Diterpenes, Sesquiterpenes, and a C_{15}-Acetogenin from the Marine Red Alga *Laurencia mariannensis*

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In addition to 10 known compounds (**7**–**16**), one new brominated diterpene, 10-hydroxykahukuene B (**1**), two new sesquiterpenes, 9-deoxyelatol (**2**) and isodactyloxene A (**3**), one new brominated C_{15}-acetogenin, laurenmariallene (**4**), and two new naturally occurring halogenated sesquiterpenes (**5** and **6**) that were previously obtained as intermediates in a biomimetic synthetic study of rhodolaureol and rhodolauradiol have been isolated and identified from the organic extract of the marine red alga *Laurencia mariannensis*. The structures of these compounds were established by spectroscopic methods. The antibacterial and antifungal activities of new compounds **1**–**4** were evaluated.

The marine red algal species of the genus *Laurencia* (family Rhodomelaceae, order Ceramiales) are widely distributed along the coast in tropical and subtropical areas around the world. Previous investigations have demonstrated that species of this genus are prolific producers of halogenated secondary metabolites consisting of sesquiterpenes, diterpenes, triterpenes, and nonterpenoid C_{15}-acetogenins.[1] *L. mariannensis* is widely distributed from the tropical to subtropical regions in the Pacific. To date, only two papers describing chemical investigations of *L. mariannensis* have been published, demonstrating the presence of halogenated sesquiterpenes and C_{15}-acetogenins.[2,3]

As part of our continuing efforts directed toward the discovery of structurally interesting and biologically active compounds from Chinese marine red algal species of the Rhodomelaceae,[4–9] we have examined the chemical constituents of a sample of *L. mariannensis* that was collected from Hainan and Weizhou Islands of People's Republic of China. These efforts resulted in the identification of six new natural products, including one brominated diterpene, 10-hydroxykahukuene B (**1**), two sesquiterpenes, 9-deoxyelatol (**2**) and isodactyloxene A (**3**), one brominated C_{15}-acetogenin, laurenmariallene (**4**), and two halogenated sesquiterpenes (**5** and **6**) that were previously obtained as intermediates in a biomimetic synthetic study of rhodolaureol and rhodolauradiol.[10] In addition, 10 known compounds, elatol (**7**),[11] deschloroelatol (**8**),[11] (+)-(10*S*)-bromo-*β*-chamigrene (**9**),[11] nidificene (**10**),[12] obtusane (**11**),[13] (−)-(10*R*)-bromo-α-chamigrene (**12**),[11] isoafricanol (**13**),[14] (1′*R*,2*S*,2″*E*,5*R*,6*R*)-2-(1′-bromoethyl)-2,5-dimethyl-6-(penta-2″,4″-dienyl)tetrahydropyran (**14**),[15] irieol C (**15**),[16] and pinnaterpene C (**16**),[17] were also identified. Among these metabolites, **1** is a brominated diterpene with a unique prenylated chamigrane skeleton possessing a decalin ring system. This is the second report of this kind of compound.[18] In addition, the structural types exemplified by the known compounds **13** and **14** are rarely encountered as metabolites of *Laurencia* species. This report describes the isolation and structure determination of compounds **1**–**16**, as well as the evaluation of the antibacterial and antifungal activities of new compounds **1**–**4**.

Results and Discussion

The EtOAc-soluble fraction derived from the crude extract of dried, powdered *L. mariannensis* was purified by a combination of Si gel and Sephadex LH-20 column chromatography, as well as by preparative TLC, to yield compounds **1**–**16**.

