groups including α,β-unsaturated ketones, lactones, α,β-unsaturated esters, nitriles, and hydrazones. In one case (entry 3), the reaction was carried out in two steps and intermediate dithio ester **3** was isolated. The two-step procedure, however, offered no improvement in overall yield.

Several observations concerning the choice of base in these reactions are noteworthy. First, when 2-methylcyclohexanone was treated with 2 equiv of 4-methyl-2,6-di-*tert*-butylphenoxide[7] and 2.5 equiv of carbon disulfide in THF for 12 h and then quenched with methyl iodide, a single product was obtained which was identical in all respects (TLC, NMR, and IR) with ketene dithioacetal **6** prepared by the procedure utilizing LHDS. No methyl β-keto dithio ester resulting from addition of the more substituted enolate to carbon disulfide was observed. Second, two examples (entries 5 and 6) reveal that the reaction is sometimes sensitive to the choice of base. Here, LDA afforded low yields of conjugated ketene dithioacetals and significant amounts of condensation material. Good yields of conjugated ketene dithioacetals could be obtained from γ-butyrolactone and methyl crotonate (entries 5 and 6, respectively) when lithium hexamethyldisilazide was employed as the base.

In summary, this one-step procedure allows for the facile preparation of ketene dithioacetals conjugated to a variety of functional groups. Investigations into synthetic applications of conjugated ketene dithioacetals are in progress in our laboratory.

Experimental Section

Proton NMR spectra were recorded on either a Varian EM-360L or JEOL FX-90Q instrument. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane as internal standard. Infrared spectra were recorded on a Perkin-Elmer 710B grating spectrophotometer. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analysis were determined by Galbraith Laboratories, Inc., Knoxville, TN.

Hexamethyldisilazane was distilled and stored over 3-Å molecular sieves. Diisopropylamine was distilled over CaH_2 and stored over KOH. Tetrahydrofuran was distilled from sodium–benzophenone prior to use.

1,1-Bis(methylthio)-2-(carbomethoxy)-1,3-butadiene (10). A solution containing 50 mL of dry THF and 8.25 g (51.1 mmol) of freshly distilled hexamethyldisilazane was cooled under nitrogen to 0–5 °C, and 21.3 mL (2.3 M in hexane, 51.1 mmol) of *n*-butyllithium was added. After 15 min the solution was cooled to −78 °C and 9.13 g (51.0 mmol) of freshly distilled HMPA was added. Approximately 30 min later, 4.93 g (49.3 mmol) of methyl crotonate in 5 mL of dry THF was added dropwise over a period of 30 min. The solution was stirred at −78 °C for an additional 20 min and 3.88 g (51.0 mmol) of carbon disulfide was added in one addition. The solution immediately turned red and was allowed to warm to 0 °C over a 2-h period, whereupon the solution was cooled to −78 °C and a solution of lithium hexamethyldisilazide [prepared from 8.25 g (51.1 mmol) of hexamethyldisilazane and 21.3 mL (51.1 mmol) of *n*-butyllithium] in 50 mL of THF was added via double-tipped needle. The solution was stirred at −78 °C for 30 min upon completion of the addition and 14.48 g (102 mmol) of methyl iodide was added in one addition. The solution was allowed to warm to room temperature over a period of 1 h and then stirred at room temperature for 2 h. The dark solution was poured into saturated aqueous ammonium chloride and extracted with ether. The combined organic phase was washed with saturated aqueous ammonium chloride, water, brine, and dried over magnesium sulfate. Removal of solvent in vacuo gave 10.0 g of crude material. Purification by column chromatography (silica gel, petroleum ether/10% diethyl ether, v/v) afforded pure ketene dithioacetal **10**: 7.1 g (71% yield); IR (CCl_4) 3080 (w), 3000 (m), 2920 (s), 1740 (vs), 1605 (m), 1440 (s), 1310 (vs), 1295 (vs), 1200 (vs), 1165 (vs), 990 (s), 918 (s) cm^{-1}; NMR (CCl_4) δ 2.32 (s, 3 H), 2.35 (s, 3 H), 3.80 (s, 3 H), an ABC pattern [5.10 (dd, J_{AB} = 1 Hz, J_{AC} = 17 Hz, 1 H), 5.22 (dd, J_{BA} = 1 Hz, J_{BC} = 11 Hz, 1 H), 6.87 (dd, J_{CA} = 17 Hz, J_{CB} = 11 Hz, 1 H)].

