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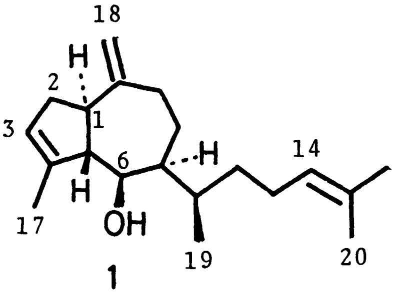
NEW HYDROAZULENOID DITERPENES FROM THE MARINE ALGA DICTYOTA DICHOTOMA

Nobuyasu ENOKI, Ryoichi ISHIDA[†], Shiro URANO[††], Masamitsu OCHI[†††],
Takashi TOKOROYAMA[††††], and Takeshi MATSUMOTO[*]
Department of Chemistry, Faculty of Science, Hokkaido University,
Sapporo 060; [†]Muroran Institute of Technology, Muroran 050;
[††]Tokyo Metropolitan Institute of Gerontology, Tokyo 173;
[†††]Faculty of Science, Kochi University, Kochi 780;
[††††]Faculty of Science, Osaka City University, Osaka 558

Abstract: Four new diterpenes have been isolated from a Japanese brown alga and their structures have been shown to be expressed by 2, 3, 4 and 5, on the basis of spectral and chemical means.

Since the structure of the first hydroazulenoid diterpene pachydictyol A (1) was reported by Fenical et al.,[1)] an increasing number of diterpenes of this series have been isolated from brown algae and characterized[2)]. We report here the isolation and structure determination of four new diterpenes of this class, dictytriene A (2), dictytriene B (3), dictyone (4) and dictyriol (5). The former two compounds are hitherto unknown parent hydrocarbons of this series and the latter two are the first examples of this category in which the side chain double bond is oxygenated.



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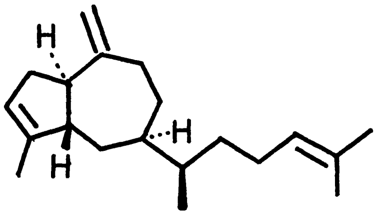

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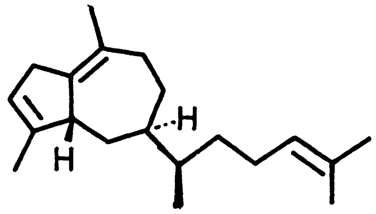

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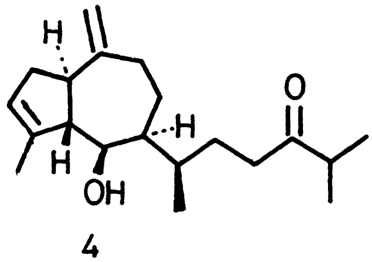

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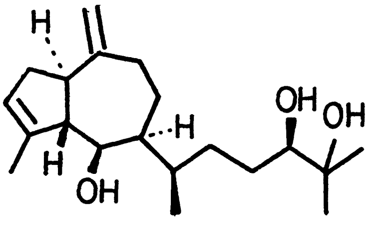

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The alga *Dictyota dichotoma* (wet 16 kg) was collected in July 1979 at Oshoro Bay, Hokkaido and immediately extracted with MeOH ar room temperature. The extracts (108 g) gave on vacuum distillation (130-180 °C/10^{-3} mmHg) a viscous oil (56 g), which on being passed through a column (SiO_2, benzene-AcOEt) afforded successively a mixture (208 mg) of hydrocarbons 2 and 3, pachydictyol A (1) (2.3 g), ketone 4 (88 mg) and triol 5 (750 mg). The hydrocarbons were further separated by preparative glc (SE-30, 200 °C, He) to give pure 2 (81 mg) and 3 (75 mg). 2: oil, $[\alpha]_D^{22}$+37° (c 0.28, cyclohexane); IR 1670 cm^{-1}; MS m/z 272 (M^+), 159 (base peak, dimethylcyclopentanotropylium cation); MW m/z found 272.2478, calcd for $C_{20}H_{32}$ 272.2478. 3: oil, $[\alpha]_D^{22}$+54.4° (c 0.29, cyclohexane); IR 1645 cm^{-1}; MS m/z 272 (M^+), 159 ($M-C_8H_{17}$, base peak; MW m/z found 272.2478, calcd for $C_{20}H_{32}$ 272.2478. The ^1H nmr spectrum of 2 exhibited peaks at $\delta(CDCl_3)$ 0.75 (3H, d, J=6 Hz), 1.60 (3H, s), 1.67 (6H, s), 4.47 (1H, s), 4.57 (1H, s), 5.04 (1H, t, J=5 Hz) and 5.43 (1H, br s). Comparison of these shift values with those of 1 suggested that 2 is the parent hydrocarbon of the alcohol 1. Formula 2 thus deduced was supported by the ^{13}C chemical shift values (Table 1). For the purpose of confirming the suggested structural formula, pachydictyol A was treated with MsCl-Et_3N (CH_2Cl_2/-20 °C) to yield a mesylate, which on being reduced with $LiAlH(Et)_3$ afforded a hydrocarbon, identical in all respects including the specific rotation value with 2. The second triene 3 was isomeric with 2 and moreover, the ^1H nmr spectral data of 3 [$\delta(CDCl_3)$ 0.70 (3H, d, J=6 Hz), 1.61 (3H, s), 1.66 (6H, s), 1.68 (3H, s), 5.11 (1H, t, J=5 Hz), 5.40 (1H, br s)] indicated the presence of a tetrasubstituted double bond bearing a methyl group instead of the gem-disubstituted double bond of 2. Therefore it was concluded that triene B is the $\Delta^{1,10}$ analog of 2. The ^{13}C chemical shifts and their multiplicities (Table 1) are also in conformity with this formulation.$^{3)}$

