CHEMISTRY LETTERS, pp. 1233-1234, 1980. © The Chemical Society of Japan 1980

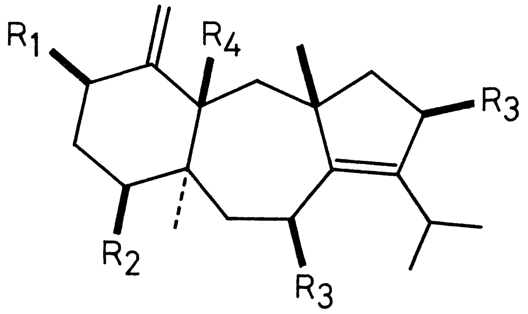
AMIJIDICTYOL, A NEW DITERPENOID FROM THE BROWN SEAWEED *DICTYOTA LINEARIS*: X-RAY CRYSTAL AND MOLECULAR STRUCTURE

Masamitsu OCHI and Masanori WATANABE
Faculty of Science, Kochi University, Akebono-cho, Kochi 780
Masaru KIDO, Yasuji ICHIKAWA, and Iwao MIURA
Laboratories of Natural Products Chemistry, Otsuka Pharmaceutical Co. Ltd., Kawauchi-cho, Tokushima 771-01
and
Takashi TOKOROYAMA
Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558

The structure of a new diterpenoid, amijidictyol, isolated from the brown seaweed *Dictyota linearis* has been determined as 4 on the basis of spectral evidence and X-ray analysis.

In the previous paper,[1] we have reported the isolation of three novel diterpenoids, amijiol (1), isoamijiol (2), and 14-deoxyamijiol (3), from the brown seaweed *Dictyota linearis*. We describe herein the structure of an additional diterpenoid, amijidictyol, isolated from the same alga.

Amijidictyol (4), $C_{24}H_{36}O_6$, mp 187-189 °C, $[\alpha]_D$ -40° ($CHCl_3$), was isolated in 0.016% yield from a methanol extract of fresh alga by careful silica gel column chromatography, and its spectral properties revealed the tricyclic structure containing the linear 6-7-5 ring system of 1, 2, and 3. The IR spectrum ($CHCl_3$) showed the presence of two hydroxyl groups at 3600 and 3460 cm^{-1}. The detailed ^1H NMR ($CDCl_3$) analysis at 400 MHz were consistent with the structure 4: δ 5.86 (dd, J=11.3 and 7.0 Hz, 7-H), 5.78 (dd, J=7.3 and 5.7 Hz, 10-H), 4.89 and 4.78 (each br s, 15-H_2), 3.89 (d, J=7.6 Hz, 4-OH), 3.45 (m, 4-H), 3.45 (s, 14-OH), 2.72 (qq, J=7.0 and 7.0 Hz, 17-H), 2.05 and 2.04 (each s, 2 MeCO), 1.52 (s, 16-H_3), 1.01 and 0.95 (each d, J=7.0 Hz, 18- and/or 19-H_3), and 0.70 (s, 20-H_3). This structure was also



1 $R_1=R_3=H$, $R_2=R_4=OH$
2 $R_1=R_4=OH$, $R_2=R_3=H$
3 $R_1=R_3=R_4=H$, $R_2=OH$
4 $R_1=H$, $R_2=R_4=OH$, $R_3=OAc$

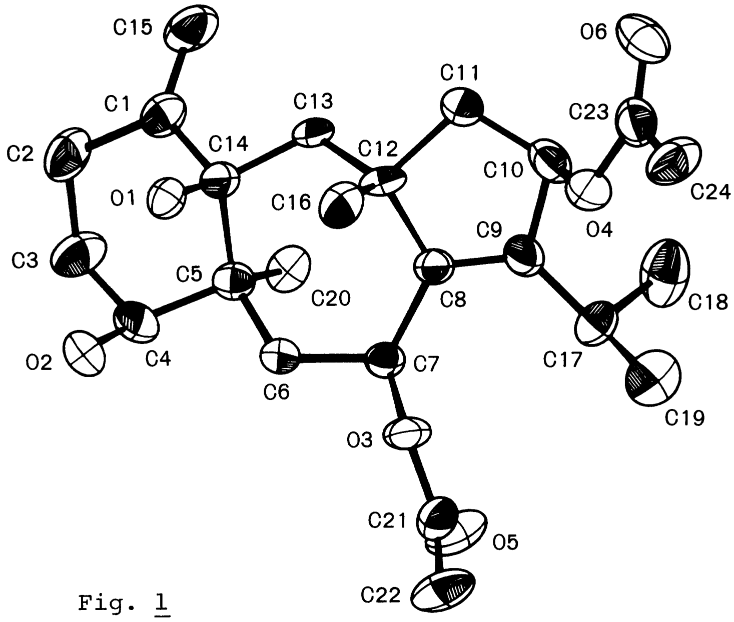


Fig. 1

supported by the ^{13}C NMR ($CDCl_3$) data at 100 MHz assisted with off-resonance and selective proton-noise decoupling technique which showed the presence of four methyls (δ 18.0, 19.8, 22.6, and 28.1), five methylenes (δ 26.5, 30.5, 34.3, 49.7, and 51.4), one methine (δ 27.1), three oxygen-bearing methines (δ 68.0, 78.4, and 80.7), together with three fully substituted carbon atoms (δ 43.0, 49.3, and 81.0), one tetrasubstituted double bond (δ 145.0 and 146.5), one exocyclic methylene group (δ 110.7 and 152.2), and two acetate (δ 21.58, 21.63, 171.2, and 171.7).

The assigned structure 4 was confirmed by X-ray analysis of the single crystal. Crystal data; a=6.243(3), b=12.820(6), c=14.440(6) Å, β=99.58(4)°, space group $P2_1$, Z=2. The intensity data were collected in ω scan mode on a Syntex R3 four-circle diffractometer using a graphite monochromated Mo-Kα radiation ($2\theta \leq 60°$). A total of 3475 independent reflection were collected, among which 2445($I>2\sigma(I)$) were classed observed. The intensity data were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by the direct method using MULTAN in Syntex XTL program. The hydrogen atoms were located in difference map computed after block-diagonal least-squares anisotropic refinements of nonhydrogen atoms. The final refinement cycle gave R=0.076, in which all hydrogen atoms were added as fixed parameters. Figure 1 shows a computer generated perspective drawing of 4. As anticipated from the spectral data the 6- and 7-membered rings are joined in a trans-fashion. The work described here does not define the absolute configuration of 4. The bridgehead methyl at C-5 has the α-configuration, all other substituents are β.

Reference

1) M. Ochi, M. Watanabe, I. Miura, M. Taniguchi, and T. Tokoroyama, *Chem. Lett.*, 1980, 1229.

(Received July 24, 1980)