Anal. Calcd for $C_8H_{12}O_2S_2$: C, 47.02; H, 5.93. Found: C, 47.19; H, 5.98.

Conjugated ketene dithioacetals listed in Table I were prepared according to the above procedure, utilizing either lithium diisopropylamide (procedure A) or lithium hexamethyldisilazide (procedure B) as the base. **6**: IR (CCl_4) 2985, 2940, 2875, 1700, 1380, 1320, 1135, 875, 853 cm^{-1}; NMR ($CDCl_3$) δ 1.13 (d, *J* = 6.0 Hz, 3 H), 1.24–2.22 (m, 4 H), 2.32 (s, 3 H), 2.34 (s, 3 H), 2.36–2.71 (m, 2 H), 3.02–3.36 (m, 1 H). **7**: IR (CCl_4) 2960, 2905, 1688, 1425, 1335, 1220, 1085, 1035, 890 cm^{-1}; NMR (CCl_4) δ 1.00 (t, *J* = 7.5 Hz, 3 H), 1.95 (s, 3 H), 2.15 (s, 3 H), 2.23 (s, 3 H) 2.53 (q, *J* = 7.5 Hz, 2 H). **8**: IR (CCl_4) 2970, 2920, 1630, 1605, 1385, 1300, 1200, 1115, 1010, 930 cm^{-1}; NMR ($CDCl_3$) δ 1.19 (d, *J* = 6.5 Hz, 6 H), 2.24 (s, 3 H), 2.30 (s, 3 H) 2.34 (t, *J* = 5.5 Hz, 2 H), 3.03 (t, *J* = 5.5 Hz, 2 H), 4.34 (septet, *J* = 6.5 Hz, 1 H), 5.31 (s, 1 H). Anal. Calcd for $C_{12}H_{18}O_2S_2$: C, 55.77; H, 7.04. Found: C, 55.52; H, 6.95. **9**: IR (CCl_4) 2975, 2910, 1740, 1560, 1435, 1370, 1218, 1080, 1040, 960, 900 cm^{-1}; NMR (CCl_4) δ 2.45 (s, 3 H), 2.47 (s, 3 H), 2.98 (t, *J* = 7.0 Hz, 2 H), 4.22 (t, *J* = 7.0 Hz, 2 H). Anal. Calcd for $C_7H_{10}O_2S_2$: C, 44.20; H, 5.31. Found: C, 44.05; H, 5.39. **11**: IR (CCl_4) 2925, 2200, 1540, 1430, 920 cm^{-1}; NMR (CCl_4) δ 2.05 (s, 3 H), 2.40 (s, 6 H). Anal. Calcd for $C_6H_9NS_2$: C, 45.24; H, 5.80. Found: C, 45.46; H, 5.70. **12**: IR (CCl_4) 2995, 2980, 2930, 2865, 1550, 1470, 1465, 1440, 1050, 1025, 890 cm^{-1}; NMR ($CDCl_3$) δ 2.12 (s, 3 H), 2.20 (s, 3 H), 2.27 (s, 3 H), 2.90 (s, 6 H), 7.73 (br s, 1 H). Anal. Calcd for $C_8H_{16}N_2S_2$: C, 47.02; H, 7.88. Found: C, 47.01; H, 7.91.

Methyl 2-Methyl-3-oxopentanedithioate (3). The ketone enolate of 2-pentanone (1.74 g, 20.2 mmol) was generated with lithium diisopropylamide in THF at −78 °C as described above. Carbon disulfide (1.69 g, 22.2 mmol) was added in one addition and the solution was stirred at −78 °C for 2 h. Methyl iodide (3.12 g, 22.0 mmol) was added and the solution was allowed to warm to room temperature over a period of 1 h. The solution was poured into saturated aqueous ammonium chloride and extracted with ether. The combined organic phase was washed with saturated aqueous ammonium chloride, water, brine, and dried over magnesium sulfate. Removal of solvent in vacuo gave 3.48 g of crude material. Purification by column chromatography (silica gel, petroleum ether/10% diethyl ether, v/v) afforded pure dithio ester **3**: 3.26 g (92% yield); IR (CCl_4) 2960, 2920, 1720, 1450, 1410, 1375, 1345, 1180, 960, 923 cm^{-1}; NMR (CCl_4) δ 0.97 (t, *J* = 8.0 Hz, 3 H), 1.43 (d, *J* = 7.5 Hz, 3 H), 1.87–2.67 (m, 2 H), 2.63 (s, 3 H), 4.23 (q, *J* = 7.5 Hz, 1 H).

