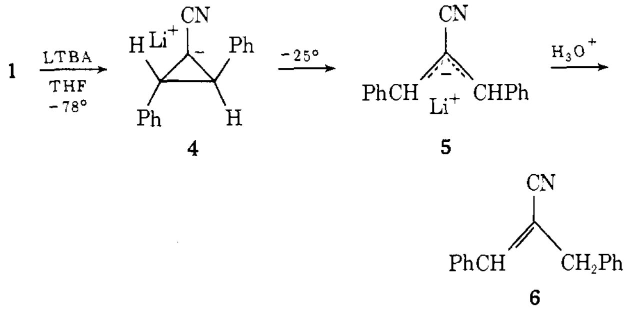
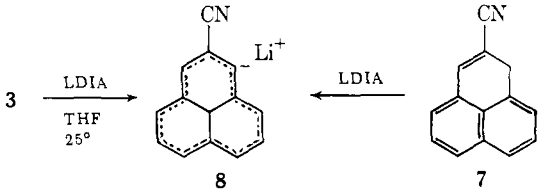
At $-25°$ the anions prepared from **1** and **2** with 0.1 *M* LTBA in THF produced magenta solutions (λ_{max} 556 nm, log ϵ 4.62) due to 2-cyano-1,3-diphenylallyllithium (**5**).[6] Hydrolysis of the magenta solutions produced a 1 : 1 mixture of *cis*- and *trans*-α-benzylcinnamonitrile (**6**) with no by-products detectable by pmr or glpc. Nearly identical preparation of **5** and **6** by treatment of **1** with LDIA in THF was reported earlier by Boche and Martens.[8] The anion prepared from **3** with 0.1 *M* LDIA in THF at $\geq 25°$ slowly produced a blue solution with a visible spectrum qualitatively the same as that obtained by treatment of 2-cyanophenalene (**7**)[3] with LDIA in THF (λ_{max} 644 nm, log ϵ 3.89). We attribute this spectrum to the 2-cyanophenalenyl anion (**8**). Acidification of the blue solutions produced 5- or 8-cyanophenalene. However, when the course of formation of **8** from **3** was followed quantitatively by glpc at 25°, at no time did the yield of **8** exceed 25%, because **8** disappeared at a rate competitive with its rate of formation, and because the anion of **3** underwent side reactions leading to products not detected under our glpc conditions. Earlier Wittig and coworkers[3] reported that treatment of **3** with LDIA in THF for 15 min at 20° and reisolation of nitriles gave 17% of **3**, 69% of the syn isomer of **3**, and 0.34% of **7**.





Rate constants for ring opening of the anions of **1** and **2** prepared with 0.05–0.1 *M* LTBA in THF were determined by following the appearance of the visible absorption of **5** over ranges of -29.6 to $-19.2°$ for **1** and -28.5 to $-8.6°$ for **2**. Rate constants were independent of LTBA concentration. The ratio of rate constants for conversion of the anions to **5** at $-25.0°$ was $k_1/k_2 = 42$. When the anion **4** was prepared with LDIA its rate constant for ring opening at $-25.0°$ was 0.49 times as fast as that for **4** prepared with LTBA. The rate data for opening of the anion of **2** lead to $\Delta H^{\ddagger} = 18.1 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3.5 \pm 4.0$ cal deg^{-1} mol^{-1} at $-25°$.[9] Initial rate constants for conversion of the anion of **3**, prepared from LDIA in THF, to **8** were measured by following the appearance of visible absorption of **8** at 36° over the first 1–4% of the reaction (in which the loss of **8** is negligible). An average value of $7.9 \pm 0.4 \times 10^{-6}$ sec^{-1} was obtained. Extrapolation of the rate data for the anion of **2** to 36° and inclusion of a factor of 2.0 for greater reactivity with LTBA than with LDIA shows that the anion of **2** opens 1.1×10^4 times faster than the anion of **3**.

