36 H). $^{13}C$ NMR (25 °C): 158.2 (0), 153.9 (0), 148.3 (0), 133.5 (0), 131.1 (1), 129.9 (0), 129.4 (0), 129.3 (1), 128.9 (1), 126.7 (1), 126.3 (1), 115.0 (0), 114.6 (0), 112.2 (0), 86.4 (0), 35.1 (0), 31.3 (3). IR: 2229. UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\epsilon$): 432 nm (4.19), 328 (4.75), 292 (4.94). High resolution mass spectrum: molecular ion 1032.4628; calcd for $C_{72}H_{56}N_8$ 1032.4630.

**Acknowledgment.** Preliminary electrochemistry was carried out by J. R. Valentine, the variable-temperature $^1H$ NMR study was conducted by R. King, and mass spectra were measured by Dr. E. Larka. This work was supported by a grant from the Office of Naval Research.

**Supplementary Material Available:** NMR data of **5**-CN (1 page). Ordering information is given on any current masthead page.

# Antitumor Xenicane and Norxenicane Lactones from the Brown Alga *Dictyota dichotoma*

Midori O. Ishitsuka, Takenori Kusumi, and Hiroshi Kakisawa*

*Department of Chemistry, The University of Tsukuba, Tsukuba, Ibaraki, Japan 305*

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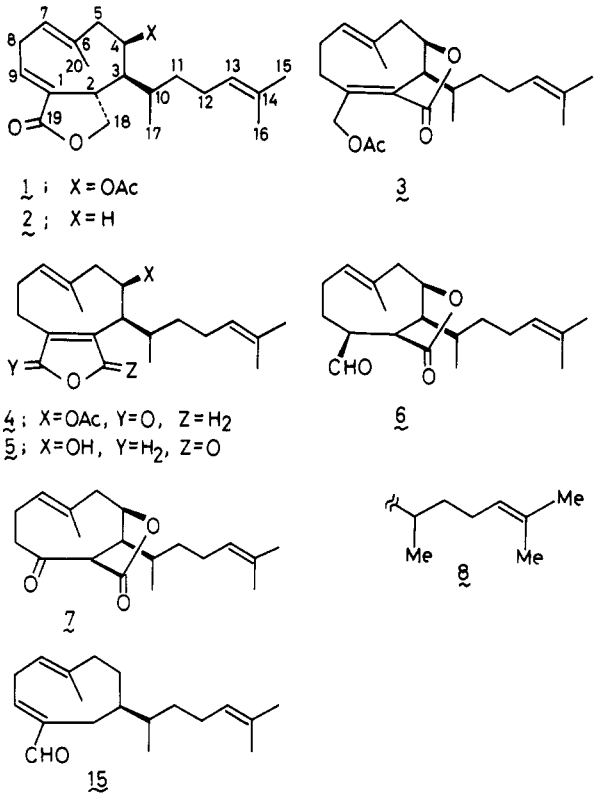
New xenicane diterpenes, 4-acetoxydictyolactone (**1**), dictyotalide A (**6**), dictyotalide B (**3**), and nordictyotalide (**7**), possessing a cyclononane carbon framework, have been isolated from the brown alga *Dictyota dichotoma*, and their structures have been spectroscopically and chemically elucidated. The conformations of these compounds have been determined on the basis of 2D-NOESY spectra. Dictyotalide B (**3**) possesses a highly strained double bond which is located at a bridgehead position of the 9-oxabicyclo[6.2.1]undecane skeleton. The compounds exhibit significant cytotoxic activity against B16 mouse melanoma cells.

Brown algae of the Dictyotaceae family are peculiar in that they produce a series of unique diterpenes consisting of medium-sized rings.[1] Among the diterpenes isolated from seaweeds, xenicanes comprise one of the most interesting classes of compounds because they are composed of a cyclononane skeleton that is seldom found in other natural products. Xenicanes have also been isolated as the ingredients of soft corals and sponges.[2] Herein we describe the structures of four new xenicane lactones from the brown alga *Dictyota dichotoma*, viz., 4-acetoxydictyolactones (**1**), dictyotalide A (**6**) and B (**3**), and nordictyotalide (**7**).