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Registry No. 1, 17649-90-0; 2, 28248-88-6; 3, 79299-97-1; 4, 79299-98-2; 6, 79299-99-3; 7, 51507-08-5; 8, 79300-00-8; 9, 21441-31-6; 10, 79300-01-9; 11, 79300-02-0; 12, 79300-03-1; cyclohexanone, 108-94-1; 2-methylcyclohexanone, 583-60-8; 2-pentanone, 96-22-0; 3-(1-methylethoxy)-2-cyclohexen-1-one, 58529-72-9; γ-butyrolactone, 96-48-0; methyl crotonate, 18707-60-3; propanenitrile, 107-12-0; propanal dimethylhydrazone, 7422-93-7.

Secondary Metabolites from a Red Alga (*Laurencia intricata*): Sesquiterpene Alcohols[1a]

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We recently described the isolation and characterization of a new, 15-carbon nonterpenoid enyne, bermudenynol

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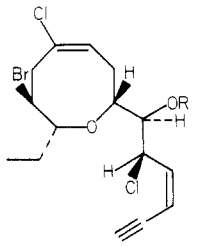
(**1a**), and its acetate (**1b**) from the red alga *Laurencia*

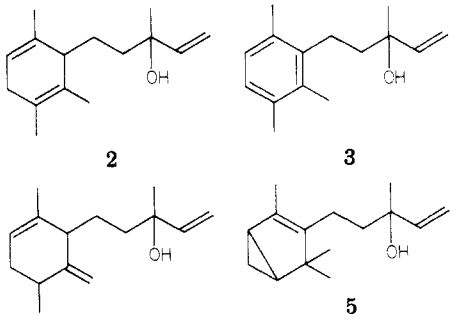


1a, R = H
b, R = $COCH_3$

intricata, collected in Bermuda.[2] We now report the isolation and characterization from this alga of four sesquiterpene alcohols. One of these, bicyclolaurencenol, possesses a novel bicyclic skeleton and seems to represent a biogenetic link between two groups of sesquiterpenes previously found in various *Laurencia* species.

^1H NMR analysis of the less polar components obtained by acetone extraction of *L. intricata* indicated the presence of a mixture of terpenoids containing a vinyl group. Silica gel chromatography, followed by chromatography on silver nitrate impregnated silica, provided pure samples of four closely related sesquiterpene alcohols.

Two of these compounds, both characterized by a rearranged isoprenoid skeleton, were readily identified by their infrared, ^1H NMR, and mass spectra as **2** and **3**,



previously characterized from *L. nidifica* by Sun et al.[3,4] The third component was also recognized on the basis of its spectral data to be another known rearranged sesquiterpene alcohol, dactylenol, **4**, recently characterized from extracts of the sea hare *Aplysia dactylomela* by Schmitz et al.[5] Although several species of sea hares are known to browse on *Laurencia* spp., a dietary source of dactylenol had not been identified. *L. intricata* may well be such a source.

