated under reduced pressure to give an oil (4.4 g). Chromatography of the oil on silica gel (440 g) with benzene-hexane (2:3) afforded the fraction I containing 1 (2.52 g), the fraction II containing 1 and 2 (250 mg), and the fraction III containing 2 (320 mg). The fraction I (2.52 g) was chromatographed on 13% $AgNO_3$ impregnated silica gel (170 g) with EtOAc-hexane (5:95) to give 1 (1.80 g) as a colorless liquid. The fraction II (250 mg) was chromatographed on silica gel (56 g) with $CHCl_3$-hexane (2:3) to afford 1 (130 mg) as a colorless liquid and a mixture containing 2 (130 mg): further chromatography of the latter on 13% $AgNO_3$ impregnated silica gel (17 g) with EtOAc-hexane (1:8) gave 2 (30 mg) as a colorless liquid. The fraction III (320 mg) was chromatographed on 13% $AgNO_3$ impregnated silica gel with EtOAc-hexane (1:10) to yield 2 (60 mg) as a colorless liquid. The total smount of 1 and 2 obtained were 1.93 g (2.4 x 10^{-3}%. R_f 0.50; silica gel TLC, $CHCl_3$-hexane (1:1)) and 90 mg (1.1 x 10^{-4}%. R_f 0.45; silica gel TLC, $CHCl_3$-hexane (1:1)), respectively. Pure 1 and 2 were obtained by preparative GLC using a 5% SE-30 on Chromosorb W column (6.4 mm x 1.5 m) at 140 °C (He as carrier gas; flow rate 60 ml/min): retention time, 7.0 min for 1 and 7.0 min for 2.

1: $C_{13}H_{22}O_2$, colorless liquid, $[\alpha]_D^{27}$ +13° (*c* 1.30, $CHCl_3$); IR (CCl_4) 3020, 1740, 1238, 1103 cm^{-1}; ^1H NMR (Table); ^{13}C NMR δ 14.0(q), 21.0(q), 22.6(t), 27.5(t), 29.3(t), 31.6(t), 32.5(t), 74.3(d), 116.4(t), 123.8(d), 133.0(d), 136.5(d), 169.7(s); MS m/z 150 (M^+ - AcOH), 99. (Found: C, 74.03; H, 10.75. $C_{13}H_{22}O_2$ requires: C, 74.24; H, 10.54%).

2: $C_{13}H_{20}O_2$, colorless liquid, $[\alpha]_D^{22}$ +20° (*c* 1.00, $CHCl_3$); IR (neat) 3010, 1741, 1641 (weak), 1236, 1022 cm^{-1}; ^1H NMR (Table); ^{13}C NMR δ 14.2(q), 20.6(t), 21.1(q), 25.7(t), 32.3(t), 74.1(d), 116.6(t), 123.9(d), 126.8(d), 131.2(d), 132.1(d), 136.2(d), 169.9(s); MS m/z 148 (M^+ - AcOH), 99. [HRMS. Found: 148.1271 (M^+ - AcOH). $C_{11}H_{16}$ requires: 148.1252].

Transformation of dictyoprolene 1 and neodictyoprolene 2 into (3*R*)-(-)-undecan-3-ol. A solution of 1 (24 mg) in EtOH (1 ml) in the presence of PtO_2 (5 mg) was stirred in the atmosphere of H_2 at room temperature for 1 h. After removal of the catalyst by filtration, the filtrate was concentrated to give an oil. Separation of the oil by preparative TLC (benzene) afforded a colorless oil (19.5 mg, 81%), $[\alpha]_D^{25}$ +10.7° (*c* 1.00, EtOH), which was identified as (3*R*)-(+)-3-acetoxyundecane by comparison of the spectral properties with those of the authentic specimen. The authentic compound was prepared by acetylation (Ac_2O - pyridine) of (3*R*)-(-)-undecan-3-ol.[9] Following the same procedures as described above, 2 (17 mg) afforded (3*R*)-(+)-3-acetoxyundecane (10.7 mg, 61%) after purification by preparative TLC.

To a stirred solution of (3*R*)-(+)-3-acetoxyundecane (19 mg) in MeOH (1 ml) was added a solution (1.5 ml) of NaOMe in MeOH (prepared from 100 mg of Na and 10 ml of anhydrous MeOH) at 0 °C under nitrogen. The solution was stirred at room temperature for 16 h and neutralized at 0 °C with 2N HCl solution. The mixture was concentrated and extracted with CH_2Cl_2 (3 x 18 ml). The combined organic extracts were dried and concentrated, and the resulting oil was purified by preparative TLC (2:1 hexane-Et_2O) to give a colorless liquid (12.3 mg, 80%), $[\alpha]_D^{22}$ -7.1° (*c* 0.57, EtOH), which was identified as (3*R*)-(-)-undecan-3-ol[9] [lit.[9] $[\alpha]_D^{20}$ -6.22° (*c* 5, EtOH)] by comparison of the spectral (IR, ^1H NMR, and MS) properties with those of the authentic specimen.

