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STRUCTURES AND CONFORMATIONS OF NEW NINE-MEMBERED RING DITERPENOIDS FROM THE MARINE ALGA DICTYOTA DICHOTOMA

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Abstract: New nine-membered ring diterpenes acetyldictyolal (**2**), hydroxyacetyldictyolal (**4**) isodictyohemiacetal (**5**) and dictyodiacetal (**7**) have been isolated. Their structures and approximate conformations have been determined by spectral and chemical means.

The brown algae of the family Dictyotaceae belonging to the order Dictyotales produce many diterpene skeletons, some of which are prenylated counterpart of known sesquiterpene systems[1)]. However, the cyclononane skeleton such as found in dictyodial (**1**)[2)] is not encountered in sesquiterpenes. We wish to report herein the isolation and structures of four new cyclononane diterpenes from Dictyota dichotoma.

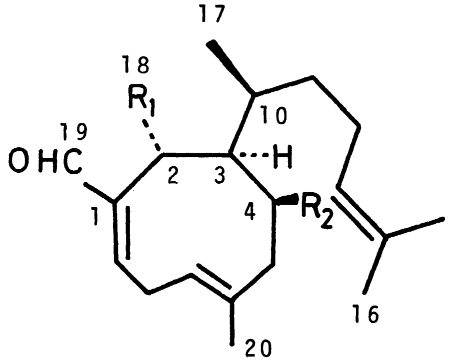
The alga was collected in July 1980 at Oshoro bay, Hokkaido and immediately extracted with methanol at rt. Crude methanol extracts were purified by silica gel chromatography using increasing concentration of ether in hexane as eluant. Final purification of the compounds was achieved by semipreparative high speed liquid chromatography. Acetyldictyolal (**2**) [0.002% yield from the wet alga) showed $[\alpha]_D^{19}$-104° (c 0.5, $CHCl_3$) and ir ν_{max} (neat) 1745, 1690 cm^{-1} due to an α,β-unsaturated carbonyl group. The molecular formula $C_{22}H_{34}O_3$ was established by high-resolution mass measurement (m/z M^+ Found 346.2515; Calcd 346.2509). Comparison of the ^1H and ^{13}C nmr spectra (Table 1, 2) of **2** with those of dictyodial (**1**)[2)] suggested that its structure may be expressed by formula **2**. In order to confirm the suggested structural formula, acetyldictyolal was reduced with $LiAlH_4$ in THF at rt to afford a diol. Treatment of this diol with PCC in CH_2Cl_2 at rt yielded as expected dictyolactone (**3**)[2)]. Coupling constants of **2**, in particular null $J_{2,3}$, $J_{3,10}$ and one of the $J_{4,5}$ values, indicated that its conformation in solution is almost identical with that of **1** in solid state[2)] and is expressed approximately by formula **2***. It should be noted that the barrier to rotation around the C_3-C_{10} is high in this compound ($J_{3,10}$=0)[4)].

Hydroxyacetyldictyolal (**4**) (0.001% yield from the alga) showed $[\alpha]_D^{19}$-180° (c 0.5, $CHCl_3$), ir ν_{max} (neat) 3500, 3200, 1690, 1745 cm^{-1} and the molecular formula $C_{22}H_{34}O_4$ (m/z M^+ Found 362.2464; Calcd 362.2458). Comparison of ^{13}C nmr signals of **4** with those of acetyldictyolal (**2**) indicated that the obvious difference was the absence of C-4 signal at 28.5(t), and the presence of a secondary alcoholic carbon at 75.5(d) in the spectrum of **4** (Table 2). The C-4 proton showed

Table 2. ^{13}C nmr(25 MHz, $CDCl_3$)

Carbon	**2**	**4**	**5**	**7**
1	150.1s	150.6s	145.6s	145.7s
2	42.2d	37.8d	45.9d	47.1d
3	46.1d	50.4d	53.9d	48.1d
4	28.5t	75.5d	28.3t	75.6d
5	41.4t	49.0t	40.7t	45.2t
6	138.9s	138.1s	134.6s	133.6s
7	123.9d^{a}	124.6d^{a}	124.7d^{a}	125.3d^{a}
8	29.1t	29.3t	29.9t	29.0t
9	156.8d	156.7d	120.0d	128.3d
10	32.0d	32.1d	31.7d	31.2d
11	38.0t	38.2t	38.0t	38.0t
12	26.2t	26.3t	26.2t	25.9t
13	124.9d^{a}	124.9d^{a}	124.7d^{a}	124.3d^{a}
14	130.9s	131.1s	131.0s	131.5q
15	17.3q^{b}	17.6q	17.7q^{b}	17.8q
16	25.7q	25.5q	25.7q	25.7q
17	16.8q^{b}	17.6q	17.1q^{b}	17.8q
18	63.1t	63.9t	100.6d	106.7d^{b}
19	196.1d	196.0d	71.3t	107.0d^{b}
20	17.7q^{b}	20.1q	17.7q^{b}	19.5q
OAc	21.1q	20.5q		21.4q
	170.7s	170.7s		169.9s
OMe				54.8q
				55.4q

