Tetrahedron Letters,Vol.24,No.40,pp 4341-4342,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

EPOXYDICTYMENE, A NEW DITERPENE FROM THE BROWN ALGA DICTYOTA DICHOTOMA

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Abstract: Structure of epoxydictymene (**1**), a new tetracyclic diterpene from *Dictyota dichotoma*, has been determined mainly on the basis of X-ray analysis.

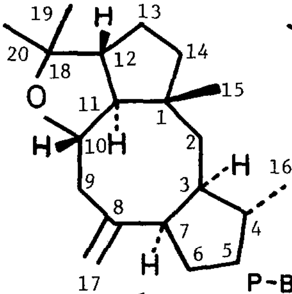
The brown algae of the family Dictyotaceae have yielded a variety of novel natural products.[1] Previously we reported isolation and structure determination of new cyclononane and hydroazulene diterpenes[2] from *Dictyota dichotoma*. We wish to report here the structure determination by X-ray analysis of p-bromophenylurethane derivative **2** of a diterpene having a novel fusicoccin-like tricyclic carbon skeleton.

Methanol extraction of the fresh alga (20 kg), collected in July 1980 at Oshoro bay, Hokkaido, followed by silica gel chromatography (AcOEt-hexane) and semipreparative high speed liquid chromatography (μPorasil, AcOEt-hexane, 5:95) yielded the new diterpene (215 mg), epoxydictymene (**1**), oil, $C_{20}H_{32}O$, m/z M^+ Found 288.2495, Calcd 288.2455; $[\alpha]_D^{18}$ +78.1° (c 0.9, hexane). The absence of the bands due to hydroxyl and carbonyl groups and presence of a band at 1140 cm^{-1} in the IR spectrum of **1** suggested that the oxygen atom of **1** was contained in an ether linkage. The ^1H-NMR spectrum of **1** exhibited four methyl signals, i. e. two singlet signals at δ 1.17 and 1.26 due to methyl groups on carbon bearing oxygen, a singlet signal at 0.89 due to a methyl on a quaternary carbon and a doublet signal at 1.01. The low field region of the ^1H-NMR spectrum displayed two singlet signals ascribable to an exomethylene group at δ 4.77 and 4.98, and a doublet of triplets at 3.57 (J=10, 7 Hz) due to the ethereal proton. The ^{13}C-NMR spectrum confirmed the presence of the exomethylene group (δ 114.1t, 145.8s), the ether linkage (74.6d, 77.7s), five methine groups (43.2, 43.8, 50.8, 57.4, 59.5, each d), six methylene groups (20.2, 34.1, 34.6, 41.1, 44.4, 48.3, each t), and four methyl groups (19.1, 24.0, 24.3, 29.2, each q). Therefore, epoxydictymene (**1**) was tetracyclic and contained an exomethylene and an ether group. However, since it seemed difficult to obtain further clue for structure determination from these data, X-ray studies of a suitable derivative was attempted.

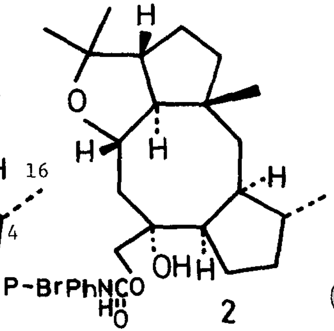
Oxidation of **1** with 1 equivalent of OsO_4 and pyridine in ether yielded an epimeric mixture of alcohols (α/β=1:1). Treatment of the mixture with p-bromophenylisocyanate in benzene yielded the corresponding mixture of p-bromophenylurethane derivatives, which was separated by column chromatography. Only the β-derivative was crystallized from methanol to give 2, mp 111°.

The crystal data for 2 were as follows: $C_{27}H_{38}NO_4Br\cdot CH_3OH$, monoclinic, space group C2, a=19.443(4), b=11.658(1), C=13.489(s) Å, β=112.16(1)°, Z=4, $2\theta<130°$ were collected on an automated four-circle diffractometer with graphite-monochromated Cu Kα radiation.[3] The structure was solved by the Monte Carlo direct method.[4] The absolute configuration was determined by taking account of the anomalous dispersion of bromine atoms for Cu Kα radiation. The final R value was 0.045.[5] The molecular skeleton of 2 thus obtained is shown in Fig. 1.

Probably the new epoxyditerpene is biosynthesized from bicyclic dollabelladiene[6] which is also present in the same alga, through a transannular cyclization. It may be of interest that the produced tetracyclic skeleton is very much more strained than its hypothetical precursor. Ophiobolin-A[7] and fusicoccin[8] which have similar skeleton with different stereochemistry, are much less strained than the new skeleton, according to inspection of models.



1



2

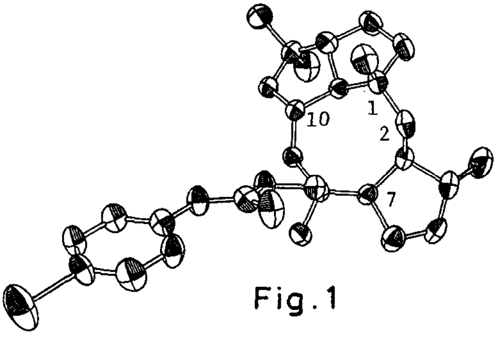


Fig.1

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(Received in Japan 14 June 1983)