1-Undecen-5-yn-3-ol 5. Commercially available zinc powder (750 mg, 11.5 mmol) was washed successively with 10% HCl solution for 2 min, H_2O four times, MeOH three times, ether three times, and benzene once, and dried *in vacuo* under nitrogen. To a stirred suspension of activated zinc in THF (0.2 ml) was added dropwise a solution of acrolein (325 mg, 5.80 mmol) and 1-bromo-2-octyne[10] (670 mg, 3.54 mmol) in THF (3 ml) at 40 °C under nitrogen. The mixture was stirred at 60 °C for 1 h, cooled, and poured into an AcOH-H_2O (1:9) solution (1.5 ml). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 18 ml). The organic layer and the ethereal extracts were combined. The organic solution was dried and concentrated, and the residual oil (830 mg) was chromatographed on silica gel with Et_2O-hexane (1:2) to afford 5 (96 mg, 17%) as a colorless liquid. Further purification by preparative GLC with a 5% SE-30 on Chromosorb W column (6.4 mm x 1.5 m) at 140 °C provided an analytical sample of 5. IR 3540, 3420, 3090, 1645 (weak), 935, 850 cm^{-1}; ^1H NMR (90 MHz) δ 0.89 (3H, br t, J = 6.0), 1.3-1.5 (6H, m), 2.18 (2H, m), 2.23 (1H, br s, OH), 2.40 (2H, m), 4.22 (1H, dt, J = 5.0, 5.5), 5.15 (1H, dd, J = 10.0, 2.0), 5.29 (1H, dd, J = 17.8, 2.0), 5.95 (1H, ddd, J = 17.8, 10.0, 5.5); MS m/z 166 (M^+), 165, 110, 109. (Found: C, 79.24; H, 11.20. $C_{11}H_{18}O$ requires: C, 79.47; H, 10.91%).

Esters, 6a and 6b. A mixture of 3β-acetoxy-5-androstene-17β-carboxylic acid[11,12] (340 mg, 0.94 mmol) and oxalyl chloride (8.76 g, 69 mmol) was stirred at 60 °C for 1 h and concentrated to dryness. The residue was dissolved in toluene and the mixture was concentrated to give the acid chloride as amorphous powder. To a stirred solution of the acid chloride in toluene (2 ml) was added a solution of 4-dimethylaminopyridine (150 mg, 1.23 mmol) in toluene (2 ml), and the mixture was stirred at 60 °C for 1 h. To the mixture was added a solution of 5 (91 mg, 0.55 mmol) in toluene (2 ml). The resulting mixture was stirred at 50 °C for 36 h, cooled, and filtered with suction. The filtrate was concentrated and the residual oil (340 mg) was separated by preparative TLC ($CHCl_3$) to give a mixture of 6a and 6b (255 mg). A portion of the mixture (190 mg) was separated by preparative TLC on 13% $AgNO_3$ impregnated silica gel (benzene) to afford 6a (79 mg, 38%, R_f 0.36) and 6b (82 mg, 39%, R_f 0.19). 6a: mp 51.5-52.5 °C (MeOH-EtOH); $[\alpha]_D^{26}$ -4.9° (*c* 0.65, benzene); IR 1722, 1258, 1032, 940 cm^{-1}; ^1H NMR (100 MHz) δ 0.70 (3H, s), 0.90 (3H, br t, J = 6.0), 1.03 (3H, s), 2.03 (3H, s), 4.64 (1H, m), 5.2-5.4 (4H, m), 5.91 (1H, ddd, J = 17.6, 10.0, 6.0); MS m/z 508 (M^+), 448, 343, 299. (Found: C, 77.94; H, 9.91. $C_{33}H_{48}O_4$ requires: C, 77.91; H, 9.51%). 6b: amorphous powder; $[\alpha]_D^{26}$ -30.3° (*c* 0.85, benzene); IR 1722, 1258, 1032, 940 cm^{-1}; ^1H NMR (100 MHz) δ 0.72 (3H, s), 0.90 (3H, br t, J = 6.0), 1.03 (3H, s), 2.03 (3H, s), 4.64 (1H, m), 5.2-5.4 (4H, m), 5.91 (1H, ddd, J = 17.6, 10.0, 6.0); MS m/z 508 (M^+), 448, 343, 299.

cis-Olefinic ester 7a. To a solution of 6a (23 mg, 0.045 mmol) in benzene (1.6 ml) were added the Lindlar catalyst (18.5 mg) and a benzene-quinoline (19:1) solution (0.4 ml). The mixture was stirred in the atmosphere of H_2 at room temperature for 2 h and filtered. Concentration of the filtrate afforded an oil, which was separated by preparative TLC (4:1 hexane-Et_2O, developed twice) to give 7a (21 mg, 91%) as amorphous powder: IR 1720, 1252, 1033, 936 cm^{-1}; ^1H NMR (100 MHz) δ 0.69 (3H, s), 0.90 (3H, br t, J = 6.0), 1.03 (3H, s), 2.03 (3H, s), 4.60 (1H, m), 5.1-5.6 (6H, m), 5.84 (1H, ddd, J = 17.0, 10.0, 5.9); MS m/z 450 (M^+ - AcOH), 343, 330 [HRMS. Found: 450.3472 (M^+ - AcOH). $C_{31}H_{46}O_2$ requires: 450.3497].