If disrotatory opening of cyclopropyl anions was allowed by orbital symmetry, the anion of **3** would open as readily as its acyclic models, the anions of **1** and **2**. In fact, we might expect the anion of **3** to open faster because the 2-cyanophenalenyl anion (**8**) is a weaker base than the 2-cyano-1,3-diphenylallyl anion (**5**).[10] Since the anion of **3** is forbidden geometrically to open conrotatory, we conclude in agreement with theory that conrotatory electrocyclic opening of cyclopropyl anions is preferred by at least the $\Delta\Delta G^{\ddagger} = 5.7$ kcal/mol obtained from relative rates of opening of the anions of **2** and **3** at 36°. Conrotatory opening of the anion of **2** probably is retarded by phenyl–proton interaction in the transition state, which can explain why opening of the anion of **1** proceeds still faster.[13] Therefore, 5.7 kcal/mol is only a lower limit for the extent to which the orbital symmetry allowed mechanism is favored over any other.

Acknowledgments. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work, and Standard Oil Co. of California and Phillips Petroleum Co. for fellowships which supported M. N.

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(6) The visible spectrum of **5** in THF is nearly the same as that of 1,3-diphenylallyllithium in THF.[7]

(7) (a) H. H. Freedman, V. R. Sandel, and B. P. Thill, *J. Amer. Chem. Soc.*, 89, 1762 (1967); (b) J. W. Burley and R. N. Young, *J. Chem. Soc., Perkin Trans 2*, 1843 (1972); (c) J. W. Burley and R. N. Young, *ibid.*, 835 (1972).

(8) G. Boche and D. Martens, *Angew. Chem., Int. Ed. Engl.*, 11, 724 (1972).

(9) Boche and Martens[8] report $\Delta H^{\ddagger} = 19.0 \pm 1.5$ kcal/mol and $\Delta S^{\ddagger} = 2.5$ eu for opening of **4** prepared with LDIA in THF. At $-24.5°$ our rate constant for opening of **4** with LDIA is 5.2 times greater than theirs. Although they do not mention their experimental method, we suspect that the difference may be attributed to a medium effect associated with much higher substrate and perhaps higher base concentrations in their experiments.

(10) We estimate from literature data that the pK_a of phenalene[11] is *ca.* 18 and the pK_a of 1,3-diphenylpropene[12] is *ca.* 28 on Streitwieser's[12] scale

(11) V. Boekelheide and C. E. Larrabee, *J. Amer. Chem. Soc.*, 72, 1245 (1950).

(12) A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *ibid.*, 89, 63 (1967).

(13) Analogous retardation of opening of cis 3,4-disubstituted cyclobutenes is well documented.[14]

(14) (a) J. I. Brauman and W. C. Archie, Jr., *J. Amer. Chem. Soc.*, 94, 4262 (1972); (b) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, 7, 559 (1968), and references in each.

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Received July 9, 1973

Oppositol, a Brominated Sesquiterpene Alcohol of a New Skeletal Class from the Red Alga, *Laurencia subopposita*

Sir:

Marine algae of the genus *Laurencia* (family Rhodomelaceae) have produced fascinating brominated secondary metabolites of three general structural types: sesquiterpene aromatics[1] typified by laurinterol (**1**),

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(1) (a) T. Irie, M. Suzuki, E. Kurosawa, and T. Masamune, *Tetrahedron*, 26, 3271 (1970); (b) T. Irie, M. Suzuki, and Y. Hayakawa, *Bull. Chem. Soc. Jap.*, 42, 843 (1969); (c) T. Irie, M. Suzuki, Y. Yasanari, E. Kurosawa, and T. Masamune, *Tetrahedron*, 25, 459 (1969).

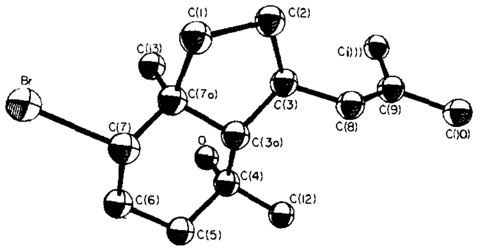
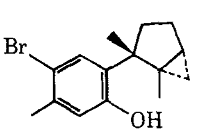
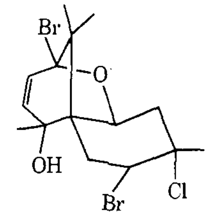


Figure 1. A perspective drawing of the X-ray model of oppositol.

