flavors. We have not experimentally evaluated the furanones in either leek or shallot oil; however, due to their overall similarity to onion oil, we suspect the furanones play no significant flavor role in these products.

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Volatile Halogen Compounds in the Alga *Asparagopsis taxiformis* (Rhodophyta)

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The essential oil of *Asparagopsis taxiformis*, an edible red alga in Hawaii, is composed of mainly bromine- and iodine-containing haloforms with smaller amounts of other halogenated methanes and several halogenated ethanes, ethanols, formaldehydes, acetaldehydes, acetones, 2-propanols, 2-acetoxypropanes, propenes, epoxypropanes, acroleins, and butenones.

Limu kohu, which in Hawaiian means the supreme seaweed, is highly prized for its aroma and flavor (Abbott et al., 1974). Scientifically known as *Asparagopsis taxiformis* (Delile) Collins et Harvey, this red alga is a dioecious, gametophytic plant that alternates in its life cycle with a heteromorphic sporophyte known as *Falkenbergia rufanolosa* (Harvey) Schmitz. Curiously the male and female plants are odoriferous whereas the asexual plant is not. In a preliminary communication (Burreson et al., 1975) we reported that the major constituent in the essential oil of Hawaiian *A. taxiformis* is bromoform (**1**). More interestingly, we found that iodine-containing haloforms, the major one being dibromoiodomethane (**2**), are also present in the essential oil. Furthermore, several halogenated acetones and butenones were identified in the oil, suggesting strongly to us that the haloforms are formed in vivo by the well-known haloform reaction of methyl ketones. We have now carried out a more extensive examination of the volatile constituents of Hawaiian *A. taxiformis*, the subject of this paper, and have identified to date 42 components of the essential oil, 24 of these unreported by us in our earlier report (Table I).

ISOLATION

Male and female plants of *A. taxiformis*, which were not separated for this investigation, were obtained from the reefs on the Waikiki side of Diamond Head, Oahu between Sept, 1974 and June, 1975. The freshly collected, wet plants were processed for essential oil by drying the seaweed in a vacuum and trapping the volatile oil and water in a dry ice cooled condenser. The essential oil was separated from water by extraction with methylene chloride. Unfortunately, this latter procedure prevented us from determining whether substances such as chloroform and carbon tetrachloride were present in the oil. The essential oil, which was initially completely colorless, quickly developed a violet color on exposure to air and light due to the formation of iodine. Free molecular iodine, however, did not appear to be present in the live plants.

Separation of the essential oil was best achieved by chromatography on silica gel. Ten major fractions were collected and analyzed by Fourier transform proton magnetic resonance (^{1}H NMR) spectroscopy and gas chromatography–mass spectrometry (GC–MS). Fraction 1 contained three 1,1,3,3-tetrahalopropenes (**30–32**), a carbon tetrahalide (**10**), and a hexahaloacetone (**25**). Fractions 2 and 3 consisted of mostly haloforms (**1–3, 5**), but traces of other halogenated alkanes (**7, 9, 13**) were also present in fraction 2. Halogenated acetones (**17, 20–22**) and butenones (**38–42**), a 1,3,3-trihaloepoxypropane (**29**), and a trace of a carbonyl dihalide (**11**) were found in fractions 4–6. Fractions 7 and 8 were complex mixtures and none of the components have been characterized yet. Fraction 9 was mostly biogenetically unrelated benzaldehyde. Fraction 10 was also a complex mixture, but contained mostly a 2-haloethanol (**12**) and a small amount of a dihaloacetaldehyde (**14**). Compounds such as **30** and **38** were not formed during the chromatography as signals for these compounds were clearly visible in both the ^{1}H NMR and carbon-13 magnetic resonance (^{13}C NMR) spectra of the essential oil. Unfortunately, many of the iodinated compounds in the essential oil did not survive the adsorption chromatography. Iodoform (**4**), for example, could be readily seen in the ^{1}H NMR and mass spectra of the crude essential oil, but after chromatography on silica gel none of the fractions contained any iodoform. GC–MS analysis of fractions resulting from separation of the essential oil by molecular distillation or gel filtration

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Table I. Volatile Constituents of Hawaiian *Asparagopsis taxiformis*