4-Acetoxydictyolactone (**1**), $[\alpha]_D$ -224° (*c* 0.86, $CHCl_3$), $C_{22}H_{32}O_4$ (*m/e* 360.2290), shows IR absorption bands at 1760 and 1740 $cm^{-1}$ assignable to $\gamma$-lactone and acetoxy [$^1H$ NMR $\delta$ 2.03 (3 H, s)] groups, respectively. Analysis of the $^1H$ and $^{13}C$ NMR (Experimental Section) and mass (*m/e* 109) spectra revealed that a 6-methyl-5-hepten-2-yl group (**8**), the typical side chain of the Dictyotaceae diterpenes, was present. The $^1H$ and $^{13}C$ NMR spectra were very similar to those of dictyolactone (**2**).[3] The placement of an acetoxy group at C-4 was determined on the basis of the coupling pattern for H-4 [$\delta$ 5.27 (dd, J = 4.5, 2.3 Hz)]. Consideration of the coupling patterns of the ring protons together with observation of the NOEs (depicted in **1a**) enabled us to propose the relative stereochemistry at C-2, -3, and -4 and the conformation (**1a**) for 4-acetoxydictyolactone. The conformation is essentially the same as that of dictyolactone (**2**) inferred by X-ray analysis.[3]




Dictyotalide B (**3**), $C_{22}H_{32}O_4$ (*m/e* 360.2338), $[\alpha]_D$ +50.3° (*c* 0.59, $CHCl_3$), is an isomer of **1**. The presence of a $\gamma$-lactone ring, an acetoxy group, the side chain **8**, and a trisubstituted olefin bearing a methyl group was apparent from the spectral properties (Table I). The $^1H$ NMR spectrum of dictyotalide B lacked the downfield olefin proton signal corresponding to H-9 of **1**, strongly suggesting

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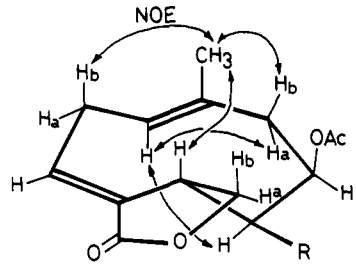
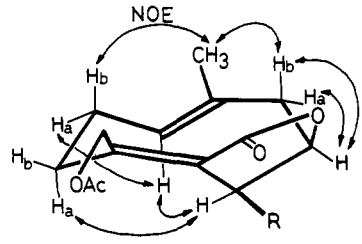
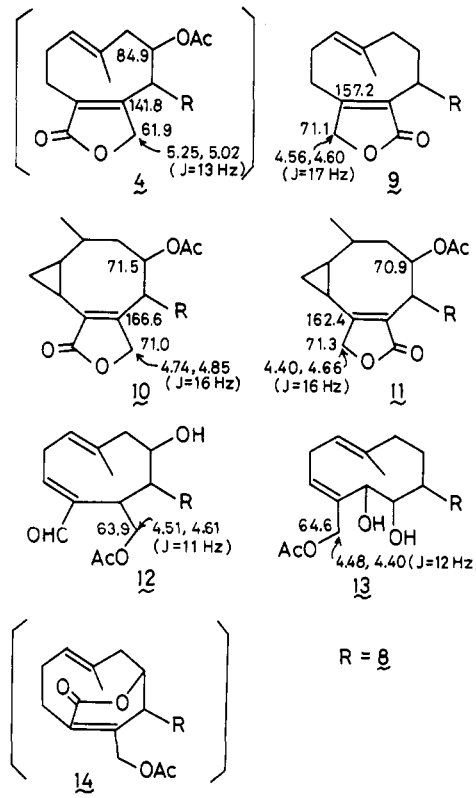



