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CHAMIGRANE METABOLITES FROM *LAURENCIA OBTUSA* AND *L. SCOPARIA*

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Key Word Index—*Laurencia*; Rhodomelaceae; Rhodophyta; marine algae; sesquiterpene; chamigrane; laurencenone.

Abstract—Four new chamigranes with an enone function in ring A have been isolated from *Laurencia obtusa* together with deschloroelatol, a new natural product, elatol and iso-obtusol. *Laurencia scoparia* yielded elatol and five other chamigranes, one of which is new. New structures were determined by spectroscopic and chemical methods.

INTRODUCTION

The red algal genus *Laurencia* is the source of an ever-growing multitude of metabolites of diverse structure, particularly terpenes and acetogenins [1–6]. We report some additions to the chamigrane group of sesquiterpenes found in *L. obtusa* and *L. scoparia*.

RESULTS AND DISCUSSION

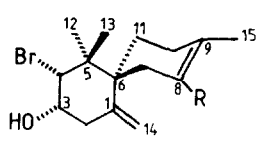
Laurencia obtusa

This alga is widely distributed, and plant material has been examined *inter alia* from the coasts of California [7], England [8], Italy [9], Turkey [10], and the Canary Islands [11], each collection containing different metabolites. A recent account [12] of new metabolites in Jamaican *L. obtusa* prompts us to report further products from *L. obtusa* also collected in Jamaican waters.

An initial, dried sample (100 g) was extracted with methanol—toluene, and the ether-soluble portion was fractionated by CC and prep. LC. Three compounds were isolated of which elatol (**1**) and iso-obtusol (**3**) are known [11, 12, 14], while deschloroelatol (**2**), previously obtained [11] by reduction of obtusol with lithium aluminium hydride is a new natural product. González *et al.* [11] showed that iso-obtusol could be quantitatively converted into elatol by stirring in a hexane suspension of silica gel. On repeating the experiment with Florisil (which we used for chromatography) iso-obtusol was recovered unchanged, and iso-obtusol was also recovered quantitatively when subjected to LC at a lower flow-rate which trebled the original elution time. Hence elatol is a genuine metabolite of *L. obtusa* and not an artefact.

Compounds **1** to **3**, and their acetates, were identified by comparison with literature values and direct comparison of ^{1}H NMR and IR spectra. As the published NMR data [11, 13, 15] on these compounds are scattered, and there are some gaps and ambiguities, we have made a complete analysis using proton 2D COSY data and ^{13}C–^{1}H correlation maps, and the results are presented in Table 1 [4]. The COSY experiment on elatol revealed long-range coupling between H-15 and H-10 which allowed the unambiguous assignment of the C-11 and C-12 protons, and the observation of long-range (unresolved) coupling of one of the *gem*-dimethyl groups to the adjacent proton on C-4 distinguished between the equatorial and axial methyl groups as only the latter would be expected to show long-range coupling to H-4. Thus all the proton signals could be assigned unambiguously, and from the 2D heteronuclear correlation map assignment of all the protonated carbons was then straightforward. The remaining carbon signals were attributed from literature values [11] and by comparison with the ^{13}C spectrum of deschloroelatol. Insufficient deschloroelatol was available for 2D work and spectral assignments were made by comparison with elatol and published values [11, 14] on appropriate related compounds. For iso-obtusol a complete sequence of decoupling experiments gave the connectivities for the three isolated proton systems, from which a full assignment could be made. The ^{13}C analysis was effected by reference to the spectrum of laurencenone A (**4**) and published data [16]. Owing to lack of material a ^{13}C–^{1}H 2D correlation map could not be derived so unfortunately some ambiguities still remain (see Table 1).