Compound **1** was obtained as a colorless oil. EIMS data exhibited a characteristic $[M - H_2O]^+$ fragment ion cluster at *m*/*z* 448/446/444 (1:2:1), suggesting the presence of two bromine atoms in **1**. The molecular formula was determined as $C_{20}H_{32}Br_2O_2$ on the basis of HRESIMS (*m*/*z* 487.0654 $[M + Na]^+$, calcd for $C_{20}H_{32}{}^{79}Br^{81}BrO_2Na$, 487.0647), indicating four degrees of unsaturation. The ^{1}H NMR spectrum (Table 1) displayed four methyl singlets, three double-doublets attributed to methines bonded to heteroatoms, and a pair of broad singlets characteristic of an exocyclic methylene group. The ^{13}C NMR spectrum (Table 2) along with the DEPT and HSQC experiments revealed the presence of four methyl, seven methylene, four methine, and five quaternary carbon atoms. A detailed comparison of the NMR data with those reported for kahukuene B, a brominated diterpene possessing an unprecedented prenylated chamigrene structure that was isolated from the Hawaiian marine red alga *L. majuscula*,[18] revealed the similarity of the molecules. In contrast to kahukuene B, compound **1** possessed an additional secondary hydroxy group at C-10. This was suggested by the replacement of a carbon signal that would correspond to the C-10 methylene unit of kahukuene B with an oxygenated methine carbon at δ_C 74.8 in the ^{13}C NMR spectrum of **1**. Similarly, in the ^{1}H NMR spectrum of **1**, the signals for H_2-10 of kahukuene B were replaced by an oxygenated methine double-doublet at δ_H 3.31 (dd, J = 10.9, 5.3 Hz). In the HMBC spectrum, the observed long-range (^3J) correlations (Figure 1), including those from H_3-16 to C-2, C-6, and C-17, from H_3-17 to C-2, C-6, and C-16, from H-18a and H-18b to C-4 and C-6, from H_3-19 to C-8 and C-10, and from H_3-20 to C-8, C-12, and C-14, confirmed the planar structure for **1**.

The relative configuration of **1** was determined to be the same as that for kahukuene B by analysis of coupling constants and NOESY correlations, as well as by comparison with those of literature reports. The large coupling constant (J = 10.9 Hz) of H_{ax}-10 with H_{ax}-11 indicated an equatorial position for the hydroxy group at C-10. In the NOESY spectrum, the observed correlations of H-10 with H-8, H-12, and H_3-19 indicated the *cis*-orientation for these protons. On the other hand, no NOESY correlations between H_3-20 and the adjacent H-8 and H-12 were observed, while correlations of H_3-20 with H_{ax}-7, H_{ax}-11, and H_{ax}-15 were clearly displayed in the NOESY spectrum. This was consistent with the

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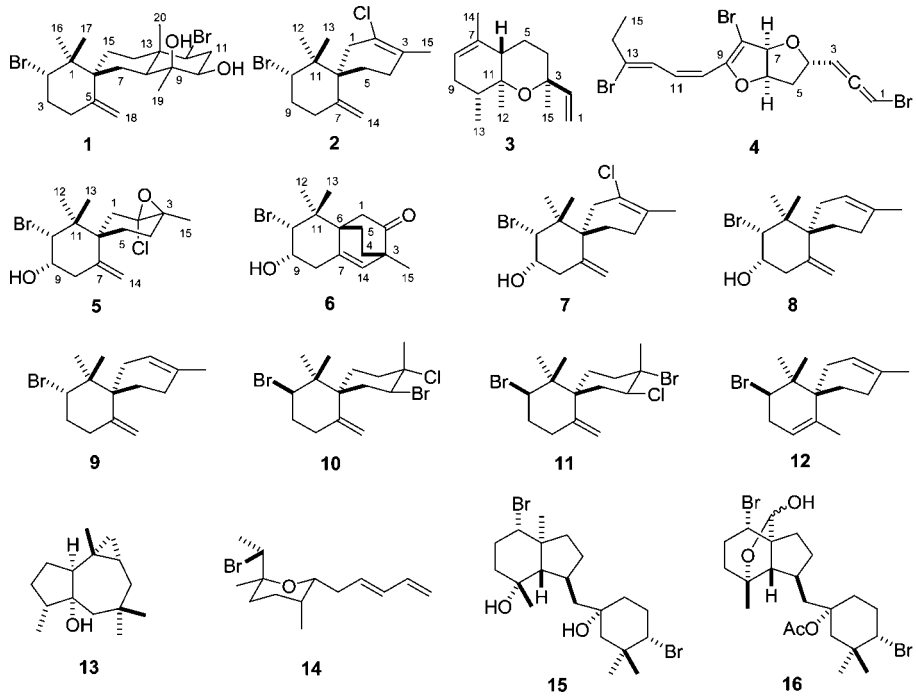

