Structure of Pachyaldehyde, a Novel Norditerpene from the Brown Alga, *Pachydictyon coriaceum*

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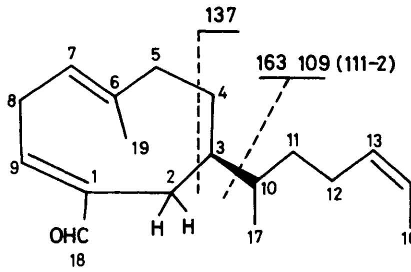
From a methanol extract of the brown alga, *Pachydictyon coriaceum*, a new norditerpene, pachyaldehyde (**1**), has been isolated, and its structure, together with the conformation, has been determined spectroscopically.

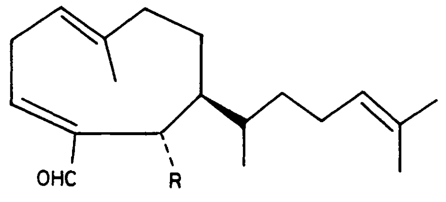
Unique compounds have been found in the brown algae of the family Dictyotaceae.[1] From the species *Pachydictyon coriaceum*, we have isolated new diterpenes which have carbon skeletons quite different from those of terrestrial diterpenes.[2] Further fractionation of a methanol extract of *P. coriaceum* afforded another new diterpene, pachyaldehyde [(**1**); 3 mg from 6 kg of the fresh alga], composed of nineteen carbon atoms.

The proton-noise decoupled ^{13}C n.m.r. spectrum of pachyaldehyde (**1**), $[\alpha]_D^{23}$ −40°(*c* 0.21, $CHCl_3$), contains nineteen signals. The multiplicities of the carbon signals (off-resonance spectrum), which indicate the number of the protons, and the molecular ion at *m/z* 274 in the mass spectrum suggest the molecular formula $C_{19}H_{30}O$ for pachyaldehyde. The high resolution mass spectrum supports this formula (M^{+}, *m/z* 274.229, $C_{19}H_{30}O$ requires 274.230). The ^{13}C n.m.r. spectrum contains signals due to six olefinic carbon atoms (three C=C's) and an aldehydic carbon atom (δ 195.9), which show that pachyaldehyde is monocyclic. The presence of an α,β-unsaturated aldehyde moiety was shown by the i.r. bands at 2720, 1685 (CHO), and 1610 cm^{-1} (C=C), and the ^1H n.m.r. (90 MHz) signals at δ 9.32 (CHO) and 6.69 (*H*–C=C–CHO).



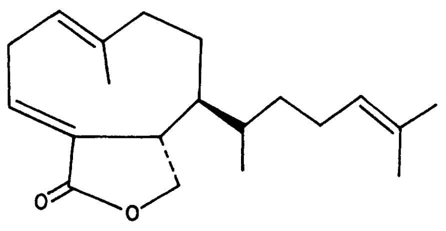
pachyaldehyde

(1)

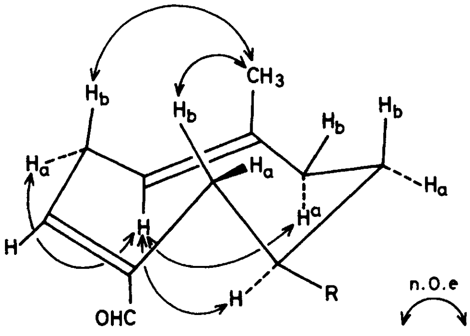


(2) R=CH2OAc

(3) R=CHO



(4)



(A)

Table 1. The ^{13}C n.m.r. data^{a} for pachyaldehyde (**1**), acetyldictyolal (**2**), dictyodial (**3**), and dictyolactone (**4**).

C atom	δ (**1**)	δ (**2**)	δ (**3**)	δ (**4**)
1	149.4	150.1	148.5	135.4
2	29.5	42.3	56.5^{c}	43.8
3	45.8	46.9	48.5	47.1
4	28.0	28.5	29.1	28.6
5	40.4	41.4	40.7	40.1
6	137.1	138.3	137.9	136.4
7	122.3	122.1	122.3	122.8
8	29.1	29.1	28.7^{c}	30.3
9	155.3	156.9	157.4	139.5
10	36.7	32.1	32.7	32.5
11	35.7	38.0	37.6	37.2
12	26.4	26.2	25.7	25.6
13	125.2	124.9	124.4	124.1
14	130.8	130.9	130.9	131.1
15	25.7	25.7	25.4	25.4
16	17.7^{b}	17.7	17.4	17.5
17	14.8	16.8	17.0	17.1
18	195.9	195.9	194.2	172.5
19	17.6^{b}	17.3	17.1	17.5
20	—	63.1	203.5	67.8

[a] Chemical shifts are relative to the centre line of $CDCl_3$. [b] Assignment may be reversed. [c] Assignment of these signals appearing in ref. 5 should be corrected to those shown here.

