

Halogenated sesquiterpenes and non-halogenated linear C₁₅-acetogenins from the marine red alga *Laurencia composita* and their chemotaxonomic significance

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1. Subject and source

Laurencia composita Yamada is a marine red alga belonging to the family Rhodomelaceae (order Ceramiales, class Rhodophyceae, and phylum Rhodophycota). It occurs mainly in the northwest part of the Pacific Ocean (Masuda et al., 1996). The material used in this research was collected in May 2007 off the coast of Nanji Island in the East China Sea, Zhejiang Province, PR China. A voucher specimen (HZ0705a) was deposited in the Institute of Oceanology, Chinese Academy of Sciences, Qingdao, China.

2. Previous work

Until now, only two papers have been published concerning the secondary metabolites of *L. composita* indicating the presence of chamigrane sesquiterpenes such as 2,10-dibromo-3-chloro-7-chamigrene, 2,10-dibromo-3-chloro-7-chamigren-9-ol, johnstonol, pacifenol, prepacifenol, and prepacifenol epoxide. In addition, C₁₅-acetogenins such as laurencenyne, *trans*-laurencenyne, and neolaurencenyne have also been reported from this species (Masuda et al., 1996, 2002).

3. Present study

During our continuing investigations of the chemical constituents of Chinese marine red algae of the Rhodomelaceae (Duan et al., 2006, 2007; Ji et al., 2007a,b,c,d,e; Li et al., 2007, 2008a,b), we examined the chemical constituents of a sample of *L. composita* collected off the coast of Nanji Island at Zhejiang Province, China. The dried and powdered material (1.5 kg) was

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extracted with $\text{CHCl}_3/\text{MeOH}$ 1:1 (v/v). The concentrated extracts were partitioned between H_2O and EtOAc. The EtOAc-soluble portion was subjected to column chromatography (CC) on silica gel, eluting with a gradient of increasing concentrations of EtOAc in petroleum ether (PE), to give six fractions (Fr. I–Fr. VI). Fr. I (eluted with PE) was further purified by CC over silica gel (PE) and by preparative TLC (cyclohexane) to afford **2** (22.9 mg), **3** (21.9 mg), **5/6** (12.6 mg, 2:3), **11** (11.2 mg), and **12** (10.0 mg). Fr. II (eluted with PE/EtOAc 100:1) was purified by CC over Sephadex LH-20 ($\text{CHCl}_3/\text{MeOH}$, 1:1) and by preparative TLC (PE/ CHCl_3 , 3:1; PE/ CHCl_3 , 1:1; and CHCl_3) to afford **1** (3.3 mg), **7** (14.4 mg), and **8** (8.9 mg). Fr. IV (eluted with PE/EtOAc 10:1) was purified by CC over Sephadex LH-20 ($\text{CHCl}_3/\text{MeOH}$, 1:1) and silica gel (PE/EtOAc, 10:1) as well as by preparative TLC (PE/EtOAc, 10:1) to afford **4** (640.4 mg) and **9** (22.6 mg). Fr. V (eluted with PE/EtOAc 3:1) was purified by CC over Sephadex LH-20 ($\text{CHCl}_3/\text{MeOH}$, 1:1) and silica gel (PE/EtOAc, 4:1) as well as by preparative TLC as above, to afford **10** (20.2 mg).

The structures of the isolated metabolites (compounds **1–12**, Fig. 1) were unambiguously elucidated by detailed analysis of NMR and mass spectra, and by comparison of these data with values in the literature. The compounds identified included two new rearranged chamigrane sesquiterpenes, which were named as 2-bromospironippol (**1**) and laurencomposidiene (**2**), and ten known compounds 2,10-dibromo-3-chloro-7-chamigrene (**3**) (Wright et al., 1991), 2,10-dibromo-3-chloro-7-chamigren-9-ol (**4**) (Suzuki et al., 1988), nidificene (**5**) (McPhail et al., 1999), obtusane (**6**) (González et al., 1979), 2,10-dibromo-3-chloro-7 α ,8 α -epoxychamigrane (**7**) (Ojika et al., 1982), 2,10-dibromo-3-chlorochamigrane-7,9-diene-5-ol (**8**) (Kimura et al., 1999), pacifenol (**9**) (de Nys et al., 1993; Kaiser et al., 2001), johnstonol (**10**) (Kaiser et al., 2001), laurencenyne (**11**) (Kigoshi et al., 1986), and *trans*-laurencenyne (**12**) (Kigoshi et al., 1986).