Type of compound	No.	Structure	Estimated % in oil by wt[a]
Haloforms	1	$CHBr_3$	80
	2	$CHBr_2I$	5
	3	$CHBrI_2$	2
	4	CHI_3	
	5	$CHBr_2Cl$	
	6	$CHBrClI$	
Dihalomethanes	7	CH_2Br_2	
	8	CH_2BrI	
	9	CH_2I_2	
Carbon tetrahalides	10	CBr_4	
Carbonyl dihalides	11	COI_2	
2-Haloethanols	12	ICH_2CH_2OH	1
1,2-Diahaloethanes	13	$BrCH_2CH_2I$	
Halogenated acetaldehydes	14	Br_2CHCHO	
Halogenated acetones	15	CH_3COCH_2Br	
	16	CH_3COCH_2I	
	17	$CH_3COCHBr_2$	2
	18	$BrCH_2COCH_2Br$	
	19	$BrCH_2COCH_2I$	
	20	CH_3COCBr_3	1
	21	CH_3COCBr_2Cl	
	22	$BrCH_2COCHBr_2$	
	23	$ICH_2COCHBr_2$	
	24	$Br_2CHCOCHBr_2$	
	25	$Cl_3CCOCCl_3$	
Halogenated 2-propanols	26	$BrCH_2CH(OH)CHBr_2$	
Halogenated 2-acetoxypropanes	27	$BrCH_2CH(OAc)CHBr_2$	
	28	$Br_2CHCH(OAc)CHBr_2$	
Halogenated 1,2-epoxypropanes	29	$BrCH_2CH\underset{\diagdown}{\overset{\diagup}{O}}CHBr_2$	
1,1,3,3-Tetrahalopropenes	30	$Br_2C{=}CHCHBr_2$	2
	31	$Br_2C{=}CHCHBrCl$	
	32	$Br_2C{=}CHCHCl_2$	
	33	$BrIC{=}CHCHBr_2$	
3,3-Dihaloacroleins	34	$Br_2C{=}CHCHO$	
Halogenated butenones	35	$Br_2C{=}CHCOCH_3$	
	36	$Br_2C{=}CHCOCH_2Br$	
	37	$Br_2C{=}CHCOCH_2I$	
	38	$Br_2C{=}CHCOCHBr_2$	2
	39	$Br_2C{=}CHCOCHBrCl$	
	40	$BrClC{=}CHCOCHBr_2$	
	41	$Cl_2C{=}CHCOCHBr_2$	
	42	$BrClC{=}CHCOCHBrCl$	

[a] All other constituents in this column are present in less than 1%.

revealed seven other iodinated compounds (**6**, **8**, **16**, **19**, **23**, **33**, and **37**) which also could not be detected in any of the silica gel fractions. In addition, nine other components, including a trihalogenated 2-propanol (**26**), two halogenated isopropyl acetates (**27**, **28**), a 3,3-dihaloacrolein (**34**), and other halogenated acetones (**15**, **18**, **24**) and butenones (**35**, **36**), were identified in the molecular distillation or gel filtration fractions.

Sporophytic plants of the epiphytic *F. rufanolosa* were collected at the Natatorium, Waikiki in the spring of 1975. No essential oil could be obtained from this seaweed and none of the compounds found in *A. taxiformis* were detected in the extract.

STRUCTURE DETERMINATION AND SYNTHESIS

Structure elucidation of the compounds listed in Table I by spectroscopic methods was generally straightforward. Many of the compounds had already been described in the chemical literature and we were therefore able to confirm structures by simply comparing the natural compound with an authentic sample obtained either by synthesis or from a commercial source (Supplementary Material; see paragraph at end of paper). Compounds **1**–**7**, **9**, **10**, **12**–**18**, **20**–**22**, **24**, **25**, **30**–**32**, and **34** were identified in this manner.

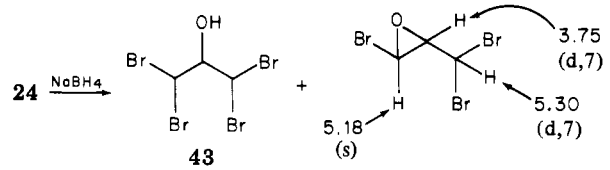
Bromoiodomethane (**8**) was not compared with an authentic sample.

Carbonyl diiodide (**11**) is not a known compound and no attempt was made on our part to synthesize it. Its structure followed from mass spectral data coupled with its chromatographic behavior on silica gel. The mass spectrum of **11** showed a molecular ion and fragment ions for $IC{\equiv}O^+$ and I^+ and **11** cochromatographed with **17** and other ketones rather than with **13** and the haloforms.

1-Bromo-3-iodoacetone (**19**) and 1,1-dibromo-3-iodoacetone (**23**) were identified from their mass spectra which both showed a molecular ion and a base peak at m/e 169 for $ICH_2C{\equiv}O^+$. Bromination of iodoacetone in aqueous sodium bicarbonate produced a very small amount of **19** (but not **23**) along with small amounts of 1-bromo-1-iodoacetone and 1,1-diiodoacetone. Iodoacetone, **19**, and **23** are the only iodinated acetones that we have been able to detect in the essential oil to date. Only a few iodinated acetones (besides **16**) have been previously described in the literature. 1,1,1-Triiodoacetone has been prepared by the reaction of sodium iodide with **20** in acetone (Birkofer and Brune, 1958) and 1,3-diiodoacetone and 1,1,3,3-tetraiodoacetone are products of the iodination of acetonedicarboxylic acid in water (Lederer, 1898).