The IR, NMR and MS spectra of dictyone (4) [oil, $[\alpha]_D^{28}$+48.5°(c 1.15 $CHCl_3$); IR 3600, 3200, 1700, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (3H, d, J=6 Hz), 1.08 (6H, d, J=6 Hz), 1.80 (3H, br s), 3.91 (1H, m), 4.46 (2H, s), 5.29 (1H, br s), ^{13}C NMR δ ($CDCl_3$) see Table 1; MS m/z 304 (M^+), 159 (base peak); MW m/z found 304.2369, calcd for $C_{20}H_{32}O_2$ 304.2376] implied that it is a hydroxyketone closely related to 1 and its carbonyl group is present on the side chain instead of the double bond of 1 and its carbonyl group is present on the side chain instead of the double bond of 1, since the isobutenyl group characteristic to 1 is lacking in 4 (^1H and ^{13}C NMR). The structure including absolute configuration was determined by chemical transformation of dictyone (4)$^{4)}$ to pachydictyol A. Dictyone (4) was reduced with $LiAlH_4$ in THF at 25 °C to afford an isomeric mixture. Treatment of this diol with p-toluenesulfonyl chloride in pyridine at 0 °C yielded a tosylate, which upon treatment with DBU in benzene at 25 °C was converted into an alcohol, identical in all respects [IR, ^1H NMR, MS and optical rotation] with pachydictyol A.

Dictytriol (5) [mp. 92-93 °C, $[\alpha]_D^{24}$+80.7° (c 0.63, $CHCl_3$); IR 3600, 3200, 1635 cm^{-1}; MS m/z 322 (M^+), 159 (base peak); MW m/z found 322.2523,calcd for $C_{20}H_{34}O_3$ 322.2525)] exhibited ^1H NMR signals at $\delta(CDCl_3)$ 0.95 (3H, d, J=6 Hz), 1.22(3H, s), 1.28 (3H, s), 1.77 (3H, br s), 3.40 (1H, m), 3.96 (1H, br s), 4.79

(2H, s), 5.38 (1H, m) and ^{13}C NMR signals shown in Table 1. These data indicated that the triol has a structure very similar to that of pachydictyol A except for the absence of the trisubstituted double bond and the presence of a secondary-tertiary glycol group in the eight-carbon side chain of 5. As expected treatment of 5 with $TiCl_3$-$LiAlH_4$ in THF at reflux for 8 h yielded an alcohol[5)] which was identical with pachydictyol A in all respects. The CD spectrum of 5 in $CHCl_3$ in the presence of $Eu(fod)_3$ showed a negative Cotton effect at 314 nm ($\Delta\varepsilon$-5.2). Therefore dictytriol has the 14-R absolute configuration[6)] and its full structure is expressed by formula 5.

Table 1. ^{13}C nmr data[a] of 1, 2, 3, 4 and 5

Carbon	1[b]	2	3	4	5
1	46.1	45.1,d[d]	124.3,s	45.8,d	45.9,d
2	33.9	30.5,t[e]	32.0,t	33.9,t	33.8,t
3	123.9	122.1,d	125.0,d	123.4,d	123.8,d
4	141.5	134.3,s	134.0,s	142.2,s	141.5,s
5	60.4	44.8,d[d]	39.2,d	59.2,d	59.8,d
6	75.1	26.8,t[c]	26.9,t[c]	73.7,d	74.1,d
7	47.7	44.2,d	42.3,d	48.9,d	48.7,d
8	23.5	24.7,t	21.5,t	23.7,t	24.2,t
9	40.6	36.3,t[e]	32.5,t	40.5,t	40.5,t
10	152.5	152.8,s	131.0,s	152.5,s	152.3,s
11	35.1	31.2,d	31.6,d	34.2,d	32.8,d
12	34.8	35.8,t	35.9,t	37.9,t	33.8,t
13	25.7	26.3,t[c]	26.3,t[c]	27.2,t	27.8,t
14	124.7	124.6,d	124.6,d	216.0,s	76.7,s
15	131.4	130.1,s	130.1,s	40.9,d	73.1,s
16	25.7	25.7,q	25.7,q	18.3,q[c]	24.2,q
17	15.9	23.8,q	23.6,q	16.0,q	16.0,q
18	107.1	103.0,t	18.5,q	106.8,t	107.0,t
19	17.5	13.3,q	13.9,q	18.0,q[c]	17.7,q
20	17.7	17.7,q	17.7,q	18.3,q[c]	23.1,q

[a] δ Values are relative to TMS in $CDCl_3$.

[b] A. F. Rose and J. J. Sims, Tetrahedron Lett., 1977, 2935.

[c,d] Signals within a column may be reversed.

[e] Large deshielding δ-effect of the C-6 hydroxyl group is observed for this skeleton. On the other hand in cyclohexane, shielding δ-effect of a hydroxyl group is reported: H-J. Schneider and V. Hoppen, Tetrahedron Lett., 1974, 579.

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3) Since 1979 we have examined terpenoids of Dictyota dichotoma collected at the same area and on the same days. However, the hydrocarbons were isolated only from the seaweed collected in 1979 and 1980. The alga of 1981 and 1982 did not contain the hydrocarbons. It may be of chemotaxonomical interest that content of these and other constituents (unpublished results) of this alga is changeable depending upon subtle differences in environmental conditions.

4) Dictyone might be an artifact.

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