Other metabolites were detected in the first sample of *L. obtusa* and when a larger sample (500 g, dry wt) was extracted four compounds, laurencenones A–D, were isolated in addition to those discussed above. The ^{1}H NMR spectrum of laurencenone A, $C_{15}H_{22}BrClO$, showed the presence of a Me–C=CH– moiety, a *gem*-dimethyl, an isolated methyl and an isolated methylene group, and a halogenated methine function. These fragments, the molecular formula, and the presence of a quaternary carbon resonating at δ43.11 provided strong evidence for a sesquiterpenoid structure of the chamigrane type. The chemical shift of the methyl singlet at δ1.96 together with an equatorial methine proton (δ4.56, *br t*, $J = 4$ Hz) implies that the halogens are located diaxially in ring B (see **4**). This is confirmed by the ^{13}C



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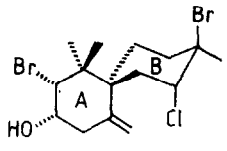
2 R = H



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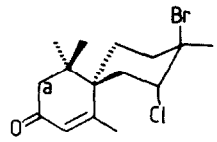

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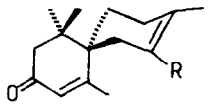

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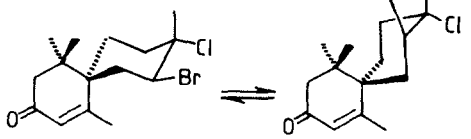
6 R = H



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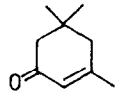

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Table 1. ^{1}H and ^{13}C NMR* assignments for compounds **1–3**

	1				2				3			
C	^{1}H	Mult.	*J* (Hz)	^{13}C	^{1}H	Mult.	*J* (Hz)	^{13}C	^{1}H	Mult.	*J* (Hz)	^{13}C
1				142.72				141.72				147.2
2 ax	2.72	*ddddd*	6.5, 3, 15, 1.5, 1.5		2.74	*d(br)*	15, 2		2.71	*t*	12, 12	
				39.59				27.49				39.1
2 eq	2.38	*dd*	15,3		2.60	*d(br)*	15, 2		2.32	*dd*	12, 4	
3	4.13	*m*	6.5, 6, 3	72.48	4.13	*dd*	6, 3	72.29	3.71	*m*		69.6
4	4.71	*d*	3	70.76	4.61	*d*	3	71.80	4.42	*d (br)*	3	76.7
5				44.01				42.94				43.5
6				49.98				46.97				44.1
7 ax	2.59	*m*			2.25	*m*			2.80	*dd*	16, 3.5	
				39.24				37.97				33.7†
7 eq	2.30	*d (br)*	12.5		2.25	*m*			3.15	*d (br)*	16	
8				128.61	5.28	*m*		132.35	4.56	*m*		65.0
9				124.81				119.28				71.2
10 ax	2.08	*dd (br)*	~15, 12		~1.9	*m*			2.20	*m*		
				29.89				29.94				33.1†
10 eq	2.00	*dd (br)*	~15, 5		~1.9	*m*			~1.85	*m*		
11 ax	1.59	*ddd*	17, 12, 5		~1.8	*m*			~1.85	*m*		
				25.95				25.69				33.0†
11 eq	1.78	*d (br)*	17		~1.8	*m*			2.00	*m*		
12	1.06	*s*		24.67	1.09	*s*		22.47	1.08	*s*		25.2‡
13	1.05	*s*		20.98	1.08	*s*		23.86	1.31	*s*		25.5‡
14	5.01	*t (br)*	1.5, 1.5	114.84	5.08	*s (br)*		115.07	5.14	*s (br)*		113.8
	4.85	*s (br)*			4.80	*s (br)*			4.97	*s (br)*		
15	1.66	*d (br)*	1.2	19.49	1.72	*s (br)*		20.31	1.89	*s*		24.8‡
OH	3.58	*d*	6						3.88	*d*	8.5	

*^{1}H at 250 MHz and ^{13}C at 62.9 MHz in Me_2CO-d_6 with TMS as internal reference.
†,‡Assignments may be interchanged.

