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AMIJIOL, ISOAMIJIOL, AND 14-DEOXYAMIJIOL, THREE NEW DITERPENOIDS FROM THE BROWN SEAWEED *DICTYOTA LINEARIS*

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Three new diterpenoids have been isolated from the brown seaweed *Dictyota linearis*, and their structures determined by ^{1}H and ^{13}C NMR spectroscopy.

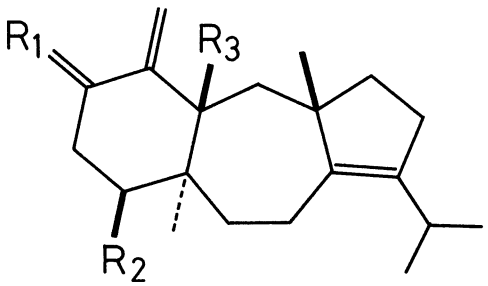
Recent investigations of the brown algae of the family Dictyotaceae have resulted in the isolation of the interesting secondary metabolites.[1] During a search of the biologically active constituents of marine algae,[2] we have examined the methanol extract of *Dictyota linearis* ("Itoamiji" in Japanese), which was found to have an antimicrobial activity against *Bacillus subtilis* and *Penicillium crustosum*. Careful silica gel column chromatography of the crude extract of fresh alga gave three new diterpenoids,[3] amijiol (1), isoamijiol (2), and 14-deoxyamijiol (3) in 0.015, 0.026, and 0.002% yield respectively. We propose the linear tricyclic structures 1 - 3 for these compounds.[4]

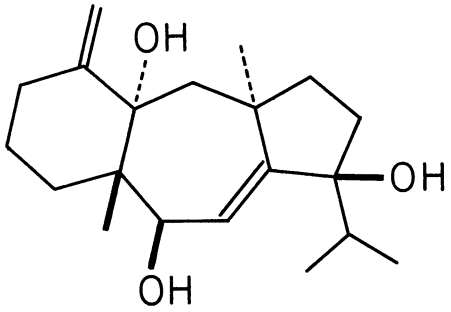
Amijiol (1), $C_{20}H_{32}O_2$, mp 180-181 °C, showed $[\alpha]_D$ -126° ($CHCl_3$) and ν_{max} ($CHCl_3$) 3600, 3480, 3090, 1640, and 905 cm^{-1}. The ^{13}C NMR data for 1 assisted with off-resonance and selective proton-noise decoupling technique, as summarized in structure 1, showed the presence of four methyls, seven methylenes, one methine, one oxygen-bearing methine, together with three fully substituted carbon atoms, one tetrasubstituted double bond, and one exocyclic methylene.

The pertinent ^{1}H NMR data, completely assigned by an extensive decoupling study and NOE measurements, are shown in structure 1a; the gross structure with a linear 6-7-5 ring system was established by following observations. Four angular positions are occupied by two methyls, one hydroxyl group, and one double bond. The marked deshielding of 12-methyl would be reasonably interpreted through the consideration of the paramagnetic anisotropy by 14β-OH disposed in 1,3-diaxial relationship. In the ^{1}H NMR spectrum of the acetate (4), $C_{22}H_{34}O_3$, mp 96-97 °C, the signal of 14β-OH proton appeared as a doublet (J=2.3 Hz) at δ 3.64 by a long-range coupling with 13α-H. This unusual W-coupling across C-O-H bonding should be caused by the hydrogen bonding to the carbonyl oxygen of 4β-OAc. The signal of 5-methyl exhibited a long-range coupling (J=∿0.1 Hz) with 6β-H which was

considerably deshielded by two axial hydroxyl groups at C-14 and C-4. Observation of a 10% NOE on 13α-H upon irradiation of one of 15-H signals revealed the presence of the contiguous C_1-C_{14}-C_{13} carbon atoms bearing substituents shown in structure 1. From these observations, we deduced the structure 1 for amijiol. This deduction is supported by consideration of the spectral data of the congeners, isoamijiol (2) and 14-deoxyamijiol (3), as follows.