1,1,3-Tribromo- (**26**) and 1,1,3,3-tetrabromo-2-propanol (**43**) and the corresponding isopropyl acetates (**27**, **28**) have not been previously described. As expected, reduction of

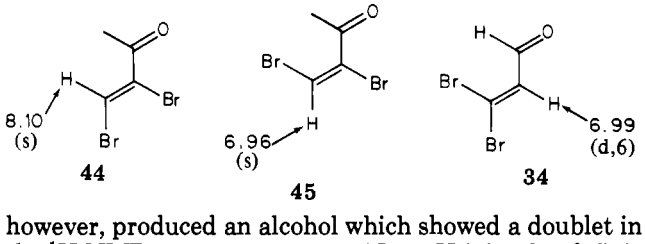
22 and 24 with sodium borohydride gave 26 and 43 and after acetylation 27 and 28, respectively. On one occasion reduction of 24 led interestingly to an appreciable amount of *trans*-1,3,3-tribromoepoxypropane (29), along with 43; apparently the sodium borohydride medium was basic enough in this particular experiment for the oxide to form. Natural 29 proved to be identical in all respects with synthetic 29. Epoxide 29 was also produced when we attempted to form the tosylate of 43. We have concluded



that the geometry of the epoxide ring is trans as no coupling is observed between the C_1 and C_2 protons in the ^1H NMR spectrum of 29.

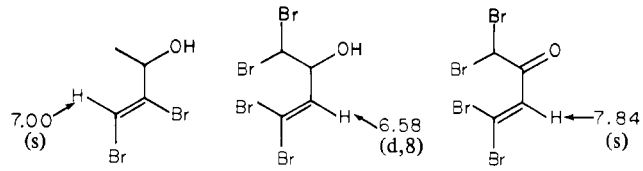
The structure of the tribromoiodopropene was established from its mass spectrum which showed a 1:3:3:1 molecular ion cluster at m/e 402, 404, 406, and 408 and a very strong fragment ion cluster at 323, 325 (base peak), and 327, attributed to loss of an allylic bromine from the molecular ion. The lack of a substantial M − I peak suggested to us that the iodine was not in an allylic position. By analogy with other halogenated propenes in the essential oil, we concluded that this compound is a 1,3,3-tribromo-1-iodopropene (33).

The major halogenated butenone is a tetrabromobutenone. Its mass spectrum exhibited a molecular ion cluster and 1:2:1 fragment ion clusters at m/e 211, 213 (base peak), and 215 for $C_2HBr_2C{\equiv}O^+$ and m/e 171, 173, and 175 for dibromomethyl ion, consistent with either a 1,1,3,4- or 1,1,4,4-tetrabromobutenone structure. Since the signal for the olefinic proton resonated at rather low field (δ 7.84), we erroneously concluded in our earlier communication (Burreson et al., 1975) that this proton was on C-4 and cis to the carbonyl group. Its position compared reasonably well with the chemical shift of the C-4 proton of (*Z*)-3,4-dibromobutenone (44, δ 8.10), but not with the chemical shifts of the C-4 proton of (*E*)-3,4-dibromobutenone (45, δ 6.96) and the C-2 proton of 34 (δ 6.99). Sodium borohydride reduction of the tetrabromobutenone,



however, produced an alcohol which showed a doublet in the ^1H NMR spectrum at δ 6.58 (J = 8 Hz) for the olefinic proton (Woolard et al., unpublished work). A coupling constant of this magnitude is only compatible with placing a proton on the adjacent carbon. By comparison (*Z*)-3,4-dibromo-3-buten-2-ol (46) showed a sharp singlet for the olefinic proton. The alcohol is therefore 1,1,4,4-tetrabromobut-3-en-2-ol (47) and this has been proven by synthesis (Woolard et al., unpublished work). The structure for the tetrabromobutenone must then be revised from (*Z*)-1,1,3,4-tetrabromobutenone to 38.

4,4-Dibromobutenone (35), 1,4,4-tribromobutenone (36), 1-iodo-4,4-dibromobutenone (37) and 1,4,4-tribromo-1-chlorobutenone (39) were identified from their mass spectra which exhibited 1:2:1 ion clusters for $Br_2C{=}CHC{\equiv}O^+$ with appropriate molecular ion clusters and



halomethyl fragments. A second tribromochlorobutenone (40) was also present in the essential oil and its mass spectrum showed a dibromomethyl ion cluster and a 4:5:3 ion cluster at m/e 167, 169 (base peak), and 171 for $BrClC{=}CHC{\equiv}O^+$. Due to insufficient material we were not able to establish the stereochemistry of the chlorine and bromine on the double bond of 40. 1,1-Dibromo-4,4-dichlorobutenone (41) was also identified from its mass spectrum which showed a strong ion cluster at m/e 123, 125, and 127 for $Cl_2CC{=}CHC{\equiv}O^+$ and a dibromomethyl ion cluster at m/e 171, 173, and 175. Finally, a second dibromodichlorobutenone was concluded to be 42 from mass spectral data.

Seven of the compounds in the essential oil (6, 26, 27, 29, 31, 39, and 42) have asymmetric carbons and therefore may have optical activity. None, however, have been collected in sufficient quantities to determine optical properties.

While our work was in progress Fenical (1974) reported the isolation and characterization of several bromine- and chlorine-containing acetones from *A. taxiformis* (Delile) Trev. collected in the Gulf of California. The major polyhaloacetone was 22, with smaller amounts of 18, 24, 1-bromo-3-chloroacetone, 1,1-dibromo-3-chloroacetone, 1,3-dibromo-1-chloroacetone, and 1,1,3-tribromo-3-chloroacetone. Halogenated butenones were also found in *A. taxiformis* from Lower California, the major one a tribromobutenone. Smaller amounts of a tetrabromobutenone, a tribromochlorobutenone, and a dibromochlorobutenone were also identified, but the positions of the two bromines on the double bond were not determined for any of the compounds. Most likely these four ketones are 4,4-dibromobutenones. The chemical shifts reported for the olefinic protons, however, are at somewhat higher field (δ 7.40–7.65) compared with what we find for 38.

