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HALOFORMS IN THE ESSENTIAL OIL OF THE ALGA ASPARAGOPSIS TAXIFORMIS (RHODOPHYTA)

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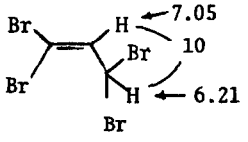
The red alga Asparagopsis taxiformis (Delile) Collins and Hervey, known as limu kohu (the supreme seaweed) in Hawaii, is the favorite edible seaweed of most Hawaiians. Prompted by a report that A. taxiformis has a strong flavor and develops an iodine odor on standing[1] and by an interest in the odoriferous constituents of algae[2], we have examined the essential oil of this highly odoriferous seaweed and have found that the major constituent is bromoform ($CHBr_3$), with smaller amounts of several chlorine- and iodine-containing haloforms ($CHClBr_2$, $CHClBrI$, $CHBr_2I$, $CHBrI_2$, and CHI_3), carbon tetrahalides (CBr_4), tetrahalopropenes (1-4), polyhalobut-3-en-2-ones (5, 6, 8, 9), monohaloacetones (10, 11), and 3,3-dihaloacroleins (12).

A. taxiformis (76 g. dry wt.) was collected at Waikiki in October. The wet plants were placed in a large vacuum desiccator and the volatile material was collected with water in vacuo on the finger of a Dry Ice cooled condenser. The oil was transferred into methylene chloride and the dried extract ($MgSO_4$), which turned violet (formation of iodine) on standing, was evaporated to give 330 mg. of essential oil. In the proton nmr spectrum (CCl_4) of the oil, there was a very strong singlet at δ 6.80 (48% of total proton integration) corresponding exactly with the chemical shift of bromoform. Smaller singlets at δ 6.36 (7% of integration), δ 5.72 (2% of integration) and δ 4.88 (< 1% of integration) coincided with those of dibromoiodomethane, diiodobromomethane and iodoform, respectively. In addition to molecular ions from bromoform (m/e 250, 252, 254 and 256) and iodoform (m/e 394) in the mass spectrum of the oil, there were strong molecular ions at m/e 298, 300, and 302 (relative intensities 1:2 1) for dibromoiodomethane and ions of equal intensity at m/e 346 and 348 for diiodobromomethane. Intense fragments ions resulting from loss of iodine or bromine from the molecular ions were

also present in the mass spectrum. The presence of bromoform, dibromoiodomethane, diiodobromomethane, and iodoform in the oil was confirmed by glc (6' x 1/8" column of 3% OV-17 on Gas-Chrom Q) comparison with authentic samples at 65° and 95°. Analysis of the low boiling fraction of the essential oil by gas chromatography-mass spectrometry (3% OV-17 on 80/100 Supelcoport at 60°) disclosed traces of dibromochloromethane [retention time, 1 4 min, molecular ions at 206, 208, 210, and 212 (relative intensities 1.8 5.2:4:1)], bromochloroiodomethane [retention time, ca 3.5 min; molecular ions at 254, 256, and 258 (relative intensities 4 4 1)], and tetrabromomethane [retention time, 9.8 min, identical with that of an authentic sample, molecular ions at 328, 330, 332, 334, and 336]. No mono- or dihalomethanes were found. The formation of molecular iodine in the methylene chloride solution of the essential oil is due to a photochemical air oxidation of iodoform and other iodine-containing haloforms.

Polyhalopropenes were also found in the essential oil. The major one was 1,1,3,3-tetrabromopropene (1, 4% of the essential oil) and its mass spectrum exhibited a molecular ion cluster at m/e 354, 356, 358, 360, and 362 (relative intensities 1 3.5·5 3.5 1). Its pmr spectrum and gc retention time were identical with a synthetic sample made by the reaction of 3,3-dibromoacrolein with acetyl bromide in the presence of aluminum chloride;[3] 1,1,3-tribromo-3-chloropropene (2) was formed as a minor product in this reaction. Small amounts of 2 [molecular ion cluster at m/e 310, 312, 314, 316, 318 (rel intensities 3:12:9.6:1)], 1,1-dibromo-3,3-dichloropropene (3) [molecular ion cluster at m/e 266, 268, 270, 272, 274 (rel intensities 4 14:12:4:1)] and an isomer of 1,3,3-tribromo-1-iodopropene (4) [molecular ion cluster at m/e 402, 404, 406, 408 (rel. intensities 1·2:2:1)] were identified in the high



