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NEW DITERPENES FROM THE BROWN ALGA PACHYDICTYON CORIACEUM

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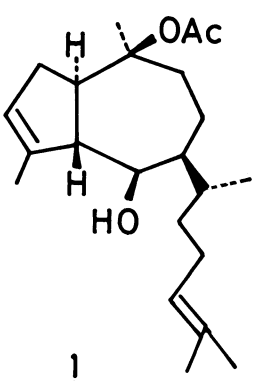
Three new diterpenes, which possess a cyclononane skeleton, have been isolated from the brown alga Pachydictyon coriaceum, and their structures have been determined spectroscopically.

The brown alga Pachydictyon coriaceum (sanadagusa), which grows widely along the Japanese coast, has been disclosed to be rich in terpenoid constituents.1-3) This seaweed produces the diterpenoid metabolites possessing various types of carbon frameworks such as perhydroazulene [e.g. acetyldictyol C (1)],1) cyclononane [e.g. acetyldictyolal (2)],1) bicyclo[4.3.1]decane [acetylsanadaol (3)],2) and bicyclo[7.2.0]undecane [e.g. acetylcoriacenone (4)].3) In this letter we wish to describe the structures of three new diterpenes having a cyclononane skeleton, which are designated as neodictyolactone (5), 18-acetoxydictyolactone (9), and isodictyoacetal (10).



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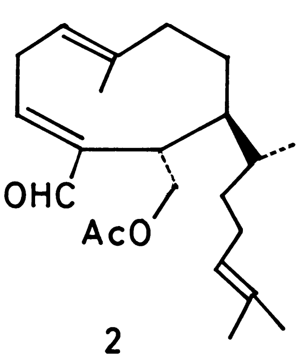

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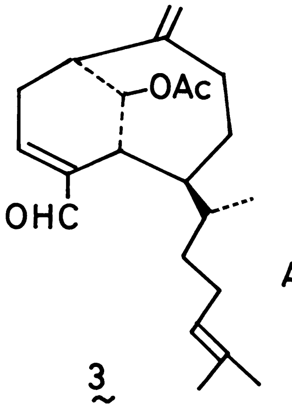

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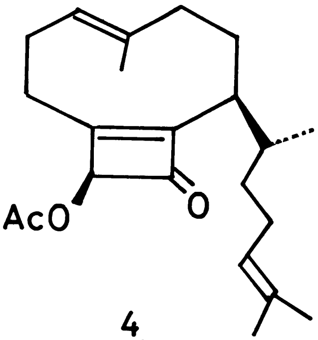