Isoamijiol (2),[5] $C_{20}H_{32}O_2$, mp 128-128.5 °C, $[\alpha]_D$ -45° ($CHCl_3$), had the spectroscopic properties very similar to those of 1. ν_{max} ($CHCl_3$) 3600, 3480, 3090, 1640, and 885 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 152.1 (C-1), 139.9 (C-8), 139.7 (C-9), 113.8 (C-15), 81.4 (C-14), 76.4 (C-2), 51.1 (C-12), 47.5 (C-13), 43.3 (C-11), 42.3 (C-5), 33.0 (C-4), 31.7 (C-6), 30.0 (C-3), 27.6 (C-10), 27.0 (C-17), 26.8 (C-16), 22.6 (C-7), 21.4 (C-19), 20.5 (C-18), and 17.8 (C-20); ^1H NMR ($CDCl_3$) δ 5.09 and 5.02 (each br s, 15-H_2), 4.30 (ddd, J=3.4, 3.4, and 0.5 Hz, 2-H), 2.63 (qq, J=6.9 and 6.9 Hz, 17-H), 1.34 (s, 16-H_3), 0.95 and 0.92 (each d, J=6.9 Hz, 18- and 19-H_3), and 0.77 (s, 20-H_3). The ^{13}C and ^1H NMR spectra of 2 and 1 are distinct from one another essentially only in the chemical shifts of the oxygen-bearing methine carbon and the methine proton attached to an oxygenated carbon atom respectively. This fact suggests that 2 has a structure close to that of 1, in which 4β-OH in 1 is replaced by 2β-OH. This was confirmed by the oxidation of 2 to yield an enone (5), $C_{20}H_{30}O_2$, mp 134-135 °C, ν_{max} ($CHCl_3$) 3600, 1695, and 1610 cm^{-1}. Thus structure 2 is assigned to isoamijiol.





(6)