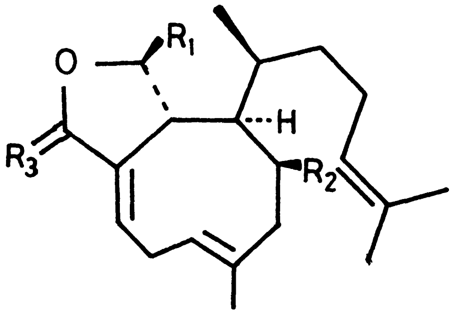
[a,b] Assignments in the same column can be reversed.



1; R$_1$=CHO, R$_2$=H

2; R$_1$=CH_2OAc, R$_2$=H

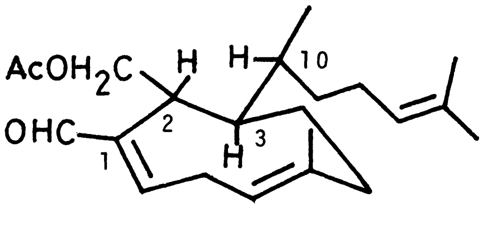
4; R$_1$=CH_2OAc, R$_2$=OH



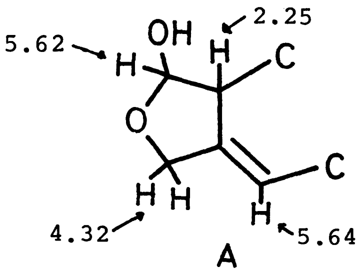
3; R$_1$=H, R$_2$=H, R$_3$=O

5; R$_1$=OH, R$_2$=H, R$_3$=H,H

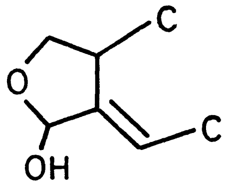
7; R$_1$=OMe, R$_2$=OAc, R$_3$=OMe,H



2*



A



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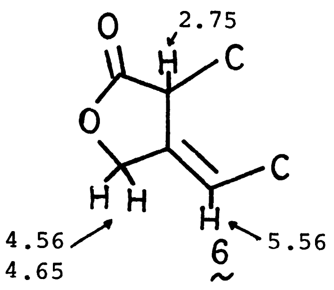

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Table 1. ^1H nmr (400 MHz, $CDCl_3$, J values in Hz)

proton	2	4	5	7
2	2.72(brt, J=7.5)	3.18(brt, J=8)	2.25(brs)	2.95(brs)
3		1.97(brs)		2.05(brs)
4		4.22(dd, J=5, 2)		5.22(dd, J=5, 2)
5	1.91(dd, J=12, 6)	2.08(dd, J=13, 5)	1.99(brdt, J=12, 4)	2.12(dd, J=12, 5)
	2.27(brdt, J=12, 3)	2.39(brdd, J=13, 2)		2.48(dd, J=12, 3.5)
7	5.34(brdd, J=12, 3.5)	5.21(brdd, J=12, 3.5)	5.40(dd, J=12, 3.5)	5.40(dd, J=12, 3.5)
8	2.95(brddd, J=16, 8, 3.5)	3.00(brddd, J=16, 8, 3.5)	2.56(brddd, J=16, 8, 3.5)	2.69(brddd, J=16, 8, 3.5)
	3.24(ddd, J=16, 12, 3.5)	3.31(ddd, J=16, 12, 3.5)	3.07(ddd, J=16, 12, 3.5)	3.13(ddd, J=16, 12, 3.5)
9	6.74(dd, J=8, 3.5)	6.80(dd, J=8, 3.5)	5.64(dd, J=8, 3.5)	5.90(dd, J=8, 3.5)
10	2.19(sextet, J=7)	2.30(sextet, J=7)	1.81(sextet, J=7)	1.98(sextet, J=7)
11	1.08(m)	1.07(m)	1.15(m)	1.22(2H, brq, J=7)
	1.15(m)	1.22(m)	1.24(m)	
12	1.85(2H,q,J=7)	1.82(2H,q,J=7)	1.94(2H,q,J=7)	1.95(2H,q,J=7)
13	5.06(brt, J=7)	5.02(brt, J=7)	5.09(brt, J=7)	5.08(brt, J=7)
15	1.66(brs)	1.66(brs)	1.68(brs)	1.68(brs)
16	1.57(brs)	1.56(brs)	1.59(brs)	1.59(brs)
17	0.85(d, J=7)	0.99(d, J=7)	0.92(d, J=7)	0.86(d, J=7)
18	4.48(dd, J=10, 7.5)	4.51(dd, J=11, 8)	5.62(brs)	5.11(brs)
	4.55(dd, J=10, 7.5)	4.61(dd, J=11, 8)		
19	9.30(d, J=1.5)	9.31(d, J=1.5)	4.32(2H,brs)	5.14(brs)
20	1.76(brs)	1.99(brs)	1.73(brs)	1.80(brs)
OAc	1.97(s)	1.99(brs)		2.30(s)
OCH_3				3.25(s)
OCH_3				3.35(s)