Synthesis of (+)-dictyoprolene 1. A solution of 7a (77 mg, 0.15 mmol) in THF (2.5 ml) was added dropwise to a stirred solution of $LiAlH_4$ (20 mg, 0.53 mmol) in THF (1 ml) at -30 °C under nitrogen. The mixture was stirred at 0 °C for 1 h, diluted with 20% MeOH - Et_2O (1 ml), filtered with the aid of Celite, and washed thoroughly with THF. The combined filtrates were dried and concentrated to give an oil. Separation and purification by preparative TLC ($CHCl_3$) provided (3*S*,5*Z*)-(+)-1,5-undecadien-3-ol 10 (19 mg, 75%) as a colorless oil: $[\alpha]_D^{18}$ +13.3° (*c* 0.95, $CHCl_3$); IR 3560, 1000, 935, 870 cm^{-1}; ^1H NMR (100 MHz) δ 0.90 (3H, br t, J = 6.0), 1.30 (6H, m), 1.64 (1H, br s, OH), 2.07 (2H, dt, J = 7.0, 6.0), 2.33 (2H, t, J = 6.0), 4.16 (1H, dt, J = 6.0, 6.0), 5.14 (1H, dd, J = 10.0, 1.5), 5.27 (1H, dd, J = 17.4, 1.5), 5.4-5.7 (2H, m), 5.93 (1H, ddd, J = 17.4, 10.0, 6.0); MS m/z 150 (M^+ - H_2O), 112, 57. (Found: C, 78.48; H, 12.42. $C_{11}H_{20}O$ requires: C, 78.51; H, 11.98%).
A solution of (3*S*,5*Z*)-(+)-1,5-undecadien-3-ol 10 (19 mg, 0.11 mmol) in Ac_2O (0.2 ml) - pyridine (0.5 ml) was stirred at room temperature for 12 h and concentrated to give an oily residue. Separation and purification by preparative TLC ($CHCl_3$) afforded (+)-1 (24 mg, quantitative) as a colorless liquid. Further purification by preparative GLC under the conditions employed for isolation of 1 (*vide ante*) gave (+)-1 as a colorless liquid: $[\alpha]_D^{25}$ +11.1° (*c* 1.17, $CHCl_3$). The IR, ^1H NMR, and mass spectra and the TLC behaviors (several solvent systems) of synthetic (+)-1 proved identical with those of natural 1.

Synthesis of (±)-neodictyoprolene 2. A solution of (3*Z*,6*Z*)-3,6-nonadienal 8[13] (10 mg, 0.072 mmol) in THF (1 ml) was added to a stirred 0.5 M solution of vinylmagnesium bromide in THF (1 ml) at 0 °C under nitrogen. The mixture was stirred at 0 °C for 30 min, diluted with saturated NH_4Cl solution (6 ml), and extracted with Et_2O (3 x 10 ml). The combined extracts were dried and concentrated to give an oily residue (14 mg). Separation and purification by preparative TLC (15:1 $CHCl_3$-EtOAc) afforded (5*Z*,8*Z*)-(±)-1,5,8-undecatrien-3-ol (2.6 mg, 22%) as a colorless oil: IR 3620, 3450, 1644 (weak), 1114, 992, 926, 862 cm^{-1}; ^1H NMR (90 MHz) δ 0.97 (3H, t, J = 7.5), 1.74 (1H, br s), 2.06 (2H, m), 2.35 (2H, dd, J = 6.0, 6.0), 2.81 (2H, dd, J = 5.7, 5.7), 4.17 (1H, dt, J = 5.7, 6.0), 5.0-5.2 (2H, m), 5.2-5.7 (4H, m), 5.92 (1H, ddd, J = 17.4, 10.1, 5.7); MS m/z 148 (M^+ - H_2O), 119, 110.
A solution of (5*Z*,8*Z*)-(±)-1,5,8-undecatrien-3-ol (2.6 mg, 0.016 mmol) in Ac_2O (0.05 ml) - pyridine (0.2 ml) was stirred at room temperature for 10 h and concentrated. Separation of the residual oil by preparative TLC ($CHCl_3$) gave (±)-2 (3.2 mg, 98%) as a colorless liquid. The IR, ^1H NMR, and mass spectra and TLC behaviors (several solvent systems) of synthetic (±)-2 were identical with those of natural 2.

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