tanes, the stereochemistry of which correlates with observations of Johnson and co-workers in the respective epoxides.[6,9] In fact treatment of the epoxide[9] derived from ketone **8** (prepared via conditions of Johnson and co-workers)[6] with 1.5 equiv of reagent **2** in Me_2SO at 40 ± 2 °C for 20 h affords oxetane **8** in 78% yield, thus confirming the intermediacy of epoxides **3** in the formation of oxetanes **4.** It appears that epoxides **3**[10] are very susceptible to nucleophilic attack and ring opening by excess reagent **2** to intermediates of the type **5** under these reaction conditions. Temperature seems to be of critical importance in the conversion of ketone **8** into the respective oxetane. At 40 ± 2 °C the only product isolated is oxetane **8;** however, at 45 ± 2 °C 2-[4-*tert*-butylcyclohexenyl]ethanol is formed in 17% yield as a side product. Nevertheless oxetanes of the type depicted in structure **4** can now be conveniently prepared by a one-step synthesis from ketones **1** by using 3 equiv of the sodium anion of dimethyl *N*-(*p*-toluenesulfonyl)sulfoximine (**2**) in Me_2SO at 40–45 °C for 16 to 20 h. Further experiments on the synthesis, stereochemistry, and utilization of 2,2-disubstituted oxetanes are in progress.

Acknowledgment. We thank the Robert A. Welch Foundation for the funds (Grants No. E-518) to support this research.

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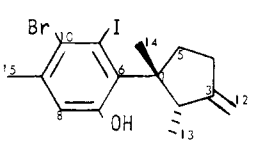
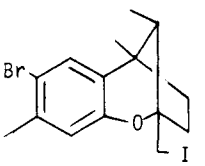
Marine Natural Products. 18. Iodinated Sesquiterpenes from the Red Algal Genus *Laurencia*[1]

Sir:

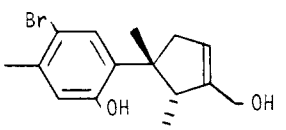
In recent years a great deal of attention has been focused on the secondary metabolites of marine algae. In particular, the genus *Laurencia* has been found to be a source of bromo and bromochloro nonisoprenoids, sesquiterpenes, and diterpenes.[2] Among these, brominated and nonbrominated aromatic sesquiterpenes have been extensively reported.[3] In this communication we report the isolation of two iodobromo aromatic sesquiterpenes (**1, 2**), the first examples of iodinated sesquiterpenes, and a new compound (**3**) of the laurene type.



(1)

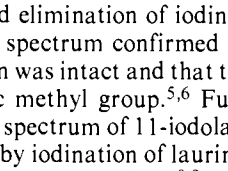


(2)

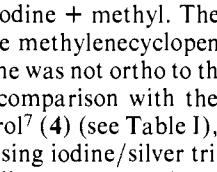


(3)

Laurencia nana Howe, collected at Isla Mujeres, Mexico, was air dried and Soxhlet extracted with dichloromethane. Column chromatography of the crude oil (17.6 g) resulted in the ready identification of filiformin[4] and 10-bromo-7-hydroxylaurene.[4] After storage of the column fractions in hexanes in the freezer, 14 mg of a new metabolite slowly solidified. The ^1H NMR spectrum displayed resonances due to a secondary methyl coupled to an allylic proton, a quaternary methyl, and two exocyclic protons, thus demonstrating a similarity to the ^1H NMR spectrum of the major metabolite, 10-bromo-7-hydroxylaurene. However, the aromatic region of the ^1H NMR spectrum displayed only one resonance and the aromatic methyl resonance was shifted downfield. The infrared and the ultraviolet spectra also supported the idea that this was a hydroxy laurene derivative. Analysis of the low resolution mass spectrum indicated a molecular formula of $C_{15}H_{18}BrIO$ and showed elimination of iodine and iodine + methyl. The ^{13}C NMR spectrum confirmed that the methylenecyclopentane portion was intact and that the iodine was not ortho to the aromatic methyl group.[5,6] Further, comparison with the ^{13}C NMR spectrum of 11-iodolaurinterol[7] (**4**) (see Table I), prepared by iodination of laurinterol using iodine/silver trifluoroacetate in chloroform,[8,9] gave excellent agreement (aromatic ring portion) with the natural compound. Consideration of these data[10] led to the assignment of the structure as that of 10-bromo-7-hydroxy-11-iodolaurene (**1**).



