Fitoterapia 83 (2012) 1191–1195

Contents lists available at SciVerse ScienceDirect

Fitoterapia

journal homepage: www.elsevier.com/locate/fitote

Sesquiterpenes from the marine red alga *Laurencia composita*

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ARTICLE INFO

Article history:
Received 26 May 2012
Accepted in revised form 25 June 2012
Available online 14 July 2012

Keywords:
Laurencia composita
Sesquiterpene
Chamigrane
Eudesmane

ABSTRACT

Four new chamigrane derivatives, laurecomin A (**1**), laurecomin B (**2**), laurecomin C (**3**), and laurecomin D (**4**), one new naturally occurring sesquiterpene, 2,10-dibromo-3-chloro-7-chamigren-9-ol acetate (**5**), and three known halogenated structures, deoxyprepacifenol (**6**), 1-bromoselin-4(14),11-diene (**7**), and 9-bromoselin-4(14),11-diene (**8**), were isolated from the marine red alga *Laurencia composita* collected from Pingtan Island, China. The structures of these compounds were unambiguously established by 1D, 2D NMR and mass spectroscopic techniques. The bioassay results showed that **2** was active against both brine shrimp and fungus *Colletotrichum lagenarium*.

1. Introduction

The marine red algae of genus *Laurencia* are widely distributed throughout the world, and about ten species from China Sea were chemically investigated so far. As a result of the continuous program, more than one hundred compounds including about 50 new ones represented by halogenated terpenes, C_{15}-acetogenins, and ploybromoindoles have been discovered, and some of them are biologically active [1–3]. Among our investigated species, *Laurencia composita* from Nanji Island has been found to be a prolific producer of halogenated chamigrane sesquiterpenes [4,5], which encouraged us to further examine the molecular diversity of this species from other places. The effort on the sample from Pingtan Island resulted in the isolation and identification of four new chamigrane derivatives, laurecomin A (**1**), laurecomin B (**2**), laurecomin C (**3**), and laurecomin D (**4**), one new naturally occurring sesquiterpene, 2,10-dibromo-3-chloro-7-chamigren-9-ol acetate (**5**) [6], and three known halogenated structures, deoxyprepacifenol (**6**) [7], 1-bromoselin-4(14),11-diene (**7**) [8], and 9-bromoselin-4(14),11-diene (**8**) [8]. In this report, we focus on the preparation, structure elucidation, and bioactivity of compounds **1**–**8** in detail (Fig. 1).

2. Experimental

2.1. General

NMR spectra were recorded at 500 and 125 MHz for ^{1}H and ^{13}C, respectively, on a Bruker Avance III 500 NMR spectrometer using TMS as internal standard. High resolution mass spectra were determined on an Autospec Premier P776 mass spectrometer. IR spectra were obtained on a JASCO FT/IR-4100 Fourier Transform InfraRed spectrometer. Quantum chemical calculations were operated using Gaussian 09 software (IA32W-G09RevC.01). HPLC separation was carried out on an Elite HPLC system (P270 pump, UV230+ detector, Dalian Elite Analytical Instruments Co., Ltd, Dalian, China) using an Eclipse XDB-C18 (5 μm, 9.4×250 mm) column. Column chromatography was performed with silica gel (100–200 and 200–300 mesh, Qingdao Haiyang Chemical Co., Qingdao, China) and Sephadex LH-20 (Pharmacia). Precoated silica gel plates (GF-254, Qingdao Haiyang Chemical Co., Qingdao, China) were used for preparative TLC purification. All solvents were of analytical grade.

2.2. Plant material

The marine red alga *L. composita* was collected from Pingtan Island of China in May, 2010 and was identified by one of the authors (N.-Y.J.). A voucher specimen (MRA100501) has been

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doi:10.1016/j.fitote.2012.07.001

