was found to apply for **3c**. The CD spectrum of **3c** showed a negative chiroptical effect at 237 nm and a positive band at 222 nm. The "dibenzoate chirality" rule, in conjunction with the established relative stereochemistry, requires therefore a 1*S*,2*R*,3*R* stereochemistry which agrees with that obtained by chemical methods.[13]

The techniques described here for assigning absolute stereochemistry to diol **2** are presently being applied to the other dihydrodiols obtained with *P. putida* 39/D. Interestingly, the diol groups in (+)-*cis*-1(*R*),2(*S*)-dihydroxy-1,2-dihydronaphthalene (**1**) and dihydrodiol **2** have the same absolute stereochemistry when the methine CH in **1** and the methyl group in **2** are treated as the same position.[14] All of the monosubstituted benzenes which are substrates for the mutant yield dihydrodiols with a high degree of optical activity, while disubstituted benzenes such as *p*-chloro- and *p*-bromotoluene yield optically inactive diols. In contrast, *p*-fluorotoluene is converted to a diol with high optical activity. Seemingly, the enzyme has a bulk tolerance at only one of the ring positions adjacent to the double bond at which the diol group is introduced. Thus, in the toluene series of substrates, the bulky chloro and bromo groups may be confused with methyl, while the fluoro group is sufficiently small that one mode of binding predominates and a highly optically active product is produced. Determination of absolute stereochemistry for this series of dihydrodiols will provide a test of this hypothesis.

[13] The absolute stereochemistry of the Diels–Alder adduct between the diacetate of **2** and *p*-bromophenyltriazolinedione has been deduced by X-ray crystallography and agrees with the assignment made here. We are indebted to Dr. R. E. Davis, Department of Chemistry, University of Texas at Austin, for disclosure of this information to us prior to publication.

[14] The diol (**1**) from naphthalene was obtained from a different *Pseudomonas* mutant.[6]

[15] This work was supported in part by grants from the Robert A. Welch Foundation (Grant No. F-440) and the National Institutes of Health, U. S. Public Health Service (Grant No. ES-00537). D. T. G. is a recipient of a Career Development Award, No. 1-K04 ES 70088 from the National Institutes of Health, U. S. Public Health Service.

Herman Ziffer,* Donald M. Jerina
National Institute of Arthritis,
Metabolism and Digestive Diseases
National Institutes of Health
Bethesda, Maryland 20014

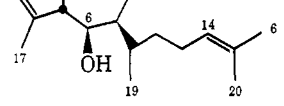
David T. Gibson,[15] Val M. Kobal
Department of Microbiology, University of Texas
Austin, Texas 78712
Received February 27, 1973

Marine Natural Products. VIII. Pachydictyol A, an Exceptional Diterpene Alcohol from the Brown Alga, *Pachydictyon coriaceum*[1]

Sir:

Marine algae of the family Dictyotaceae, particularly the genera *Dictyopteris*[2–4] and *Taonia*,[5] are known for the interesting secondary metabolites they produce. *Pachydictyon coriaceum*, a member of this family, is found on the Pacific coast of California, south from Santa Barbara to Baja California. We report here the structure of one of the constituents of *P. coriaceum*, which we have found to have mild antibiotic activity *vs. Staphyloccus aureus*.

Hexane extraction of the air dried seaweed followed by column chromatography on silica gel resulted in the isolation of a new diterpene alcohol, pachydictyol A (**1**) (0.7% dry weight of alga), $[\alpha]^{30}\text{D}$ +106° (cyclohexane). A composition of $C_{20}H_{32}O$ was indicated by the mass spectrum of **1** ($M^+ = m/e$ 288) and confirmed by elemental analysis of its α-naphthylurethane derivative (mp 114–115°). The infrared spectrum of **1** showed bands at 2.87 (OH), 6.12 (C=C), and 11.23 μ ($C{=}CH_2$).



Nmr spectra of **1** and added increments of $Eu(dpm)_3$ were analyzed using a recently developed graphical method.[6] The following chemical shift assignments were made: δ 5.30 (1 H, m, H-3), 5.10 (1 H, t, H-14), 4.72 (2 H, s, H-18), 3.85 (1 H, broad s, H-6), 1.75 (3 H, d, H-17), 1.67 (3 H, s, H-20), 1.60 (3 H, s, H-16), 0.97 (3 H, d, H-19).