Table 2. ^{1}H N.m.r. (400 MHz) data for pachyaldehyde (**1**).

Protc	δ^{a}	Proton	δ^{a}
2	2.43 (dd)	9	6.69 (br. dd)
	1.51 (d)	10	1.66 (m)
3	1.28 (ddd)	11	1.20 (m)
4	1.55 (dddd)	12	1.90 (m)
	1.39 (dq)	13	5.05 (br. t)
5	1.98 (dt)	15	1.66 (br. s)
	2.21 (ddd)	16	1.57 (br. s)
7	5.39 (br. dd)	17	0.85 (d)
8	2.96 (ddd)	18	9.32 (s)
	3.23 (ddd)	19	1.75 (br. s)

[a] In $CDCl_3$ at 28 °C and from Me_4Si as an internal standard. J(H–H) values in Hz: (2a–2b) 14, (2a–3) 7, (2b–3) 0, (4a–4b) 12, (4b–3) 12, (4a–5a) 5, (4a–5b) 3, (4b–5a) 12, (4b–5b) 4, (5a–5b) 12, (7–8a) 4, (7–8b) 12, (8a–8b) 16, (8a–9) 8, (8b–9) 3, (13–12) 7, (17–10) 7; others not resolved.

The proton at δ 6.69 (9-H, dd, J 8, 3 Hz) is coupled with the methylene protons appearing at δ 3.23 (8-H$_b$, ddd, J 16, 12, 3 Hz) and 2.96 (8-H$_a$, ddd, J 16, 8, 4 Hz). The methylene protons are further coupled with the olefinic proton at δ 5.39 (7-H, dd, J 12, 4 Hz), irradiation of which resulted in sharpening of the methyl signal at δ 1.75 (19-Me, br. s). These data indicate the partial structure ($\mathrm{OHC{-}\underset{|}{C}{=}CH{-}CH_2{-}CH{=}\underset{|}{C}{-}Me}$).

The presence of the 6-methylhept-5-en-2-yl group, the side chain which is frequently encountered in the diterpenes isolated from the Dictyotaceae algae, was evident from the mass fragment at m/z 109,[2a] and also the ^{13}C n.m.r. signals which correspond well with the side chain carbon atoms [see structure (**1**) and Table 1].[2a] The ^{13}C n.m.r. spectrum shows the presence of three additional methylene and one methine groups. Biogenetic considerations led to the structure (**1**) [or its alternative having the side chain at C(4)] for pachyaldehyde. The configuration of the double bond at C[1(9)] was deduced as *E* from the upfield chemical shift of the aldehyde proton (δ 9.32) in the ^{1}H n.m.r. spectrum.[3] Also, the *E*-configuration of C(6)=C(7) was determined from the upfield ^{13}C n.m.r. chemical shift of the 19-methyl group (δ 17.6).[3]

As to the position of the side chain, C(3) was considered to be more appropriate than C(4), because the ^{13}C n.m.r. spectrum of pachyaldehyde (**1**) corresponds well with those of acetyldictyolal (**2**),[4] dictyodial (**3**),[5] and dictyolactone (**4**),[5] as shown in Table 1. Furthermore, the 400 MHz ^{1}H n.m.r. spectrum of pachyaldehyde (Table 2) established the coupling constants between the protons on the ring carbon atoms, providing the conformation of the cyclononadiene ring illustrated in (A), and also further suggesting the position of the side chain at C(3).† The nuclear Overhauser effects (n.O.e.s) found for (**1**) [depicted in (A) by arrows] are consistent with the proposed conformation.

Pachyaldehyde (**1**) is the first example of a norditerpene possessing a cyclononadiene skeleton.

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† Molecular models show that if the side chain is attached to C(4) there is no possible conformer that fits the *J* values and the n.O.e.s found for pachyaldehyde.

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