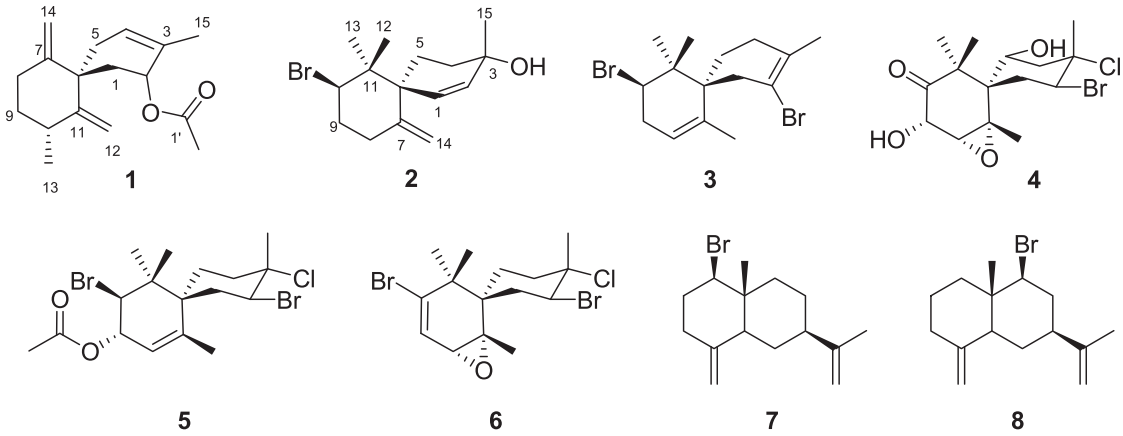

Fig. 1. Structures of compounds **1**–**8**.

deposited at the Bio-Resource Laboratory of Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences.

2.3. Extraction and isolation

The dried and powdered sample (0.7 kg) was extracted with a mixture of $CHCl_3$ and MeOH (1:1, v/v). The concentrated extract was partitioned between H_2O and EtOAc. The total extract (21.0 g) was subjected to silica gel column chromatography (CC, petroleum ether (PE)/EtOAc gradient) to give 14 fractions (Frs. 1–14), monitored by TLC. Fr. 1 eluted with PE and was purified by CC on Sephadex LH-20 ($CHCl_3$/MeOH, 1:1), preparative HPLC (MeOH/H_2O, 85:15), and preparative TLC (PE) to afford **7** (1.9 mg) and **8** (2.0 mg). Fr. 3 eluted with PE too and was further purified by CC on Sephadex LH-20 ($CHCl_3$/MeOH, 1:1) and preparative HPLC (MeOH/H_2O, 85:15) to afford **3** (1.5 mg). Fr. 7 eluted with PE/EtOAc (50:1) and was purified by CC on silica gel (PE/EtOAc, 40:1), Sephadex LH-20 ($CHCl_3$/MeOH, 1:1), and preparative HPLC (MeOH/H_2O, 85:15) to afford **1** (3.1 mg) and **6** (3.0 mg). Fr. 8 eluted with PE/EtOAc (20:1) and was purified by CC on Sephadex LH-20 ($CHCl_3$/MeOH, 1:1), silica gel (PE/EtOAc, 30:1), and preparative HPLC (MeOH/H_2O, 85:15) to give **5** (3.3 mg). Fr. 10 eluted with PE/EtOAc (10:1) and was further purified by CC on Sephadex LH-20 ($CHCl_3$/MeOH, 1:1) and MeOH recrystallization to afford **4** (10.4 mg). Fr. 12 eluted with PE/EtOAc (10:1) and was further purified by CC on Sephadex LH-20 ($CHCl_3$/MeOH, 1:1), preparative HPLC (MeOH/H_2O, 75:25), and preparative TLC (PE/EtOAc, 4:1) to give **2** (3.6 mg).

Laurecomin A (**1**): colorless oil; $[\alpha]^{18}_D$ –22.2 (*c* 0.15, $CHCl_3$); IR (KBr) ν_{max} 2927, 2858, 1736, 1635, 1446, 1373, 1246, 1026, 895 cm^{-1}; ^1H NMR data, see Table 1; ^{13}C NMR data, see Table 2; HREIMS *m/z* 260.1758 $[M]^+$, calcd for $C_{17}H_{24}O_2$, 260.1776.