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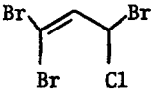

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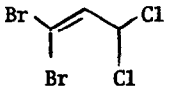


3

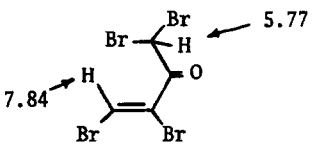
$CBrI{=}CH\text{-}CHBr_2$

4

boiling fraction of the essential oil by gc-ms. Both 2 and 3 had gc retention times identical with those of synthetic samples[3]. Intense fragment ions were observed in the mass spectra of the tetrahalopropenes for loss of an allylic halogen from the molecular ion. Since the mass spectrum of 4 exhibited a M-Br but not a M-I ion cluster, the iodine must be attached at C-1.

Compounds containing bromine and chlorine are not unusual in red algae[4], but the only iodo compounds reported from algae are the iodotyrosines[5]. Biogenetically the haloforms appear to

be degradation products of 1,1,1-trihalomethyl ketones. Mass spectral analysis of the essential oil revealed the presence of several polyhaloacetones and polyhalobut-3-en-2-ones. The major ketone (ca 2% of the essential oil), cis-1,1,3,4-tetrabromobut-3-en-2-one (5), was isolated by preparative thin layer chromatography of the high-boiling fraction of the essential oil on silica gel HF with benzene and its mass spectrum showed molecular ions at m/e 382, 384, 386, 388, 390 (relative intensities 1·3.5.5:3.5 1). The pmr chemical shift of the C-4 proton of 5 agreed well with that of cis-3,4-dibromobut-3-en-2-one (6), obtained with a smaller amount of 7 by addition of bromine to but-3-yn-2-one in CCl_4. When 7 was heated or treated with LiBr in



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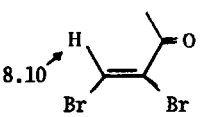

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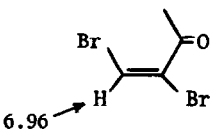
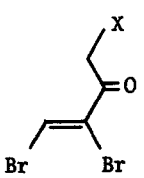
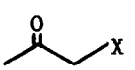


7

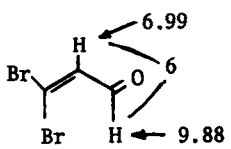
HOAc, rapid isomerization to the thermodynamically more stable[6] 6 occurred. Minor amounts of 6 [molecular ion cluster at m/e 226, 228, 230 (rel intensities 1.2:1)], cis-1,3,4-tribromobut-3-en-2-one (8) [molecular ion cluster at m/e 304, 306, 308, 310 (rel intensities 1:3:3:1)], cis-3,4-dibromo-1-iodobut-3-en-2-one (9) [molecular ion cluster at m/e 352, 354, 356 (rel intensities 1·2:1)], bromoacetone (10) [molecular ion peaks at m/e 136 and 138 (1.1)], and iodoacetone (11) [m/e 184] have been identified in the essential oil to date by gc-ms. Compounds 5, 6, 8, and 9 all show the same intense fragment ion cluster at m/e 211, 213, 215, (1.2:1) for $CHBr{=}CHBr{-}C{\equiv}O^{+}$. Ketones 6, 10 and 11[7] had identical gc retention times with those of authentic samples. Finally several aldehydes, such as 3,3-dibromoacrolein (12, identified by gc-ms, nmr,



8, X = Br
9, X = I



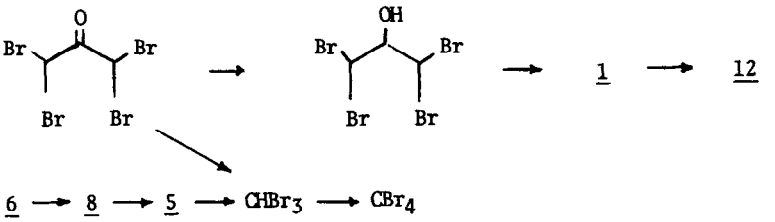
10, X = Br
11, X = I



12

and comparison with an authentic sample), are present in Asparagopsis oil.

Carbon tetrabromide is probably formed by bromination of bromoform while 1 is the result of reduction of 1,1,3,3-tetrabromoacetone to 1,1,3,3-tetrabromoisopropanol followed by dehydration. Hydrolysis of the gem-dibromo group of 1 then leads to 12. The biogenesis of the



halogenated acetones and butenones is presently unknown.

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