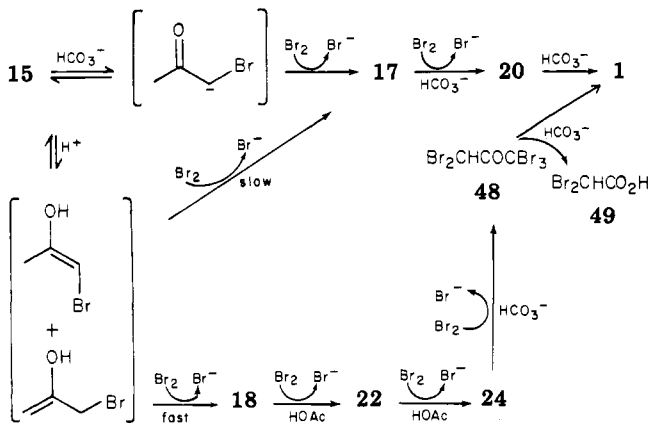
FORMATION OF ARTIFACTS

When a solution of iodoform in methylene chloride is exposed to air and light, molecular iodine is liberated. Iodine, carbon monoxide, and carbon dioxide are reported (Schmidt, 1901) to be formed when iodoform is air oxidized at 100 °C and carbonyl diiodide is probably the intermediate in the oxidation. Dichloroiodomethane has been reported (Auger, 1908) to rapidly develop a phosgene-like odor when exposed to moist air and light, due probably to carbonyl chloride–iodide. Bromochloroiodomethane has also been found (Garino and Muzio, 1926) to immediately assume a violet color and the odor of carbonyl bromide–chloride in air. Carbonyl diiodide may therefore be an artifact that results from decomposition of iodoform during the silica gel chromatography.

BIOGENESIS OF THE HALOFORMS

The haloforms are most likely formed from 1,1,1-trihaloacetones (e.g., 20 → 1 and 21 → 5). Support for the proposed biogenesis is obtained from a study of the nonenzymatic halogenation of halogenated acetones. Compounds 17 and 20 are readily produced when 15 is treated with bromine in aqueous sodium bicarbonate (Scheme I). As 20 is allowed to stand at pH 8, extensive degradation to 1 occurs. Under these conditions (pH 8) compounds 18, 22, and 24 are not formed. When the bromination is

Scheme I



carried out in an acidic medium, however, **18**, **22**, and **24** are the sole products. Further bromination of **24** does not proceed in an acidic medium but occurs readily in aqueous $NaHCO_3$ to give pentabromoacetone (**48**), the latter undergoing appreciable decomposition of 1 and dibromoacetic acid (**49**) in the presence of bicarbonate. Although **48** has not been detected in Hawaiian *A. taxiformis*, **49** is present in the aqueous extract of the dried alga (Woolard et al., unpublished work). When chloroacetone is brominated in aqueous $NaHCO_3$ 1-bromo-1-chloroacetone and **21** are formed. At pH 8 **21** also decomposes slowly to the haloform (**5**). A similar bromination of **16** in aqueous $NaHCO_3$ results in the formation of mostly **15** and **17**, but small amounts of 1-bromo-1-iodoacetone, 1,1-diiodoacetone, and the iodinated haloforms (**2** and **3**) are produced.

HALOCARBONS IN THE AIR AND IN THE SEA

Methyl chloride is the dominant halocarbon of the atmosphere (Grimsrud and Rasmussen, 1975). Lovelock (1975) has proposed that methyl chloride may have a marine origin. Marine algae such as the brown seaweed *Laminaria digitata* seem to produce extracellular methyl iodide since the seawater in the vicinity of this kelp contains 1000 times more methyl iodide than the open oceans. In the sea the methyl iodide reacts nucleophilically with chloride ion to form methyl chloride which then escapes into the atmosphere. The residence time of methyl iodide in seawater is comparable to its rate of reaction with chloride ion (Zafiriou, 1975).

Chloroform, 1,1,1-trichloroethane, tetrachloroethylene, and carbon tetrachloride have also been identified in the chlorocarbon complement of the air and these compounds do not appear to have an anthropogenic origin (Lovelock et al., 1973). Our work with *Asparagopsis* suggests that these chlorocarbons may indeed have an algal origin. The essential oil of Hawaiian *Asparagopsis* is extracellular and bromoform and carbon tetrabromide are being continually excreted into the seawater. By analogy chloroform and carbon tetrachloride could be produced by algae and excreted into the seawater and eventually exchanged into the air. It is even possible that chloroform and carbon tetrachloride are constituents of Hawaiian *Asparagopsis* but our experiment procedure will have to be modified to detect these volatile compounds.

