

CHONDRIOL, A HALOGENATED ACETYLENE FROM THE
MARINE ALGA CHONDRIA OPPOSITICLADA¹

William Fenical* and James J. Sims

Department of Plant Pathology, University of California
Riverside, California 92502

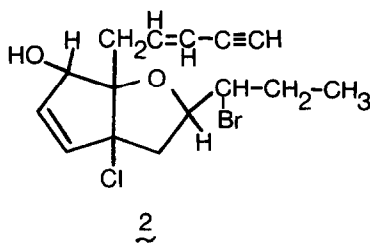
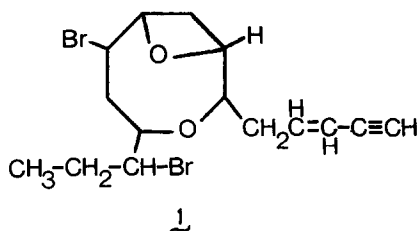
and

Phillip Radlick

Department of Chemistry, University of California
Riverside, California 92502

(Received in USA 13 November 1972; received in UK for publication 2 January 1973)

Studies of members of the red algal genus Laurencia, family Rhodomelaceae, have led to the isolation of halogen containing compounds of two different kinds, sesquiterpenes² and non-terpene,³ C₁₅ compounds 1. The non-terpene compounds appear to be derived from a common C₁₅ precursor,⁴ which is in all probability derived from a C₁₆ fatty acid. From a member of the same family, Chondria oppositoclada, we have isolated a new C₁₅ compound similar to the compounds of Laurencia but strikingly different. Chondriol, 2, was isolated by silica gel chromatography of a hexane extract as a colorless oil (0.1% dry weight). The

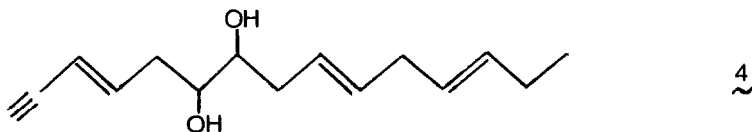
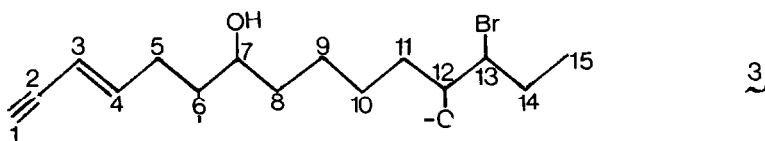


alcohol, C₁₅H₁₈O₂BrCl, (M⁺_{344,346,348} m/e), showed uv absorption at λ_{Max}^{MeOH} 221 nm (ε9800) characteristic of the enyne function. The presence of alcohol and acetylene groups was indicated by ir absorption, ν_{Max}^{film} 3400 (OH), 3290 (C≡CH)

cm^{-1} . Acetylation ($\text{Ac}_2\text{O}/\text{py}$) give a monoacetate from which chondriol could be regenerated by saponification: $\text{C}_{17}\text{H}_{20}\text{O}_3\text{BrCl}$, mp $53-54.5^\circ$, $[\alpha]_{\text{D}} + 54.9^\circ$ (MeOH), M^+ , CALCD for $\text{C}_{17}\text{H}_{20}\text{O}_3$ ^{79}Br ^{35}Cl , 386.0291; found, 386.0284.

Chondriol differs in two significant respects from previously isolated compounds.²⁻⁴ It contains both Br and Cl and a carbon-carbon bond forming a five membered ring. All previous compounds contain only bromine and are cyclic ethers. The five membered ring of chondriol bears a strong resemblance to that of the prostaglandins in functionality and stereochemistry.

The structure of chondriol is assigned on spectral data, mainly nmr spectra (Figure 1) of the alcohol and its acetate. Extensive use of decoupling along with comparison with the published spectra of laurencin^{2,5} and laureatin³ leads to the structure 2. The bromopropyl side chain and the enyne side chain give rise to nmr signals identical to the same groups in laurencin and laureatin. Proton E is the α proton of a secondary alcohol based upon its downfield shift of 1.0 ppm on acetylation. It is coupled only to two other protons F and G as shown by irradiating F and G causing E to collapse to a singlet. This defines a three carbon allylic alcohol constellation. Separation of F and G to a first order ABX pattern is observed at 220 MHz . The point of attachment of the bromopropyl side chain is seen by the coupling between I and J; I is also split by the two remaining protons H. Thus a five carbon chain containing the bromine is delimited. One more fact could be gleaned from the nmr; the chemical shift