Table 1. ^{1}H NMR Data of Compounds **1**–**6** (500 MHz, $CDCl_3$, *J* in Hz)

no.	1	2	3	4	5	6
1a		2.30 (br d, 17.4)	4.94 (dd, 10.8, 1.4)	6.07 (dd, 5.7, 1.4)	2.56 (br d, 15.4)	2.10 (d, 17.9)
1b		2.60 (br d, 17.4)	5.11 (dd, 17.5, 1.4)		2.64 (d, 15.4)	2.42 (dd, 17.9, 3.3)
2	4.64 (dd, 13.0, 4.6)		5.93 (dd, 17.5, 10.8)			
3a	2.08 (m)			5.46 (dd, 6.7, 5.7)		
3b	2.28 (m)					
4a	2.10 (m)	1.78 (m)	1.55 (m)	4.37 (m)	1.49 (m)	1.49 (m)
4b	2.28 (m)	1.93 (m)	1.59 (m)		1.88 (m)	1.66 (m)
5a		1.60 (m)	1.57 (m)	2.02 (ddd, 13.6, 10.3, 5.8)	1.50 (m)	1.51 (m)
5b		1.87 (m)	1.87 (m)	2.48 (dd, 13.6, 4.6)	1.50 (m)	1.71 (m)
6			1.73 (dd, 8.6, 3.9)	5.31 (dd, 6.0, 5.8)		
7a	1.82 (dd, 12.6, 12.4)			5.81 (d, 6.0)		
7b	2.04 (dd, 12.6, 2.0)					
8a	0.91 (dd, 12.4, 2.0)	2.19 (m)	5.28 (br s)		2.47 (m)	2.75 (m)
8b		2.31 (m)			2.55 (m)	2.97 (m)
9a		2.05 (m)	1.62 (m)		4.14 (m)	4.10 (m)
9b		2.21 (m)	2.19 (br d, 17.4)			
10	3.31 (dd, 10.9, 5.3)	4.56 (dd, 12.9, 4.4)	2.08 (m)	6.64 (d, 8.1)	4.53 (d, 2.9)	4.47 (d, 4.4)
11a	2.26 (m)			7.19 (dd, 8.1, 7.6)		
11b	2.30 (m)					
12	3.80 (dd, 12.4, 4.2)	0.96 (s)	1.08 (s)	6.78 (d, 7.6)	1.03 (s)	1.18 (s)
13		1.13 (s)	0.94 (d, 6.7)		1.02 (s)	1.11 (s)
14a	1.31 (m)	4.60 (br s)	1.66 (d, 1.7)	2.76 (m)	5.15 (br s)	5.63 (br s)
14b	1.65 (m)	4.98 (br s)			5.23 (br s)	
15a	1.67 (m)	1.69 (br s)	1.27 (s)	1.27 (t, 7.6)	1.45 (s)	1.19 (s)
15b	1.74 (m)					
16	0.96 (s)					
17	1.21 (s)					
18a	4.79 (br s)					
18b	5.13 (br s)					
19	1.21 (s)					
20	1.16 (s)					

proposed *trans*-orientation between H_3-20 and H-8 and H-12. In addition, a NOESY correlation between H-2 and H-7b supported the *cis*-relationship assigned for H-2 and CH_2-7. The chemical shift values as well as coupling constants in **1** were similar to those of kahukuene B, further supporting these conclusions.[18] The above spectroscopic evidence established the relative configuration and resulted in the assignment of the structure of **1**, which was named as 10-hydroxykahukuene B. It should be noted that in the literature report[18] the configuration at C-2 for kahukuene B appeared to be incorrectly represented.

Compound **2** was obtained as a colorless oil. The EIMS exhibited a characteristic fragment ion peak cluster at *m/z* 283/281 (1:1, [M − Cl]$^+$). The molecular formula was determined as $C_{15}H_{22}BrCl$ on the basis of high-resolution ESIMS (*m/z* 317.0670 [M + H]$^+$, calcd for $C_{15}H_{23}{}^{79}Br^{35}Cl$, 317.0672), suggesting four degrees of unsaturation. The ^{1}H NMR spectrum (Table 1) showed three methyl singlets, one double-doublet attributed to a methine bonded to a heteroatom, and a pair of broad singlets characteristic of an exocyclic methylene unit. The ^{13}C NMR spectrum (Table 2), along with DEPT and HSQC data, revealed the presence of 15 carbon atoms (three methyl, six methylene, one methine, and five non-protonated carbon atoms). A detailed comparison of the NMR data with those reported for elatol (**7**) revealed that **2** differed from **7** only at C-9.[11] The oxygenated methine signals at δ_H 4.14 (m, H-9)