1a




3a

at first that dictyotalide B had either structure 4 or that of its C-18 carbonyl isomer (4; X = OAc, Y = $H_2$, Z = O), in which the $C_9(C_1)$ double bond of 1 had migrated to $C_1(C_2)$. Although a certain stereochemical arrangement for dictyotalide B based on structure 4 seemed to satisfy all observed coupling patterns and NOEs, we noticed some conflicts in the chemical shifts of several protons and carbons when compared with those of several other diterpenes (9–13) isolated from Dictyotaceae: (i) The chemical shift of C-4 ($\delta$ 84.9) was too low for the acetoxy methylene carbon of 4 (cf. 10[4] and 11[5]). (ii) The shift of C-18 ($\delta$ 61.9) was too high for the $\gamma$-carbon of the $\alpha,\beta$-unsaturated $\gamma$-lactone of 4 (cf. 9,[6] 10, 11); in addition, the geminal coupling constant ($J$ = 13 Hz) between the 18-methylene protons of 4 was too small (cf. 9–11), resembling instead that for the acetoxymethyl group (cf. 12,[7] 13[8]). (iii) The chemical shift ($\delta$ 141.8) of C-2 was much too high for the $\beta$-carbon of the unsaturated $\gamma$-lactone moiety of 4 (cf. 9–11). On the basis of these data, we next considered structures 3 and 14 for dictyotalide B. At first the structures seemed to be improbable since they appeared to violate Bredt's rule with a double bond at the bridgehead (C-1). Structure 14 proved to be such a case, since it was not possible to construct a molecular model for 14. However, the model for 3 was quite easily built and our attention was now focused on this structure. The structure was compatible with all the chemical shifts of the protons and carbons, especially C-2, C-4, and C-18, as well as with the coupling patterns for all the ring protons. Moreover, the unusually upfield chemical shift for C-1 ($\delta$ 141.8) could now be explained from inspection of a molecular model, which showed that the plane of the carbonyl group was twisted somewhat from that of the double bond ($C_1$=$C_2$). The absence of an absorption maximum above 210 nm in the UV spectrum of 3 also suggested that the lactonic




carbonyl was not fully conjugated with the double bond (cf. 1, $\lambda_{max}$ 220 nm; 2, $\lambda_{max}$ 226 nm). Eventually, dictyotalide B proved to have structure 3 on the basis of long-range carbon–proton couplings. In the COLOC spectrum ($J$ = 7 Hz), a correlation peak showing coupling between the lactonic carbonyl carbon (C-18) and H-4 was clearly observed. Also, couplings from the methylene protons on C-19 to the carbonyl carbon of the acetoxy group were present (Table I). These observations eliminated the possibility of structure 4. Conformation 3a was the most probable one, since it best fitted the coupling patterns and NOEs found for dictyotalide B.

The $Z$ configuration of $C_1$=$C_2$ was confirmed by the following chemical transformations. Dictyotalide B was saponified (NaOH/dioxane) and treated with acetic anhydride in pyridine, yielding a 1:2 mixture of 3 and 5. Although the hydroxy group at C-4 of 5 could not be acetylated owing to severe steric hindrance from the side chain on C-3,[9] the lactone formation agreed with the $Z$ configuration of the 1-olefin group. The geminal coupling constant for 19-$H_2$ ($\delta$ 4.68 and 4.73, $J_{gem}$ = 17 Hz) is, as expected, different from that corresponding to 3 ($\delta$ 5.25 and 5.02, $J_{gem}$ = 13.3 Hz), but coincident with those of 9–11.

Structure 6 of dictyotalide A, $[\alpha]_D$ −102° ($c$ 0.71, $CHCl_3$), $C_{20}H_{30}O_3$ ($m/e$ 318.2196), was deduced in essentially the same manner: The occurrence of side chain 8, an aldehyde group ($^1$H NMR $\delta$ 9.56, IR 2700 and 1725 cm$^{-1}$), a trisubstituted olefin ($\delta$ 5.40) having an allylic methyl ($\delta$ 1.86), and a $\gamma$-lactone (1760 cm$^{-1}$) was confirmed from its spectral properties (Table II). We assigned the $E$ configuration to the geometry of 6-olefin because a cross peak due to the NOE between H-7 and H-5 was observed in the NOESY spectrum; this was despite the fact that the chemical shift ($\delta$ 22.4) of C-20 was low for an allylic methyl which is trans to the olefin proton. The presence of the cross peak from

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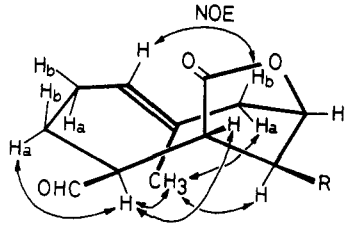
(9) Ishitsuka, M.; Kusumi, T.; Tanaka, J.; Kakisawa, H. *Chem. Lett.* **1982**, 1517.

