Tetrahedron Letters,Vol.26,No.14,pp 1731-1734,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

NEW TRICARBOCYCLIC CYCROPROPANOID DITERPENES FROM THE BROWN ALGA DICTYOTA DICHOTOMA

Nobuyasu Enoki, Ryoichi Ishida, Shiro Urano, and Takeshi Matsumoto
Department of Chemistry, Faculty of Science, Hokkaido University,
Sapporo 060, JAPAN

Abstract: The structures 1, 2, and 3 have been proposed for three new diterpenes from Dictyota dichotoma mainly on the basis of spectroscopic evidence.

In previous papers we reported the isolation and structure determination of new hydroazulene1) and cyclononane2) diterpenes from Dictyota dichotoma. We wish to report here the structure determination of three new diterpenes containing an unconventional cyclopropyl ether moiety, tricyclodictyofuran A (1), B (2), and C (3). The alga (16 kg) was collected in July 1979 at Oshoro bay, Hokkaido and immediately extracted with MeOH at room temperature. The crude extracts were fractionated repeatedly by silica gel chromatography using increasing concentrations of ether in hexane as eluent to give 1, 2 and 3 in amounts of 14, 10, and 3 mg respectively. Tricyclodictyofuran A (1) was isolated as a colorless oil, $[\alpha]_D^{25}$+26.7 (c 1.8, $CHCl_3$), ν(neat) 3600-3200, 1185 cm^{-1}, and had molecular formula $C_{20}H_{30}O_2$ (m/z M^+ 302.2242, Calcd 302.2247). In its mass spectrum important peaks were seen at 284 (M^+-H_2O), 82 ($C_6H_{10}^+$) and 69 ($C_5H_9^+$). Out of the two oxygen atoms of 1, at least one oxygen atom was present as a hydroxyl group (IR). The ^1H-NMR ($CDCl_3$, 200 MHz) (Table 1) spectrum suggested the presence of the monoolefinic eight-carbon side chain characteristic to the diterpenoids1,2,3) of this alga [δ 1.01 (3H, d, J=6 Hz), 1.62 (3H, brs), 1.69 (3H, brs) and 5.11 (1H, t, J=6 Hz)], one methyl on a quaternary carbon, two oxygen-bearing methine groups (4.38 and 3.41), one oxygen-bearing methylene group (3.86 and 4.17), and two coupled olefinic protons [5.51 (1H, d, J=6 Hz), 5.35 (1H, dd, J=6, 2 Hz)] in the molecule, which was therefore tetracyclic. Since three oxygen-bearing carbon atoms were found, the second oxygen atom was assigned to an ether. The small J value (6 Hz) of the vicinal olefinic protons suggested that the double bond was on a cyclopentene ring. Comparison of these data with those of its p-bromophenylurethane derivative 4 (Table 1) indicated that the peak at δ 4.38 of 1 was responsible for a hydroxy-bearing methine group. Exhaustive double resonance studies of 4 at 400 MHz, coupled with biogenetic considerations, allowed to characterize all of its protons as shown in Table and implied structure 4 with conformation 5. Almost null value of vicinal coupling constant of the C_2-C_3 protons (dihedral angle$\sim$105°) may be in part ascribed to the presence of the C_2 oxygen atom.$^{4)}$

Further evidence for the suggested structure was obtained by NOE difference spectrum studies of **4** (400 MHz). Enhancement of the signal intensity of C_2-ether proton, C_5-olefinic proton, $C_{7\alpha}$ proton, and C_9-proton was clearly observed when the 20-methyl peak was irradiated (Fig 1). Although relative stereochemistry at C-11 in the side chain could not be determined by NMR, 9S, 11R relative configuration was allotted since **1** was supposed to be biogenetically related to a dictyofuran$^{2,3,5)}$ derivative as shown in Fig 2. Difference between the δ values of 18-methyls of **1** and **2**, lacking the 8β-hydroxyl group (Fig 3), indicates that 18-methyl of **1** is close to the 8β-hydroxyl group. Since a conformation with parallel C_{10-19} and C_{11-12} bonds would be unstable, the proximity of C_{18} and 8β-OH and $J_{9,11}$ of 5 Hz mean that stereochemistry and predominant conformation of the side chain is expressed by Fig 3, in agreement with the above assignment.$^{6)}$ Tricyclodictyofuran B (**2**), oily product, $[\alpha]_D^{21}$+25.7 (c 0.3, cyclohexane), had molecular formula $C_{20}H_{30}O$ (m/z M^+ 286.2337, Calcd 286.2298). The infrared spectrum of this compound showed the absence of a hydroxyl group and presence of an ether linkage (1185 cm^{-1}). The ^{1}H-NMR spectrum was strongly reminiscent of that of **1** (Table 1), apart from the signals due to replacement of the secondary hydroxyl group by a proton. These results led to structure **2** for tricyclodictyofuran B, whose ^{13}C-NMR spectrum confirmed the proposed structure (Fig 4). In conformity with the proposed formula, the ^{13}C-^1H coupling constant of C_2 was quite large, being 194.1 Hz, although $J_{C(3)-H}$ was not clearly observable by overlapping of signals. Tricyclodictyofuran C (**3**), oil, $[\alpha]_D^{21}$+27.4 (c 0.27, cyclohexane) had molecular formula $C_{21}H_{32}O_2$ [m/z M^+ 316.2404. 284 (M^+-MeOH)]. The salient difference between the ^{1}H-NMR spectrum of **3** and that of **2** resided in the absence of the double doublet peaks at 3.69 and 3.99 and the presence of a doublet peak due to an acetal proton [4.98 (d, J=5 Hz)] and a methoxyl peak at 3.38 (Table 1). In **3**, the signal due to 10β-H appeared at significantly higher field than that of **2**. Therefore a 19β methoxy structure **3** was assigned for this compound.$^{7)}$ The inferred structure suggests, however, that the compound could be an artifact of the corresponding hemiacetal.

