p-toluenesulfonic acid. Reduction of the keto alcohol **14** with sodium borohydride in absolute ethanol at 0° for 10 min gave aeroplysinin-1 (**1**) in 60% yield. The synthetic racemate was identical in all respects with an authentic sample of (±)-aeroplysinin-1, prepared by mixing equal quantities of both natural enantiomers. This synthesis of aeroplysinin-1 (**1**) and isoaeroplysinin-1 (**2**) constitutes a novel approach to the synthesis of arene glycols and has the added advantage that both cis and trans glycols can be prepared stereospecifically.[13]

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(10) Mp 103–108°; ir (Nujol) 3420, 2260, 1635, and 1585 cm^{-1}; NMR ($CDCl_3$–C_3D_6O) δ 2.78 and 2.82 (ABq, 2 H, $J = 16$ Hz), 3.71 (s, 3 H), 4.22 (d, 1 H, $J = 6$ Hz), 4.59 (s, 1 H), 4.94 (d, 1 H), and 6.35 (s, 1 H).
(11) Ir (Nujol) 3350, 2260, 1610, and 1580 cm^{-1}; NMR ($CDCl_3$) δ 2.75 (s, 2 H), 3.12 (bs, 2 H), 3.79 (s, 3 H), and 6.44 (s, 1 H).
(12) Authentic aeroplysinin-1 diacetate was prepared by standard procedures from a sample of authentic aeroplysinin-1, kindly supplied to us by Dr. M. F. Stempien. We were unable to form isoaeroplysinin-1 diacetate directly from isoaeroplysinin-1.
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1-Iodo-3,3-dibromo-2-heptanone, 1,1,3,3-Tetrabromo-2-heptanone, and Related Compounds from the Red Alga *Bonnemaisonia hamifera*[1]

Sir:

During the course of our extensive investigations of marine organisms collected off Baja California while aboard the R/V Alpha Helix, a small sample of the red alga *Bonnemaisonia hamifera* (AHBE-21-III-74-1-103)[2] indicated extraordinarily high lipid total halogen content, high lipid bromine content, high antimicrobial activity against *Bacillus subtilis*, and a remarkably persistent, sweet odor associated with the wet alga.[3]

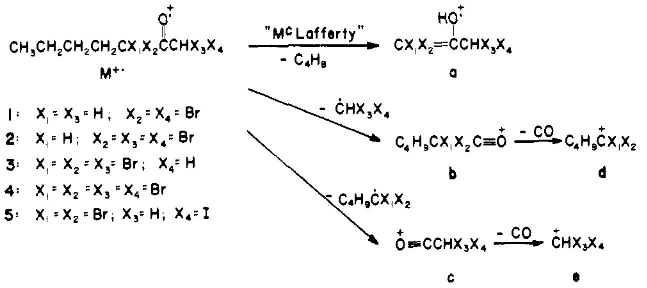

Figure 1. Mass spectral fragmentations of **4** and related halogenated heptanones. Values (*m/e*) for the individual molecular and fragment ions are found in Table I.

In an attempt to identify the compound or compounds responsible for the halogen content, antimicrobial activity, and characteristic odor of *B. hamifera*, a large sample of the alga was ground under ethanol, filtered, concentrated in a rotary evaporator, redissolved in petroleum ether, and chromatographed over silicic acid to give a sample of 1,1,3,3-tetrabromo-2-heptanone (**4**), isolated in ca. 0.01% yield (wet weight) from the alga. Compound **4** displays the characteristic odor of *B. hamifera* and shows activity at the 100 μg/ml level against the fungi *Monosporium apiospermum* and a *Geotrichum* species, at the 500 μg/ml level against *S. pyogenes* and *D. pneumoniae*, and at the 1 mg/ml level against *S. aureus*, *S. faecalis*, *K. pneumoniae*, and 15 additional fungal species.

The electron impact (EI) mass spectrum of **4** displayed no molecular ion except at reduced ionizing potential and maximum sensitivity, when the typical tetrabromo isotope pattern (symmetrical quintet) could be observed at *m/e* 426, 428, 430, 432, and 434. A far more intense ion in the EI spectrum, also containing four bromine atoms, was found at *m/e* 370, resulting from a McLafferty rearrangement (Figure 1, ion a), and the acylonium ions characteristic of α-cleavage of ketones were found at *m/e* 255 and 199 (Figure 1, ions b and c, both ions containing two bromine atoms). Alkyl ions stabilized by the two attached bromine atoms were also observed, at *m/e* 227 and 171 (Figure 1, ions d and e, two bromine atoms each). These fragments, which were confirmed by high resolution data (Table I) allow assignment of the structure $C_4H_9CBr_2COCHBr_2$. The infrared spectrum (CCl_4) of **4** shows carbonyl absorption characteristic of an α-halo ketone at 1738 cm^{-1}, and its nmr spectrum (60 MHz, CCl_4, ppm from TMS) shows absorption for a *n*-butyl group (CH_3, 1.00 t; $(CH_2)_2$, 1.2–1.8 m; deshielded $-CH_2-$, 2.4–2.7 m) and a deshielded singlet at 6.83 ppm ($-C(=O)CHBr_2$). Together, the ir, NMR, and mass spectral data assign structure **4**. The compound was synthesized by the (slightly modified) method of Rappe and Andersson.[4] Properties of the synthetic compound (ir, NMR, TLC, GC, and odor) were identical with those of the natural product. This compound (**4**) and the others in Table I are the first simple brominated aliphatic ketones observed in nature.[5]

