Biochemical Systematics and Ecology 64 (2016) 1–5

Contents lists available at ScienceDirect

Biochemical Systematics and Ecology

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

# Halogenated eudesmane derivatives and other terpenes from the marine red alga *Laurencia pinnata* and their chemotaxonomic significance

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ARTICLE INFO

*Article history:*
Received 5 September 2015
Received in revised form 31 October 2015
Accepted 17 November 2015
Available online 26 November 2015

*Keywords:*
Rhodomelaceae
*Laurencia pinnata*
Sesquiterpene
Eudesmane
Diterpene

ABSTRACT

Chemical investigation of the marine red alga *Laurencia pinnata* collected from Nanji Island of China resulted in the isolation and identification of three new eudesmane (selinane) sesquiterpenes, 1β-bromoselin-11-en-4α-ol (**1**), 1β-bromo-4α,5α-epoxyselinane (**2**), and 1β-bromoselin-3,11-diene (**3**), and one new 6,8-cycloeudesmane sesquiterpene, 1β-bromo-6,8-cycloselin-4(15)-ene (**4**), together with one known eudesmane sesquiterpene, 1β-bromoselin-4(15),11-diene (**5**), two known chamigrane sesquiterpenes, 2,10-dibromo-3-chlorochamigr-7-ene (**6**) and 2,10-dibromo-3-chlorochamigr-7-en-9-ol (**7**), one kahukuane diterpene, kahukuene B (**8**), and one parguerane diterpene, 15-bromoparguer-9(11)-en-16-ol (**9**). These halogenated isolates were found in *L. pinnata* for the first time, and they support the taxonomic position of this species under the genus *Laurencia*. Eudesmane derivatives (**1**–**5**) are predominant and rarely reported from this genus, and they may be taken as chemotaxonomic markers for *L. pinnata* in the future.



## 1. Subject and source

*Laurencia pinnata* Yamada is a marine red alga belonging to the family Rhodomelaceae (order Ceramiales, class Rhodophyceae, and phylum Rhodophycota), which is also named *Laurencia pinnatifida*, that is mainly distributed in the Northwest Pacific Ocean, the West Pacific Ocean, the Indian Ocean, and the Mediterranean (Wang et al., 2013; Ji and Wang, 2014). The algal sample (1–3 cm high, dark red) used in this experiment was collected from Nanji Island of China in May, 2007 and identified by the third author. A voucher specimen (HZ0705b) for inspection was deposited in the Institute of Oceanology, Chinese Academy of Sciences.

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http://dx.doi.org/10.1016/j.bse.2015.11.010
0305-1978/

## 2. Previous work

Previous chemical studies on *L pinnata* have resulted in the discovery of more than thirty new secondary metabolites (Wang et al., 2013; Ji and Wang, 2014), including five chamigrane and two laurane sesquiterpenes, such as pinnatazane, pinnatifidone, pinnatifenol, pinnatifinone, and pinnatifate (González et al., 1984; Atta-ur-Rahman et al., 1988; Bano et al., 1988; Atta-ur-Rahman, 1989; Ahmad and Ali, 1991a, 1991b); eight diterpenes, pinnaterpenes A–C with an irieane skeleton, pinnatols A–D with a labdane skeleton, and prepinnaterpene (Fukuzawa et al., 1982, 1985a, 1985b); one polyether triterpene, dehydrothyrsiferol (González et al., 1984); sixteen $C_{15}$-acetogenins, such as laurepinnacin, isolaurepinnacin, E-dihydrorhodophytin, cis-pinnatifidenyne, trans-pinnatifidenyne, and pinnatifidine (Fukuzawa and Masamune, 1981; González et al., 1982; Norte et al., 1989, 1991); and two steroids, pinnasterol and acetylpinnasterol (Fukuzawa et al., 1981).