Pachydictyol A formed an acetate with difficulty and was oxidized with Jones reagent to a ketone (ir 5.88 μ, 7-ring C=O).

The structure, including absolute stereochemistry, of **1** was obtained by an X-ray crystallographic analysis of its *p*-bromophenylurethane derivative (mp 107–109°, needles from ethanol). Weissenberg and precession photographs showed monoclinic symmetry and space group $P2_1$. The unit cell constants, $a = 13.392$ (9), $b = 19.28$ (2), $c = 5.195$ (5) Å, and $\beta = 103.45$ (2)°, were determined from a least-squares fit of 12 carefully centered high angle reflections, using Mo $K\alpha_1$ radiation (λ 0.70926 Å). The density of the crystal measured by flotation was 1.22 g cm^{-3}, while that calculated for two molecules of $C_{27}H_{36}O_2NBr$ in a unit cell is 1.204 g cm^{-3}.

Intensity data were collected on a computer controlled Picker four-circle diffractometer, using Mo $K\alpha$ radiation made monochromatic by Bragg reflection from a graphite crystal. Reflections having 2θ values up to 38° (1005 unique reflections) were collected by the 2θ–θ scan technique at a scan rate of 1°/min and a scan range of 1.9°. During the period of data collection, three standard reflections were measured after every 75 reflections. At the end of data collection the crystal turned yellowish brown with the decomposition showing up equally in the three standard reflections as a monotonic 15% loss of intensity. The intensities were scaled to the initial standards and corrected for Lorentz polarization effects.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations, using 951 reflections which were greater than 2σ (the

---

[1] Paper VII in this series: *J. Org. Chem.*, submitted for publication.

[2] T. Irie, K. Yamamoto, and T. Masamune, *Bull. Chem. Soc. Jap.*, **37**, 1058 (1964).

[3] J. A. Pettus, Jr., and R. E. Moore, *J. Amer. Chem. Soc.*, **93**, 3087 (1971).

[4] W. Fenical, J. J. Sims, R. M. Wing, and P. C. Radlick, *Phytochemistry*, **11**, 1161 (1972).

[5] A. G. Gonzalez, J. Darias, and J. D. Martin, *Tetrahedron Lett.*, 2729 (1971).

[6] R. M. Wing, T. A. Early, and J. J. Uebel, *Tetrahedron Lett.*, 4153 (1972).

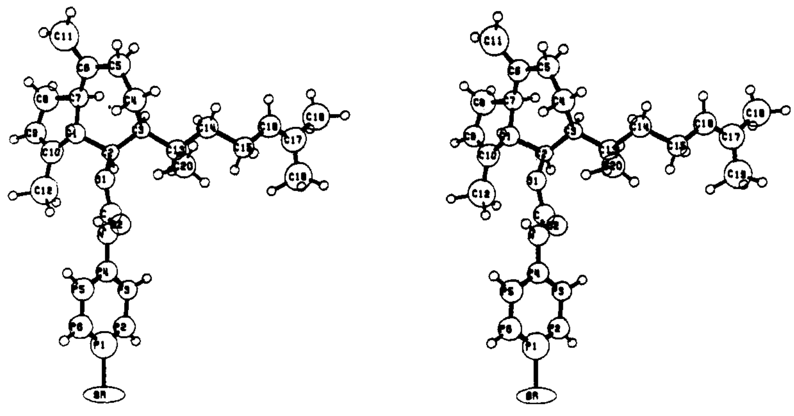


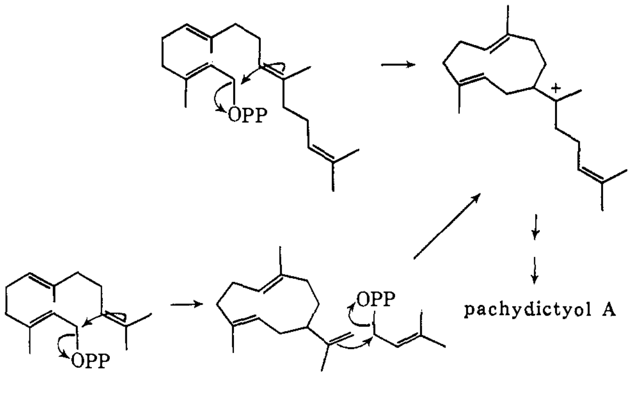
Figure 1. A stereo view of pachydictyol A *p*-bromophenylurethane.