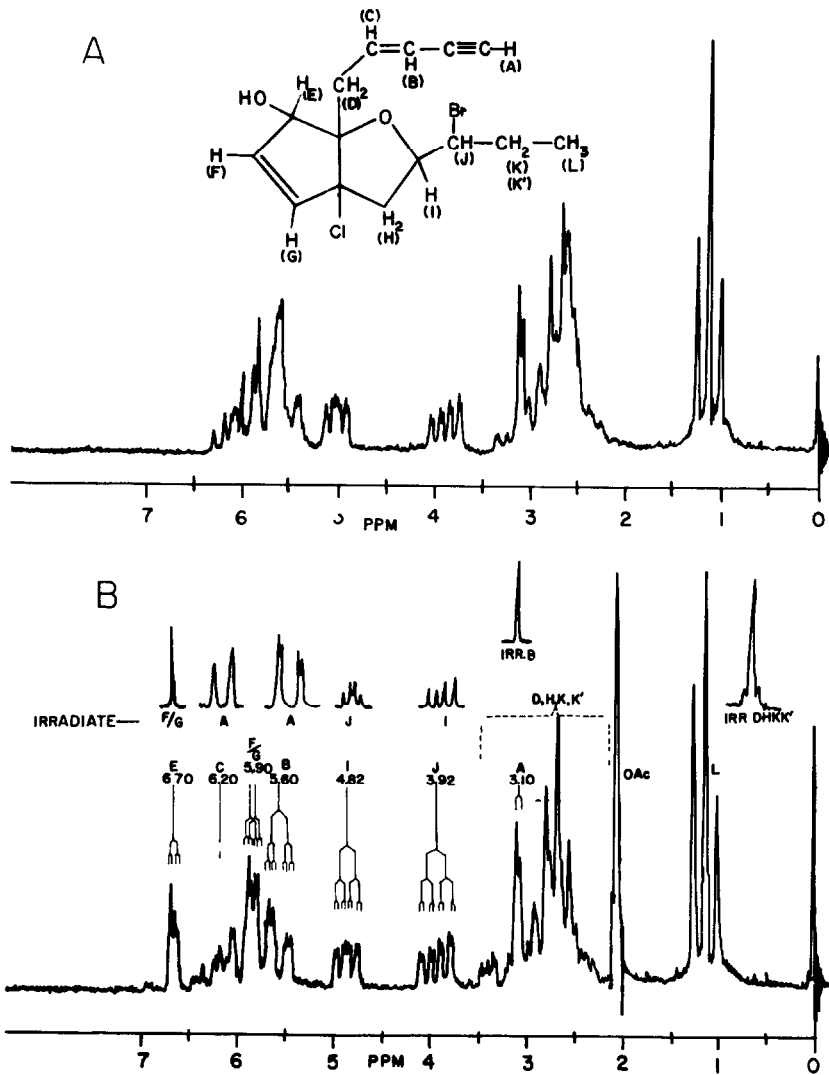


FIG 1 60 MHz NMR Spectra of Chondriol(A) and Chondriol Acetate(B) With Spin Decoupling Data

of I is the same as the protons attached to ethers in laurencin and laureatin. From the empirical formula only three atoms are left unaccounted for, two carbon atoms and a chlorine. The preceding three partial structures must be connected by two quaternary carbon atoms. The most rational way of doing this is part structure 3. This structure makes sense of all the decoupling data and agrees well with 4, the compound proposed by Irie as a common precursor to laurefucin, laurencin, laureatin and isolaureatin.⁴ If one now joins C-6 in 3 to the oxygen at C-12, in accordance with the precursor 4, then joins C-6 and C-10 by a single bond and places a chlorine at the only remaining valence at C-10, the structure of chondriol 2 is generated.

While definitive evidence to indicate the relative stereochemistry of 2 was not obtained, analysis of molecular models dictates a preference for the cis ring fused isomer.

Acknowledgment

The authors wish to express thanks to Dr. Isabella A. Abbott, Hopkins Marine Station for the identification of this alga and to Miss Delilah Squatrito for obtaining the optical rotation data.

This work is a result of research sponsored by NOAA Office of Sea Grant, Department of Commerce, under Grant #USDC 2-35208 with the Institute of Marine Resources. The US Government is authorized to produce and distribute reprints for governmental purposes not withstanding any copyright that may appear hereon.

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