Table I. $^1H$ and $^{13}C$ NMR ($CDCl_3$) Spectral Data of Dictyotalide B (3)[a]

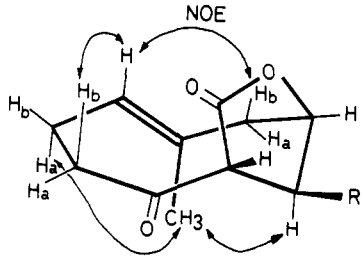
| position no. | $^1H$ NMR | $^{13}C$ NMR | C–H long-range couplings[b] |
|---|---|---|---|
| 1 | | 141.8 (s) | H-8a, H-9a, H-9b, H-19 |
| 2 | | 133.3 (s) | H-3, H-4, H-9a, H-9b, H-19 |
| 3 | 2.52 (d, 8.5) | 50.7 (d) | H-5b, H-17 |
| 4 | 4.73 (dd, 3.4, 2.3) | 84.9 (d) | H-5b |
| 5a | 2.18 (dd, 13.7, 3.4) | 44.2 (t) | |
| 5b | 2.60 (dd, 13.7, 2.3) | | |
| 6 | | 135.7 (s) | H-4, H-5b, H-20 |
| 7 | 5.07 (br dd, 12.1, 4.8) | 125.9 (d) | H-5b, H-9b, H-20 |
| 8a | 2.46 (ddt, 12.3, 4.8, 3.5) | 29.7 (t) | H-9a, H-9b |
| 8b | 2.11 (qd, 12.3, 3.5) | | |
| 9a | 1.87 (td, 12.3, 3.5) | 33.5 (t) | H-8b, H-19 |
| 9b | 2.54 (dt, 12.3, 3.5) | | |
| 10 | 1.49 (dqm, 8.5, 6.6) | 34.5 (d) | H-17 |
| 11 | 1.38 (m) | 33.5 (t) | |
| | 0.96 (m) | | |
| 12 | 2.00 (m) | 25.7 (t) | |
| | 1.85 (m) | | |
| 13 | 5.00 (br t, 7.0) | 124.0 (d) | H-15, H-16 |
| 14 | | 132.0 (s) | H-15, H-16 |
| 15 | 1.66 (br s) | 25.8 (q) | |
| 16 | 1.57 (br s) | 17.8 (q) | |
| 17 | 0.92 (d, 6.6) | 17.3 (q) | |
| 18 | | 169.3 (s) | H-3, H-4 |
| 19 | 5.25 (d, 13.3) | 61.9 (t) | |
| | 5.02 (d, 13.3) | | |
| 20 | 1.38 (br s) | 19.2 (q) | |
| Ac | | 170.8 (s) | H-19, H-Ac |
| | 2.10 (s) | 21.0 (q) | |

[a] $^1H$ and $^{13}C$ NMR spectra were recorded at 500 and 125 MHz, rspectively. Chemical shifts are reported as $\delta$ values, and $J$ values are given in hertz in parentheses. Multiplicities and assignments of the carbon signals were determined by INEPT and C–H COSY experiments. [b] $J$ = 7 Hz.

H-3 to the lactonic carbonyl carbon (C-18) in the COLOC spectrum of dictyotalide A is consistent with structure **6**. On the basis of the NOEs and the coupling patterns of the protons, the stereochemistry and conformation of dictyotalide A were inferred to be as shown in **6a**.




6a




7a

In the $^1H$ NMR spectrum (500 MHz; 25 °C) of dictyotalide A (**6**), the proton signals are accompanied by small peaks appearing around each peak. For example, besides the singlet at $\delta$ 9.56 due to the aldehyde proton, there are two other singlets at $\delta$ 9.58 and 9.55. The integral ratio of the three peaks is 5:1:1. When the $^1H$ NMR spectrum was recorded at 105 °C (DMSO-$d_6$), most of the small signals had disappeared and the aldehyde signals became a single singlet, indicating that dictyotalide B exists in three conformations with **6a** being the major one.