Laurecomin B (**2**): colorless crystals; m.p. 108–111 °C; $[\alpha]^{12}_D$ –49.7 (*c* 0.10, $CHCl_3$); IR (KBr) ν_{max} 3298, 2962, 2854, 1454, 1122, 899 cm^{-1}; ^1H NMR data, see Table 1; ^{13}C NMR data, see Table 2; HREIMS *m/z* 298.0910 $[M]^+$, calcd for $C_{15}H_{23}BrO$, 298.0932.

Laurecomin C (**3**): colorless oil; $[\alpha]^{22}_D$ –186.9 (*c* 0.03, $CHCl_3$); IR (KBr) ν_{max} 2927, 1678, 1446, 1377, 841 cm^{-1}; ^1H

Table 1
^1H NMR Data for **1**–**4** (500 MHz, δ in ppm, *J* in Hz).

No.	1[a]	2[a]	3[a]	4[b]
1a	1.69 (dd, 13.0, 8.6)	5.70 (dd, 10.4, 2.4)	2.33 (dm, 17.9)	2.30 (dd, 15.2, 12.9)
1b	2.51 (brd, 13.0)		2.73 (dm, 17.9)	2.46 (dd, 15.2, 3.9)
2	5.11 (brs)	5.77 (dd, 10.4, 1.7)		4.70 (dd, 12.9, 3.9)
4a	5.68 (brs)	1.51 (ddd, 13.8, 13.6, 3.0)	2.13 (m)	2.35 (dd, 14.9, 4.1)
4b		1.63 (dm, 13.8)	2.13 (m)	2.53 (dd, 14.9, 14.4)
5a	2.29 (brd, 14.2)	1.79 (dm, 13.6)	1.64 (m)	5.22 (dd, 14.4, 4.1)
5b	2.50 (brd, 14.2)	1.93 (ddd, 13.6, 13.6, 2.9)	1.86 (ddd, 12.6, 10.6, 7.4)	
8a	2.22 (ddd, 13.8, 4.3, 2.3)	2.24 (m)	5.25 (brs)	3.64 (d, 3.2)
8b	2.63 (ddd, 13.8, 13.7, 5.0)	2.43 (m)		
9a	1.05 (m)	2.11 (m)	2.54 (ddm, 18.2, 10.8)	4.06 (d, 3.2)
9b	1.94 (m)	2.22 (m)	2.66 (ddd, 18.2, 6.8, 1.9)	
10	2.56 (m)	4.61 (dd, 12.2, 4.6)	4.66 (dd, 10.8, 6.8)	
12a	4.72 (s)	1.09 (s)	0.94 (s)	1.21 (s)
12b	4.72 (s)			
13	1.05 (d, 6.4)	1.09 (s)	1.13 (s)	1.43 (s)
14a	4.53 (s)	4.63 (brs)	1.67 (brs)	1.57 (s)
14b	4.72 (s)	4.91 (brs)		
15	1.61 (brs)	1.23 (s)	1.81 (brs)	1.78 (s)
2'	2.04 (s)			

[a] Recorded in $CDCl_3$.
[b] Recorded in CD_3COCD_3.

Table 2
^{13}C NMR Data for **1–5** (125 MHz, δ in ppm).

No.	1[a]	2[a]	3[a]	4[b]	5[a]
1	37.4 (t)	133.0 (d)	40.9 (t)	32.1 (t)	39.2 (t)
2	71.8 (d)	135.1 (d)	119.6 (s)	58.4 (d)	62.3 (d)
3	130.5 (s)	66.8 (s)	132.5 (s)	70.6 (s)	70.7 (s)
4	125.1 (d)	33.6 (t)	31.2 (t)	43.9 (t)	40.1 (t)
5	33.0 (t)	22.4 (t)	30.7 (t)	70.4 (d)	31.4 (t)
6	46.9 (s)	51.4 (s)	47.3 (s)	47.2 (s)	47.8 (s)
7	151.2 (s)	146.8 (s)	139.4 (s)	60.2 (s)	144.6 (s)
8	32.2 (t)	32.5 (t)	122.4 (d)	59.8 (d)	121.7 (d)
9	38.7 (t)	34.4 (t)	36.4 (t)	73.7 (d)	75.4 (d)
10	33.0 (d)	64.1 (d)	62.0 (d)	208.2 (s)	62.9 (d)
11	157.8 (s)	42.2 (s)	41.6 (s)	47.7 (s)	46.0 (s)
12	104.6 (t)	18.1 (q)	16.9 (q)	22.4 (q)	18.0 (q)
13	19.0 (q)	25.9 (q)	24.8 (q)	24.5 (q)	25.0 (q)
14	107.8 (t)	114.0 (t)	23.2 (q)	18.4 (q)	25.7 (q)
15	18.9 (q)	29.6 (q)	22.9 (q)	30.5 (q)	24.1 (q)
1'	171.0 (s)				170.4 (s)
2'	21.2 (q)				21.1 (q)