CARCINOGENICITY AND TOXICITY OF HALOCARBONS

Limu kohu (*A. taxiformis*) is the favorite edible seaweed in Hawaii. The presence of haloforms and other halogenated compounds in the essential oil suggests that limu kohu should be a poisonous seaweed to eat, but to our knowledge there has never been a single case of illness attributed to the ingestion of this alga. Generally, alkyl and vinyl halides are alkylating agents and a number of them have been shown to be either carcinogenic or toxic. Methyl iodide (Druckrey et al., 1970), carbon tetrachloride (Reuber and Glover, 1970), 1,2-dibromoethane and 1,2-dibromo-3-chloropropane (Olson et al., 1973), vinyl chloride (Maltoni and Lefemine, 1974), and trichloroethylene (Seltzer, 1975), for example, are carcinogenic in animals and carbon tetrabromide and dichlorodibromomethane (Rudali, 1967) and 2-chloroethanol (Browning, 1965) are poisonous. Vinyl chloride is carcinogenic in humans (*Chem. Eng. News*, 1974) on the basis of epidemiological evidence and recently 2-chlorobutadiene has been implicated as a human carcinogen according to a Russian study (*Chem. Eng. News*, 1975). Little, however, is known about the physiological properties of most of the compounds in *A. taxiformis*. Bromoform, the major constituent, has been used as a sedative. Whether limu kohu should be considered a dangerous seaweed to eat will have to await further study.

EXPERIMENTAL SECTION

Proton magnetic resonance (^1H NMR) spectra were determined at 100 MHz on a Varian HA-100 spectrometer and carbon-13 magnetic resonance (^{13}C NMR) spectra were obtained at 25.15 MHz on a Varian XL-100 spectrometer equipped with a Digilab Fourier transform system. Chemical shifts are reported in δ units (parts per million) relative to Me_4Si (δ 0) as an internal standard in $CDCl_3$. Methine, methylene, and methyl carbons were identified by single frequency off-resonance decoupling with the proton decoupler at δ 14. Gas chromatography–mass spectrometry (GC–MS) was carried out with a Hewlett-Packard 5700 gas chromatograph coupled through a double-stage jet separator to a JEOL JMS-01SG-2 double focusing mass spectrometer operating at 70 eV. All GC retention times were determined on a 6 ft × $^1/_8$ in. stainless steel column of 3% OV-17 on 80/100 Supelcoport which was heated isothermally at 60 °C for 4 min after injection, then temperature programmed from 60 to 200 °C at 8 °C per min, and finally heated isothermally at 200 °C using a helium flow rate of 30 ml/min.

Isolation of Oil. In a typical experiment, wet *Asparagopsis taxiformis* plants collected at Waikiki were placed in a large vacuum desiccator and the volatile material collected with water in vacuo on the finger of a dry ice cooled condenser. The colorless oil was transferred into CH_2Cl_2 and the dried extract ($MgSO_4$), which turned violet on standing due to the formation of iodine, was evaporated to give 330 mg of halogen-containing essential oil (0.43% based on the weight of the dried seaweed that remained). When 1–2 g of wet *Falkenbergia rufanolosa* plants was processed only a trace of volatile, nonodoriferous oil was obtained. No volatile halogen-containing compounds could be found in *F. rufanolosa* oil by GC–MS analysis.

Fractionation of the Essential Oil of *A. taxiformis*. (a) *Absorption Chromatography.* The essential oil (1 g) was applied to a 1.5 m × 2.5 cm column of silica gel (Bio-Sil A) at 5 °C. The chromatogram was developed with hexane and the column effluent was assayed continuously for uv absorption at 254 and 280 nm. Fractions 1 (20 mg), 2 (650 mg), and 3 (20 mg) were eluted with hexane, fractions 4 (25 mg), 5 (25 mg), 6 (10 mg), 7 (5 mg), 8 (5 mg), and 9 (5 mg) with 50% methylene chloride–hexane, and fraction 10 (25 mg) with 10% ethanol–ether. Each fraction was analyzed in detail by ^1H NMR spectroscopy and GC–MS. The percentages of the major compounds in each fraction are based on relative ^1H NMR integrations whereas the

percentages of the minor compounds are based on relative peak areas of the GC trace.

In fraction 1, 1,1,3,3-tetrabromopropene (**30**, 80%, retention time 12.7 min) is the major constituent; 1,1,3-tribromo-3-chloropropene (**31**, 10%, t_R = 10.8 min), carbon tetrabromide (**10**, 3%, t_R = 8.3 min), 1,1-dibromo-3,3-dichloropropene (**32**, 3%, t_R = 8.7 min), and hexachloroacetone (**25**, 1%, t_R = 9.8 min) are minor constituents.

In fraction 2, bromoform (**1**, 90%, t_R = 2.9 min) is the major constituent; dibromoiodomethane (**2**, 2%, t_R = 7.2 min), **30** (2%), **31** (0.2%), dibromochloromethane (**5**, 0.2%, t_R = 1.3 min), 1-bromo-2-chloroethane (**13**, <0.1%, t_R = 3.4 min), dibromomethane (**7**, <0.1%, t_R = 0.8), and diiodomethane (**9**, <0.1%, t_R = 5.2 min), are minor constituents.