Table 2. ^{13}C NMR Data of Compounds **1–6** (125 MHz, $CDCl_3$)

no.	1	2	3	4	5	6
1	44.1 qC	38.8 CH_2	110.1 CH_2	73.8 CH	41.1 CH_2	42.7 CH_2
2	65.2 CH	128.1 qC	148.2 CH	202.3 qC	84.2 qC	212.2 qC
3	36.1 CH_2	124.4 qC	73.1 qC	99.7 CH	64.1 qC	48.8 qC
4	33.9 CH_2	29.3 CH_2	34.0 CH_2	73.6 CH	27.7 CH_2	30.7 CH_2
5	146.6 qC	25.4 CH_2	21.7 CH_2	40.5 CH_2	21.1 CH_2	28.3 CH_2
6	49.0 qC	49.1 qC	46.0 CH	86.0 CH	48.2 qC	39.0 qC
7	23.7 CH_2	145.2 qC	135.6 qC	82.5 CH	142.5 qC	143.4 qC
8	45.3 CH	33.1 CH_2	120.6 CH	123.3 qC	38.6 CH_2	34.9 CH_2
9	73.7 qC	35.5 CH_2	33.3 CH_2	160.9 qC	72.0 CH	72.3 CH
10	74.8 CH	64.8 CH	33.5 CH	107.1 CH	70.2 CH	66.2 CH
11	38.5 CH_2	42.7 qC	76.2 qC	130.9 CH	42.9 qC	45.8 qC
12	63.1 CH	17.5 CH_3	22.9 CH_3	120.4 CH	20.7 CH_3	23.7 CH_3
13	39.8 qC	23.8 CH_3	14.8 CH_3	143.5 qC	24.2 CH_3	27.1 CH_3
14	38.0 CH_2	112.8 CH_2	21.7 CH_3	25.4 CH_2	116.2 CH_2	128.6 CH
15	24.0 CH_2	19.4 CH_3	26.9 CH_3	14.8 CH_3	19.2 CH_3	17.4 CH_3
16	17.6 CH_3					
17	23.7 CH_3					
18	114.5 CH_2					
19	25.1 CH_3					
20	14.2 CH_3					

and δ_C 72.1 (C-9) observed in the spectrum of **7** were replaced by nonoxygenated methylene protons at δ_H 2.05 and 2.21 (both m, H_2-9) and δ_C 35.5 (CH_2, C-9) in the NMR spectrum of **2**, which suggested that **2** is a 9-deoxy derivative of **7**. HMBC correlations (Figure 1), from H_3-12 to C-6, C-10, and C-13, from H_3-13 to C-6, C-10, and C-12, from H-14a and H-14b to C-6 and C-8, and from H_3-15 to C-2 and C-4, further supported the proposed planar structure for **2**.

The relative configuration of **2** was assigned by comparison with those of literature reports for similar compounds. The relative configurations at C-6, C-10, and C-11 were assigned to be the same as for 10-hydroxykahukuene B (**1**), elatol (**7**), deschloroelatol (**8**), and (+)-(10*S*)-bromo-*β*-chamigrene (**9**), by detailed comparisons of NMR data.[11] The above evidence established the structure of **2**, which was named 9-deoxyelatol.