spectrum wherein C-9 appears at δ68.2 (*s*) and C-8 at δ65.3 (*d*). These values are within the normal range for these carbons in 9-bromo-8-chlorochamigrenes and exclude di-equatorial alternatives [14]. Ring A, in laurencenone A, contains an enone function, uncommon in the chamigrane series. This is evident from the ^{13}C NMR spectrum which includes a carbonyl resonance at δ197.6 and vinyl carbons at δ169.6 and 127.8, IR absorption at 1670 cm^{-1}, and UV absorption at 239 nm ($\varepsilon \sim 11000$). Spectroscopically ring A shows a marked resemblance to isophorone (**8**) which supports the conclusion that laurencenone A has structure **4** (λ_{max}^{EtOH} calcd 239 nm). The alternative structure with ring B attached to C_a (see **4**) is ruled out by the absence of long-range coupling between the allylic methyl and the methylene protons (cf. **1**). Complete ^1H and ^{13}C assignments are listed in Table 2.

Laurencenone B, $C_{15}H_{21}ClO$, is very similar to A but the methyl singlet at δ1.96 in the ^1H NMR spectrum is replaced by a broad doublet at δ1.75 suggesting that ring B is of the elatol (**1**) type, and hence laurencenone B has structure **5**. That was confirmed when A was quantitatively converted into B by stirring in ether over silica gel. This dehydrobromination corresponds to the conversion **3**→**1** implying, in both cases, a conformation change on the silica surface prior to elimination of hydrogen bromide. The ^1H NMR assignments of laurencenone B are given in Table 2; unfortunately the sample decomposed before a ^{13}C NMR spectrum could be run.

Laurencenone C, $C_{15}H_{22}O$, is deschlorolaurencenone B. Its ^1H NMR spectrum (see Table 2) differs from that of B in that a second vinyl proton signal is observed at δ5.62 coupled to an allylic methyl at δ1.76. Structure **6** was confirmed by dehalogenation of laurencenone A to give C by reduction in ether with zinc and a trace of acetic acid at 0°. The ease of this reaction (predominantly an E2 elimination [17, 18], cf. **7**→**6** below) provides further confirmation of the *trans* diaxial configuration of laurencenone A.

Additional support for structures **4**–**6** comes from their mass spectra. Whereas laurencenone A (**4**) fragments, like isophorone (**8**), by initial cleavage of ring A,

$$M^+(A, m/z\ 332) \xrightarrow{-C_4H_8} 276\ (56\%) \xrightarrow{-Br} 197\ (100)$$

$$\xrightarrow{-HCl} 162(60)$$

in the spectra of laurencenone B (**5**) and C (**6**), there is a significant ion at *m/z* 150 which must arise by retro-Diels–Alder fragmentation of ring B leading to the base peak (for C) at *m/z* 107.

$$M^+(C, m/z\ 218) \xrightarrow{-C_5H_8} 150(30\%)$$

$$\xrightarrow{-Me} 135(24) \xrightarrow{-CO} 107(100)$$

Laurencenone D is isomeric with A (**4**), and can also be reduced with zinc and acetic acid to form C (**6**). The mass spectra of D and A are virtually identical except for intensity differences but the NMR spectra of D show that two inter-converting isomers are present (in acetone solution). Most lines are broad and several occur in pairs. For example the H-8 methine signal was observed as two multiplets, one at δ4.88 ($J = 10$ and 4 Hz) typical of an axial proton, and the other at δ4.50 (*br t*, $J = 4$ Hz) for an equatorial proton. When the signal at δ4.88 was irradiated at low power both it and the signal at δ4.50 disappeared, and similar irradiation of the δ4.50 signal also eliminated that at δ4.88. In another cross-saturation [19] experiment, two quaternary methyl singlets at δ1.71 and 1.83 were removed from the spectrum when either signal was irradiated, and the same result obtained when either of two very broad ($\nu_{\frac{1}{2}} \sim 10$ Hz) methyl signals at δ0.95 and 1.13 were irradiated. Clearly, two interconverting isomers are present which are represented by **7**. The proton assignments are listed in Table 2. The ^{13}C NMR spectrum also consists of broadened lines and some pairs. The halogenated carbons are observed as four lines at δ71.4, 69.0, 62.2 and 61.0. The pair at δ71.4 and 62.2 correspond to the diequatorial configuration, and as the other pair at δ69.0 and 61.0 are outwith the normal range for *trans* diaxial halogenated C-8 and C-9 carbons, with bromine at C-9 [15], they provide further evidence for structure **7**.

