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DICTYMAL, A NEW SECO-FUSICOCCIN TYPE DITERPENE FROM THE BROWN ALGA DICTYOTA DICHOTOMA

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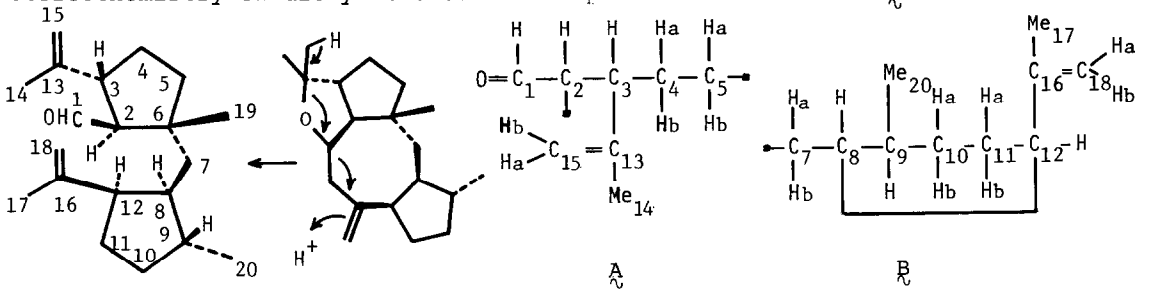
Abstract: The structure of dictymal, a new seco-fusicoccin type diterpene isolated from the brown alga Dictyota dichotoma, has been determined mainly on the basis of the 2D NMR studies.

In the course of our continuing studies of the chemical constituents of the title alga[1], a new diterpene aldehyde, designated as dictymal, was isolated from the alga collected at Oshoro Bay, Hokkaido. We wish to describe the structure determination of this metabolite.

Methanol extracts of the fresh alga were fractionated by silica gel column chromatography repeatedly to yield dictymal (1), as a colorless oil, $C_{20}H_{32}O$ (m/z M^+ Found 288.24309, Calcd 288.24519), $[\alpha]_D^{18}$ +16.4° (c 0.88, $CHCl_3$). Dictymal showed in its IR and ^1H NMR spectra[2] the presence of an aldehyde group [ν 2820, 2720 and 1720 cm^{-1}; δ 9.57 (1H, d, J=3 Hz)], two isopropenyl groups [ν 3060, 1640 and 890 cm^{-1}; δ 1.57 and 1.63 (each 3H, br s), 4.70, 4.74, 4.78 and 4.89 (each 1H, br s)], a tertiary methyl group [δ 0.87 (3H, s)] and a secondary methyl group [δ 0.94 (3H, d, J=7)]. Those spectral data and five degrees of unsaturation seemed to indicate 1 to be a bicyclic compound. The 2D NMR COSY spectrum revealed the presence of two partial structures, A and B, which were supported by the 2D NMR relayed coherence transfer COSY spectrum[3]. The spectrum showed the eleven contour plots exhibited by the following two-proton pairs, (H-2, H-4a), (H-2, H-4b), (H-3, H-5a), (H-3, H-5b), (H-7a, H-9), (H-7a, H-12), (H-8, Me-20), (H-9. H-12), (H-10a, H-12), (H-10b, H-12) and (H-12, Me-20). By three plots, (H-7a, H-9), (H-8, Me-20) and (H-9, H-12), H-8 was assigned to a vicinal proton of H-9, though $J_{8,9}$ was ∿0 Hz. J values were obtained by the 2D NMR J resolved spectrum[4]. Each carbon, except for three quaternary carbons (δ 147.2, 147.0 and 48.0), was characterized by the 2D NMR C-H COSY spectrum[5]. The former two carbons were assigned to C-13 and 16 on account of those chemical shifts and the latter was to the uniden-

tified 20th carbon, C-6. Therefore, through the ^1H assignments, the carbon skelton was given and the planner structure of 1 was established. Relative stereochemistries of both rings were determined by the NOEs observed with respect to those five pairs of protons, (H-1, H-3), (H-1, Me-19), (H-3, Me-19), (H-8, Me-20) and (H-12, Me-20). Dictymal was considered to be biogenetically derived from epoxydictymene (2)[6] which was also found in the same alga. The stereochemistry of dictymal should be represented as formula 1[7].



1 2 A B

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2) 1: ν_{max}^{film} 3060, 2820, 2720, 1720, 1640 and 890 cm^{-1}; δ (500 MHz, C_6D_6) 0.87 (3H, s; Me-19), 0.94 (3H, d, J=7 Hz; Me-20), 1.06 (1H, dddd, J=13, 9, 8, 6; H-10a), 1.24 (1H, ddd, J=12, 8, 5; H-5b), 1.30 (1H, dd, J=14, 6; H-7a), 1.44 (1H, dddd, J=12, 10, 8, 5; H-4a), 1.44 (1H, ddd, J=10, 6, 4; H-8), 1.51 (1H, dd, J=14, 4; H-7b), 1.51 (1H, dt, J=12, 5; H-5a), 1.54 (1H, dtd, J=13, 9, 8; H-11b), 1.57 (3H, br s; Me-14), 1.63 (3H, br s; Me-17), 1.67 (1H, dtd, J=13, 8, 4; H-11a), 1.73 (1H, ddt, J=12, 10, 5; H-4b), 1.75 (1H, quint d, J=7, 6; H-9), 1.86 (1H, dddd, J=13, 9, 7, 4; H-10b), 2.36 (1H, dd, J=10, 3; H-2), 2.52 (1H, dt, J=10, 8; H-12), 3.01 (1H, q, J=10; H-3), 4.70 (1H, br s; H-15a), 4.74 (1H, br s; H-18b), 4.78 (1H, br s; H-15b), 4.89 (1H, br s; H-18a) and 9.57 (1H, d, J=3; H-1); δ (126 MHz, C_6D_6) 21.0 (q; C-14), 22.3 (q; C-20), 23.0 (q; C-19), 23.3 (q; C-17), 29.2 (t; C-11), 29.5 (t; C-4), 32.5 (t; C-10), 40.5 (t; C-5), 41.1 (d; C-9), 42.0 (t, C-7), 46.5 (d; C-8), 46.6 (d; C-3), 48.0 (s; C-6), 50.8 (d; C-12), 65.2 (d; C-2), 110.8 (t; C-15), 112.7 (t; C-18), 147.0 and 147.2 (each s; C-13 and C-16) and 203.7 (d; C-1).

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