References

1) N. Enoki, R. Ishida, S. Urano, M. Ochi, T. Tokoroyama, and T. Matsumoto, Chem. Lett., 1837 (1982).

2) N. Enoki, H. Shirahama, E. Osawa, S. Urano, R. Ishida, and T. Matsumoto, Chem. Lett., 1399 (1983).

3) J. Finer, J. Clardy, W. Fenical, L. Minale, R. Ricco, J. Battaile, M. Kirkup, and R. E. Moore, J. Org. Chem., 44, 2044 (1979).

4) For the effect of electronegative substitutents on J's see for examle L. M. Jackman and S. Sternhell, "Application of N.M.R. Spectroscopy in Org. Chem.," 2nd ed, Pergamon Press, (1969), pp. 283-284.

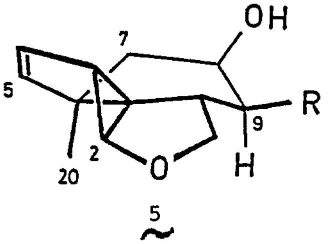
5) In ref 2), the relative configuration at the chiral center of the side

chain of 1 through 5 is errorneously drawn. The configuration should be inverted.

6) Since the hypothetical precursor (Fig 2) in turn is seemingly derived from dilophol with 11R configuration [N. Enoki, H. Shirahama, A. Furusaki, K. Suehiro, E. Osawa, R. Ishida, and T. Matsumoto, Chem. Lett., 459 (1984)], the absolute configuration of the tricyclodictyofurans may be expressed by 1-3.

7) An OR group causes the proton eclipsed by it to appear at higher field. L. M. Jackman and S. Sternhell, "Application of N.M.R. Spectroscopy in Org. Chem.," 2nd ed, Pergamon Press, (1969), pp. 232-234.