Compound **1** was obtained as a colorless oil. The EI mass spectrum exhibited a characteristic molecular ion cluster at m/z 300/298 (1:1), indicating the presence of one bromine atom. The molecular formula was deduced to be $\text{C}_{15}\text{H}_{23}\text{BrO}$ on the basis of the EI mass spectrum, in conjunction with the ^1H , ^{13}C , and DEPT NMR data (Table 1), suggesting four degrees of unsaturation. The ^1H NMR spectrum (Table 1) displayed three methyl singlets at δ_{H} 1.09 (s, H₃-12), 1.21 (s, H₃-15), and 1.55 (br s, H₃-14), one methyl doublet at δ_{H} 0.99 (d, $J = 6.6$ Hz, H₃-13), one halogenated or oxygenated methine double-doublet at δ_{H} 4.17 (dd, $J = 10.6, 4.8$ Hz, H-2), and one broad olefinic singlet at δ_{H} 5.23 (br s, H-8). The ^{13}C NMR and DEPT data (Table 1) revealed the presence of four methyl, four methylene, three methine, and four non-protonated carbon atoms, including three quaternary sp^3 carbons. Detailed comparison of the NMR data with those reported for spironippol, a non-halogenated sesquiterpene identified from *L. nipponica*, revealed that **1** differed from spironippol mainly at C-2 (δ_{C} 57.3 for **1** and 71.8 for spironippol) (Fukuzawa et al., 1981). The bromine atom was located at C-2 by virtue of its relatively upfield chemical shift at δ_{C} 57.3 (de Nys et al., 1993; Kaiser et al., 2001). Observed ^1H – ^1H COSY correlations between H₂-1 and H-2,

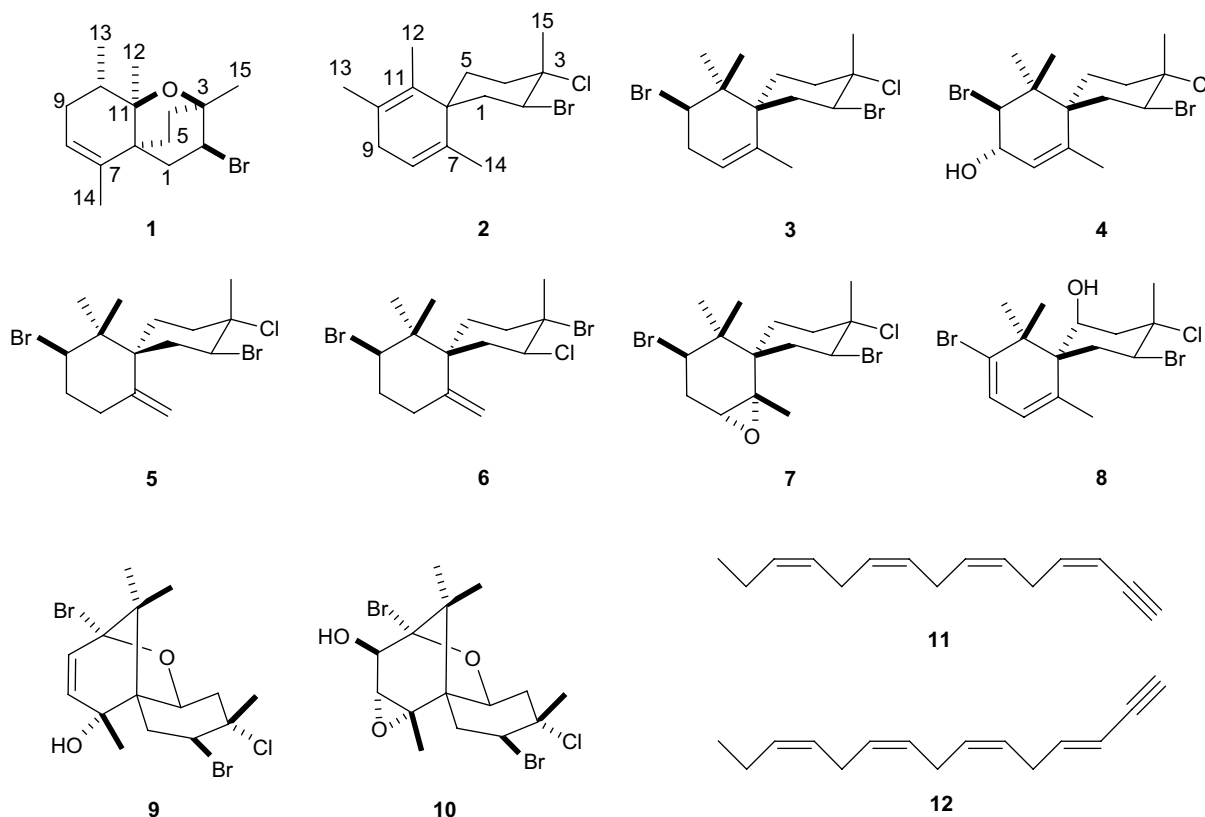


Fig. 1. Chemical structures characterized.

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