It is conceivable that A (**4**) could be an artefact derived from **3** by dehydrobromination and rearrangement, and **5** and **6** might be derived similarly from **1** and **2**, respectively. We think that is unlikely because all four laurencenones were observed when *L. obtusa* was rapidly extracted with methanol–toluene and the extract examined immediately by ^1H NMR using the C-9 methyl signals for identification.

Laurencia scoparia

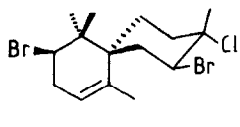
This species, also collected in Jamaica, has not been previously examined. Extraction and fractionation, as before, yielded elatol (**1**), and the chamigranes **9** to **13**, of which **9** and **10** had been found already in an unidentified *Laurencia* [20]. When the present work was done the epoxides **11** to **13** were new but **11** and **12** have since been isolated [21] from another unidentified species (possibly *L. flagellifera*) collected in Florida. Recently, the structure of **10** has been confirmed by X-ray analysis [22]. The physical properties of our samples of **9** to **12** are in complete agreement with those published [20, 21] except that we obtained **11** and **12** as crystalline solids rather than oils.

Compound **13**, $C_{15}H_{24}BrClO_3$, is also a chamigrene from its NMR characteristics. The spectra reveal the presence of two isolated methyl groups, a *gem*-dimethyl group, another quaternary carbon at δ49.28, corresponding to C-6, three methylene and two hydroxyl groups. The NMR spectra are generally similar to those of **11** [21] suggesting a 8,9-dihalo-1,2-epoxide structure. A bromomethine signal at δ5.06 (*dd*, $J = 12.5$ and 6 Hz) shows that the bromine is equatorial, and the ^{13}C shift for C-9 at δ70.20 implies [16] that the chlorine is axial. From a 2D COSY experiment, followed by specific decouplings, a hydroxyl group could be assigned to C-11 and must be equatorial as H-11 (δ4.00 *dd*, $J = 14$ and 4 Hz) is clearly axial. Ring B is thus defined as in **13**, and the second hydroxyl group must be in ring A. The COSY and decoupling data show that the second hydroxymethine proton at δ3.74 is coupled to both of the ring A methylene protons and to the epoxymethine proton, and as all the couplings are small ($J = 4.0$, 3.0 and 2.0 Hz) the hydroxyl group is axial. The epoxymethine proton is coupled to only one of the methylene protons ($J = 2.1$ Hz). The spectroscopic evidence is therefore in accord with structure **13** in which the dihedral angle be-

Table 2. ^1H and ^{13}C NMR*

	4				5		
C	^1H	Mult.	J (Hz)	^{13}C	^1H	Mult.	J (Hz)
1				169.61			
2	5.33	*s (br)*		127.80	5.90	*s (br)*	
3				197.63			
4	2.51	*d*	18	48.96	ax 2.70	*d*	18
					eq 2.10	*d*	18
5				42.25			
6				43.11			
7 ax	2.09‡	*dd*	16, 4	39.44	2.3–1.6	*m*	
7 eq	3.03‡	*dd*	16, ~4				
8	4.56	*t (br)*	4, 4	65.30			
9				68.21			
10 ax	2.24	*ddd*	15, 12, 4	36.57	2.3–1.6	*m*	
10 eq	1.80	*m*					
11 *ax*	~2.15	*m*		24.20	2.3–1.6	*m*	
11 eq	1.85	*dt*	14, 4				
12	1.17	s		24.20‡	1.03	*s*	
13	0.99	*s*		23.86‡	0.98	*s*	
14	2.20	*d*	2	31.27	1.98	*d*	2
15	1.96	*s*		25.55	1.75	*d (br)*	~4

*^1H at 360, 250 and 60 MHz and ^{13}C at 90 and 62.9 MHz in Me_2CO-d_6 with TMS
†Unassigned signals at δ48.9, 48.8, 42.3, 42.2, 41.9, 41.8, 40.9, 40.6, 37.6, 34.9.
‡Assignments may be interchanged.