[a] Recorded in $CDCl_3$.
[b] Recorded in CD_3COCD_3.

NMR data, see Table 1; ^{13}C NMR data, see Table 2; HREIMS *m/z* 362.0056 $[M]^+$, calcd for $C_{15}H_{22}Br_2$, 362.0068.

Laurecomin D (**4**): colorless crystals; m.p. 118–120 °C; $[\alpha]^{12}_D$ −130.1 (*c* 0.18, acetone); IR (KBr) ν_{max} 3460, 2927, 2854, 1736, 1670, 1454, 1385, 1084, 906 cm^{-1}; ^{1}H NMR data, see Table 1; ^{13}C NMR data, see Table 2; HREIMS *m/z* 380.0399 $[M]^+$, calcd for $C_{15}H_{22}BrClO_4$, 380.0390.

2.4. Bioassay

Antifungal activity against plant pathogens (*Colletotrichum lagenarium* and *Fusarium oxysporum*) and toxicity against brine shrimp (*Artemia salina*) were tested as described previously [9,10], with amphotericin B (inhibitory diameter 8 and 7 mm at 30 μg/disk, respectively) and thyrsiferol (lethal rate 100% at 100 μg/mL) as positive controls, respectively.

3. Results and discussion

Compound **1** was obtained as a colorless oil. The IR absorption band at 1736 cm^{-1} indicated the presence of a carbonyl group. The molecular formula $C_{17}H_{24}O_2$ was established by HREIMS (*m/z* 260.1758 $[M]^+$, calcd for $C_{17}H_{24}O_2$, 260.1776), requiring six degrees of unsaturation. The ^{1}H NMR spectrum (Table 1) along with the HSQC experiment showed two methyl singlets, one methyl doublet, four singlets characteristic of four olefinic methylene protons, two broad singlets ascribable to an oxygenated methine and an olefinic proton. The ^{13}C NMR spectrum (Table 2) along with the DEPT and HSQC experiments delineated seventeen signals, arising from three methyls, six methylenes, three methines, and five quaternary carbons. An analysis of the NMR data revealed **1** could possess an acetylated rearranged chamigrane derivative [4,11]. The ^{1}H–^{1}H COSY correlations (Fig. 2) indicated the presence of three structural units, including –CH_2–CH– (C-1 to C-2), =CH–CH_2– (C-4 to C-5), and –CH_2–CH_2–CH–CH_3 (C-8 to C-13). The connectivity of them at quaternary C-3, C-6, C-7, and C-11 was established by the key HMBC correlations from H-12 to C-6 and C-10, from H-13 to C-9, C-10, and C-11, from H-14 to C-6, C-7, and C-8, from H-15 to C-2, C-3, and C-4, and from H-1 to C-5, C-6, C-7, and C-11 (Fig. 2). The acetoxyl group was confirmed by the HMBC correlation from H-2′ to C-1′, which was bonded to C-2 by its downfield chemical shifts (δ_H 5.11 and δ_C 71.8). The relative configuration was deduced by the NOESY spectrum. H-8b, H-9b, and H-10 were located on the same side by the strong NOESY correlations of H-9b with H-8b and H-10, while the vicinal orientation of H-1b, H-2, and H-8b was placed on the basis of NOESY correlations of H-1b with H-2 and H-8b. Additionally, the same direction of H-5a and H-14a was placed according to NOESY correlation between them. The lowest-energy conformer (Fig. 3) was generated by the Dreiding force field in MarvinSketch and further optimized using density function theory (DFT) at the B3LYP/6–31 G(d) level in Gaussian 09 [12], which matched well with the NOESY data. The above evidence established the structure of **1**, trivially named laurecomin A.