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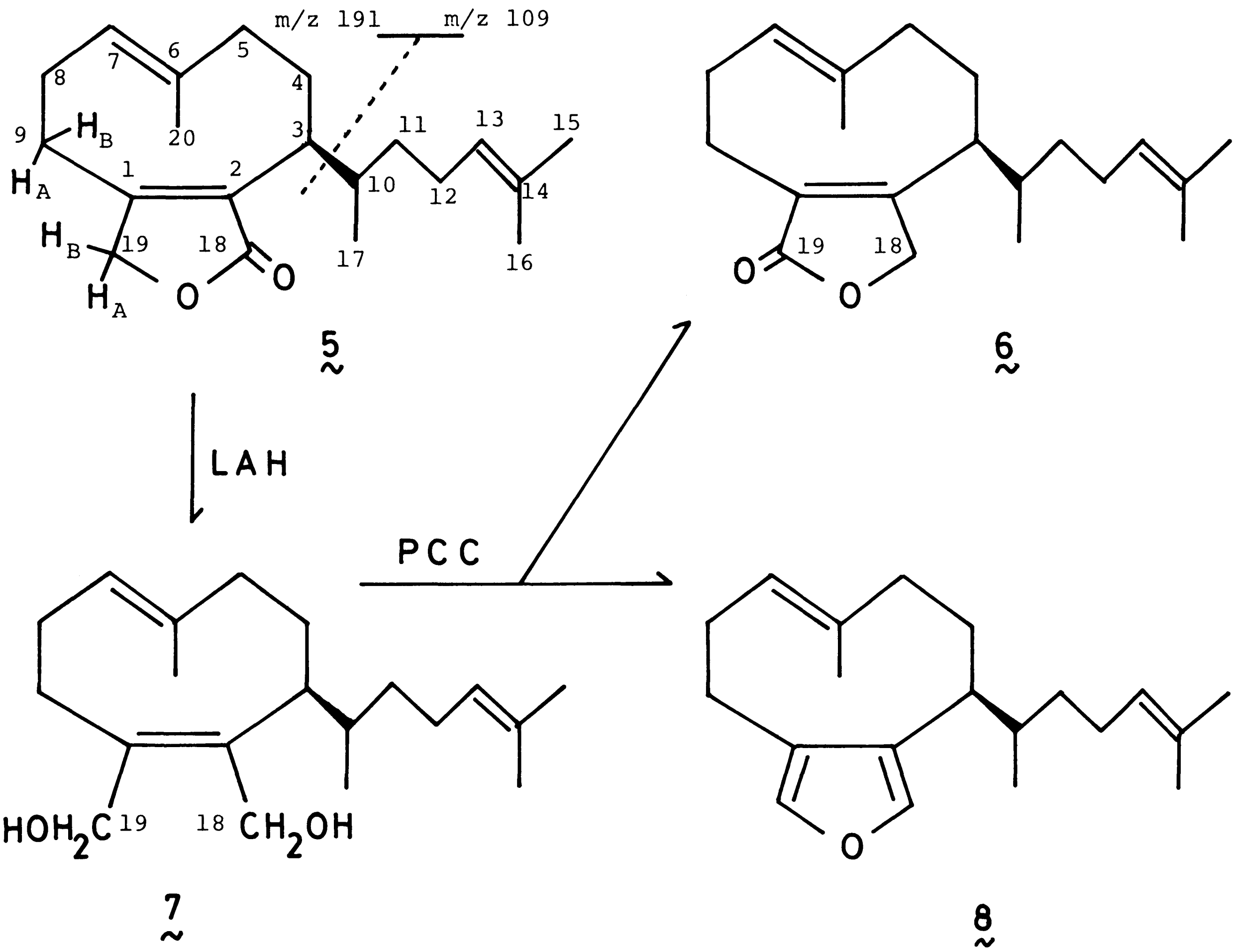
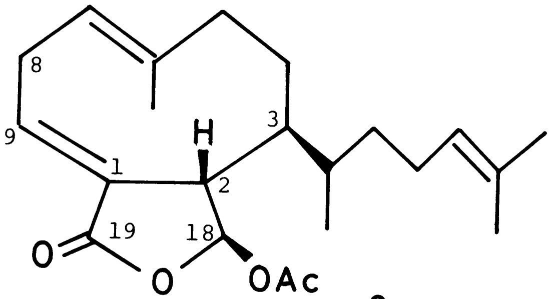
Neodictyolactone,4) $C_{20}H_{30}O_2$, $[\alpha]_D$ -43.4° (c 0.29, $CHCl_3$), shows IR bands at 1750 (s) and 1645 (w) cm^{-1} attributable to an α,β-unsaturated γ-lactone moiety, the presence of which was confirmed by the UV maximum at 220 nm (ε 7800) and a ^1H-NMR (90 MHz) signal at δ 4.56 (2H,s) ascribable to the methylene protons at the γ-position. From the MS fragments at m/z 109 and 191 (See the structure 5.) together with the ^{13}C-NMR spectrum, it is obvious3) that 6-methyl-5-hepten-2-yl group, a side chain, is included in this compound. The ^{13}C-NMR spectrum reveals the presence of another trisubstituted olefin bearing a methyl group [δ 15.8 (q;20-C), 123.5 (d;7-C), 140.0 (s;6-C)], and also four methylene and one methine groups in



addition to the aforementioned moieties, which indicates that one more ring other than the lactone ring is included in neodictyolactone. The configuration of the trisubstituted olefin is deduced to be E from the chemical shift (δ 15.8) of the olefinic methyl. In the ^{1}H-NMR spectrum, this methyl group appears as a broad singlet at δ 1.26. This highly shielded olefinic methyl is reminescent of acetylcoriacenone (4),[3] in which the olefinic methyl is shielded by a transannular effect of the cyclobutene group. These facts together with biogenetic considerations allowed us to propose two possible structures 5 and 6 for neodictyolactone. The position of the lactonic carbonyl, C-18 (5) or C-19 (6), was determined by the following chemical transformations. Neodictyolactone was reduced with LAH to afford the diol 7 [δ 4.11 (2H,ABq,J=11 Hz), 4.12 (2H,s)]. The diol was treated with PCC in dichloromethane, giving rise to a lactone together with dictyofuran T (8),[5] the formation of which supported the carbon framework of neodictyolactone. In this oxidation process, it is likely that the less hindered hydroxyl group (C-19) of the diol 7 would be oxidized in preference to the more hindered one (C-18),[6] so that the resulting lactone would have the 19-keto structure (6).[7] This lactone was different from neodictyolactone in TLC, GC, and MS; therefore, the structure 5 is assignable to neodictyolactone. NOEDS experiments (400 MHz) are consistent with the structure 5; on irradiation at δ 4.60 (19-H_B), significant NOE's were detected for the signals of 9-H_B (δ 2.3) and 20-Me (δ 1.26).

