pulsions exist in **3**, they would be removed through formation of **4**.[11]

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[11] The hypothesis that an electronic substituent effect is the controlling factor in stabilizing the localization occurring in the observed pathway is not attractive. If one can transfer evidence from esr data for the electron distribution in the first excited state, it is clear that β positions in naphthalenes and in benzocyclobutenes have very little spin density to be stabilized or destabilized by substituents such as *tert*-butyl; see R. D. Rieke, S. E. Bales, P. M. Hudnall, and C. F. Meares, *J. Amer. Chem. Soc.*, **93**, 697 (1971), for benzocyclobutene esr data and I. Goldberg and B. M. Peake, manuscript to be published for *tert*-butylnaphthalene esr data.

[12] Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for Grant 5150-D4 in support of R. W. F. We also acknowledge the National Cancer Institute for Grant 11,421-07 for support of W. L. M. We are grateful to Professor N. O. Smith for detailed discussions on the error analysis of our kinetic data. A part of this research has been presented by J. E. Anderson, R. W. Franck, and W. L. Mandella, 3rd Northeast Regional Meeting of the American Chemical Society, Abstracts, p 182.

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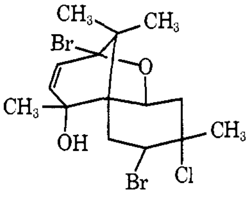
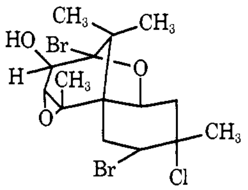
Marine Natural Products. IV. Prepacifenol, a Halogenated Epoxy Sesquiterpene and Precursor to Pacifenol from the Red Alga, *Laurencia filiformis*[1]

Sir:

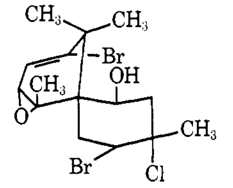
Recently we described the isolation of pacifenol (**1**)[2] and johnstonol[1] (**2**) from *L. pacifica* and *L. johnstonii*, respectively. Marine algae of the genus *Laurencia* were first noted for producing terpenoids containing bromine.[3,4] In addition, the isolation of **1** and **2**, which contain both bromine and chlorine as well as an unusual tricyclic ring structure, makes this genus an important one for the study of marine natural products.



1



2



3

In the course of further work on this interesting group of algae, we have isolated the probable precursor of pacifenol, prepacifenol (**3**). Accordingly, hexane extraction of *L. filiformis* followed by evaporation of the hexane and recrystallization of the partly crystalline residue from hexane gave prepacifenol (**3**) (yield, 0.3% dry plant): $C_{15}H_{21}O_2Br_2Cl$; *m/e* $M^+ = 430, 428, 426$; high resolution $M^+ - H_2O$ *m/e* = 409.9477 (calcd for $C_{15}H_{19}O^{79}Br^{81}Br^{35}Cl$, 409.9472). The nmr spectrum (100 MHz, $CDCl_3$) of **3** indicated at δ 1.88 (s), 1.63 (s), 1.42 (s), and 1.24 (s) four methyl groups, at 2.4 (m) four methylene protons, at 3.02 (d, $J = 3$ Hz) one α-epoxy proton, at 4.72 (four lines, X of ABX) one proton α to bromine, at 4.41 (four lines) one proton α to hydroxyl, and at 6.25 (d, $J = 3$ Hz) one vinyl proton. That prepacifenol was an alcohol was indicated by infrared absorption at 3.5 μ coupled with the disappearance of a one-proton nmr signal (d, $J = 5$ Hz) at δ 1.50 after a D_2O exchange experiment. On analysis of these data for prepacifenol, in particular comparison of its nmr spectrum with the nmr spectra of **1** and **2**, structure **3** was proposed for prepacifenol. Confirmation of this structure was provided in convincing fashion by the conversion of **3** to **1** in almost quantitative yield upon treatment with *p*-toluenesulfonic acid in benzene. The pacifenol so produced was identical with that previously isolated from *L. pacifica*. The conversion of **3** to **1** also occurred on heating **3** to its melting point. Depending upon the rate of heating, **3** melts from 109 to 126°, solidifies, and remelts at 147°. Thin layer chromatography of the residue shows complete conversion to **1**. The cyclization also occurs in high yield under conditions of chromatography upon neutral alumina.

Our original isolation procedure for **1** from *L. pacifica* involved the use of silica gel chromatography and therefore it was possible that pacifenol was an artifact.[2] Indeed, chromatography of prepacifenol on silica gel resulted in quantitative conversion of pacifenol. We conducted a new extraction of *L. pacifica* using the procedure described above which led to the exclusive isolation of prepacifenol. The new extraction gave only prepacifenol and no pacifenol. Thus, our report that pacifenol is present as a natural product in *L. pacifica* is incorrect. However, pacifenol does exist as a natural product in *L. tasmanica*. Extraction of this alga using the new procedure led to pacifenol (0.25% of dry plant) as the major compound.

Acknowledgment. One of us (J. J. S.) wishes to express his gratitude to the Australian National University for a Research Fellowship (1971–1972) and to Professor A. J. Birch, Research School of Chemistry, Australian National University, for the hospitality of his laboratory where this work was carried out. We are grateful to Dr. H. B. S. Womersley, University of Adelaide, for identification of the algae.

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[1] For paper III of this series see: J. J. Sims, W. Fenical, R. M. Wing, and P. Radlick, *Tetrahedron Lett.*, 195 (1972).

[2] J. J. Sims, W. Fenical, R. M. Wing, and P. Radlick, *J. Amer. Chem. Soc.*, **93**, 3774 (1971).

[3] T. Irie, M. Suzuki, E. Kurosawa, and T. Masamune, *Tetrahedron*, **26**, 3271 (1970); M. Suzuki, E. Kurosawa, and T. Irie, *Tetrahedron Lett.*, 4995 (1970), and previous papers cited within.

[4] S. Itô, K. Eudo, T. Yoshida, and M. Kodama, *Chem. Commun.*, 186 (1967).

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Short-Lived Intermediates. IV. Adamantene[1]

Sir:

The recent syntheses of bicyclo[3.3.2]non-1-ene[2] have generated considerable interest in the synthesis and

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[1] Part III: J. E. Gano, *Chem. Commun.*, 1491 (1971).

[2] (a) J. R. Wiseman, *J. Amer. Chem. Soc.*, **89**, 5966 (1967); (b) J. A. Marshall and H. Faubl, *ibid.*, **89**, 5965 (1967).