Compound **2** was obtained as colorless crystals. The IR spectrum exhibited an absorption band at 3298 cm^{-1}, suggesting the presence of a hydroxyl group. The molecular formula was determined to be $C_{15}H_{23}BrO$ on the basis of HREIMS (*m/z* 298.0910 $[M]^+$, calcd for $C_{15}H_{23}BrO$, 298.0932), consistent with four degrees of unsaturation. The ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) along with the DEPT and HSQC data delineated signals characteristic of three tertiary methyl groups (C-12, C-13, and C-15), one sp^2 methylene (C-14), four sp^3 methylenes (C-4, C-5, C-8, and C-9), one halogenated methine (C-10), two olefinic methines (C-1 and C-2), two sp^3 quaternary carbons (C-3, C-6, and C-11), and one olefinic quaternary carbon (C-7). The NMR data of **2** were similar to those of 10-bromo-7α,8α-expoxychamigr-1-en-3-ol except for the presence of signals for an exocyclic double bond and a sp^3 methylene and the lack of signals for an expoxy moiety and a methyl group [3]. So, **2** was deduced to be an β-chamigrene derivative, which was confirmed by the HMBC correlations from H-14 to C-6 and C-8 and ^{1}H–^{1}H COSY correlations of H-9 with H-8 and H-10. The other ^{1}H–^{1}H COSY and HMBC correlations further verified the structure of **2** to be 10-bromo-β-1-chamigren-3-ol (Fig. 2), trivially named laurecomin B. The relative configuration was the same as that of 10-bromo-7α,8α-expoxychamigr-1-en-3-ol by their identical NMR data and NOESY correlations between H-10 and H-5a, H-5b.

Compound **3** isolated as a colorless oil was assigned the molecular formula $C_{15}H_{22}Br_2$ by the interpretation of HREIMS.

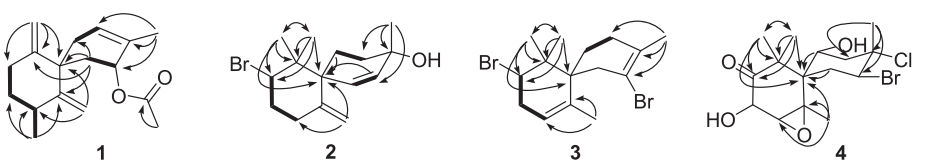

Fig. 2. Key correlations in ^{1}H–^{1}H COSY (bold lines) and HMBC (arrows) spectra of **1–4**.

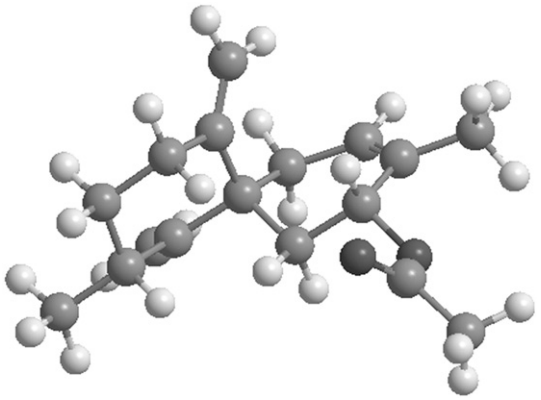

Fig. 3. Optimized stereo structure in chloroform of **1**.

The ^{1}H NMR spectrum (Table 1) showed four methyl singlets, one double doublet attributable to a halogenated methine, and one broad singlet assignable to an olefinic proton. The ^{13}C NMR spectrum (Table 2) exhibited fifteen resonances, classified into four methyls, four methylenes, two methines, and five quaternary carbons by the DEPT and HSQC experiments. The above NMR data closely resembled those for 2,10-dibromochamigra-2,7-dien-9-ol [13]. However, the hydroxylated methine in 2,10-dibromochamigra-2,7-dien-9-ol was replaced by the methylene group (C-9) in **3**, which was confirmed by the ^{1}H–^{1}H COSY correlations of H-9 with H-8 and H-10. The other ^{1}H–^{1}H COSY and HMBC correlations further verified the structure of **3** to be 2,10-dibromochamigra-2,7-diene (Fig. 2), trivially named laurecomin C. The relative configuration at C-6 was the same as that of 2,10-dibromochamigra-2,7-dien-9-ol by the NOESY correlation between H-5a and H-10.