Although dictyotalide A showed a single spot or peak on TLC (hexane/ethyl acetate) and GC (OV-1; 200 °C), reverse-phase HPLC ($MeOH/H_2O$) appeared to show two peaks. Reinjection of each component immediately after separation again revealed two peaks. We first thought the two peaks were the conformational isomers of dictyotalide A, but found they were due to an equilibrated mixture of the aldehyde and hemiacetals formed by the action of methanol on the aldehyde group: the $^1H$ NMR signal of the aldehyde proton greatly weakened in the protic solvent ($CD_3OD/D_2O$).

Nordictyotalide (**7**), $[\alpha]_D$ −31° (*c* 0.43, $CHCl_3$) exhibited 19 signals in the $^{13}C$ NMR spectrum. HRMS confirmed the compound to be a norditerpene, which showed a molecular peak at *m/e* 304.2026 ($C_{19}H_{28}O_3$). The presence of a carbonyl (IR 1705 $cm^{-1}$; $^{13}C$ NMR $\delta$ 207.3) and a $\gamma$-lactonic carbonyl (IR 1770 $cm^{-1}$; $^{13}C$ NMR $\delta$ 176.5) group with side chain **8** was revealed by the spectral data. The $^1H$ NMR spectrum (500 MHz) shows well-separated signals, and assignment of the coupling patterns of protons and chemical shifts of carbons (Table II) was done by using $^1H$–$^1H$ and $^1H$–$^{13}C$ COSY spectra; the structure **7** was deduced for nordictyotalide. Especially noticeable is that H-9b shows a signal far downfield ($\delta$ 3.46) in the $^1H$ NMR spectrum. This anomaly could be explained by assuming conformation **7a**, where the proton was located close to the lactonic carbonyl (C-18) and seriously deshielded by the anisotropic effect from the carbonyl group. Actually, the conformation **7a** proved to be reasonable since NOEs were found as depicted in the structure.

From *Pachydictyon coriaceum* we have isolated pachyaldehyde (**15**),[10] another norxenicane. The present norditerpene, nordictyotalide (**7**), has a novel carbon framework different from that of **15**. Biosynthetically, both norditerpenes may be derived by elimination of C-19

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Table II. $^1H$ and $^{13}C$ NMR ($CDCl_3$) Spectral Data of Dictyotalide A (6) and Nordictyotalide (7)[a]

| position no. | 6 | | 7 | |
|---|---|---|---|---|
| | $^1H$ NMR | $^{13}C$ NMR | $^1H$ NMR | $^{13}C$ NMR |
| 1 | 2.14 (dd, 10, 2) | 57.6 (d) | | 207.3 (s) |
| 2 | 3.32 (dd, 3, 2) | 40.4 (d) | 2.83 (d, 2) | 60.5 (d) |
| 3 | 1.79 (ddd, 5, 3, 2) | 52.6 (d) | 2.33 (dt, 5.5, 2) | 47.1 (d) |
| 4 | 4.58 (dt, 4, 2) | 81.4 (d) | 4.56 (dt, 4, 2) | 81.6 (d) |
| 5a | 1.97 (dd, 15, 4) | 40.7 (t) | 1.94 (dd, 15, 4) | 41.2 (t) |
| 5b | 2.74 (br d, 15) | | 2.68 (br d, 15) | |
| 6 | | 130.8 (s) | | 132.2 (s)[b] |
| 7 | 5.40 (br dd, 12, 5) | 128.5 (d) | 5.62 (ddq, 12, 4, 1.8) | 126.4 (d) |
| 8a | 2.38 (dtd, 13, 12, 5) | 28.9 (t) | 2.69 (qd, 12, 6) | 25.5 (t)[c] |
| 8b | 2.33 (m) | | 2.16 (br ddd, 12, 6.5, 4) | |
| 9a | 2.08 (ddd, 13, 5, 2) | 25.5 (t) | 2.18 (br dd, 11, 6) | 36.8 (t) |
| 9b | 2.18 (dddd, 13, 12, 10, 4.5) | | 3.46 (ddd, 12, 11, 6.5) | |
| 10 | 1.58 (qdm, 7, 5) | 36.8 (d) | 1.60 (qdm, 6.8, 5.5) | 36.6 (d) |
| 11 | 1.30 (m) | 33.5 (t) | 1.32 (m) | 33.3 (t) |
| | 1.14 (m) | | 1.10 (dddd, 15, 13, 9, 5.5) | |
| 12 | 2.02 (m) | 25.7 (t) | 2.05 (m) | 25.7 (t)[c] |
| | 1.93 (m) | | 1.92 (m) | |
| 13 | 5.04 (br t, 7) | 123.9 (d) | 5.04 (br t, 7) | 123.7 (d) |
| 14 | | 132.2 (s) | | 131.6 (s)[b] |
| 15 | 1.67 (br s) | 25.8 (q) | 1.66 (d, 1.3) | 25.7 (q) |
| 16 | 1.58 (br s) | 17.8 (q) | 1.58 (d, 1.0) | 17.7 (q) |
| 17 | 0.89 (d, 7) | 15.8 (q) | 0.87 (d, 6.8) | 15.4 (q) |
| 18 | | 178.7 (s) | | 176.5 (s) |
| 19 | 9.56 (s) | 199.7 (d) | | |
| 20 | 1.86 (br s) | 22.4 (q) | 1.63 (d, 1.8) | 21.2 (q) |