Compound **3** was obtained as a colorless oil. The molecular formula was determined to be $C_{15}H_{24}O$ by high-resolution ESIMS (*m/z* 243.1718, $[M + Na]^+$, calcd for $C_{15}H_{24}ONa$, 243.1724), suggesting four degrees of unsaturation. The ^1H NMR spectrum (Table 1) showed two methyl singlets, two methyl doublets, one broad singlet attributed to an olefinic proton at δ_H 5.28 (1H, br s, H-8), and three double-doublets assigned to the protons of an isolated vinyl group. The ^{13}C NMR spectrum (Table 2) along with DEPT and HSQC data again revealed the presence of 15 carbon atoms including four methyl, four methylene, four methine, and three nonprotonated carbon atoms. $^1H-^1H$ COSY correlations indicated the presence of three spin systems, including CH_2═CH− (C-1 to C-2), $-CH_2-CH_2-CH-$ (C-4 to C-6), and ═CH$-CH_2-CH-CH_3$ (C-8 to C-13). HMBC correlations (Figure 1) from H-12 to C-6 and C-10, from H-13 to C-9 and C-11, from H-14 to C-6 and C-8, and from H-15 to C-2 and C-4 established the connections of the above three spin systems to carbons C-3, C-7, and C-11, respectively. According to the molecular formula, compound **3** contains only one oxygen atom. However, two oxygenated carbons (C-3 at δ_C 73.1 and C-11 at δ_C 76.2) were observed in the ^{13}C NMR spectrum, which implied a cyclic ether linkage between C-3 and C-11. The above evidence resulted in the elucidation of a planar structure for **3**, which was identical with that for dactyloxene A.[19] However, the NMR data of **3** were not exactly the same as those of dactyloxene A, suggesting that **3** is a stereoisomer of dactyloxene A.

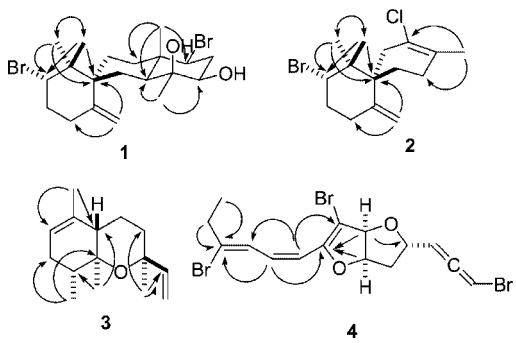

Figure 1. Key HMBC correlations for compounds **1–4**.

The relative configuration of **3** was determined upon analysis of NOESY data. In the NOESY spectrum, the signals for H_3-13 and H_3-15 both showed NOESY correlations with H-12, suggesting a *cis*-orientation for these three methyl groups. H-6 should be *trans* to the C-12 methyl group, since no cross-peak was detected between H-6 and H_3-12 in the NOESY data. On the basis of these data, the structure of compound **3** was assigned as shown. This metabolite, which we have named isodactyloxene A, is a new stereoisomer of dactyloxene A having a *trans*-orientation for C-12 and C-15.[19]

Compound **4** was also obtained as a colorless oil. The EIMS exhibited a characteristic fragment ion peak cluster at *m/z* 308/306 (1: 1, $[M - 2Br]^+$). The molecular formula was determined as $C_{15}H_{15}Br_3O_2$ on the basis of high-resolution ESIMS (*m/z* 490.8477 $[M + Na]^+$, calcd for $C_{15}H_{15}{}^{79}Br^{81}Br_2O_2Na$, 490.8480), indicating seven degrees of unsaturation. The ^1H NMR spectrum (Table 1) included one methyl triplet, three oxygenated methine, and five olefinic resonances. The ^{13}C NMR spectrum (Table 2) along with DEPT and HSQC data also revealed the presence of 15 carbon atoms including one methyl, two methylene, eight methine, and four nonprotonated carbon atoms. The presence of a bromoallene moiety was indicated by the characteristic carbon resonances observed at δ_C 73.8 (CH, C-1), 202.3 (C, C-2), and 99.7 (CH, C-3) in the ^{13}C NMR spectrum.[8,20] The $^1H-^1H$ COSY correlations indicated the presence of three spin systems, including ═CH$-$CH$-CH_2-$CH$-$CH− (C-3 to C-7), −CH═CH−CH═ (C-10 to C-12), and CH_3-CH_2- (C-14 to C-15). The two cyclic ether linkages between C-4 and C-7 and between C-6 and C-9 were established by HMBC correlations (Figure 1) from H-7 to C-4 and from H-6 to C-9, respectively. Other HMBC correlations from H-7 to C-9, from H-10 to C-8 and C-12, from H-11 to C-9 and C-13, and from H-14 and H-15 to C-13 established the connections of the above three structural units at carbons C-8, C-9, and C-13, respectively. The above evidence led to assignment of the planar structure **4** for this metabolite.