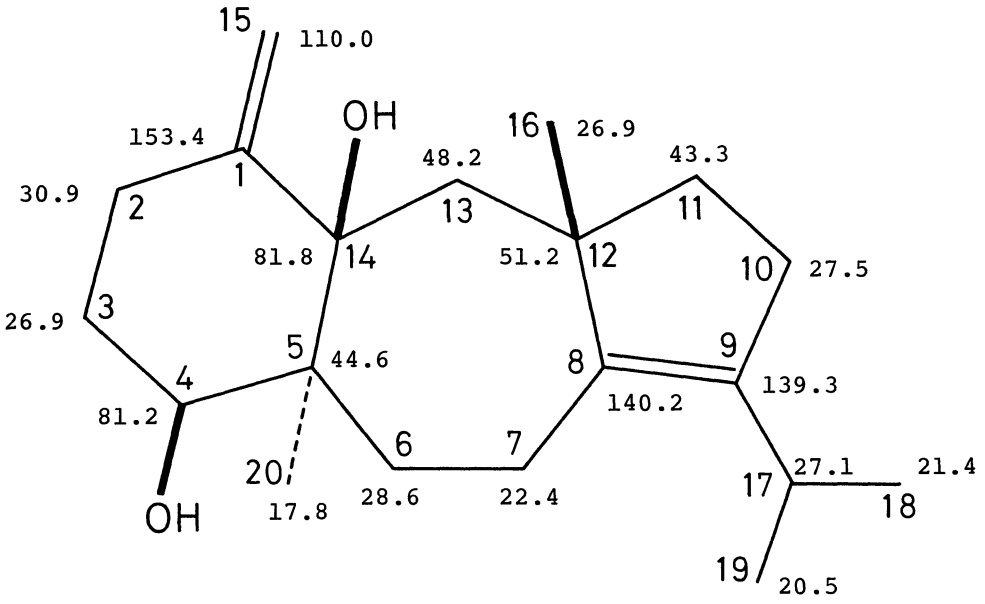
(1) $R_1 = H_2$, $R_2 = R_3 = OH$

(2) R_1 = α-H, β-OH, R_2 = H, R_3 = OH

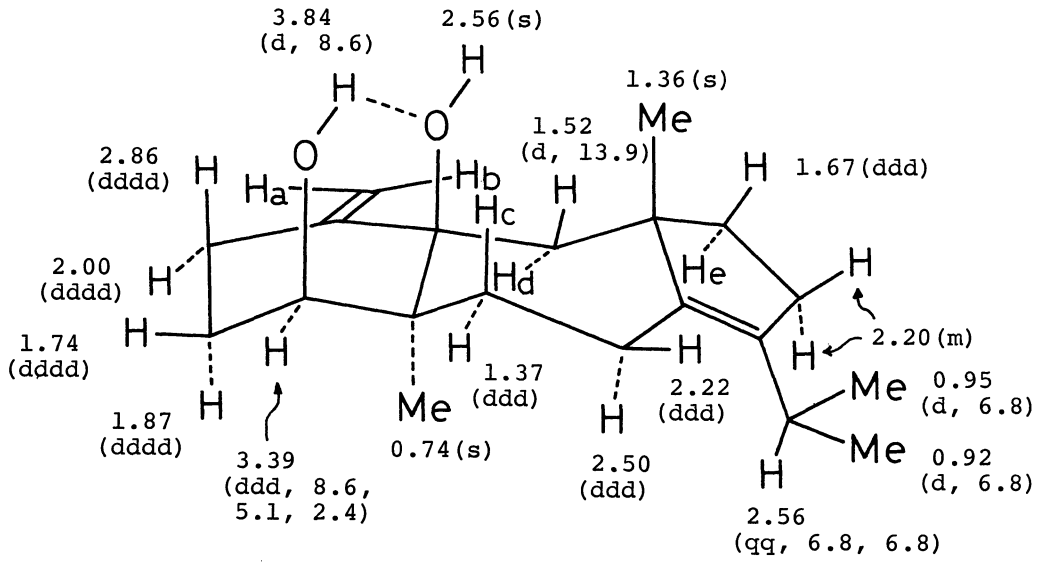
(3) $R_1 = H_2$, $R_2 = OH$, $R_3 = H$

(4) $R_1 = H_2$, R_2 = OAc, $R_3 = OH$

(5) $R_1 = O$, $R_2 = H$, $R_3 = OH$



(1) Amijiol; ^{13}C NMR data (100 MHz, δ/ppm) for $CDCl_3$ solution.



(1a); ^{1}H NMR data for 1; 400 MHz; $CDCl_3$ solution; δ values; multiplicity and J values (in Hz) in parentheses. Ha: δ 4.83 (dd, 1.5, 1.0), Hb: δ 4.88 (dd, 1.5, 1.5), Hc: δ 2.92 (ddd), Hd: δ 2.03 (d, 13.9), He: δ 1.57 (ddd).

A close structural similarity of 14-deoxyamijiol (3),[5] $C_{20}H_{32}O$, mp 103-104 °C, $[\alpha]_D$ -79° ($CHCl_3$), to 1 was indicated by the following spectral data analogous to those of 1. ν_{max} ($CHCl_3$) 3630, 3080, 1640, and 890 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 152.8 (C-1), 140.8 (C-8), 139.7 (C-9), 107.6 (C-15), 79.4 (C-4), 50.0 (C-12), 43.6 (C-5), 42.3 (C-13), 41.3 (C-11), 40.3 (C-14), 36.8 (C-2), 31.8 (C-6), 31.5 (C-3), 27.5 (C-10), 26.9 (C-17), 24.2 (C-16), 22.4 (C-7), 21.2 (C-18), 21.0 (C-19), and 16.9 (C-20); ^1H NMR ($CDCl_3$) δ 4.80 (ddd, J=1.6, 1.6, and 1.3 Hz, 15-Ha), 4.56 (ddd, J= 1.6, 1.6, and 1.6 Hz, 15-Hb), 3.42 (dd, J=3.4 and 3.4 Hz, 4-H), 2.67 (ddd, J=10.0, 6.0, and 1.6 Hz, 14-H), 2.59 (qq, J=7.0 and 7.0 Hz, 17-H), 1.09 (s, 16-H_3), 0.93 and 0.92 (each d, J=7.0 Hz, 18- and 19-H_3), and 0.65 (s, 20-H_3). These evidence reveal the replacement of the tertiary hydroxyl group at C-14 in 1 by a hydrogen atom. Therefore, 14-deoxyamijiol must be represented by the structure 3.

Structures 1 - 3 are closely related to that of dolatriol (6), a cytotoxic diterpenoid recently isolated from a mollusk *Dolabella auricularia*.[6] The occurrence of amijiol and its congeners in a marine alga of the genus *Dictyota* may support the possibility that dolatriol is of dietary origin. Strange to say, three clavularane derivatives having a similar 6-7-5 ring system have been isolated from an octocoral *Clavularia inflata*[7] which hardly feeds on such a seaweed.

We thank Dr. M. Ohno, Usa Marine Biological Institute, Kochi University, for identification of alga.

References and Notes

1) J. Finer, J. Clardy, W. Fenical, L. Minale, R. Riccio, J. Battaile, M. Kirkup, and R. E. Moore, *J. Org. Chem.*, 44, 2044 (1979) and references cited therein.
2) For previous article see M. Ochi, H. Kotsuki, S. Inoue, M. Taniguchi, and T. Tokoroyama, *Chem. Lett.*, 1979, 831.
3) These compounds did not show an evident antimicrobial activity against *B. subtilis* and *P. crustosum* at a concentration of 100 μg/ml.
4) The structure of the congener, amijidictyol, was determined to have the same carbon skeleton by X-ray method; M. Ochi, M. Watanabe, M. Kido, Y. Ichikawa, I. Miura, and T. Tokoroyama, submitted for publication.
5) The detailed ^1H NMR data for isoamijiol and 14-deoxyamijiol were consistent with the structures shown.
6) G. R. Pettit, R. H. Ode, C. L. Herald, R. B. Von Dreele, and C. Michel, *J. Amer. Chem. Soc.*, 98, 4677 (1976).
7) J. C. Braekman, D. Daloze, R. Schubert, M. Albericci, B. Tursch, and R. Karlsson, *Tetrahedron*, 34, 1551 (1978).

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