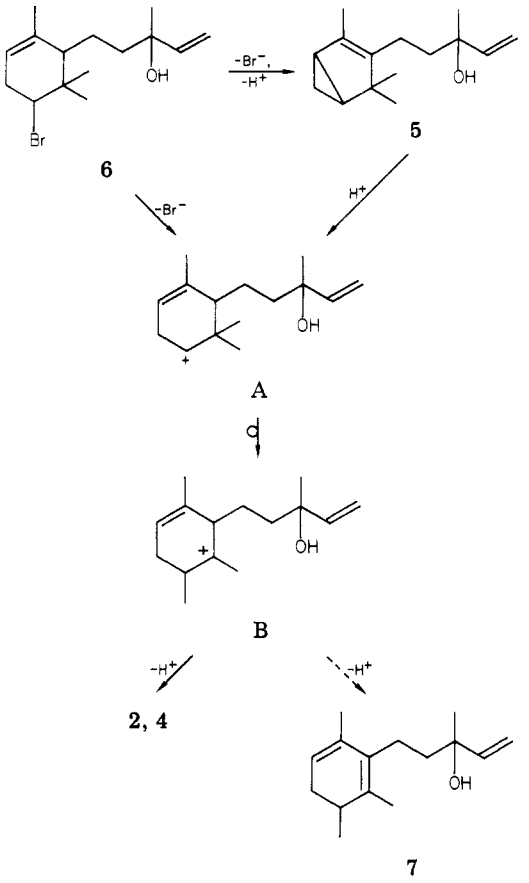


Figure 1.

The fourth sesquiterpene alcohol from this alga, bicyclolaurencenol, which was the most mobile on silver nitrate impregnated silica gel, proved to be the most interesting. Its molecular weight (*m/e* 220) demonstrated constitutional isomerism with **2** and **4** ($C_{15}H_{24}O$) and the similarity of the mass spectral fragmentation patterns in the three isomers mandated quite similar structures for the three molecules. The ABX system in the olefinic region of the ^1H NMR spectrum (δ 5.96, 5.27, 5.07), the methyl singlet at δ 1.27, and the infrared absorption at 3580 cm^{-1} attested to the presence of the methyl vinyl carbinol moiety characteristic of this series. High-field ^1H NMR resonances at δ 0.64 and −0.11 were indicative of the presence of a cyclopropane and corresponded closely to data reported for bicyclo[3.1.0]hex-2-ene.[6] The relatively low molar extinction coefficient (ϵ 3400) of the ultraviolet absorption maximum of bicyclolaurencenol was best accomodated by a vinyl cyclopropane chromophore. Considerable alkyl substitution on the chromophore was suggested by the wavelength of the absorption maximum and was corroborated by the presence of a vinyl methyl signal at δ 1.66 and the absence of olefinic signals, other than the ABX system, in the ^1H NMR spectrum. Additional methyl singlets at δ 1.04 and 0.99 suggested a geminal dimethyl group and, therefore, an unrearranged sesquiterpene skeleton. Careful consideration of these and the remaining spectral data led us to structure **5** for bicyclolaurencenol.

Bicyclo[3.1.0]hex-2-enes do not appear to have been found previously among algal metabolites. However, structure **5** is obviously closely related to its rearranged congenors **2**–**4**, as well as to the unrearranged α-snyderol (**6**).[7] One possible biosynthetic scheme relating these

(1) (a) Contribution No. 849 from the Bermuda Biological Research Station. (b) Work performed while the author was on leave from the USDA, Forest Service, Northeastern Forest Experiment Station, Warren, PA. (c) Present address: Department of Chemistry, Montana State University, Bozeman, MT 59717.

(2) Cardellina, J. H., II; Horsley, S. B.; Clardy, J. C.; Leftow, S. R.; Meinwald, J., submitted for publication in *Can. J. Chem.*

(3) Sun, H. H.; Warasekiewicz, S. M.; Erickson, K. L. *Tetrahedron Lett.* **1976**, 585.

(4) The hydroxyl bearing carbon atom in **3** appears to have the *R* configuration on the basis of a comparison of the specific rotation of **3** with those of (−)-(*R*)-linalool, $[\alpha]_D$ −21.5° (Ohloff, G.; Klein, E. *Tetrahedron* **1962**, *18*, 37), (−)-(*R*)-nerolidol, and (−)-(*R*)-geranylinalool, $[\alpha]_D$ −10.1° (Kimland, B.; Norin, T. *Acta Chem. Scand.* **1967**, *21*, 825). Possessing optical rotations of identical sign and similar magnitude, alcohol **3** and the three models have a similar array of substituents on the chiral carbon; the only difference is the aromatic ring rather than a double bond three carbons distant from the chiral center. The same stereochemistry can be inferred for **2**, since it autoxidizes to **3**.[3]

(5) Schmitz, F. J.; McDonald, F. J.; Vanderah, D. N. *J. Org. Chem.* **1978**, *43*, 4220.

