cleus via organoboranes. The use of *B*-alkyl-9-BBN derivatives makes this procedure superior to the S_N2 reaction for hindered alkyl groups. In addition, we have found that the formation of the "ate" complex activates the 3 position to attack by carbon electrophiles. These results, as well as applications to other aromatic systems, will be the subject of forthcoming publications.

The following procedure is representative.[12,13] A dry 50-mL round-bottom flask equipped with a septum-capped side arm and reflux condenser was connected to an oil bubbler. The system was purged with nitrogen and maintained under nitrogen until after the oxidation. To this flask was added 5 mL of THF and 0.682 g (2.5 mmol) of *N*-benzenesulfonylindole.[10] To this solution maintained at −12 °C was added 1.60 mL (3 mmol) of *tert*-butyllithium. The flask was allowed to stir in air for 20 min, cooled to −80 °C, and 0.428 mL (3.00 mmol) of triethylborane was added. The solution was stirred for 10 min, and 0.84 g of I_2 in 3 mL of THF was added. The solution was stirred for 1 h at −80 °C and allowed to warm to room temperature. The residual borane was washed three times with 3 mL of 3 N NaOH then oxidized by addition of 2 mL of 3 N NaOH followed by the dropwise addition of 2 mL of 30% hydrogen peroxide. After stirring at room temperature for 1 h, the organic layer was diluted with ether, separated, washed with water, and dried ($MgSO_4$) and the solvent was removed under vacuum to give 0.62 g of a crude brown solid. Recrystallization from methanol gave 0.39 g (57%) of analytically pure 1-(benzensulfonyl)-2-ethylindole (mp 95.0–96.5 °C).

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Alan B. Levy

Department of Chemistry
State University of New York
Stony Brook, New York 11794

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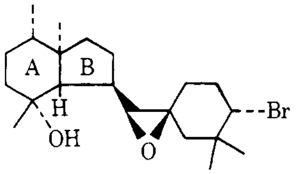
Isolation and Structure of Angasiol[1]

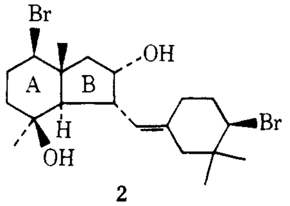
Summary: The structure and absolute configuration of a new dibromoditerpene designated angasiol has been determined by X-ray crystallographic techniques.

Sir: The seaweeds have developed very effective enzyme systems for utilizing halide ions in synthesis of halogenated terpenes.[2] Marine red algae (*Rhodophyta* phylum), especially members of the genera *Laurencia* and *Plocamium,* have proved to be quite adept at halogen atom incorporation.[3] Certain mollusk herbivores consume such algae and accumulate some of the halogenated constituents for their chemical defense mechanism. A useful illustration is provided by the gastropod (subclass Opisthobranchia) *Aplysia californica* feeding on *Laurencia* and *Plocamium* seaweeds.[4]

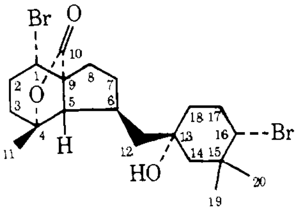
Two new dibromoditerpenes, irieol A (1) and iriediol (2), were recently isolated from a Gulf of California *Laurencia* sp. by Fenical and colleagues,[5] and X-ray crystallographic methods were used to derive structures 1 and 2. But assignment of absolute configurations could not be made with certainty and structure 2 according to the crystallographic data should represent the A/B ring enantiomer of 1. We now wish to report that the South Pacific Ocean (East Australia) sea hare *Aplysia angasi* contains an apparently related dibromoditerpene designated angasiol (3), that accompanies the cytotoxic component aplysistatin (4).[6] The discovery of angasiol provides the first evidence that some sea hares may store exogenous dibromoditerpenes of the new irieol A type for certain biosynthetic processes.[7] After the absolute configuration of angasiol had been established by X-ray methods, comparison with irieol A (1) revealed the same absolute configuration at six chiral centers, according to the original tentative assignment for 1.[1,2]



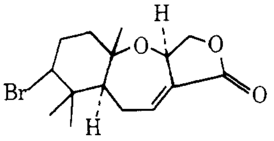
1



2



3



4

Angasiol (3) was isolated (Supplementary Material) from a chloroform-soluble fraction in turn obtained through a solvent-partitioning sequence applied to a 2-propanol extract of *Aplysia angasi.* Careful chromatography using a Merck size C prepacked column[8] and elution with 9:1 ligroin–ethyl acetate led to angasiol (3, 0.007% yield, as needles from acetone–hexane, mp 189–191 °C) corresponding to empirical formula $C_{20}H_{30}Br_2O_3$: mass spectrum *m/e*, 458/460/462 (M − H_2O), 379/381 (M − H_2O − Br), 378/380 (M − H_2O − HBr); ORD and CD in methanol gave positive plain curves; IR (KBr) 3500 (s), 1765, 1210, 1150, and 575 cm^{-1}. The broad band decoupled ^{13}C NMR spectrum[9] of angasiol revealed the presence of 20 carbon atoms, and the off-resonance decoupled spectrum confirmed the molecular formula. The ^{13}C NMR spectra indicated the presence of a γ-lactone carbonyl (δ 176.56) and an associated tertiary alkoxy group (83.55), a tertiary alcohol (72.43), two quaternary carbon atoms without