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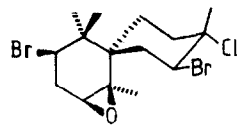

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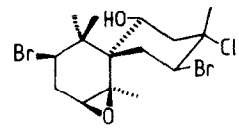

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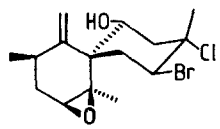

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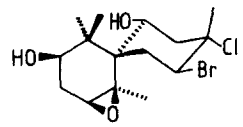

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tween H-2 and $H_{eq}-3$ is close to 90° and zero coupling is therefore expected, and the almost planar *W* pathway between H-2 and H-4 accounts for the 4 Hz coupling constant. The ^{13}C spectrum was analysed by reference to that of **10** and chemical shift additivity constants [23]. Full assignments are given in Table 3.

EXPERIMENTAL

Isolation. L. obtusa was collected at Negril, Jamaica, washed, and air-dried. The first batch (100 g) was extracted with MeOH–toluene (3:1) (3 × 500 ml) in a Waring Blender. After filtration, the combined solns were dried ($MgSO_4$) and evapd at 50° to a viscous dark green oil (2 g, 2%). The Et_2O-soluble portion was chromatographed in cyclohexane–EtOAc over Florisil (50 g) using gradient elution, monitored by 60 MHz ^1H NMR. Appropriate fractions were further purified by prep. LC on a 5μ Zorbaxsil column (12 × 250 mm) and 5% EtOAc–cyclohexane as mobile phase to give, in order of elution, deschloroelatol (50 mg, 0.05%), elatol (60 mg, 0.06%), and isoobtusol (4 mg, 0.04%). The second batch (500 g) was worked-up in the same way using 10% EtOAc–cyclohexane to elute the

assignments for compounds **4–7**

6			**7**			
^{1}H	Mult.	*J* (Hz)	^{1}H	Mult.	*J* (Hz)	^{13}C†
						167.3
5.95	*s (br)*		5.84	*s (br)*		127.8
						128.2
						197.5
ax 2.75	*d*	18	2.7–1.8	m		
eq 2.2	*d*	18				
2.3–1.6	*m*		2.7–1.8	*m*		
5.62	*s (br)*		4.88	*dd*	~10, 4	61.0
			4.50	*t (br)*	~4, 4	62.2
						69.0
						71.4
2.3–1.6	*m*		2.7–1.8	*m*		
2.3–1.6	*m*		2.8–1.8	*m*		
1.03	*s*		1.13	*s (br)*		~25
0.97	*s*		0.95	*s (br)*		~24
1.99	*d*	2	2.20	*s (br)*		31.8
1.76	*d (br)*	~4	1.71	*s*		
			1.83			

as internal reference.

Table 3. ^{1}H and ^{13}C NMR* assignments for compound **13**

C	^{1}H	Mult.	*J* (Hz)	^{13}C
1				61.32
2 eq	2.77	*dd*	4, 2	57.34
3 ax	2.00	*ddd*	16, 3, 2	
				42.84
3 eq	2.17	*dd*	16, 2	
4 eq	3.74	*ddd*	4, 3, 2	83.44
5				46.98
6				49.28
7 ax	2.15	*dd*	14, 12.5	
				34.39
7 eq	2.50	*dd*	14, 6	
8 ax	5.06	*dd*	12.5, 6	59.79
9				70.20
10 ax	2.70	*dd*	14, 12.5	
				41.46
10 eq	2.59	*dd*	12.5, 4	
11 ax	4.00	*dd*	14, 4	77.09
12	1.27	*s*		21.71
13	1.11	*s*		29.32†
14	1.85	*s*		28.92†
15	1.57	*s*		28.17†
HO-1	3.49	*s (br)*		
HO-10	5.12	*s (br)*		

*^{1}H at 360 MHz and ^{13}C at 90 MHz in $CDCl_3$ with TMS as internal reference.