The relative configuration of **4** was determined by analysis of NOESY data and coupling constants, as well as by comparison

with literature data. The observed NOESY correlations from H-7 to H-3 and H-6 indicated a *cis* relative orientation for these protons. The coupling constant between H-6 and H-7 ($J = 6.0$ Hz) supported the *cis*-orientation for H-6 and H-7 upon comparison with that of okamurallene.[20] In addition, the absence of NOESY correlation between H-4 and H-6 and H-7 also supported the above deduction. The double bond at C-10 was assigned the *Z*-geometry on the basis of the coupling constant (8.1 Hz) between H-10 and H-11. The geometry of the double bond at C-12 was also assigned as *Z* on the basis of an observed NOESY correlation between H-12 and H_2-14. In view of the strong positive optical rotation, the configuration of the bromallene moiety in **4** was assigned as *S* by comparison with a literature report as well as by application of Lowe's rule.[20,21] These data established the structure of **4**, which was named laurenmariallene.

Compounds **5** and **6** were previously reported as intermediates in a biomimetic synthetic study of rhodolaureol and rhodolauradiol. However, they are isolated and reported here as natural products for the first time. Their structures were confirmed by analysis of 1D NMR, 2D NMR, and MS data in comparison with literature values.[10] During our separation procedures, compound **6** was invariably produced in the course of the purification of **5**. Thus, **6** might be an artifact of the isolation process, since Si gel was used in the synthetic process to form **6** from **5**.[10]

To date, only two papers have been published describing chemical investigations of *L. mariannensis*, leading to isolation of a total of five metabolites including one halogenated C_{15}-acetogenin and four halogenated sesquiterpenes.[2,3] In our case, two kinds of halogenated diterpenes (**1**, **15**, and **16**), three kinds of halogenated (**2**, **5**–**12**) or nonhalogenated (**3** and **13**) sesquiterpenes, a halogenated nonterpenoid C_{15}-acetogenin (**4**), and one other metabolite (**14**) have been identified, reflecting the molecular diversity in the secondary metabolite composition of this variety of *L. mariannensis*.

Compounds **1**–**4** were assayed for antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*, as well as antifungal activity against *Candida albicans* and *Aspergillus niger* using standard agar diffusion tests.[22] The results indicated that **1** exhibited weak activities against *S. aureus* and *E. coli* with an inhibition diameter of 6.5 mm, and **4** exhibited weak activity against *E. coli* with an inhibition diameter of 7.0 mm. None of the tested compounds displayed any antifungal activity.

Experimental Section

General Experimental Procedures. Optical rotations were measured on an ATAGO POLAX-L polarimeter. UV spectra were determined on a Spectrumlab 54 UV–visible spectrophotometer. IR spectra were recorded on a Nicolet NEXUS 470 FT-IR spectrophotometer. 1D and 2D NMR spectra were obtained at 500 and 125 MHz for ^{1}H and ^{13}C, respectively, on a Bruker Avance 500 MHz NMR spectrometer in $CDCl_3$ with TMS as internal standard. Mass spectra were recorded using a VG Autospec 3000 mass spectrometer. Column chromatography (CC) was performed with Si gel (200–300 mesh, Qingdao Haiyang Chemical Co., Qingdao, China) and Sephadex LH-20 (Sigma). TLC was carried out with precoated Si gel plates (GF-254, Qingdao Haiyang Chemical Co., Qingdao, China).

Plant Material. The marine red alga *Laurencia mariannensis* Yamada was collected at Hainan and Weizhou Islands of People's Republic of China, in March and April 2006, respectively, and was identified by one of the authors (L.-P.D). A voucher specimen (HZ06M04b) has been deposited at the Key Laboratory of Experimental Marine Biology of the Institute of Oceanology, Chinese Academy of Sciences.