The second new diterpene, 18-acetoxydictyolactone (9),[8] has the molecular formula $C_{22}H_{32}O_4$, suggesting that an acetoxyl group is present in addition to a diterpenoid framework. The UV maximum at 224 nm (ε 8200), the IR bands at 1785 and 1640 cm^{-1}, and the ^1H-NMR signal at δ 7.06 due to an olefinic proton are suggestive of an α-alkylidene-γ-lactone structure. This proton (9-H) is deduced to be adjacent to a doubly allylic methylene protons (8-H_2; δ 2.8-3.4) as in dictyolactone (12),[9] because irradiation on the latter affected the signals at δ 7.06 (9-H) and also at 5.37 (7-H). The acetoxyl group has to be located at C-18, since the signal of the methine proton on the carbon bearing the acetoxyl group shifts down to δ 6.68. These findings allowed us to deduce the structure of this compound to be 9, and the other spectral properties are compatible with this structure. The relative configurations at C-2, 3, and 18 of 9 were assigned as illustrated in the structure from the consideration of the null coupling constants between H-18 and H-2, as well as H-2 and H-3. (Molecular models reveals that the dihedral angles formed by each of these protons are 90° in 9.)



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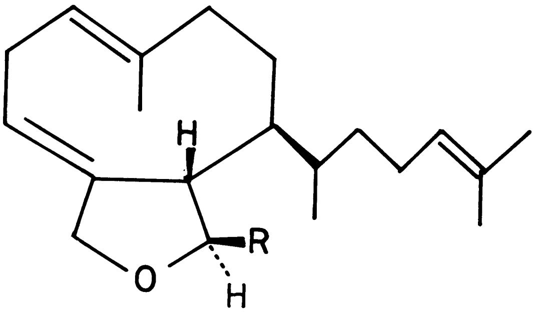
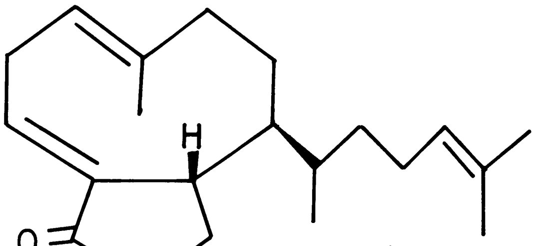


10 : R=OMe
11 : R=OH



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In the similar way as described for neodictyolactone and 18-acetoxydictyolactone, the structure of the third new diterpene, isodictyoacetal,[10] $[\alpha]_D$ -7.7° (c 0.75, $CHCl_3$), was elucidated to be 10. On hydrolysis of 10 (TsOH in dioxane-water) there was obtained a hemiacetal, which exhibits an acetalic methine proton signal at δ 5.65 in the ^1H-NMR spectrum. This chemical shift and also other spectral features of this product are identical with those reported for isodictyohemiacetal (11).[11] As observed in 18-acetoxydictyolactone (9), the coupling constants, J_{2-3} and J_{2-18}, in the ^1H-NMR spectrum of 10 are zero, which led to the assignment of the relative configurations at C-2, 3, and 18 as seen in the structure.

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References

1) M. Ishitsuka, T. Kusumi, J. Tanaka, and H. Kakisawa, Chem. Lett., 1982, 1517.

2) M. Ishitsuka, T. Kusumi, and H. Kakisawa, Tetrahedron Lett., 1982, 3179.

3) M. Ishitsuka, T. Kusumi, H. Kakisawa, Y. Kawakami, Y. Nagai, and T. Sato, J. Org. Chem., 48, 1937 (1983).