(6) Schneider, M. P.; Crawford, R. J. *Can. J. Chem.* **1970**, *48*, 628.

sesquiterpenoids is given in Figure 1. In this scheme, solvolysis of 6 with participation of the homoallylic double bond would give rise to 5.[8] Protonation of the tetrasubstituted double bond of the bicyclo[3.1.0]hex-2-ene ring system of 5 or solvolysis of 6 without double bond participation could lead to cation A, which upon rearrangement to cation B provides an immediate precursor for 2 and 4. (Another likely deprotonation product from B, 7, has not yet been observed.) On this basis, bicyclolaurencenol is simply the cyclopropylcarbinyl cousin of the homoallylic halide, α-snyderol, and its rearranged dehydrohalogenation products.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer, ultraviolet spectra on a Beckman DB-G spectrophotometer, and optical rotations on a Perkin-Elmer Model 141 polarimeter. Mass spectra were obtained on an Associated Electronic Industries MS-902 mass spectrometer operated at 70 eV. ^{1}H NMR spectra were obtained on a Varian EM-390 spectrometer; chemical shifts are reported in parts per million (δ units) downfield from tetramethylsilane as an internal standard. Only well-resolved resonances are described.

Isolation of Sesquiterpene Alcohols 2, 3, 4, and 5. Specimens of *Laurencia intricata* were collected at depths of 1–3 feet in Castle Harbour, Bermuda in October 1979, and preserved in acetone prior to analysis. The acetone extracts were decanted and concentrated under reduced pressure. The residual aqueous phase was extracted with CH_2Cl_2 to yield a dark green syrup (4.5 g), which was chromatographed on Florisil. Fourteen fractions were collected from the Florisil column (136 g) by elution with mixtures of hexane, ethyl acetate, and methanol of gradually increasing polarity. ^{1}H NMR analysis of fractions 1–3 indicated the presence of a series of sesquiterpenes containing vinyl groups. Further chromatography of fractions 1–3 on silica gel (135 g of Biosil A, 200–400 mesh), eluting with hexane–ether (9:1) gave a mixture of sesquiterpenes. The mixture was separated on silica gel (44 g Woelm, 32–63 μm) impregnated with 10% $AgNO_3$; elution with hexane–ether mixtures yielded the four sesquiterpene alcohols 5, 2, 3, and 4. Final purification of each component was accomplished by gel filtration through Sephadex LH-20 (2 × 100 cm) with CH_2Cl_2–MeOH (1:1). Alcohol 2 was obtained as a colorless oil [15 mg, $[\alpha]^{25}_D$ + 29.0° (*c* 0.84, $CHCl_3$)], 3 as a colorless oil [18 mg, $[\alpha]^{25}_D$ −12.1° (*c* 0.48, $CHCl_3$)], dactylenol, 4, as a colorless oil (62 mg).

Bicyclolaurencenol (5). Bicyclolaurencenol (30 mg) was obtained as a colorless oil: $[\alpha]^{25}_D$ −16.1° (*c* 0.67, $CHCl_3$); IR (CCl_4) ν_{max} 3580, 3045, 1640, 990, 915 cm^{-1}; UV (cyclohexane) λ_{max} 227 nm (ε 3400); ^{1}H NMR ($CDCl_3$) δ 5.96 (1 H, dd, *J* = 17.25, 10.5 Hz), 5.27 (1 H, dd, *J* = 17.25, 1.5 Hz), 5.07 (1 H, dd, *J* = 10.5, 1.5 Hz), 1.66 (3 H, s), 1.27 (3 H, s), 1.04 (3 H, s), 0.99 (3 H, s), 0.64 (1 H, m, *J* = 8.1, 7.8, 3.6 Hz), −0.11 (1 H, m, *J* = 3.8, 2.7 Hz); mass spectrum, *m/e* (relative intensity) 220 (M^+, 18), 202 (4), 187 (12), 145 (8), 135 (23), 134 (71), 133 (15), 122 (15), 121 (64), 120 (28), 119 (100), 107 (17), 105 (25), 94 (14), 91 (20), 81 (13), 79 (11), 77 (12), 71 (12), 55 (10), 43 (16); mol wt calcd for $C_{15}H_{24}O$ 220.1827, found 220.1837.

