successive treatment with ethanethiol and DPPA, hydrogen chloride, and benzoyl chloride.

Although this investigation is still in its preliminary stages, the data in Table I suggest that the procedures herein described provide a one-step method for preparing thiol esters containing reactive functions under mild reaction conditions.

Supplementary Material Available. Ir and nmr data for all compounds as well as microanalytical data for new compounds 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, 24× 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 of $2.00 for microfiche, referring to code number JOC-74-3302.

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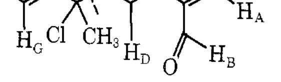
Cartilagineal. An Unusual Monoterpene Aldehyde from Marine Alga

Summary: A unique monoterpene aldehyde, $C_{10}H_{11}OCl_3$, has been isolated from the ether soluble extract of the red marine alga *Plocamium cartilagineum* (L.) Dixon and its structure has been determined from spectroscopic data.

Sir: Marine algae of divisions *Rhodophyta* and *Phaeophyta* have recently been found to elaborate antibiotics of a wide range of structural types.[1] The essential oils from certain brown alga have been shown to contain a number of C_{11} hydrocarbons some of which exhibit gamone activity.[2] Both red and brown algae have also been observed as possessing components with toxic activity,[3] while very little attention has been given to the isolation and identification of such compounds.

In connection with our interest in marine chemical products we have examined an abundant red alga, *Plocamium cartilagineum* (L.) Dixon (*Plocamium coccineum var. pacificum*),[4] native to the Pacific coast whose ether soluble components are toxic to goldfish. There are several unique monoterpenes in this fraction and we report below the characterization of an odoriferous polychlorinated aldehyde.

Hplc purification of the $CHCl_3$–CH_3OH (85:15) extract of the wet alga (2 Kg, dry weight) afforded an α,β-unsaturated aldehyde (0.01%) as a viscous liquid [ir 3070, 2950, 2860, 2740, 1690 cm^{-1}; uv λ_{max} 245 (ϵ 15,800, EtOH)] which could be distilled [Kugelrohr point, 130° (0.1 mm)] but decomposed upon prolonged standing in air. A molecular formula of $C_{10}H_{11}OCl_3$ was deduced from the mass spectra: M^+ 252, 254, 256, 258; $M^+ - Cl$ 217, 219, 221; $M^+ - Cl - HCl$ 181, 183; $M^+ - 3Cl$ 147. The base peak $M^+ - C_6H_5OCl_2$, 89, 91 was accompanied by a less intense fragment $M^+ - C_4H_6Cl$ 163, 165, 167. These data along with magnetic resonance experiments (Tables I and II) enabled us to deduce structure 1. In particular a 3-chloro-1-butenyl substituent was required by the mass spectral fragmentation and pmr assignments of a tertiary methyl group and a clean vinylic ABX pattern (J = 17.0, 10.5, and 1.0 Hz) at δ 5.26, 5.40, and 6.06. On the other hand a somewhat unusual architecture was indicated for the enal function. The aldehyde proton (H_B) appeared as a sharp doublet, J = 2.0



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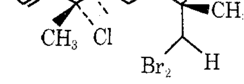

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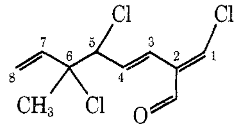
Table I
100-MHz Pmr Data for Cartilagineal (1)

Proton	δ, ppm[a]	Pattern[b]	J, Hz[c]	Spin decoupling
H_A	7.05	s		
H_B	9.04	d	2.0	irr at H_C, s
H_C	6.49	d of dd	15.3, 2.0, 1.0	irr at H_B, br d (J = 15.3) irr at H_E, sharp dd (J = 15.3, 2.0)
H_D	7.05	dd	15.3, 8.5	irr at H_C, d (J = 8.5) irr at H_E, d (J = 15.3)
H_E	4.47	br d	8.5	
H_F	6.06	dd	17.0, 10.5	
H_G	5.40	dd	17.0, 1.0	
H_H	5.26	dd	10.5, 1.0	
CH_3	1.71	s		

[a] Relative to internal TMS. [b] s, singlet; d, doublet; dd, doubled doublet; d of dd, doublet of doubled doublets. [c] J's are based on a first-order analysis and in some cases represent close, approximate values.

Table II
25.1-MHz Cmr Data for Cartilagineal (1)



Carbon	δ, ppm[a]	Multiple[b] pattern	J, Hz[c]
1	143.9	d	193
2	137.3	s	
3	122.5	d	158
4 or 7	134.0	d	170 or 168
5	69.5	d	155
6	71.5	s	
7 or 4	139.5	d	168 or 170
8	116.3	t	160
O=C	189.3	d	175
CH_3	24.6	q	128

[a] Relative to TMS. [b] H^1 coupled spectra obtained *via* the alternatively pulsed H^1 decoupling technique: O. Ganson and W. Shittenhelm, *J. Amer. Chem. Soc.*, **93**, 4294 (1971). [c] Error, ±1 Hz.