[a] $^1H$ and $^{13}C$ NMR spectra were recorded at 500 and 125 MHz, respectively. Chemical shifts are reported as $\delta$ values, and $J$ values are given in hertz in parentheses. Multiplicities and assignments of the carbon signals were determined by INEPT and C–H COSY experiments. [b,c] These assignments can be interchanged.

and C-18 from dictyodial[3] or its congeners.

Cytotoxic activities ($IC_{50}$, $\mu g/mL$) of the present diterpenoids against B16 mouse melanoma cells are as follows: 4-acetoxydictyolactone (1), 1.57; dictyotalide A (6), 2.57; dictyotalide B (3), 0.58; nordictyotalide (7), 1.58.

## Experimental Section

Infrared spectra were recorded on a Hitachi 215 grating spectrophotometer, and ultraviolet spectra were recorded on a Hitachi 340 spectrophotometer. Optical rotations were measured on a JASCO DIP-181 polarimeter, using a 10-cm microcell. $^1H$ and $^{13}C$ NMR spectra were recorded on JEOL JNM-FX-90Q and Bruker AM-500 spectrometers; chemical shifts are reported relative to $Me_4Si$ ($\delta$ 0), and coupling constants are given in hertz. High-resolution mass spectra were taken on a JEOL JMS-DX-300 spectrometer. Low-resolution mass spectra were obtained from a Hitachi RMU-6M mass spectrometer.

**Materials.** *D. dichotoma* (25 kg) was collected at Yagachi, Okinawa, in June 1983. (The alga was identified by Prof. Y. Yokohama, and the reference specimen is preserved at The Experimental Station of Marine Biology, The University of Tsukuba.) The seaweed was soaked in MeOH immediately after collection and allowed to stand for 1 week. The MeOH was decanted, and the residual material was again extracted with fresh MeOH for 1 week. The combined MeOH extracts were concentrated, and the residue was successively washed with hexane, dichloromethane, and ethyl acetate. The hexane extract was concentrated to give a dark green residue (100 g), and this material was separated by chromatography on silica gel (Merck, Kieselgel 60; 1 kg). Elution with gradient proportions of hexane and ethyl acetate yielded a fraction (430 mg), which was further separated by flash chromatography on silica gel (Wakogel C-300; 35 g, $CH_2Cl_2$) followed by separation with preparative TLC (Merck, Kieselgel 60, $GF_{254}$; $CH_2Cl_2$) to give 4-acetoxydictyolactone (1; 13 mg). Dictyotalide A (6; 18 mg) and B (3; 10 mg) and nordictyotalide (7; 8 mg) were obtained in essentially the same manner as described above from the hexane extract.