bromine atom was treated anisotropically). After convergence to a weighted residue, R_w (based on $|F|$), of 10.8% the absolute configuration was confirmed using the anomalous dispersion effect of the bromine atoms (R_w = 11.3% for the enantiomer).[7] At this stage, all hydrogen atoms were located from a difference Fourier map. Hydrogen atoms were included in the structure factor calculation but not in a further refinement. The refinement converged to a final R_w of 8.4%. The standard deviation of an observation of unit weight is 1.98.

An interesting question to consider is the biosynthesis of pachydictyol A. The perhydroazulene ring system of pachydictyol A is previously unknown among diterpenes. The ring system is well known in sesquiterpenes and one is tempted to consider pachydictyol A as a sequiterpene to which an isoprene unit has been added. Such a biogenesis is obvious for the many flavanoids to which one or more isoprene units have been added[8] but has not previously been proposed for any terpenoid.

The diterpenes are normally considered to be derived from geranylgeraniol. Pachydictyol A could be derived from this precursor by cyclization analogus to farnesol in sesquiterpene biosynthesis (Scheme I).

Scheme I. Possible Biosyntheses of Pachydictyol A



There are two other compounds among the diterpenes, artemisene and biflorin, which also resemble sesquiterpenes and for which this biosynthesis has been proposed.[9]

Acknowledgment. This work is a result of research sponsored by NOAA Office of Sea Grant, Department of Commerce, under Grant No. USDC 2-35208.

D. R. Hirschfeld, William Fenical, George H. Y. Lin
Richard M. Wing, Phillip Radlick, James J. Sims*
Departments of Plant Pathology and Chemistry
University of California, Riverside, California 92502

Received March 24, 1973

---

[7] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

[8] T. A. Geissman and D. H. G. Crout, "Organic Chemistry of Secondary Plant Metabolism," Freeman, Cooper and Co., San Francisco, Calif., 1969, pp 242–246.

[9] T. K. Devon and A. I. Scott, "Handbook of Naturally Occurring Compounds. Volume II. Terpenes," Academic Press, New York, N. Y., 1972.

Intrinsic Acidities of Carboxylic Acids from Gas-Phase Acid Equilibria

Sir:

Recently we reported[1,2] results for the gas-phase proton transfer equilibria ($B_1H^+ + B_2 = B_1 + B_2H^+$) measured with a pulsed electron beam high-pressure mass spectrometer.[2,3] The equilibrium constants and their temperature dependence allow the evaluation of free energy and enthalpy changes for the reactions and permit the measurement of the intrinsic basicity of the compounds in absence of a solvent.

Similar measurements, but at much lower pressure and constant temperature, have been made by several groups,[4–6] using ion cyclotron spectrometers.

The present communication represents an extension of the proton transfer work to equilibria involving the acids HA.

$$A_1^- + A_2H = A_1H + A_2^- \qquad (1)$$

The results, measured with the same instrument,[2,3] are given in Table I.

The data were obtained by passing through the ion source a carrier gas (O_2, N_2, or Ar) at 4 Torr, typically containing the weaker acid HA at some 100 mTorr and

---

[1] J. P. Briggs, R. Yamdagni, and P. Kebarle, *J. Amer. Chem. Soc.*, **94**, 5128 (1972).

[2] R. Yamdagni and P. Kebarle, to be submitted for publication.

[3] A. J. Cunningham, J. D. Payzant, and P. Kebarle, *J. Amer. Chem. Soc.*, **94**, 7627 (1972).

[4] E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, D. Holtz, J. L. Beauchamp, and R. W. Taft, *ibid.*, **94**, 4724 (1972).

[5] D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **94**, 4726 (1972).

[6] W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *ibid.*, **94**, 471 (1972).