The remaining compounds in Table I were identified in other column chromatographic fractions. As seen in Figure 1, these compounds are less brominated derivatives of 2-heptanone, obtained in less than 0.001% yield (wet weight) from the algae. Their mass spectral fragmentations to give ions a–e (Figure 1) established them as halogenated methyl pentyl ketones and assigned the degree of halogenation at the α- and α′-carbons. Although the mass spectra above would in principle allow four carbon skeletons for ketones **1–3** and **5**, the structures shown were confirmed by the observation that by-products in the synthesis of **4** from 2-heptanone had identical mass spectra and GC retention times

Table I. Gas Chromatographic and Mass Spectrometric Data for *B. hamifera* Components

Compound[a]	Retention time[b]	Mass spectral fragment,[a] *m/e* (no. of halogens) (relative intensity)[c] [precise mass][d]					
		M^+	a^+	b^+	c^+	d^+	e^+
1	0.44	270 (Br_2) (0)	214 (Br_2) (8)	177 (Br) (2)	121 (Br) (19)	149 (Br) (9)	93 (Br) (8)
2	0.66	348 (Br_3) (0)	292 (Br_3) (1)	177 (Br) (3)	199 (Br_2) (1)	149 (Br) (12)	171 (Br_2) (2)
3	0.77	348 (Br_3) (0)	292 (Br_3) (2)		121 (Br) (68)	227 (Br_2) (10)	93 (Br) (13)
4[e]	1.00	426 (Br_4) (0)	370 (Br_4) (1) [373.6795 (− 0.5)]	255 (Br_2) (3) [256.8998 (0.2)]	199 (Br_2) (8) [200.8372 (− 0.3)]	227 (Br_2) (17) [228.9045 (− 0.3)]	171 (Br_2) (10) [172.8424 (− 0.1)]
5[f]	1.02	396 (Br_2I) (0) [397.8201 (+ 0.1)]	340 (Br_2I) (1)		169 (I) (84) [168.9148 (0.1)]	227 (Br_2) (12)	141 (I) (17) [140.9200 (0.0)]

[a] For structures, see Figure 1. [b] Relative to compound 4 equal 1.00. [c] Per cent of base peak. [d] Measured (by peak matching) on the center peak of quintuplets (Br_4) and triplets (Br_2), the lower mass peak of doublets (Br), except as noted. Figures in parentheses indicate mmu deviation from calculated values. [e] Additional peaks measured: *m/e* 188.9916 (+ 0.1), $C_7H_{10}BrO$ (M − Br_3), *m/e* 148.9789 (0.0), $C_5H_8{}^{81}Br$ (d − HBr). [f] Additional peaks measured: *m/e* 316.9036 (− 0.1), $C_7H_{11}BrIO$ (M − Br); *m/e* 148.9786 (− 0.3), $C_5H_8{}^{81}Br$ (d − HBr); *m/e* 127.9121 (0.1), HI; *m/e* 126.9043 (0.0), I; *m/e* 111.0806 (− 0.4), $C_7H_{11}O$ (M − Br_2I).

and cochromatographed (GC) with **1–3** obtained from *B. hamifera*.

Among the compounds identified by GC–mass spectra is 1-iodo-3,3-dibromo-2-heptanone (**5**), which gave peaks at *m/e* 396 (M, symmetrical Br_2 triplet at 396, 398, 400) and at *m/e* 340, 169, 227, and 141 (a, c, d, and e, respectively) as well as peaks at *m/e* 127 and 128 (I^+ and $HI^{+\cdot}$). High resolution mass spectrometric data (Table I) agreed with these assignments. Compound **5** is especially significant among those in Table I since it represents the first example of a natural product containing both iodine and bromine and also structurally departs from the only other known iodinated natural substances, which are thyroxine related compounds.[5]

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The Photochemistry of β,γ-Epoxy Cyclic Ketones

Sir:

In striking contrast to the extensive investigation of the photochemistry of α,β-epoxy ketones,[1] only scattered reports have appeared concerning aspects of the photochemis-