4) 5; IR (CCl_4) 1750(s), 1645(w), 1160(w), 1050(m), 1030(m) cm^{-1}; MS m/z 302(M^+, 5%), 287(14), 257(100), 201(62), 191(35), 187(33), 147(41), 145(41), 109(48), 82(38), 69(47); ^1H-NMR (400 MHz) δ 0.98(3H,d,J=6.5 Hz,17-Me), 1.26, 1.54, 1.64 (each 3H,bs,20,16,15-Me), 4.56, 4.60(each 1H,d,J=17 Hz,19-H_2), 4.98(1H,bt,J=7 Hz,13-H), 5.22(1H,dd,J=12,4 Hz,7-H); ^{13}C-NMR ($CDCl_3$) δ 15.8(q,20-C), 17.6(q, 16-C), 18.0(q,17-C), 25.0*(t,12-C), 25.6(q,15-C), 25.8*(t,8-C), 28.4(t,9-C), 32.1(t,4-C), 33.1(d,10-C), 35.2(t,11-C),40.5(t,5-C), 43.1(d,3-C), 71.1(t,19-C), 123.5(d,7-C), 124.7(d,13-C), 131.1(s,14-C), 133.2(s,2-C), 140.0(s,6-C), 157.4 (s,1-C), 173.8(s,18-C).

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

6) H. H. Sun, F. J. McEnroe, and W. Fenical, J. Org. Chem., 48, 1903 (1983).

7) 6; MS 302(M^+), 221, 191, 149, 109, 82 (base), 69. ^1H-NMR spectrum is essentially the same as that of neodictyolactone (5).

8) 9; IR (CCl_4) 1785, 1750, 1640, 1180, 1160, 950 cm^{-1}; MS m/z 360(M^+,2%), 343(4), 300(27), 257(31), 229(39), 137(53), 109(48), 82(100), 81(61), 69(33); ^1H-NMR (90 MHz,$CDCl_3$) δ 1.03(3H,d,J=6 Hz,17-Me), 1.57, 1.67, 1.69 (each3H,bs,16,15, 20-Me), 2.55(1H,bs.2-H), 2.8-3.4(2H,m,8-H_2), 5.03(1H,bt,J=7 Hz,13-H), 5.37(1H, bdd,J=11,5 Hz,7-H), 6.68(1H,s,18-H), 7.06(1H,bdd,J=7,3 Hz,9-H); ^{13}C-NMR ($CDCl_3$) δ 17.3*(17-C), 17.6*(20-C), 17.7(16-C), 21.0(CH_3CO), 25.7(15-C), 26.0(12-C), 29.1(4-C), 30.0(8-C), 32,9(10-C), 37.7(11-C), 40.1(5-C), 47.0(2-C), 50.9(3-C), 96.0(18-C), 122.8(7-C), 124.0(13-C), 131.9(14-C), 132.4(1-C), 136.9(6-C), 143.1 (9-C).

9) 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).

10) 10; IR (CCl_4) 1090. 1045, 925 cm^{-1}; MS m/z 318 (M^+,17%), 286(13), 243(20), 215 (43), 205(46), 203(63), 147(100), 133(77), 109(48), 107(68), 69(59); ^1H-NMR (90 MHz, $CDCl_3$) δ 0.91(3H,d,J=6 Hz,17-Me), 1.58, 1.66, 1.71(each 3H,bs,16,15, 20-Me), 2.26(1H,bs,2-H), 3.24(3H,s,OMe), 4.29(2H,bs,19-H_2), 5.07(1H,s,18-H), 5.07(1H,bt,J=7 Hz,13-H), 5.40 (1H,bdd,J=11,4 Hz,7-H), 5.50(1H,m,9-H); ^{13}C-NMR ($CDCl_3$) δ 17.2(17-C), 17.7(16-C), 17.7(20-C), 25.7(15-C), 26.3(12-C), 28.4(4-C), 29.8(8-C), 31.6(10-C), 38.1(11-C), 40.7(5-C), 45.9(2-C), 53.0(3-C), 54.3(MeO), 71.1(19-C), 107.4(18-C), 119.0(9-C), 124.8(13-C), 125.8(7-C), 131.2(14-C), 134.6(6-C), 146.1(1-C).

11) N. Enoki, R. Ishida, and T. Matsumoto, Chem. Lett. , 1982, 1749.

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