ferent predictions for II, they are in essential agreement with respect to the barrier to ring closure for I.

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(17) P. Dowd and K. Sachdev, *J. Am. Chem. Soc.*, **89**, 715 (1967).

(18) K. Takeda, H. Yoshida, K. Hayashi, and S. Okamura, *Bull. Inst. Chem. Res., Kyoto Univ.*, **45**, 55 (1967); T. Yamaguchi, M. Irie, and H. Yoshida, *Chem. Lett.*, 975 (1973); H. Yoshida and O. Edlund, *Chem. Phys. Lett.*, **42**, 107 (1976).

(19) There is one apparent exception[6d] in which a MINDO/2 procedure has been used to suggest that the splitting between the (0,0,0) triplet and the (0,0,90) singlet of I is 11 kcal/mol, a value which is smaller than that calculated using other methods.[6] However, the (MINDO/2) calculations[6d] place the heat of formation of the ground-state triplet of I at 50 kcal/mol, only 2 kcal/mol higher than that of methylenecyclopropane.[16] Other conclusions of the MINDO/2 calculations have also been questioned.[6a,b]

(20) (a) This barrier may not be >7 kcal/mol. As an example, the prediction[6c] of a 9-kcal/mol barrier for the conversion of the singlet of I to methylene-cyclopropane would place the singlet state below the triplet state, contrary to recent findings with regard to the multiplicity of the ground state of the molecule of I. (b) The existence of an activation barrier for the conversion of singlet of I to the triplet state of I would make the 82-kcal/mol estimate ΔH_f be too low; an activation barrier for the conversion of singlet of I to methylenecyclopropane would cause the estimated ΔH_f to be too high. Since the two possible barriers tend to cancel one another, the 82-kcal/mol estimate may be not too far from the true value.

(21) Cf. R. Breslow, *Acc. Chem. Res.*, **6**, 393 (1973), and references cited therein; M. J. S. Dewar, *Adv. Chem. Phys.*, **8**, 65 (1965); M. L. Herr, *Tetrahedron*, **32**, 2835 (1976).

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Neoconcinndiol Hydroperoxide, a Novel Marine Diterpenoid from the Red Alga *Laurencia*

Sir:

The rarity of the hydroperoxide functionality in nature[1] prompts us to report here the structure of a unique diterpene hydroperoxide **1** which was isolated from extracts of the red seaweed *Laurencia snyderiae* (Dawson).[2] The structural similarity of **1** to the known diterpene concinndiol,[3] also isolated from *L. snyderiae*, prompts us to suggest the trivial name neoconcinndiol hydroperoxide for this metabolite.

Conventional silica gel column chromatography of the CHCl₃–MeOH (1:1) extract of the fresh algae furnished

1   **2**
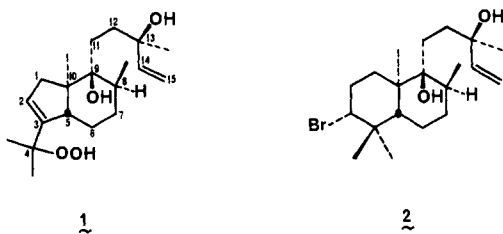
fractions, one of which (100% diethyl ether eluent) deposited crystals of **1**, $[\alpha]^{22}_D$ −35° (*c* 0.8, CH₃OH), mp 158–159 °C (0.07% extract). Inspection of the earlier fractions resulted in the isolation of major amounts of **2**, mp 122–123 °C, as determined by comparisons with standard samples from *L. concinna*.[4] High resolution mass spectrometry of **1** gave major ions at *m/e* 320.2353 for C₂₀H₃₂O₃ and *m/e* 304.2404 for C₂₀H₃₂O₂, which reflect fragmentations of M⁺ − H₂O and M⁺ − H₂O, −O, respectively, from the true molecular composition of C₂₀H₃₄O₄. The facile loss of water under mass spectral conditions is in complete analogy to the behavior noted earlier for **2**.[3] Initially, it appeared that **1** was an aldehyde, since a sharp one-proton singlet band was observed in the proton NMR spectrum (220 MHz, Me₂CO-*d₆*) at δ 9.80. The infrared spectrum of this polar compound (KBr), however, was devoid of substantial carbonyl absorption and showed, instead, intense hydroxyl absorptions. NMR D₂O addition experiments
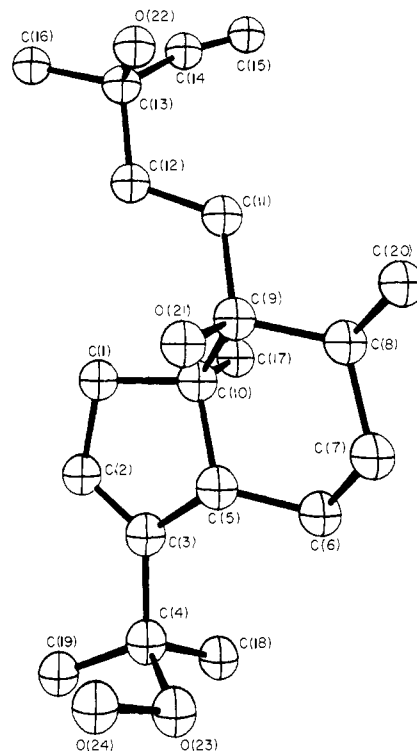
Figure 1. A computer generated perspective drawing of neoconcinndiol hydroperoxide. Hydrogens are omitted for clarity and only one orientation of the threefold disordered vinyl group (C(14) and C(15)) is shown.

