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SLIGHTLY POLAR SECONDARY METABOLITES FROM THE FAR-EASTERN BROWN ALGA *Dictyota dichotoma*

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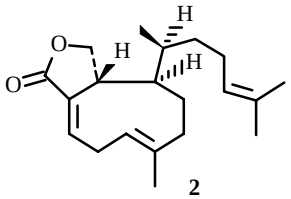
The brown alga *Dictyota dichotoma* is well-known as a source of terpenoids with bactericidal, antifungal, insectidical, antitumor, and antiviral activity. Secondary metabolites from populations of this alga growing near the shores of Japan, Australia, India, Pakistan, Greece, Italy, and Spain have been previously studied. It has been shown that the terpenoid composition depends on the collection site [1]. Nevertheless, the chemical composition of the Russian population of *D. dichotoma* inhabiting the northwest shore of the Sea of Japan has not been studied.

In continuation of our research on natural compounds from this alga species collected in Troits Bay of the Sea of Japan [2], we communicate the isolation from the ethanol extract of *D. dichotoma* (dry alga weight 53 g) another four diterpenoids (**1**-**4**).



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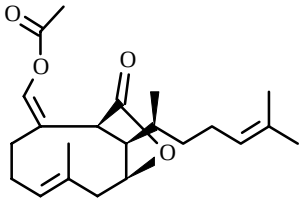

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Compound **1** (2.5 mg, 0.008% of dry weight) was isolated by column chromatography over silica gel (hexane:EtOAc, 25:1) followed by normal-phase HPLC over a column of Ultrasphere™ Si (5 μm, 9.4 × 250 mm, hexane:EtOAc, 30:1). We isolated analogously using hexane:EtOAc (10:1) and HPLC compound **2** (19.4 mg, 0.06% of dry wt.), fractions containing **3** (9.3 mg) as the main constituent, and fractions containing **4** (8.6 mg). Compounds **3** (2 mg, 0.007% of dry wt.) and **4** (3.7 mg, 0.01% of dry wt.) were purified by HPLC over columns of Ultrasphere™ Si (5 μm, 4.6 × 250 mm, hexane:EtOAc, 20:1 for **3**; 15:1 for **4**).

The structures and relative stereochemistries of **1**-**4** were found using one-dimensional and two-dimensional NMR spectroscopy (PMR and ^{13}C NMR, ^{1}H—^{1}H COSY, DEPT, HSQC, HMBC, and NOESY) and GC—MS spectra. They were identified as 18-hydroxy-3,7-dolabelladiene (**1**) [3], dictyolactone (**2**) [4], dilopholide (**3**) [5], and dictyotin B (**4**) [6]. Diterpenoids **2** and **3** were isolated for the first time from *D. dichotoma*. They were previously known as secondary metabolites of the algal-toxic mollusk *Aplysia depilans* [4] and brown alga *Dilophus ligulatus* [5], respectively. Recently **2** was isolated from the alga *Dilophus okamurae* [7]. We report for the first time the NMR spectra of dictyotin B in C_6D_6. Compounds **1** and **4** were found previously in Italian and Japanese populations of *D. dichotoma*, respectively [3, 6].

18-Hydroxy-3,7-dolabelladiene (1). Colorless oil, $[\alpha]_D^{25}$ +20.0° (*c* 0.1, $CHCl_3$), lit. [3] $[\alpha]_D$ +27.5° (*c* 1, $CHCl_3$). The PMR and ^{13}C NMR spectra ($CDCl_3$) agreed with those reported earlier [3].

GC—MS (*m*/*z*, I_{rel}, %) 290 (3) $[M]^+$, 272 (24), 257 (20), 243 (3), 229 (35), 217 (10), 203 (13), 189 (45), 175 (21), 161 (51), 147 (37), 135 (93), 121 (73), 107 (66), 95 (79), 81 (71), 67 (62), 59 (100), 55 (40).

Dictyolactone (2). Colorless oil, $[\alpha]_D^{20}$ -162.7° (*c* 1, MeOH), lit. [4] $[\alpha]_D^{25}$ -165.0° (*c* 0.9, MeOH). The PMR and ^{13}C NMR spectra ($CDCl_3$) agreed with those reported earlier [4].

GC—MS (*m*/*z*, I_{rel}, %): 302 (7), 287 (7), 257 (11), 233 (17), 221 (15), 203 (11), 189 (11), 175 (20), 151 (17), 137 (50), 119 (37), 105 (43), 91 (61), 82 (100), 69 (85), 55 (61).

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Dilopholide (3). Colorless oil, $[\alpha]_D^{20}$ -87.1° (*c* 0.1, $CHCl_3$), lit. [5] $[\alpha]_D$ -113.7° (*c* 0.86, $CHCl_3$). The PMR and ^{13}C NMR spectra ($CDCl_3$) agreed with those reported earlier [5].

GC—MS (*m*/*z*, I_{rel}, %): 360 (4) $[M]^+$, 331 (9), 218 (20), 300 (15), 285 (9), 249 (22), 231 (22), 218 (17), 207 (26), 189 (39), 175 (22), 161 (70), 147 (28), 135 (50), 119 (35), 109 (61), 93 (39), 81 (41), 77 (17), 69 (100), 55 (41).

Dictyotin B (4). Colorless oil, $[\alpha]_D^{20}$ -36.0° (*c* 0.1, $CHCl_3$), lit. [6] $[\alpha]_D^{25}$ -30.0° (*c* 0.19, $CHCl_3$).

PMR spectrum (500 MHz, C_6D_6, δ, ppm, J/Hz): 5.61 (1H, br.s), 5.23 (1H, tt, J = 7.2, 1.4), 1.95-2.10 (m), 1.75 (1H, m), 1.70 (3H, br.s), 1.65 (3H, br.s), 1.58 (3H, br.s), 1.43 (1H, m), 1.25-1.35 (m), 1.11-1.21 (m), 1.04 (1H, m), 0.99 (3H, s), 0.77 (3H, d, J = 6.9).

^{13}C NMR spectrum (125 MHz, C_6D_6, δ, ppm): 13.5, 17.7, 20.9, 22.6, 22.9, 24.0, 25.9, 26.7, 31.2, 31.3, 36.2, 39.8, 42.7, 45.2, 50.4, 71.5, 122.8, 125.4, 131.0, 134.8.

GC—MS (*m*/*z*, I_{rel}, %): 290 (7) $[M]^+$, 272 (100), 257 (7), 205 (11), 187 (36), 159 (43), 145 (25), 135 (18), 121 (54), 109 (36), 95 (54), 81 (32), 69 (46), 55 (29).

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