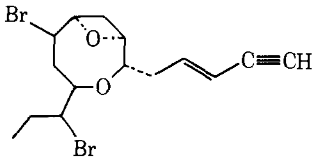
spiro-fused sesquiterpenes[2] exemplified by pacifenol (2), and nonterpene C_{15} compounds[3] of which laureatin (3) is a good example. We wish to report the isolation,



1



2



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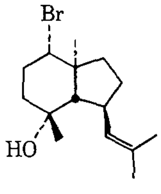
from the epiphytic red alga *Laurencia subopposita* Setchell, of a brominated sesquiterpene alcohol, which possesses moderate antibiotic activity *vs. Staphylococcus aureus.* This unusual *Laurencia* metabolite represents a new sesquiterpene skeletal class.

Repeated chromatography of the hexane extract of the air-dried seaweed[4] resulted in the isolation of a new sesquiterpene alcohol, oppositol (4) (0.1% dry weight of alga), $[\alpha]^{25}\text{D}$ −232° (*c* 0.19, EtOH), as a colorless oil which slowly crystallized, mp 54–55°. A composition of $C_{15}H_{25}OBr$ was suggested by the mass spectrum of **4** (M^+ *m/e* 300–302) and confirmed by elemental analysis. A sharp band at 3623 cm^{-1} (CCl_4) in the infrared spectrum and no reaction when subjected to acetylation (Ac_2O–pyridine, 25°) or Jones oxidation conditions suggested a hindered tertiary alcohol. The nmr spectrum[5] indicated the presence of two tertiary methyl groups and two overlapping vinyl methyl groups,[6] a vinyl proton (δ 5.02) which was shown to be part of the above dimethyl vinyl system by decoupling, and a quartet pattern (δ 3.83) typical of an axial proton on a carbon bearing a bromine atom in a cyclohexane ring.

Catalytic hydrogenation (PtO_2–EtOH) yielded dihydrooppositol, $C_{15}H_{27}OBr$, whose nmr spectrum indicated the reduction of the vinyl moiety and formation of an isopropyl group. Ozonolysis of oppositol (**4**) gave an acid $C_{12}H_{19}O_3Br$ (mp 153–154°) and a secondary aldehyde, $C_{12}H_{19}O_2Br$. Subjecting oppositol (**4**) to a refluxing solution of *p*-toluenesulfonic acid in benzene resulted in an 85% yield of 1,4-dimethyl-7-isobutylindan (**5**).[7]



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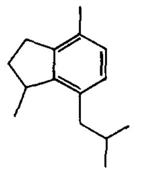

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Since the interpretation of the data could not be accommodated by any known sesquiterpene skeleton nor was it consistent with the skeleton of the aromatization product **5**, oppositol (**4**) was subjected to single-crystal X-ray diffraction analysis which led to the total structure and absolute stereochemistry.

Oppositol (**4**) crystallizes with two molecules per asymmetric unit in the triclinic space group P_1 with a = 9.64 (2), b = 7.83 (2), and c = 11.15 (3) Å, and α = 107.2 (2), β = 72.6 (2), and γ = 97.4 (1)°. All intensity data in a 2θ sphere of 100° were collected on a fully automated diffractometer using Ni-filtered Cu $K\alpha$ radiation (1.5418 Å). A decline in standard intensities of 30% and a darkening of the crystal accompanied data collection. After scaling for decomposition, Lorentz, polarization, and background corrections of 1652 reflections had $I > 3\sigma(I)$ and were judged observed. The bromine atoms were easily located in the Patterson synthesis.[8] The subsequent electron density syntheses, which were complicated by the false inversion center, were finally interpreted to yield the nonhydrogen atom skeleton of both molecules. Twenty-four fixed hydrogen atoms were located in the difference electron density synthesis. Full-matrix, least-squares refinements with anomalous scattering factor corrections for the bromine smoothly converged to a conventional discrepancy index of 0.073 (wR = 0.088) for the configuration shown and 0.075 (wR = 0.091) for its enantiomorph.[9] Figure 1 is a perspective drawing of the X-ray model.[10]

Both molecules in the asymmetric unit have the

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(2) (a) J. J. Sims, W. Fenical, R. M. Wing, and P. Radlick, *J. Amer. Chem. Soc.*, **93**, 3774 (1971); (b) J. J. Sims, W. Fenical, R. M. Wing, and P. Radlick, *Tetrahedron Lett.*, 195 (1972); (c) M. Suzuki, E. Kurosawa, and T. Irie, *Tetrahedron Lett.*, 4995 (1970); (d) J. J. Sims, W. Fenical, R. M. Wing, and P. Radlick, *J. Amer. Chem. Soc.*, **95**, 972 (1973).