Compound **4** was obtained as colorless crystals. The IR spectrum showed strong absorption bands at 3460 and 1736 cm^{-1} due to the presence of hydroxyl groups and a carbonyl group. The molecular formula $C_{15}H_{22}BrClO_4$ with four degrees of unsaturation was deduced by analysis of the HREIMS (*m/z* 380.0399 $[M]^+$, calcd for $C_{15}H_{22}BrClO_4$, 380.0390). In accordance with the molecular formula, four methyls, two methylenes, four methines, and five quaternary carbons responsible for the fifteen resonances in the ^{13}C NMR spectrum (Table 2) were distinguished by the DEPT and HSQC experiments. The NMR data showed similarity with those of deoxyprepacifenol (**6**) in parts [6], which suggested the presence of a 2-bromo-3-chloro-7,8-epoxychamigrane skeleton. Especially, the NMR data of H-2, C-2, and C-3 were in good agreement with those of the same halogenated unit in **5** and **6**, which occurred commonly in the chamigrane sesquiterpenes from *Laurencia* species [14]. This connection was confirmed by the HMBC correlations from H-14 to C-6, C-7, and C-8 and from H-15 to C-2, C-3, and C-4 (Fig. 2). The carbonyl group was attached to C-11 based on the HMBC correlations from H-12 and H-13 to C-6, C-10, and C-11, which was extended to C-8 by the HMBC correlation from downfield H-9 to C-10 and ^{1}H–^{1}H COSY correlation between H-8 and H-9. A hydroxyl group was located at C-5 by the ^{1}H–^{1}H COSY correlation of H-4 with downfield H-5, and H-5 was axial according to the coupling constants (14.4, 4.1 Hz). H-9 was *syn* to H-8 based on the little coupling constant (3.2 Hz) and NOESY correlation between them. The same orientation of C-12, C-14, and C-1 was placed by the NOESY correlations of H-14 with H-1b and H-12. The above data evidence the structure of **4** to be 2-bromo-3-chloro-7α,8α-expoxy-5,9-dihydroxychamigran-10-one, trivially named laurecomin D.

Compounds **5**–**8** were identified to be 2,10-dibromo-3-chloro-7-chamigren-9-ol acetate (**5**) [6], deoxyprepacifenol (**6**) [7], 1-bromoselin-4(14),11-diene (**7**) [8], and 9-bromoselin-4(14),11-diene (**8**) [8], respectively, based on the NMR data comparison with literature values. **5** was a new naturally occurring sesquiterpene, and its ^{13}C NMR data were described in Table 2.

In order to determine the chemical defense of compounds **1**–**8** preliminary, they were assayed against brine shrimp larvae and plant-pathogenic fungi. The results showed that only **1**, **2**, **7**, and **8** displayed potent brine shrimp toxicity with LC_{50} values of 51.1, 37.0, 15.2, and 78.7 μg/mL, respectively. An inspection of the structure-activity relationship demonstrated that exocylic double bond in **2** and epoxy group in 10-bromo-7α,8α-expoxychamigr-1-en-3-ol, respectively, might be not the key active moieties [3]. The bromine substitution at C-1 in **7** could contribute more to the brine shrimp toxicity than that at C-9 in **8** and the hydroxyl group in β-dictyopterol (lethal rate 22.3% at 100 μg/mL) [8]. Additionally, compound **2** also displayed antifungal activity against *C. lagenarium* with an inhibitory diameter of 10 mm and no compounds exhibited activity against *F. oxysporum* by the agar diffusion test at 30 μg/disk.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (41106136, 41106137), Shandong Province Natural Science Foundation (ZR2009BQ021), Chinese Academy of Sciences for Key Topics in Innovation Engineering (KZCX2-YW-QN209), and Foundation of the Chinese Academy of Sciences for President's Scholarship (awarded to N.-Y. Ji).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.fitote.2012.07.001.

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