resonance lines at δ 4.22(dd, J=5.0, 2.0 Hz) in the ^{1}H nmr spectrum. These J values indicated that the dihedral angle between C-4 and C-3 protons is about 90° and angles between C-4 proton and each of the C-5 protons are about 60°. Since **2** and **4** take the almost same conformation$^{4)}$, configuration of the C-4 hydroxyl group must be $\beta^{5,6)}$. Isodictyohemiacetal (**5**) exhibited $[\alpha]_D^{19}$-50.2° (c 0.23, $CHCl_3$), ir ν_{max} (neat) 3200, 3500, 1975, 1025 cm^{-1}. The molecular formula $C_{20}H_{32}O_2$ was established by high-resolution mass measurement (m/z M$^+$ Found 304.2411; Calcd 304.2404). The ^{13}C and ^{1}H nmr spectrum suggested the presence of a partial structure A or B [δ 100.6(d), 71.3(t); δ 2.25(1H, br s, H-2), 4.32(2H, br s, H-19), 5.62(1H, br s, H-18); δ 5.64(1H, dd, J=8, 3.5, H-9)]. Since oxidation(PDC/DME/rt/overnight), of **5** afforded lactone **6** [m/z 302 (M$^+$); ν_{max} (neat) 1775 cm^{-1}; δ($CDCl_3$) 2.75(1H,br s, H-2), 4.56 (1H, d, J=11, H-19), 4.65(1H, br d, J=11, H-19), 5.56(1H, br d, J=8, H-9)], formula **5** was assigned for isodictyohemiacetal. It can be seen from Table 1 that the dihedral angle between C-2 and C-18 protons is about 90°, thus configuration of the C-18 hydroxyl group must be β. Dictyodiacetal (**7**) (0.0008% yield from the alga) showed $[\alpha]_D^{19}$-113° (c 0.5, $CHCl_2$), ir ν_{max} (neat) 1740, 1240, 1110 cm^{-1} and molecular formula $C_{24}H_{38}O_5$ (m/z M$^+$ Found 406.2711; Calcd 406.2720). On the basis of ^{1}H and ^{13}C nmr data as shown in Table 1 and 2, formula **7** was inferred for this compound. Configuration at C-19 is not clear at present$^{7)}$.

References

1) Reviews: F. J. McEnroe, K. J. Robertson and W. H. Fenical, in NATO Conference on Marine Natural Products (Edited by D. J. Faulkner and W. H. Fenical) pp. 179-189, Plenum Press, New York (1977); D. J. Faulkner, Tetrahedron, **33**, 1421 (1977); W. H. Fenical, Marine Natural Products. Chemical and Biological Perspective (Edited by P. J. Scheuer), pp. 173-245, Vol. 2, Academic Press, New York (1978).
2) J. Finer, J. Clardy, W. H. Fenical, L. Minale, R. Riccio, J. Battaile, M. Kirkup, and R. E. Moore, J. Org. Chem., **44**, 2044 (1979).
3) The same compound has been isolated from *Pachydictyon coriaceum* and the same formula was assigned independently by the Tsukuba group (H. Kakisawa, private communication dated on April 2, 1982).
4) J. values listed in Table 1 show that the four compounds take a similar conformation, including side chain. On the contrary, according to molecular mechanics calculation (E. Osawa, H. Shirahama and T. Matsumoto, J. Amer. Chem. Soc., **101**, 4824 (1979)) the side chain of steroids rotates freely at rt.
5) In an independent work formula **4** has been assigned to a diterpenoid isolated from *Dilophus okamurai* by the Kochi University group (M. Ochi, private communication dated on July 22, 1982).
6) Comparison of ^{13}C nmr data of **2** and **4** demonstrated that the C-4 hydroxyl group shows a notable deshielding δ-effect on C-20.
7) Dictiodiacetal can be an artifact formed from the corresponding dialdehyde, which has not yet been isolated.

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