In fraction 3, **1** (40%) and **2** (40%) are the major constituents; bromodiiodomethane (**3**, 10%, t_R = 10.8 min) is a minor constituent.

In fraction 4, 1,1,4,4-tetrabromobutenone (**38**, 60%, t_R = 17.5 min) and 1,1,1-tribromoacetone (**20**, 30%, t_R = 9.8 min) are the major constituents; 1,1,4-tribromo-4-chlorobutenone (**40**, 4%, t_R = 15.6 min, mostly in low side of GC–MS peak), 1,4,4-tribromo-1-chlorobutenone (**39**, 1%, t_R = 15.6 min, mostly in high side of GC–MS peak), 1,1-dibromo-1-chloroacetone (**21**, 1%, t_R = 9.8 min), *trans*-1,3,3-tribromo-1,2-epoxypropane (**29**, 1%, t_R = 11.7 min), 1,1-dibromo-4,4-dichlorobutenone (**41**, 0.2%, t_R = 13.8 min), and 1,4-dibromo-1,4-dichlorobutenone (**42**, <<0.1%, t_R = 13.8 min) are minor constituents.

In fraction 5, 1,1-dibromoacetone (**17**, 70%, t_R = 2.9 min) and **38** (20%) are the major constituents; **20** (2%), **40** (1%), and carbonyl diiodide (**11**, <0.1%, t_R = 4.0 min) are minor constituents.

In fraction 6, **17** (95%) is the major constituent; 1,1,3-tribromoacetone (**22**, 0.5%, t_R = 12.5 min) is a minor constituent.

In fraction 10, 2-iodoethanol (**12**, 20%, t_R = 2.9 min) is a major constituent; dibromoacetaldehyde (**14**, 2%, t_R = 2.0 min) is a minor constituent.

Fractions 7 and 8 are complex mixtures, but none of the constituents have been identified. In fraction 9 benzaldehyde (95%, t_R = 4.6 min) is the major constituent.

In most cases identifications of compounds above were made by direct comparisons of the NMR spectra, GC retention times, and mass spectra with those of commercially available or synthetic samples. Most of these data are reported as supplementary material in the microfilm edition of this volume of the journal.

Spectral data of compounds that were not compared with authentic samples follow. Dibromomethane (**7**): mass spectrum *m/e* (relative intensity) 172 (30), 174 (60), 176 (30), 93 (100), 95 (100). Carbonyl diiodide (**11**): mass spectrum *m/e* (relative intensity) 282 (35), 155 (100), 127 (20). 1,1,4,4-Tetrabromobutenone (**38**): ^{1}H NMR spectrum δ 5.77 (s), 7.84; mass spectrum *m/e* 382, 384, 386, 388, 390 (1.7:7.2:10:6.6:1.6 ion cluster, <1%), 303, 305, 307, 309 (1:3:3:1 ion cluster, <1%), 275 (1), 277 (3), 279 (3), 281 (1), 211 (53), 213 (100), 215 (49), 183 (5), 185 (10), 187 (5), 171 (4), 173 (8), 175 (4), 131 (2), 133 (2), 104 (7), 106 (7). 1,4,4-Tribromo-1-chlorobutenone (**39**): mass spectrum *m/e* (relative intensity) 338, 340, 342, 344, 346 (3:9:10:5:1 ion cluster, <1%), 211 (50), 213 (100), 215 (50), 183 (10), 185 (20), 187 (10), 127 (38), 129 (41), 131 (10). 1,1,4-Tribromo-4-chlorobutenone (**40**): mass spectrum *m/e* (relative intensity) 338 (0.2), 340 (0.7), 342 (0.7), 344 (0.4), 167 (85), 169 (100), 171 (55), 139 (17), 141 (20), 143 (7). 1,1-Dibromo-4,4-dichlorobutenone (**41**): mass spectrum *m/e* (relative intensity) no M^+ ion, 171 (2), 173 (4), 175 (2), 123 (100), 125 (62), 127 (14). 1,4-Dibromo-1,4-dichlorobutenone (**42**): mass spectrum *m/e* (relative intensity) no M^+ ion, 167 (4), 169 (4), 171 (2) in fraction containing mostly **41**.