showed that the sharp band at δ 9.80 and two others at δ 2.90 and 3.61 were exchangeable hydroxyl protons. The incongruity of these chemical shifts, coupled with the loss of an oxygen atom under mass spectral conditions, suggested that the δ 9.80 exchangeable band was from a hydroperoxide group.[5] Supporting this contention, **1** gave a positive iodide–iodine test for peroxides but generated complex mixtures upon attempted NaBH₄ reduction to the corresponding alcohol.

The NMR spectrum of **1** contains a number of features which can now be assigned to structural facets of **1**. However, initially, only the relatedness to **2** could be concluded. Structural features associated with the six-carbon side chain were observed at shifts analogous to those from **2**. Specifically, the isolated vinyl group gave bands at δ 4.94 (dd, *J* = 10, 2 Hz) and δ 5.19 (dd, *J* = 15, 2 Hz) for the terminal protons (C(15)) and a band at δ 5.89)dd, *J* = 10, 15 Hz) for the C(14) olefin. Remaining in the olefin region was a single band at δ 5.43 (m), assigned to the C-2 proton, which was coupled to a set of AB double doublets (C(1) protons) at δ 3.11 and 2.61 (each *J* = 14, 4 Hz). At high field, a six-proton singlet was observed at δ 1.29 assigned to the *gem*-dimethyl at C(4), a three-proton singlet at δ 1.22 assigned to the methyl at C(13), and, finally, a three-proton doublet at δ 0.89 (*J* = 7 Hz) assigned to the secondary methyl at C(8).

The final structure assignment for neoconcinndiol hydroperoxide was provided by a combination of the aforementioned spectral studies with a single-crystal x-ray diffraction experiment. Preliminary x-ray photographs revealed that **1** crystallized from acetone in the monoclinic crystal class. Systematic absences conformed to space group *P*2₁ with accurate lattice constants of *a* = 6.797 (2) Å, *b* = 13.550 (4) Å, *c* = 10.677 (3) Å, *β* = 96.81 (3)°, and *Z* = 2. All unique reflections with *θ* ≤ 114.1° were measured using graphite monochromated Cu Kα (1.541 78 Å) x rays and after Lorentz, polarization, and background corrections, 1143 (82%), were judged observed ($F_o \geq 3\sigma (F_o)$).

The structure solution proceeded with great difficulty. The largest 100 *E*'s were initially phased by hand and their values

Scheme I
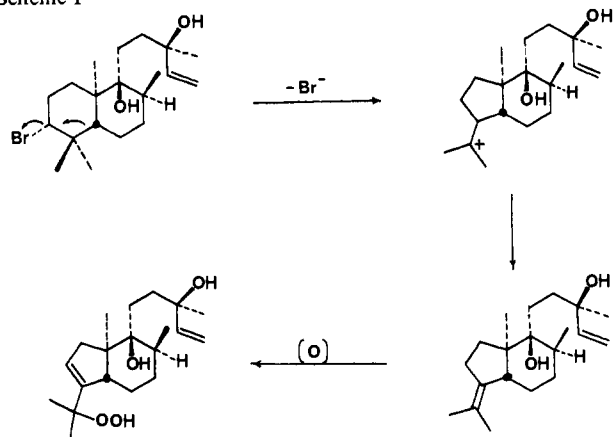
refined in the tangent formula. Phases were extended to the largest 200 E's, and a subsequent electron density synthesis revealed a plausible 23-atom fragment. Full-matrix, least-squares refinements with all atoms identified as carbons converged to a standard crystallographic residual of 12%.[6] Inspection of thermal parameters and bond distances indicated that four of the atoms should be identified as oxygens. In Figure 1, these are O(21), O(22), O(23), and O(24). It was also obvious that one of the carbon atoms was very poorly behaved, with a thermal parameter roughly twice as large as any of the other carbons and a carbon–carbon bond distance of 1.70 Å! This atom is roughly midway between the atoms labeled C(14) and C(15) in Figure 1. Since the ^{1}H NMR spectrum clearly showed a $-CH=CH_2$ group which was not present in our x-ray model, we replaced the poorly behaved atom with a disordered vinyl group. The current residual for this model is 4.9% for the observed reflections. Figure 1 presents an x-ray drawing of this model showing only one of the threefold disordered vinyl group orientations. In general, bond distances and bond angles agree well with generally accepted values. The hydroperoxide geometry is C(4)–O(23) = 1.438 (7) Å, O(23)–O(24) = 1.461 (6) Å, and $\angle$C(4)–O(23)–O(24) = 108.1 (4)°. The five- and six-membered rings are trans fused, and the relative stereochemistry at C(5), C(8), C(9), C(10), and C(13) is identical with that reported for 2.[3] Additional crystallographic details can be found in the supplemental material.