Hz,[5] derived by coupling to a vinylic proton H_C which was situated on an *E* disubstituted double bond (J_{CD} = 15.2 Hz). The other proton on this *E* double bond (H_D) was coupled to a proton on a saturated carbon (H_E, δ 4.47, J_{DE} = 8.5 Hz), and a long range coupling of ~1 Hz between H_E and H_C collapsed during spin decoupling at H_E.

These *J*'s and decoupling experiments (Table I) are suggestive of a rather rigid carbon framework containing the protons H_A, H_B, H_C, H_D, and H_E on carbons as sequenced in structure **1**, and in addition a planar transoid conformation between conjugated sets of trigonal C's provides a favorable "W" path for the long range $^4J_{BC}$ = 2 Hz.[6] The stereochemistry about the remaining double bond is suggested to be *E* by comparison of the observed chemical shift for H_A (δ 7.05) *vs.* that calculated from tables of substituent shielding constants[7] giving H_A (calculated): *Z* isomer, δ 7.44; *E* isomer, δ 7.03.

Marine algae, especially of the genus *Laurencia,* have been observed to be a rich lode of brominated sesquiterpenes,[8] even though the marine environment has ~10^2 times as much chloride *vs.* bromide.[9] Recently, however, a growing list of sesquiterpenes containing both Br and Cl within a spiro[5.5]undecane skeleton have been isolated from *Laurencia.*[1a,g,10–12] In this context cartilagineal (**1**) is quite unique because almost no halogenated monoterpenes have been reported from marine algal sources. In addition, this compound represents, to our knowledge, the first terpenoid from marine sources containing multiple halogens bonded to carbon all of which are chlorine.[13] Structurally, this aldehyde bears an intriguing resemblance to the tribromotrichloro monoterpene **2** isolated from the sea hare *Aplysia californica,*[14] and also observed to be a component of *p. coccineum* collected in Southern California.[15]

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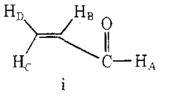

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(13) We have purified other polyhalogenated hydrocarbons from *P. cartilagineum* including one having a formula of $C_{10}H_{11}Cl_5$ (**3**). A preliminary characterization based upon its mass spectrum and magnetic resonance data (^1H and ^{13}C) suggests a structure identical with **1** but differing by the replacement of the oxo group by geminal chlorines. If this *structure is correct, then the biogenesis of* **1** *is undoubtedly via* **3.** This latter point will be discussed in a full account of our work.

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A Novel Method for the Oxidation of Primary and Secondary Alcohols to Carbonyl Compounds

Summary: a solution of sodium dichromate and sulfuric acid in dimethyl sulfoxide oxidizes primary alcohols to aldehydes and secondary alcohols to ketones; in these oxidations DMSO acts as a solvent and not as a reactant.

Sir: Recently, there has been a host of new methods reported for the oxidation of alcohols to aldehydes and ketones. The reagents employed are DMSO–*p*-toluenesulfonyl chloride and methanesulfonic anhydride,[1] DMSO–DCC,[2] DMSO–SO_3,[3] DMSO–acetic anhydride,[4] DMSO–P_2O_5,[5] DMSO–chloroformate,[6] boiling DMSO,[7] DMSO–chlorine,[8] ceric ammonium nitrate in acetic acid or acetonitrile,[9] *N*-chlorosuccinimide and dimethyl sulfide,[10] chromium trioxide in pyridine[11] and, earlier, chromium trioxide in acetone,[12] activated manganese dioxide,[13] and aqueous sodium dichromate.[14]

We report here a new method for the oxidation of alcohols to aldehydes or ketones in 80–90% yields. This method is economical, efficient, and simple to operate and consists of treating a solution of sodium dichromate dihydrate in DMSO[15] with an alcohol and concentrated sulfuric acid. To determine the role that DMSO plays in these oxidations, we found that oxidation of benzyl alcohol with $Na_2Cr_2O_7 \cdot 2H_2O$ and sulfuric acid alone at 70° led to charring and the formation of some benzoic acid. A solution of $Na_2Cr_2O_7 \cdot 2H_2O$ in DMSO at 70° caused only a slight oxidation of benzyl alcohol to benzaldehyde while the alcohol was recovered unchanged when heated with DMSO–H_2SO_4. It would appear, therefore, that DMSO acts as an excellent solvent[15] and prevents further oxidation of the carbonyl compound[7] formed and does not take part in the reaction as in other cases.[2–7] There was no evidence of the formation of methylthiomethyl ethers[2,8] of alcohols. Even if they had been formed, they would have been cleaved by the strong acid.[2] The unique feature of this method is that commercial DMSO may be used without further purification and the reaction takes 90 min for completion.

The following procedure represents the use of this oxidation for the preparation of an aldehyde.

Benzaldehyde. To a stirred solution of sodium dichromate dihydrate (10 g., 0.0332 mol) in 100 g of DMSO was added benzyl alcohol (5.4 g, 0.05 mol). Concentrated sulfuric acid (7.2 ml, 0.133 mol) was added dropwise, while the temperature was kept below