(b) *Gel Filtration.* The volatile portion of the essential oil (1 g) was removed by molecular distillation at 40 °C (2 mm) and the much less volatile residual oil (156 mg) in the distillation pot was introduced onto a 5 ft × 1 in. column of Sephadex LH-20 with 50% $CHCl_3$–MeOH. Elution was continued with the same solvent and the fractionation was continuously monitored by uv absorption at 254 and 280 nm and 6-ml fractions were collected. Analysis of the material in fractions 26–31 (58 mg) by GC–MS revealed the presence of several new compounds that were not found in the silica gel chromatography. In addition to **17** (2%), **20** (4%), **22** (1%), **30** (40%), **31** (3%), **32** (<1%), **38** (35%), **39** (1%), and **40** (4%), minor amounts of 1,3-dibromoacetone (**18**, <1%, t_R = 8.2 min), 1-bromo-3-iodoacetone (**19**, <1%, t_R = 8.2 min), 1,1-dibromo-3-iodoacetone (**23**, <1%, t_R = 12.5 min), 1,1,3-tribromo-2-propanol (**26**, 2%, t_R = 13.3 min), 4,4-dibromobutenone (**35**, 4%, t_R = 13.7 min), 1,4,4-tribromobutenone (**36**, <1%, t_R = 15.4 min), 1,3,3-tribromo-1-iodopropene (**33**, <1%, t_R = 15.4 min), 4,4-dibromo-1-iodobutenone (**37**, <1%, t_R = 15.4 min), and 1,1,3,3-tetrabromoacetone (**24**, <1%, t_R = 16.0 min) were present. Analysis of the material in fractions 32–36 (68 mg) showed that it was composed of mostly haloforms; no new compounds were identified in this fraction. In fractions 24–25 (6 mg) 1,1,3-tribromo-2-propyl acetate (**27**, 1%, t_R = 14.5 min), 1,1,3,3-tetrabromo-2-propyl acetate (**28**, 5%, t_R = 18.8 min), and 3,3-dibromoacrolein (**34**, 10%, t_R = 5.5 min) were found by GC–MS.

Many identifications of compounds above were made by direct comparisons of NMR and GC–MS data with those of authentic samples.

Spectral data of compounds that were not compared with authentic samples follow. 1,1-Dibromo-3-iodoacetone (**23**): mass spectrum *m/e* (relative intensity) 340 (4), 342 (8), 344 (4), 169 (100). 1,3,3-Tribromo-1-iodopropene (**33**): mass spectrum *m/e* (relative intensity) 402 (1.5), 404 (4), 406 (4), 408 (1.5), 323 (56), 325 (100), 327 (48), 171 (20), 173 (38), 175 (20). 4,4-Dibromo-1-iodobutenone (**37**): mass spectrum *m/e* (relative intensity) 352 (2), 354 (4), 356 (2), 211 (52), 213 (100), 215 (48), 141 (8), 127 (16).

(c) *Molecular Distillation.* The essential oil (330 mg) was separated by molecular distillation at 40 °C (2 mm) into two volatile fractions (250 mg forerun, essentially 95% **1** and 5% **2**, and 30 mg for fraction 2) and a much less volatile fraction that remained in the distillation pot (fraction 3). Small amounts of bromochloroiodomethane (**6**, <1%, t_R = 3.5 min) and bromoiodomethane (**8**, <1%, t_R = 3 min) [mass spectrum *m/e* (relative intensity) 220 (60), 222 (60), 141 (40), 93 (100), 95 (100)] were found in fraction 2 in addition to compounds already mentioned above. Iodoform (**4**, 2%, t_R = 14.0 min), bromoacetone (**15**, <1%, t_R = 1.5 min), and iodoacetone (**16**, <1%, t_R = 3.1 min) were the only new compounds to be found in fraction 3.

Bromination of Halogenated Acetones in Aqueous Bicarbonate Solution. To bromoacetone (1.36 g) in water (25 ml) containing sodium bicarbonate (3 g), bromine (3.2 g) was added and the mixture stirred for 2 h. The mixture was extracted with CH_2Cl_2 and the extract washed with sodium bisulfite solution and dried. Evaporation of the solvent gave 2.1 g of an oil which was shown to be 72% 1,1,1-tribromoacetone (**20**) [^{1}H NMR spectrum δ 2.80; mass spectrum *m/e* (relative intensity) no M^+ ion, 249 (1), 251

(2.5), 253 (2.5), 255 (1), 213 (1), 215 (2), 217 (1), 185 (1), 187 (2), 189 (1), 170 (2), 171 (2), 172 (4), 173 (4), 174 (2), 175 (2), 91 (3), 93 (3), 43 (100)], 24% **1**, 2% **17**, and 2% starting material by ^{1}H NMR analysis.

Chloroacetone (**58**, 0.92 g) was brominated in a similar manner (Barrett et al., 1971) to give 1.5 g of an oil which by ^{1}H NMR analysis was a mixture of 70% 1,1-dibromo-1-chloroacetone (**21**) [^{1}H NMR spectrum δ 2.76; mass spectrum m/e (relative intensity) no M^+ ion, 205 (9), 207 (17), 209 (13), 211 (4), 169 (13), 171 (17), 173 (7), 43 (100)], 15% **5**, 6% 1-bromo-1-chloroacetone [^{1}H NMR spectrum δ 2.50 (s, 3 H), 5.86 (s, 1 H); mass spectrum m/e (relative intensity) 170 (0.6), 172 (0.7), 174 (0.2), 127 (2.0), 129 (2.6), 131 (0.7), 43 (100)], and 7% starting material.

When iodoacetone was brominated in the same manner, however, most of the starting material was recovered together with substantial amounts of bromoacetone and 1,1-dibromoacetone. Also found were very small amounts of dibromoiodomethane, diiodobromomethane, 1-bromo-1-iodoacetone [mass spectrum m/e (relative intensity) 262 (36), 264 (36), 219 (11), 201 (11), 128 (19), 127 (19), 43 (100)], 1-bromo-3-iodoacetone (**19**) [mass spectrum m/e (relative intensity) 262 (11), 264 (11), 169 (21), 128 (100), 127 (57), 121 (36), 123 (36)], 1,1-diiodoacetone [mass spectrum m/e (relative intensity) 310 (100), 267 (12), 128 (31), 127 (30), 43 (96)], and 1,3-diiodoacetone [mass spectrum m/e (relative intensity) 310 (50), 183 (100), 169 (53), 141 (44), 128 (47), 127 (42)].