(3) (a) T. Irie, M. Suzuki, and T. Masamune, *Tetrahedron*, **24**, 4193 (1968); (b) T. Irie, M. Izawa, and E. Kurosawa, *Tetrahedron*, **26**, 851 (1970); (c) A. Fukuzawa, E. Kurosawa, and T. Irie, *Tetrahedron Lett.*, 3 (1972); (d) E. Kurosawa, A. Fukuzawa, and T. Irie, *Tetrahedron Lett.*, 2121 (1972).

(4) Collected intertidally in eelgrass at La Jolla, Calif., in January.

(5) Nmr (220 MHz, CCl_4) δ 5.02 (d, 1 H, J = 9.5 Hz), 3.83 (d of d, 1 H, J = 12, 4 Hz), 2.99 (m, 1 H), 2.28 (m, 1 H), 1.62 (s, 6 H), 1.15 (s, 3 H), and 1.05 ppm (s, 3 H). The nmr spectrum will appear with the supplementary material in the microfilm edition—see paragraph at end of paper.

(6) Resolved into two signals by the incremental addition of $Eu(fod)_3$ or acetylation using severe conditions (Ac_2O–pyridine, 90°, 82 hr) to obtain the monoacetate, mp 38–40°.

(7) Nmr (220 MHz, CCl_4) δ 6.75 (d, 1 H, J = 7 Hz), 6.74 (d, 1 H, J = 7 Hz), 3.28 (m, 1 H), 2.75 (m, 2 H), 2.40 (m, 2 H), 2.17 (s, 3 H), 1.12 (d, 3 H, J = 7 Hz), and 0.90 ppm (d, 6 H, J = 7 Hz); mass spectrum *m/e* (rel intensity) 202 (17, M^+), 187 (13), 159 (100), 145 (18), 129 (15).

(8) The following library of crystallographic programs was used: C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorith and the Programs ALFF, ALFFDP, ALFFT and FRIEDEL," U. S. Atomic Energy Commission Report IS-2625, Iowa State University-Institute for Atomic Research, Ames, Iowa, 1971; W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least Squares Program," U. S. Atomic Energy Commission Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965; C. Johnson, "ORTEP, A Fortran Crystallographic Function and Error Program," U. S. Atomic Energy Commission Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(9) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(10) See paragraph at end of paper regarding supplementary material.

same configuration and identical bond lengths and angles within experimental error (0.02 Å and 0.3°). There is a double bond between C-8 and C-9. Me-13 and the hydrogen attached to C-3a are trans disposed while the Br and OH are cis to each other. All bond distances and angles agree with generally accepted values within experimental error.[11] The only short intermolecular contact is a hydrogen bond between the hydroxyls of the two independent molecules in the asymmetric unit of 2.92 (2) Å.

In addition to this unique metabolite, we have found that *L. subopposita* also contains new compounds similar to some of those previously isolated from other *Laurencia* species.

Acknowledgment. We wish to thank Dr. William Fenical for valuable discussions. This research was supported by a grant from the National Oceanic and Atmospheric Administration office of Sea Grant, Department of Commerce, and gifts from Abbott Laboratories and Hoffmann-La Roche, Inc.

Supplementary Material Available. A listing of fractional coordinates and the nmr and mass spectra of oppositol will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-7187.

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(11) O. Kennard and D. G. Watson, "Molecular Structures and Dimensions," Crystallographic Data Centre, Cambridge, England, 1970.

(12) National Institutes of Health Special Fellow, 1972–1973, and Rutgers University Faculty Academic Study Program Participant. Address correspondence to: Department of Chemistry, Rutgers University, Newark, N. J. 07102.