Extraction and Isolation. A sample of the dried and powdered alga *L. mariannensis* (500 g) was extracted with $CHCl_3$/MeOH (1:1, v/v), and the residue was further extracted with 95% EtOH. The concentrated extracts were combined and partitioned between H_2O and EtOAc. The EtOAc-soluble fraction was chromatographed over Si gel, eluting with a step-gradient of EtOAc in petroleum ether (PE) (0–100%) to give six fractions, I−VI. Fr. I eluted with PE and was further purified by preparative TLC to afford **2** (12.7 mg), **9** (3.4 mg), and **12** (5.1 mg). Fr. II eluted with PE/EtOAc (30:1) and was also purified by preparative TLC (Si gel) to afford **3** (2.1 mg), **4** (10.3 mg), **5** (2.5 mg), **6** (2.8 mg), **7** (1.2 g), **8** (5.3 mg), **13** (8.4 mg), **14** (5.1 mg), and a mixture of **10** and **11** (23.8 mg, 2:1). Fr. IV eluted with PE/EtOAc (5:1) and was also purified by Si gel CC, Sephadex LH-20 ($CHCl_3$/MeOH, 1:1) CC, and preparative TLC to afford **1** (8.6 mg), **15** (6.9 mg), and **16** (38.3 mg).

10-Hydroxykahukuene B (1): colorless oil; $[\alpha]^{18}_D$ +8.1 (*c* 0.71, $CHCl_3$); IR (KBr) ν_{max} 3450, 3090, 2924, 2854, 1635, 1456, 1373, 1183, 1032, 901 cm^{-1}; ^{1}H NMR data, see Table 1; ^{13}C NMR data, see Table 2; EIMS *m*/*z* (%) 448 (4), 446 (8), 444 (4) $[M - H_2O]^+$, 385 (7), 383 (7), 367 (93), 365 (100), 341 (31), 339 (31), 285 (24), 267 (29); HRESIMS *m*/*z* 487.0654 $[M + Na]^+$ (calcd for $C_{20}H_{32}{}^{79}Br^{81}BrO_2Na$, 487.0647).

9-Deoxyelatol (2): colorless oil; $[\alpha]^{18}_D$ +17 (*c* 1.11, $CHCl_3$); IR (KBr) ν_{max} 2925, 2854, 1680, 1639, 1455, 1374, 900 cm^{-1}; ^{1}H NMR data, see Table 1; ^{13}C NMR data, see Table 2; EIMS *m*/*z* (%) 283 (13), 281 (14)) $[M - Cl]^+$, 239 (28), 237 (96), 201 (44), 69 (100); HRESIMS *m*/*z* 317.0670 $[M + H]^+$ (calcd for $C_{15}H_{23}{}^{79}Br^{35}Cl$, 317.0672).

Isodactyloxene A (3): colorless oil; $[\alpha]^{18}_D$ +1.2 (*c* 0.19, $CHCl_3$); IR (KBr) ν_{max} 3026, 2922, 2852, 1630, 1454, 1377, 1138, 1030, 910 cm^{-1}; ^{1}H NMR data, see Table 1; ^{13}C NMR data, see Table 2; ESIMS *m*/*z* 243 ($[M + Na]^+$); HRESIMS *m*/*z* 243.1718 $[M + Na]^+$ (calcd for $C_{15}H_{24}ONa$, 243.1724).

Laurenmariallene (4): colorless oil; $[\alpha]^{18}_D$ +190 (*c* 0.89, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ϵ) 242 (3.13), 280 (3.22) nm; IR (KBr) ν_{max} 3057, 2963, 2930, 2873, 1961, 1610, 1596, 1453, 1376, 1238, 1180, 1022, 932, 787 cm^{-1}; ^{1}H NMR data, see Table 1; ^{13}C NMR, see Table 2; EIMS *m*/*z* (%) 308 (31), 306 (34), 227 (6), 189 (72), 159 (47), 147 (100); HRESIMS *m*/*z* 490.8477 $[M + Na]^+$ (calcd for $C_{15}H_{15}{}^{79}Br^{81}Br_2O_2Na$, 490.8480).

Compound 5: colorless oil; ^{1}H NMR data, see Table 1; ^{13}C NMR, see Table 2; ESIMS *m*/*z* 353, 351, 349 $[M + H]^+$ (1:4:3).

Compound 6: colorless oil; ^{1}H NMR data, see Table 1; ^{13}C NMR, see Table 2; ESIMS *m*/*z* 315, 313 $[M + H]^+$ (1:1).

Bioassays. Antibacterial and antifungal assays were performed as previously described.[22]

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Supporting Information Available: 1D and selected 2D NMR spectra of compounds **1**–**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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