We suggest that 1 and 2 are biogenetically related via solvolysis of the C(3) equatorial bromine in 2, as depicted in Scheme I. These transformations are precedented in the solvolytic A-ring contraction reactions of 3β-tosyltriterpenes[7] and in the reactivity of ground state (enzymatic) or singlet O_2 with tetrasubstituted olefins to yield rearranged allylic hydroperoxides.

Supplementary Material Available: Fractional coordinates (Table 1), bond distances (Table 2), bond angles (Table 3), and observed and calculated structure factors (Table 4) (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) We are unaware of reports of terpenes with the hydroperoxide functionality; however, a steroidal hydroperoxide, 3α,22α-dihydroxy-7α-hydroperoxy-Δ⁵-stigmastene is a natural product; see F. G. Fisher and H. Mägerlein, *Justus*

Liebigs Ann. Chem., **636**, 88 (1960). Also, it seems secure that hydroperoxides are important intermediates in prostaglandin synthesis; see (inter alia) M. Hamberg, J. Svenson, T. Wakabayashi, and B. Samuelson, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 345 (1974).
(2) The nomenclature for this species of red seaweed has been recently revised from *L. snyderae* to *L. snyderiae;* see I. A. Abbott and G. J. Hollenberg, "Marine Algae of California", Stanford University Press, Stanford, Calif., 1976.
(3) J. J. Sims, G. H. Y. Lin, R. M. Wing, and W. Fenical, *J. Chem. Soc., Chem. Commun.*, 470 (1973).
(4) Two different collections of *L. snyderiae*, one from La Jolla and one from Santa Catalina Island, were compared. La Jolla populations contained concinndiol (2) as well as β-snyderol (3), the structure of which was reported in an earlier communication (B. M. Howard and W. Fenical, *Tetrahedron Lett.*, 41 (1976)). Santa Catalina Island populations also contained 2 and 3, but they contained, in addition, the hydroperoxide 1 and an aromatized snyderol derivative, 4, reported earlier as a component of *L. nidifica* (H. H. Sun, S. W. Waraszkiewicz, and K. L. Erickson, *Tetrahedron Lett.*, 585 (1976)). It thus appears that solvolysis of C(3) equatorial bromine in concinndiol results in bridgehead bond migration, while the analogous solvolytic rearrangement in the sesquiterpene 3 results in methyl migration.

3

4
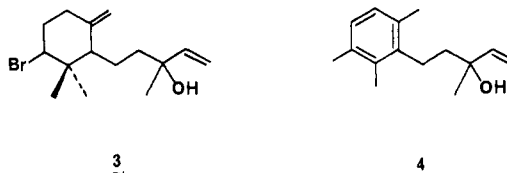
(5) Hydroperoxide protons are recognized in their nmr spectra to appear at low field. A recent example of a hydroperoxide proton at ca. 9 ppm was given in W. A. Porter, M. O. Funk, D. Gilmore, R. Isaac, and J. Nixon, *Jl Am. Chem. Soc.*, **98**, 6000 (1976).
(6) The following library of crystallographic programs was used: C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFT and FRIEDEL", USAEC 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", USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965; C. Johnson, "ORTEP, A FORTRAN Thermal-Ellipsoid Plot Program", U.S. Atomic Energy Commission Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(7) L. Ruzicka, M. Montavon, and O. Jeger, *Helv. Chim. Acta*, **31**, 818 (1948).
(8) Camille and Henry Dreyfus Foundation Teacher–Scholar Grant awardee 1972–1977.

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Nitrosoalkanes as New Ligands of Iron(II) Porphyrins and Hemoproteins

Sir:

Nitrosoalkanes or nitrosoarenes are interesting ligands because of their nitroso group which is isoelectronic with dioxygen, of their different possible modes of binding (at N or O atom, side-on or end-on), and of their low-lying π^* system[1] which should be readily available for back-bonding. However, few transition metal complexes having such ligands have been reported. Most of these are nitrosoarene complexes[2-10] and only two nitrosoalkane complexes, $CoCp(C_7H_{10}N_2O_2)$[11] and $[Ru(NH_3)_5[(NO)CH_2C(CH_3)_2OH]]^{2+}$,[12] have been isolated. In addition, very recently, the reaction of aliphatic hydroxylamines with $[Fe(CN)_5(H_2O)]^{3-}$ has been reported to give complexes identified as $[Fe(CN)_5(RNO)]^{3-}$ from their spectral characteristics, by analogy with those of the $[Fe(CN)_5(ArNO)]^{3-}$ Baudisch complexes.[13]

However, nitrosoarenes bind to hemoglobin,[14] and we recently proposed that nitrosoalkanes are the exogenous ligands of the very stable "425-, 421-, and 455-nm absorbing com-