(13) Camille and Henry Dreyfus Teacher–Scholar Grant Awardee, 1972–1977, and Fellow of the Alfred P. Sloan Foundation, 1973–1975.

*Book Reviews**

Atlas of Spectral Data and Physical Constants for Organic Compounds. Edited by J. G. Graselli (The Standard Oil Co., Ohio). CRC Press, Cleveland, Ohio. 1973. 1695 pp. $125.00.

This is an impressive work. Some two-thirds of it is an enormous table, in which about 8000 compounds are listed in alphabetical order, with melting and boiling points, density, specific rotation, solubility, infrared, ultraviolet, and nmr absorption, and mass spectrographic peaks. The spectrographic data, which are given in numerical form out of practical necessity, have been compiled from a number of major collections and form as a result a more comprehensive set than has been available heretofore, even though there are extensive gaps. Anyone who has had to face the task of tracing down a specific spectrum from the scattered published (and unpublished) sources will greatly appreciate this feature, which is the principal (and sufficient) justification for this Atlas.

The considerable problem of access to a specific datum in such a large collection has been met by providing a multifaceted set of keys. In recognition of difficulties of nomenclature, an extensive exposition of the naming system used precedes the table, which uses IUPAC and *Chemical Abstracts* names, usually inverted. There is also a comprehensive name/synonym directory, and a section showing structural formulas alphanumerically keyed to the table entries.

Nearly one-third of the atlas consists of a versatile set of indexes: Formula Index (general), Formula (hydrates), Formula (halide salts), Formula (other salts), Molecular Weight, Melting Point, Boiling Point, Infrared Band, Ultraviolet Band, NMR Shift, Mass Spectrum Molecular Weight, and Chemical Structure and Substructure Index. This last makes use of the Wiswesser Line Notation, as has been described in our review of the *Chemical Substructure Index* (Institute for Scientific Information). The great value of this index is that, by use of the permuted index technique, it allows one to locate compounds having specified structural features, independently of general size and structure. Since this index (and all the others) is keyed by alphanumeric serial number to specific entries in the table, one can retrieve spectral data for compounds of closely related structure, even if the specific compound one has in hand is not listed.

It is hardly necessary to point out that a compilation of this nature would not have been feasible without the aid of computers, which have been used not only to collate the extensive indexes, but also to convert spectral data to consistent units. The table unfortunately reports infrared absorptions either in microns or in reciprocal centimeters, according to the source, but in the infrared band index all data have been converted to wavelength (a pity the choice was not made to use wave numbers instead). The Atlas thus becomes a surrogate for a computer bank of the same information. It will take no little effort to use the Atlas for certain types of retrieval that would be almost trivial with a computer, but the cost of this resource is but a small fraction of the cost of a computer bank, and that of its operation and maintenance is nearly zero.

Lastly, a 105-page section at the beginning of the Atlas, entitled Spectroscopic Aids, is full of useful practical information, from definitions of terms to correlation tables and lists of characteristic frequencies. A short discourse on "Tracking Down Spurious Bands in Infrared Analysis," by P. J. Launer (reprinted from Perkin-Elmer "Instrument News") is a handy and useful feature, as are the many tabulations of nmr constants, reprinted from scattered sources.

This is an expensive book, but nevertheless good value for the money. One can foresee heavy use for library copies; its popularity will attest to its practical value. It is, indeed, many books in one.

Heterocyclic Chemistry. By J. A. Joule and G. F. Smith (University of Manchester). Van Nostrand-Reinhold, London and New York. 1972. ix + 362 pp. £6.25 (cloth); £2.75 (paper).

The last decade has seen a number of brave attempts to condense the vast and expanding bulk of heterocyclic chemistry between the covers of one volume. Some have taken the path of generalization, setting out general principles embracing a variety of different rings, whereas others have restricted their scope to a select number of ring systems, in order to give more detail. The present work is organized in the latter way, yet is suffused with a substantial amount of generalization and a constant plugging at principles; the result is a happy one.

This is a textbook and not a reference book; it is written in the main for graduate students but could also serve well for others wishing to become familiar with or to brush up on the subject. The authors lay heavy emphasis on the aromatic five- and six-membered

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* Unsigned book reviews are by the Book Review Editor.