(4)



(5)

High performance liquid chromatography (LC) (silica, hexanes) of an early column chromatographic fraction resulted in the isolation of filiformin,[5] α-bromocuparene,[11] bromo ether A (**5**),[12] and a compound whose spectral data were very similar

Table I. Carbon Chemical Shifts of Algal Sesquiterpenes[a]

carbon	compound 1	2	4	5	6
1	49.1	45.8	48.6	n.o.	50.1
2	48.2	44.8	29.5	44.2	48.9
3	157.7	85.1	18.7	86.2	143.6
4	28.0	36.7	25.3	35.1	124.5
5	34.6	41.4	35.4	41.8	41.9
6	135.4	129.4	135.4	129.9	137.5
7	150.7	151.8	151.9	n.o.	147.4
8	133.1	117.5	133.2	117.7	125.4
9	134.9	136.6	134.9	136.9	136.5
10	121.8	115.8	121.8	115.2	121.4
11	116.5	128.2	115.9	128.6	132.4
12	106.7	11.2	16.2	34.6	62.3
13	19.8	7.1	24.2	7.2	15.0
14	25.4	20.5	22.3	20.4	28.4
15	20.0	22.4	19.7	22.5	22.4
					168.7
					170.9
					21.6
					20.9

[a] n.o. = not observed. Chemical shifts are in parts per million from Me_4Si in $CDCl_3$.

to those of bromo ether A. The 90-MHz ^1H NMR spectrum of this compound displayed signals due to three methyl groups at 0.74 (3 H, d, J = 7 Hz), 1.37 (3 H, s), and 2.27 ppm (3 H, s), two protons on a carbon bearing halogen at 3.24 and 3.42 ppm (1 H each, AB quartet, J = 11 Hz), and two aromatic protons at 6.60 (1 H, s) and 7.10 ppm (1 H, s). The mass spectrum of this compound showed a molecular formula of $C_{15}H_{18}BrIO$. After loss of iodine, the mass spectrum was superimposable on the mass spectrum of bromo ether A (**5**) after loss of bromine. The ^{13}C NMR spectra of the two compounds were essentially identical except for the resonance of carbon 12. A shift in this resonance of −23.4 ppm can only be ascribed to replacement of a bromine with an iodine.[5,6] Consideration of these data[13] led assignment of the structure as that of iodo ether A (**2**). Iodination of 10-bromo-7-hydroxylaurene using iodine/silver trifluoroacetate in chloroform[8] gave a product in 23% yield identical in all respects with the natural product.

To facilitate separation, the later column chromatographic fractions were acetylated using acetic anhydride/pyridine. LC of the resulting oil gave filiforminyl acetate[4] and a slow-forming solid. Examination of the 90-MHz ^1H NMR spectrum of the latter compound showed the presence of four quaternary methyls, a secondary methyl, two protons α to an acetate, an olefinic proton, and two aromatic protons. The IR spectrum indicated two acetate carbonyls typical of a phenolic acetate and a primary acetate. Analysis of the mass spectrum gave a molecular formula of $C_{19}H_{23}BrO_4$. The ^{13}C NMR spectrum displayed resonances for two acetates, an aromatic ring, an aromatic methyl, and an endocyclic olefin (trisubstituted). These data[14] established the structure as that of 10-bromo-7,12-diacetoxy-$\Delta^{2,3}$-laurene (**6**). Hydrolysis of the acetates using 2% KOH/EtOH gave the unaltered diol. The IR spectrum showed hydroxyl and olefinic absorbance. Mass spectral analysis gave a molecular formula of $C_{15}H_{19}BrO_2$. The 90-MHz ^1H NMR spectrum displayed resonances for a secondary methyl, two quaternary methyls, a methine, an allylic methylene, a methylene α to a hydroxyl, a vinyl proton, two aromatic protons, and two exchangeable protons. These data[15] also supported the structure as that of 10-bromo-7,12-dihydroxy-$\Delta^{2,3}$-laurene (**3**).

The relative stereochemistry of methyls 13 and 14 in compounds **1–3** is based on ^1H NMR and ^{13}C NMR[7] analogies to related compounds.