†Assignments may be interchanged.

laurencenones. A and D were completely separated in that system on the same prep. LC column as before, and B and C were finally separated on an 8 × 500 mm column using CH_2Cl_2–cyclohexane (2:3); yields A (45 mg, 0.009%), B (40 mg, 0.008%), C (45 mg, 0.009%), and D (5 mg, 0.001%).

L. scoparia was collected at Negril and an air-dried sample (97 g) was extracted in the same way. CC over Florisil was run in cyclohexane, cyclohexane–Et_2O (5%), and cyclohexane–Et_2O (10%). Prep. LC in cyclohexane–EtOAc (5%) gave **1** and **9**, and **10–13** were separated in CH_2Cl_2–EtOAc (2%); **10**, **11**, and **13** were crystallized from cyclohexane–Et_2O (5%). Yields: **1** (40 mg, 0.04%), **9** (30 mg, 0.03%), **10** (50 mg, 0.05%), **11** (250 mg, 0.25%), **12** (40 mg, 0.04%), **13** (45 mg, 0.045%).

Laurencenone A {*rel*-(6R,8R,9R)-9-*bromo*-8-*chloro*-1,5,5,9-*tetramethylspiro*[6.6]*undec*-1-*en*-3-*one*} (**4**). An oil (Found: M^+ 332.9130. $C_{15}H_{22}{}^{79}Br^{35}ClO$ requires M 332.9134); UV λ_{max}^{EtOH} nm: 239 (ε 11 000); IR (film) cm^{-1}; 1670 (CO); EIMS (probe) 70 eV; *m/z* (rel. int.): 336 (1), 334 (5), 332 (4) $[M]^+$, 280 (18), 278 (72), 275.9921 ($C_{11}H_{14}{}^{79}Br^{35}ClO$ requires 275.9921, 56) $[M-C_4H_8]^+$, 199 (33), 197.0735 ($C_{11}H_{14}{}^{35}ClO$ requires 197.0733, 100) $[M-C_4H_8-Br]^+$, 161.0963 ($C_{11}H_{13}O$ requires 161.0966, 60) $[M-C_4H_8-Br-HCl]^+$.

Laurencenone B {*rel*-(6*R*)-8-*chloro*-1,5,5,9-*tetramethylspiro*[6.6]*undeca*-1,8-*dien*-3-*one*} (**5**). An oil (Found: M^+ 252.1288. $C_{15}H_{21}ClO$ requires M 252.1281); UV λ_{max}^{EtOH} nm; 239 (δ 11 000); IR (film) cm^{-1}: 1670 (CO); EIMS (probe) 70 eV, *m/z* (rel. int.): 254 (5), 252 (15) $[M]^+$, 198 (6), 196.0658 ($C_{11}H_{13}{}^{35}ClO$ requires 196.0655, 25) $[M-C_4H_8]^+$, 183 (18), 181.0416 ($C_{10}H_{10}{}^{35}ClO$ requires 181.0420, 56) $[M-C_4H_8-Me]^+$, 161.0968 ($C_{11}H_{13}O$ requires 161.0966, 100) $[M-C_4H_8-Cl]^+$, 150.1039 ($C_{10}H_{14}O$ requires 150.1045, 30) $[M-C_5H_7Cl]$, 135