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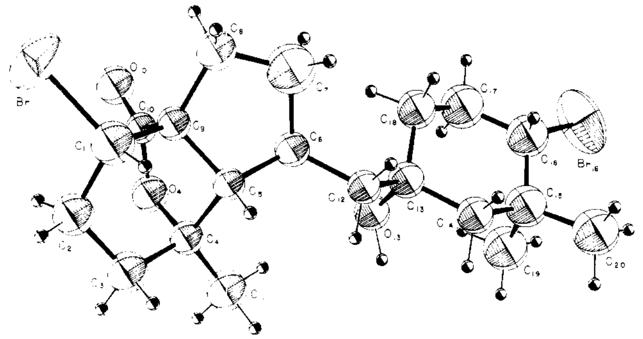

Figure 1. A perspective representation of the structure of angasiol.

electronegative atoms (61.61, 36.54), two –CHBr– groups (65.31 and 51.53 as determined by single-frequency proton decoupling), two methine carbon atoms (63.52, 35.83), eight methylene carbon atoms (51.36, 50.00, 39.79, 38.13, 32.83, 31.96, 31.63, 30.33), and three methyl groups (32.61, attached to a carbon atom bearing an electronegative substituent, 22.66, and 21.20). The ^{1}H NMR spectrum suggested that each proton on a bromine-bearing carbon atom was vicinal to a methylene with diastereotopic hydrogen atoms: 1.03 (s, 3 H), 1.24 (s, 3 H), 1.47 (s, 3 H), 1.2–2.5 (m, 18 H), 3.93 (d of d, J = 4.5, 8 Hz, 1 H), and 4.14 (d of d, J = 6.5, 11 Hz, 1 H).

Single crystals of angasiol suitable for data collection were obtained from acetone–hexane. The X-ray precession photographs displayed orthorhombic symmetry with systematically extinct reflections: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; and $00l$, $l = 2n + 1$, which conformed uniquely to the noncentrosymmetric space group $P2_12_12_1$. Least-squares refinement of 15 reflections between the angular range $3.4 \leq 2\theta \leq 17.2°$ yielded the lattice parameters a = 9.441 (3), b = 9.529 (2), and c = 23.683 (9) Å, which for z = 4 gives ρ_{calcd} = 1.49 g/cm^3 (ρ_{obsd} = 1.46 g/cm^3 by flotation in toluene–carbon tetrachloride). Diffraction intensities were measured using graphite monochromated Mo K_α radiation on a Syntex P$\bar{1}$ autodiffractometer operating in the 2θ–θ mode. Of 2841 reflections examined ($2\theta \leq 55°$) 2176 unique reflections were accepted with $|F_o| > 0$. Corrections were made for Lorentz, polarization, and absorption (μ = 38 cm^{-1}) effects.[10]

The structure was solved by standard heavy-atom techniques.[11] A comparison was made of the two configurational isomers with isotropic temperature factors for carbon and oxygen and anisotropic temperature factors for bromine using anomalous scattering factors for Br.[12] Standard residuals at convergence for the two enantiomers were R = 0.1582 and 0.1562, respectively, and the weighted residuals $R_w = (\sum_w(|F_o| - |F_c|)^2/\sum_w|F_o|^2)^{1/2}$ of 0.1240 and 0.1227, respectively, where $w = 1/\sigma_{F_o}{}^2$. Statistical significance of R_w-factor ratio at 0.995 significance level indicated the second enantiomer to be correct. Conformational and absolute configurational aspects of the angasiol molecule are presented in Figure 1. The seven chiral centers are C-1 (S), C-4 (R), C-5 (S), C-6 (S), C-9 (S), C-13 (S), and C-16 (S).

Refinement was unsuccessful when carbon and oxygen atoms were allowed to vary anisotropically. A certain degree of disorder is present and is most apparent in the large temperature factor for C-7. Results from attempts to refine alternate positions for C-7, C-12, C-14, C-18, and O-13 were inconclusive, terminating any further attempts toward anisotropic refinement. After hydrogen atoms were placed at calculated positions 1.0 Å from their respective carbon atoms, full-matrix least-squares refinement converged to final crystallographic residuals R = 0.074 and R_w = 0.072 for 875 reflections restricted to $\sin\theta/\lambda < 0.45$ and $F_o > 1.0\sigma_{F_o}$.

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Supplementary Material Available. Figures 2 and 3 showing bond angles and bond lengths, Tables I and II of atomic positional and thermal parameters of angasiol, and procedures for the isolation of angasiol (5 pages). Ordering information is given on any current masthead page.

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George R. Pettit,* Cherry L. Herald
James J. Einck, Lawrence D. Vanell
Peter Brown, Devens Gust
Cancer Research Institute and
Department of Chemistry, Arizona State University
Tempe, Arizona 85281

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Versatile Polymer-Bound Hydrogenation Catalyst. Anthranilic Acid Anchored Palladium(II) Catalysis

Summary: Anchoring the bidentate ligand anthranilic acid to chloromethylated polystyrene beads, followed by refluxing with palladium chloride, has resulted in a catalyst effecting the hydrogenation of alkenes, dienes, and even benzene. The catalyst is air-stable and has a lifetime of at least 10 000 catalytic cycles per palladium atom.