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(7) ^1H NMR (CCl_4): δ 0.57 (2 H, d, J = 6.0 Hz), 1.40 (3 H, s), 1.42 (3 H, s), 2.04 (3 H, s), 4.67 (1 H, s, D_2O), 7.77 (1 H, s), and 0.8–2.3 ppm (5 H, m).
(8) "Organic Syntheses", Collect. Vol. IV, Wiley, New York, 1963, p 547.
(9) Both 11-iodo- and 8-iodolaurinterol were formed in the reaction, with the latter predominating.
(10) Data: mp 147–153 °C dec; $[\alpha]_D$ +225° (*c* 0.24, $CHCl_3$); mass spectrum *m/e* (rel intensity) 420 (1), 422 (1), 295 (1), 293 (1), 281 (1), 279 (1), 199 (10), 149 (43), 85 (50), 83 (50), 73 (40), 71 (50), 69 (69), 67 (35), 60 (31), 57 (88), 55 (89), 43 (base), and 41 (55); UV (EtOH) 287 nm (log ϵ 3.68) and 292 (3.33); IR ($CHCl_3$) 2.84, 3.38, 6.04, 7.32, 8.29, 8.67, and 11.26 μm; ^1H NMR (CCl_4) 0.71 (3 H, d, J = 7.0 Hz), 1.24 (3 H, s), 2.07 (3 H, s), 3.00 (1 H, q, J = 7.0 Hz), 4.73 (1 H, s, D_2O), 4.90 (1 H, s), 5.00 (1 H, s), 7.53 (1 H, s), and 0.7–2.6 ppm (4 H, m).
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(12) M. Suzuki and E. Kurosawa, *Tetrahedron Lett.*, 4817 (1976).
(13) Data: mp 99–102 °C dec; $[\alpha]_D$ +29° (*c* 0.94, $CHCl_3$); high resolution mass spectrum (70 eV) *m/e* 419.9594 (calcd for $C_{15}H_{18}{}^{79}BrIO$, 419.9588); mass spectrum *m/e* (rel intensity) 422 and 420 (base), 295 (36), 293 (36), 239 (30), 237 (30), 214 (78), 201 (47), 199 (82), 169 (31), 145 (47), 128 (41), 11, (41), 107 (87), 94 (31), and 91 (32); UV (EtOH) 237 nm (log ϵ 3.89), 288 (3.34), and 298 nm (3.36); IR (CCl_4) 3.38, 6.18, 6.41, 6.76, 7.20, 8.06, 9.22, 10.73, and 11.34 μm; ^1H NMR (CCl_4) 0.74 (3 H, d, J = 7.0 Hz), 1.37 (3 H, s), 2.27 (3 H, s), 3.24 and 3.42 (2 H, AB quartet, J = 11 Hz), 6.60 (1 H, s), 7.10 (1 H, s), and 1.0–2.1 ppm (5 H, m).
(14) Data: mp 104–105 °C; $[\alpha]_D$ +74° (*c* 1.82, $CHCl_3$); high resolution mass spectrum (70 eV) *m/e* 396.0765 (calcd for $C_{19}H_{23}{}^{81}BrO_4$, 396.0760); mass spectrum *m/e* (rel intensity) 396 (4), 336 (11), 334 (11), 213 (40), 198 (73), 105 (30), 91 (38), 77 (27), and 43 (base); UV (EtOH) 231 nm (log ϵ 4.16, sh), 274 (3.20), 283 (3.16), and 290 (2.95); IR (neat) 3.14, 5.66, 5.72, 6.72, 6.88, 6.92, 7.34, 8.03, 8.14, 8.86, 9.32, 9.77, 11.02, 12.69, and 13.10 μm; ^1H NMR (CCl_4) 0.68 (3 H, d, J = 7.0 Hz), 1.27 (3 H, s), 2.04 (3 H, s), 2.28 (3 H, s), 2.39 (3 H, s), 2.56 (1 H, q, J = 7.0 Hz), 2.92 (1 H, br d, J = 5.0 Hz), 4.53 (2 H, s), 5.54 (1 H, br s), 6.90 (1 H, s), 7.26 (1 H, s), and 2.2 ppm (1 H, m).
(15) Data: mp 141–145 °C; $[\alpha]_D$ +100° (*c* 1.18, $CHCl_3$); mass spectrum *m/e* (rel intensity) 312 (2), 310 (2) 294 (4), 292 (4), 279 (4), 277 (4), 231 (4), 198 (11), 168 (20), 141 (40), 128 (30), 115 (63), 77 (base), and 51 (38); UV (EtOH) 233 nm (log ϵ 3.87), 286 (3.44), and 293 (3.42); IR (film) 2.96, 3.22, 3.40, 3.45, 6.04, 6.22, 6.71, 6.86, 7.18, 7.39, 7.99, 8.54, 9.36, 9.82, 9.09, 10.09, 10.36, 10.47, 11.40, 11.83, 12.13, and 12.48 μm; ^1H NMR (acetone-d_6) 0.72 (3 H, d, J = 7.0 Hz), 1.37 (3 H, s), 2.03 (3 H, s), 2.27 (3 H, s), 2.93 (2 H, m), 3.73 (1 H, t, J = 5.0 Hz, D_2O), 4.13 (2 H, br s, $w_{1/2}$ = 9.0 Hz), 5.51 (1 H, m), 6.77 (1 H, s), 7.19 (1 H, s), and 8.43 ppm (1 H, s, D_2O).
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Evidence Further Substantiating the $S_{RN}1$ Mechanism of Aromatic Substitution[1]

Sir:

Despite the common opinion that unsubstituted phenyl halides are unreactive with nucleophiles, several have in recent years been found to react readily with simple halobenzenes and like substrates, at room temperature or below, to form substitution products in high yield.[2] Representative reactions are those of eq 1 and 2. A few reactions of this class occur spon-

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