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Registry No. 2, 59700-20-8; 3, 79373-32-3; 4, 58542-82-8; 5, 79373-33-4.

(7) Fenical, W.; Howard, B. M. *Tetrahedron Lett.* **1976**, 41.

(8) Any halogenated sesquiterpenes, such as the snyderols, present in the extracts would most likely undergo solvolytic type rearrangements on the silver nitrate impregnated silica gel. That 5 is, in fact, a natural product was borne out by examination of the ^{1}H NMR and mass spectra of the sesquiterpene mixture prior to argentate chromatography. The mass spectrum revealed no halogen-containing fragment ions or any ions of mass larger than *m/e* 220. The ^{1}H NMR spectrum not only possessed signals for the geminal methyls of 5 but conspicuously lacked any signal near δ 4.05 for protons on the bromomethines of the snyderols. We thank referee II for informative suggestions in this regard.

Perchlorodihydrotrindene

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The pyrolysis of hexachlorocyclopentadiene[1-4] (1) or perchlorobi-2,4-cyclopentadien-1-yl[5,6] (2) gives as a major product a solid (3, mp 344–346 °C) analyzing for C_5Cl_4 (Chart I). . The structure of 3 was originally assigned as perchlorofulvalene and subsequently revised[4] to the general perchlorodihydrotrindene structure (4), on the basis of molecular weight determination (564, boiling point elevation) and degradation to trindane (5). This paper reports mass spectral data establishing unequivocally that 3 is $C_{15}Cl_{12}$ and compelling ^{13}C NMR evidence for the structural assignment of 3. The ^{13}C resonances of 1 and 3, together with the ^{13}C–^{13}C coupling constants of 1, are also assigned.

Results and Discussion

The mass spectrum of 3 gives a molecular ion (M^+·) starting at *m/e* 600 which has an isotope cluster with relative intensities corresponding to those expected from the isotopic abundances of $C_{15}Cl_{12}$. Fragmentation ion clusters are found starting at *m/e* 565, 530, 495, 460, 425, 390, and 355. These clusters may be assigned to ions arising from the loss of one to seven Cl atoms, respectively, from the molecular ion. The intensities[7] of these ions appear to vary in a systematic manner as follows: M^+·, 8; M^+· − Cl, 43; M^+· − 2Cl, 14; M^+· − 3Cl, 100; M^+· − 4Cl, 11; M^+· − 5Cl, 43; M^+· − 6Cl, 7; M^+· − 7Cl, 27.

The relative prevalence of M^+· − 3Cl could result from the loss of three allylic chlorines from the fused ring system to give a $C_{15}Cl_9^+$ ion (6) which would then have a macrocyclic ring system with 14 π electrons, satisfying the Hückel 4*n* + 2 rule for aromatic stability. Starting at *m/e* 247.5, an interesting isotope cluster (relative intensity 13) is found. Its peaks are separated by half integral mass numbers; their multiplet relative intensities are equal to those of the *m/e* 495 ion. This is compelling evidence for assigning the *m/e* 247.5 ion as $C_{15}Cl_9^{2+}$, which could arise from the loss of an electron from $C_{15}Cl_9^+$.

The chemical evidence for the trindene ring system in 3 is very strong. Degradation of 3 with lithium and *tert*-butyl alcohol gives 5,[1] a result confirmed by us. Compound 5 has also been obtained[4] by hydrogenating 3 over plati-

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(3) (a) C. F. Baranauckas, U. S. Patent 2 801 269 (1957); (b) V. Mark, *ibid.*, 3 099 693 (1963).

(4) V. Mark, *Tetrahedron Lett.*, 333 (1961).

(5) E. T. McBee, J. D. Idol, Jr., and C. W. Roberts, *J. Am. Chem. Soc.*, 77, 4375 (1955).

(6) E. T. McBee, C. W. Roberts, and J. D. Idol, Jr., *J. Am. Chem. Soc.*, 77, 4942 (1955).

(7) All relative intensities are based on the height of the highest peak of each isotope cluster, a value of 100 being arbitrarily assigned for the M^+· − 3Cl ion.

0022-3263/81/1946-5035$01.25/0