1,1,3,3-Tetrabromoacetone (3.7 g) was brominated in the same manner with 1.6 g of bromine to give 3.8 g of an oil which by ^{1}H NMR and GC–MS analysis was a mixture of 90% **1**, 5% starting material, and 5% pentabromoacetone (**48**) [mass spectrum m/e (relative intensity) no M^+ ion, 249 (9), 251 (30), 253 (28), 255 (9), 199 (53), 201 (100), 203 (49)].

Tribromination of Acetone in HOAc. To acetone (1.16 g) in glacial acetic acid (50 ml) was added 9.5 g of bromine. After discharge of the bromine color (18 h), the reaction mixture was poured into water, the mixture extracted with CH_2Cl_2, the extract washed with water and aqueous $NaHCO_3$ and dried ($MgSO_4$), and the solvent evaporated. ^{1}H NMR and GC–MS analysis of the residue (5.8 g) showed that the product was a mixture of 10% **18**, 65% **22**, and 20% **24**.

Halogenated 2-Propanols. To $NaBH_4$ (0.03 g) in MeOH (20 ml), 1,1,3,3-tetrabromoacetone (0.37 g) was added. After standing for 1 h the solvent was removed under reduced pressure and the residue extracted with methylene chloride to give 0.35 g of 1,1,3,3-tetrabromo-2-propanol (**43**, t_R = 17.2 min) [^{1}H NMR spectrum δ 3.46 (d, OH, J = 5 Hz), 4.24 (q, 1 H, J = 5 Hz), 5.96 (d, 2 H, J = 5 Hz); mass spectrum m/e (relative intensity) 372 (0.2), 374 (0.7), 376 (1), 378 (0.7), 400 (0.2), 201 (50), 203 (100), 205 (48), 122 (72), 124 (72)].

A similar reduction of 1,1,3-tribromoacetone gave 1,1,3-tribromo-2-propanol (**26**) [^{1}H NMR spectrum δ 3.30 (d, OH, J = 5 Hz), 3.66 (d, 2 H, J = 5 Hz), 4.16 (p, 1 H, J = 5 Hz), 5.40 (d, 1 H, J = 5 Hz); mass spectrum m/e (relative intensity) 294 (0.1), 296 (0.3), 298 (0.3), 300 (0.1), 201 (4), 203 (8), 205 (4), 171 (4), 173 (8), 175 (4), 123 (100), 125 (100)].

Halogenated 2-Acetoxypropanes. A solution of 1,1,3,3-tetrabromo-2-propanol (0.30 g) and acetyl chloride (5 ml) was allowed to stand 12 h. Water was added, the mixture extracted with CH_2Cl_2, and the extract washed with water and dried ($MgSO_4$). Removal of the solvent gave 1,1,3,3-tetrabromo-2-propyl acetate (**28**) [^{1}H NMR spectrum δ 2.24 (s, 3 H), 5.70 (t, 1 H, J = 5 Hz), 5.90 (d, 2 H, J = 5 Hz); mass spectrum m/e (relative intensity) no M^+ ion, 354 (1), 356 (2), 358 (5), 360 (2), 362 (1), 335 (2), 337 (4), 339 (4), 341 (2), 275 (31), 277 (100), 279 (100), 281 (31), 243 (36), 245 (66), 247 (35), 43 (base peak, >100)].

Acetylation of 1,1,3-tetrabromo-2-propanol under similar conditions gave 1,1,3-tribromo-2-propyl acetate (**27**) [mass spectrum m/e (relative intensity) no M^+ ion, 276 (2), 278 (5), 280 (5), 282 (2), 257 (1), 259 (2), 261 (1), 165 (100), 167 (100), 43 (base peak, >100)].

Halogenated 1,2-Epoxypropanes. On one occasion $NaBH_4$ reduction of 1,1,3,3-tetrabromoacetone gave in addition to **43** an epoxide (ca. 25% of the product), *trans*-1,3,3-tribromopropene oxide (**29**) [^{1}H NMR spectrum δ 5.30 (d, J = 7 Hz), 5.18 (s), 3.75 (d, J = 7 Hz); mass spectrum m/e (relative intensity) 292 (0.1), 294 (0.3), 296 (0.8), 298 (0.1), 213 (30), 215 (58), 217 (28), 185 (17), 187 (33), 189 (17), 171 (8), 173 (15), 175 (7), 105 (100), 107 (97)] which could be separated by silica gel chromatography. This compound was also formed (10% conversion) on treatment of 1,1,3,3-tetrabromo-2-propanol with *p*-toluenesulfonyl chloride in benzene (12 h reflux).

Supplementary Material Available: Spectral data (GC, NMR, MS) for identification of natural compounds discussed, by comparison with authentic samples obtained by synthesis or from commercial sources (5 pages). Ordering information is given on any current masthead page.

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