**4-Acetoxydictyolactone (1)**: low-resolution MS, $m/e$ (relative intensity) 360 ($M^+$, 4), 318 (13), 300 (30), 165 (100), 136 (90), 109 (43), 82 (41), 69 (39); IR ($CCl_4$) 1760, 1740, 1640, 1365, 1230, 1110 $cm^{-1}$; UV (EtOH) 220 nm ($\epsilon$ 8500); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 0.90 (3 H, d, $J$ = 6.7 Hz, H-17), 1.2 (2 H, m, H-11), 1.64 (1 H, m, H-10), 1.54, 1.64, 1.78 (each 3 H, d, $J$ = 1.5 Hz, H-16,15,20), 1.88 (2 H, m, H-12), 2.03 (3 H, s, Ac), 2.10 (1 H, dd, $J$ = 2.3, 1.5 Hz, H-3), 2.17 (1 H, ddd, $J$ = 13.8, 4.5, 1.0 Hz, H-5a), 2.47 (1 H, dd, $J$ = 13.8, 2.3 Hz, H-5b), 2.99 (1 H, dddd, $J$ = 17.6, 7.5, 4.0, 1.0 Hz, H-8a), 3.19 (1 H, ddt, $J$ = 17.6, 11.6, 2.2 Hz, H-8b), 3.36 (1 H, dtd, $J$ = 7.7, 2.2, 1.6 Hz, H-2), 4.10 (1 H, dd, $J$ = 9.6, 7.7 Hz, H-18b), 4.44 (1 H, dd, $J$ = 9.6, 1.6 Hz, H-18a), 4.99 (1 H, triplet of septets, $J$ = 7.1, 1.5 Hz, H-13), 5.27 (1 H, dd, $J$ = 4.5, 2.3 Hz, H-4), 5.36 (1 H, dd, $J$ = 11.6, 4.0 Hz, H-7), 6.95 (1 H, dt, $J$ = 7.5, 2.2 Hz, H-9); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 172.9 (C-19 or Ac), 169.8 (Ac or C-19), 139.8 (C-9), 134.9 (C-1), 134.9 (C-6), 132.1 (C-14), 126.5 (C-7), 123.8 (C-13), 75.6 (C-4), 68.1 (C-18), 49.8 (C-3), 45.1 (C-5), 37.6 (C-11), 36.7 (C-2), 32.3 (C-10), 29.5 (C-8), 25.8 (C-12), 25.7 (C-15), 21.5 (Ac), 19.7 (C-20), 17.8 (C-16), 17.4 (C-17).

**Dictyotalide B (3)**: low-resolution MS, $m/e$ 360 ($M^+$, 4), 318 (9), 300 (21), 232 (38), 217 (35), 189 (35), 140 (71), 109 (76), 69 (100); IR ($CCl_4$) 1750, 1640, 1220, 1170 $cm^{-1}$.

**Dictyotalide A (6)**: low-resolution MS, $m/e$ 318 ($M^+$, 36), 300 (22), 257 (40), 192 (74), 135 (100), 109 (82), 107 (100), 82 (92), 69 (64); IR ($CCl_4$) 2700, 1760, 1725, 1175 $cm^{-1}$.

**Nordictyotalide (7)**: low-resolution MS, $m/e$ 304 ($M^+$, 9), 286 (20), 271 (11), 241 (54), 151 (74), 135 (67), 109 (93), 82 (72), 69 (100), 68 (91); IR ($CCl_4$) 1770, 1705, 1170 $cm^{-1}$.

**Saponification of Dictyotalide B (3).** To a solution of 3 (0.9 mg) in dioxane (0.25 mL) was added a drop of 1 M NaOH, and the mixture was allowed to stand at room temperature for 4 h. The solution was neutralized with 1 M HCl and extracted with ether. The ether layer was dried over $MgSO_4$ and evaporated to give a crude oil, which was separated by preparative TLC, yielding 5 (0.5 mg; $C_{20}H_{30}O_3$) and another product, which was acetylated with acetic anhydride in pyridine, giving 3 (0.2 mg) identified by TLC and the $^1H$ NMR spectrum. Compound 5: MS, $m/e$ 318 ($M^+$), 300, 250, 232, 217, 140, 109, 82, 69 (base); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 0.99 (3 H, d, $J$ = 6 Hz), 1.42, 1.62 (each 3 H, br s), 1.5 (3 H, br s, overlapped with $H_2O$ signal), 3.98 (1 H, br s), 4.68, 4.73 (each 1 H, d, $J$ = 17 Hz), 4.94 (1 H, br t, $J$ = 7 Hz), 5.12 (1 H, dd, $J$ = 12, 4 Hz).

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