## 3. Present study

### 3.1. Extraction and isolation

In our continuing investigation of the chemical diversity of Chinese *Laurencia* algae (Ji et al., 2007, 2008), the marine red alga *L. pinnata* collected from Nanji Island of China was chemically examined. The dried and powdered algal material (90.0 g) was completely extracted with $CHCl_3$ followed by MeOH, and then the concentrated extracts were combined and partitioned between EtOAc and $H_2O$. The EtOAc-soluble fraction (1.3 g) was subjected to silica gel column chromatography (CC) with a step-gradient solvent system of 0–100% EtOAc in petroleum ether (PE) to give five fractions (Frs. I–V). Fr. I was eluted with PE and further purified by silica gel CC (PE) to afford an inseparable mixture of compounds **3**/**4** (4.4 mg, 3:2), along with pure compounds **5** (2.1 mg) and **6** (4.0 mg). Fr. II was eluted with PE/EtOAc (30:1) and purified by silica gel CC (PE/EtOAc, 30:1) to give **9** (2.3 mg), and the residual part was purified by preparative TLC (PE/EtOAc, 10:1) to produce **2** (2.0 mg). Fr. III was eluted with PE/EtOAc (10:1) and further purified by preparative TLC ($CHCl_3$) to afford **8** (3.7 mg). Fr. IV was eluted with PE/EtOAc (5:1) and further purified by preparative TLC ($CHCl_3$) to yield **1** (2.2 mg) and **7** (1.5 mg).

### 3.2. Structure elucidation

The structures of the isolates (Fig. 1) were determined by the analyses of NMR and mass spectra and confirmed by comparison with literature data, comprising three new eudesmane (selinane) sesquiterpenes, 1β-bromoselin-11-en-4α-ol (**1**), 1β-bromo-4α,5α-epoxyselinane (**2**), and 1β-bromoselin-3,11-diene (**3**); one new 6,8-cycloeudesmane sesquiterpene, 1β-bromo-6,8-cycloselin-4(15)-ene (**4**); three known sesquiterpenes, 1β-bromoselin-4(15),11-diene (**5**) (Ji et al., 2009), 2,10-dibromo-3-chlorochamigr-7-ene (**6**) (Wright et al., 1991), and 2,10-dibromo-3-chlorochamigr-7-en-9-ol (**7**) (Suzuki et al., 1988); and two known diterpenes, kahukuene B (**8**) (Brennan et al., 1993) and 15-bromoparguer-9(11)-en-16-ol (**9**) (Lyakhova et al., 2004).

Compound **1** was obtained as a colourless oil. The EIMS spectrum exhibits a characteristic $[M-H_2O]^+$ fragment ion cluster at *m/z* 284/282 (1:1), which suggests the presence of a bromine atom and a hydroxy group along with the IR absorption band at 3990 $cm^{-1}$. A molecular formula of $C_{15}H_{25}BrO$ was determined by HRAPPIMS (*m/z* 300.1074 $[M]^+$, calcd. for $C_{15}H_{25}^{79}BrO$, 300.1088), requiring three degrees of unsaturation. The $^1H$ NMR spectrum (Table 1) displays three methyl singlets, one double doublet ascribable to a halogenated/oxygenated methine, and one broad singlet assignable to two olefinic protons. The $^{13}C$ NMR spectrum (Table 2), along with DEPT and HSQC data, reveals the presence of three methyls, six methylenes, three methines, and three quaternary carbon atoms. A detailed NMR data comparison with those reported for cyperusol C reveals that **1** mainly differs from it at C-1 ($\delta_C$ 67.0 for **1** and 79.3 for cyperusol C) (Xu et al., 2004), which was deduced to be brominated in **1** by its upfield-shifted resonance (Ji et al., 2009). The HMBC correlations from H-12 to C-7 and C-13, from H-13

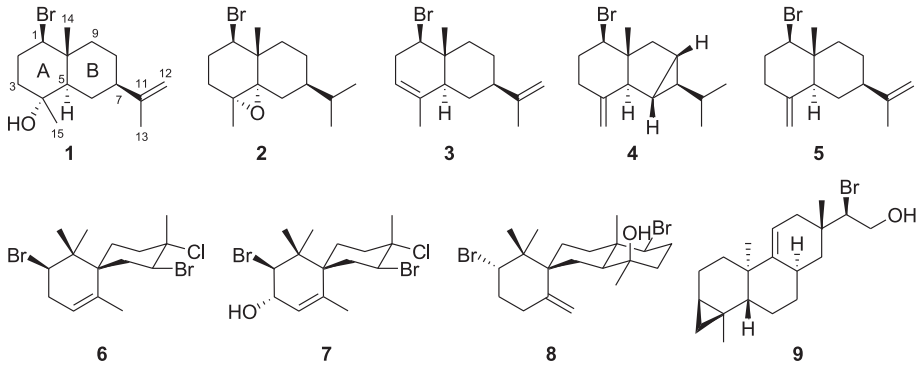


**Fig. 1.** Structures of compounds **1**–**9**.