Fig. 1



5

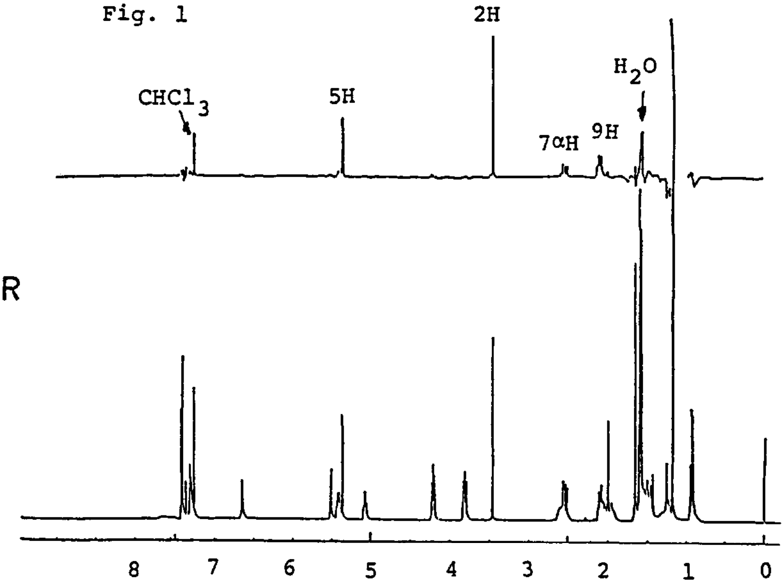


Fig. 2

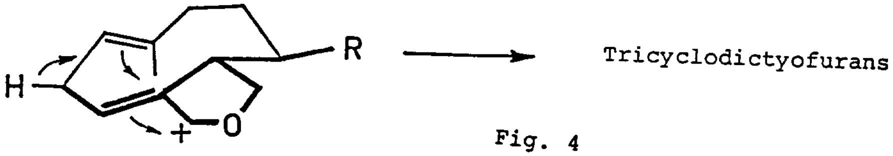


Fig. 3

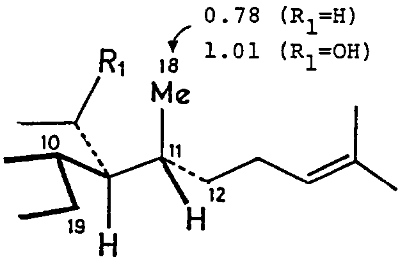
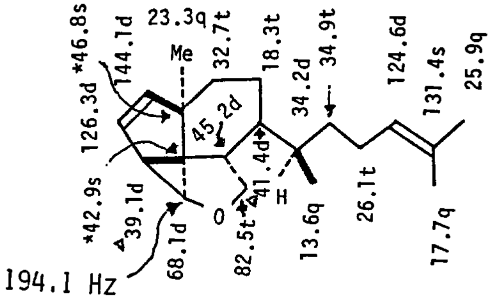


Fig. 4

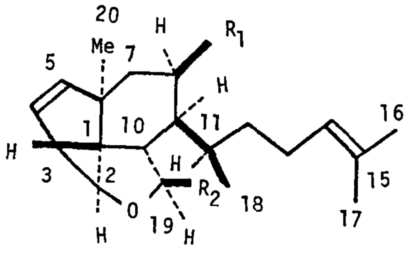


The values with * or ▵ are exchangeable.

Table 1

	1	2	3
2	3.41 (s)	3.27 (s)	3.22 (s)
3	1.93 (d, 2 Hz)	1.77 (d, 2 Hz)	1.93 (d, 2 Hz)
4	5.51 (dd, J=6, 2 Hz)	5.44 (dd, J=6, 2 Hz)	5.30 (dd, J=6, 2Hz)
5	5.35 (d, J=6 Hz)	5.22 (d, J=6 Hz)	5.24 (d, J=6 Hz)
7	2.33 (dd, J=14, 8 Hz)	2.21 (dd, J=14, 8 Hz)	-
	-	-	-
8	4.38 (ddd, J=8, 6, 5 Hz)	-	-
9	-	1.19 (m)	-
10	2.42 (ddd, J=12, 8, 7.5 Hz)	2.28 (ddd, J=12, 7, 7.5 Hz)	1.62 (m)
11	-	-	-
12	-	-	-
13	-	-	-
	-	-	-
14	5.11 (t, J=6 Hz)	5.01 (t, J=6 Hz)	5.11 (t, J=6 Hz)
16	1.62 (3H, brs)	1.68 (3H, brs)	1.62 (3H, brs)
17	1.69 (3H, brs)	1.75 (3H, brs)	1.70 (3H, brs)
18	1.01 (3H, d, J=6 Hz)	0.78 (3H, d, J=6 Hz)	0.78 (3H, d, J=6 Hz)
19	3.86 (dd, J=10, 8 Hz)	3.69 (dd, J=9, 7.5 Hz)	4.98 (d, J=5 Hz)
	4.17 (dd, J=10, 7.5 Hz)	3.99 (dd, J=9, 7 Hz)	-
20	1.13 (3H, s)	1.12 (3H, s)	1.09 (3H, s)

	4
2	3.47 (s)
3	2.03 (d, J=2 Hz)
4	5.37 (dd, J=6, 2 Hz)
5	5.42 (d, J=6 Hz)
7	1.47 (dd, J=14, 5.5 Hz)
	2.54 (dd, J=14, 9 Hz)
8	5.42 (ddd, J=9, 5, 5.5 Hz)
9	2.02 (dt, J=12, 5 Hz)
10	2.59 (ddd, J=12, 8, 7.5 Hz)
11	1.53 (m)
12	1.50 (2H, q, J=7 Hz)
13	1.95 (m)
	2.03 (m)
14	5.06 (t, J=6 Hz)
16	1.58 (3H, brs)
17	1.66 (3H, brs)
18	0.93 (3H, d, J=6 Hz)
19	4.21 (dd, J=10, 8 Hz)
	3.82 (dd, J=10, 7.5 Hz)
20	1.18 (3H, s)



1	R_1= OH,	R_2= H
2	R_1= H,	R_2= H
3	R_1= H,	R_2= OMe
4	R_1= $\text{O-}\underset{\underset{\text{O}}{\Vert}}{\text{C}}\text{-NH-}C_6H_4Br$,	R_2= H

(Received in Japan 22 December 1984)