(25), $[M-C_5H_7Cl-Me]^+$, 107 (35) $[M-C_5H_7Cl-Me-CO]^+$

Laurencenone C {*rel*-(6R)-1,5,5,9-*tetramethylspiro*[6.6]*undeca*-1,8-*dien*-3-*one*} (**6**). An oil (Found: M^+ 218.0674. $C_{15}H_{22}O$ requires M. 218.0671); UV λ_{max}^{EtOH} nm: 239 (ε 11 000); IR (film) cm^{-1}; 1670 (CO); EIMS (probe) 70 eV, *m/z* (rel. int.): 218 (21) $[M]^+$, 162 (18) $[M-C_4H_8]^+$, 150.1039 ($C_{10}H_{14}O$ requires 150.1042, 30) $[M-C_5H_8]^+$, 135 (24) $[M-C_5H_8-Me]^+$, 107 (100) $[M-C_5H_8-Me-CO]^+$.

Laurencenone D (*8-bromo-9-chloro*-1,5,5,9-*tetramethylspiro*[6.6]*undec*-1-*en*-3-*one*). A solid (Found: $M^+-Me_2C{=}CH_2$ 275.9930. $C_{11}H_{14}{}^{79}Br^{35}ClO$ requires 275.9916; UV λ_{max}^{EtOH} nm; 329 (ε 11 000); IR (nujol) cm^{-1}: 1675 (CO); EIMS (probe) 70 eV, *m/z* (rel. int.): 336 (1), 334 (5), 332 (4) $[M]^+$, 280 (5), 278 (72), 276 (20) $[M-C_4H_8]^+$, 199 (22), 197.0733 ($C_{11}H_{14}{}^{35}ClO$ requires 197.0733, 70) $[M-C_4H_9-Br]^+$, 161 55) $[M-C_4H_8-Br-HCl]^+$, 151 (85).

Chemical transformations. (i) To a soln of laurencenone A (**4**) (10 mg) in Et_2O (2 ml) was added Zn. dust (10 mg) and HOAc (5 μl). The suspension was stirred for 4 hr at 0°, filtered, diluted with Et_2O, washed with 0.1 M HCl (3 × 2 ml) and H_2O (4 × 4 ml), dried ($MgSO_4$), and evaporated to give a pale yellow oil (5 mg) identical (MS, ^1H NMR) to laurencenone C (**6**).

(ii) A soln of laurencenone A (**4**) (10 mg) in cyclohexane (10 ml) was stirred with silica gel (2 g) for 24 hr. After filtration the silica gel was dry-packed into a small bore column and eluted with Et_2O to give an oil (7 mg) identical (MS, ^1H NMR) with laurencenone B (**5**).

(iii) To a soln of laurencenone D (4 mg) and HOAc (5 μl) in Et_2O (5 ml) was added Zn dust (5 mg). After stirring at room temp. for 72 hr the mixture was worked up as in (i) to give an oil (2 mg) identical (MS, ^1H NMR) with laurencenone C (**6**).

Compound **11**. Crystals, mp. 161°; $[\alpha]_D^{20}+9.5°$ (Me_2CO; *c* 0.5).

Compound **12**. Crystals, mp 125°; $[\alpha]_D^{20}+71°$ (Me_2CO; *c* 0.5).

Compound **13**. (rel. 1*R*,3*S*,4*S*,6*R*,7*S*,8*S*,10*S*)-4-bromo-3-chloro-7,8-epoxy-1,10-dihydroxy-1,7,11,11-tetramethylspiro[6.6]undecane). Crystals, mp 191.5°; $[\alpha]_D^{20}+1°$ (Me_2CO: *c* 0.5); (Found: C, 49.07; H, 5.75. $C_{15}H_{24}BrClO_3$ requires C 48.99; H, 5.79%), EIMS (probe) 70 eV, *m/z* (rel. int.): M^+ not observed, 271 (5), 269 (25), 267 (20), 253 (12), 250.9844 ($C_9H_{13}{}^{79}Br^{35}ClO$) requires 250.9838), 249 (65), 115.0992 ($C_6H_{11}O_2$ requires 115.0997), 98 (95), 69 (100), 55 (75).

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