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Halogenated metabolites from Japanese *Laurencia* spp.

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Abstract

Further investigation of *Laurencia* species from Japanese waters, which were collected at three locations, yielded brominated metabolites, a labdane- type diterpene and a C_{15} acetogenin possessing a terminal bromoallene group. Their structures were deduced from analysis of spectroscopic data.

Keywords: *Laurencia*; Rhodomelaceae; Red alga; C_{15} acetogenin; Diterpene; Sesquiterpene; Halogenated compound; Chemotaxonomy

1. Introduction

In connection with our continuing studies (Vairappan et al., 2001; Masuda et al., 2002; Takahashi et al., 2002; Suzuki et al., 2002a,b) on chemical compositions of the red algal genus *Laurencia* from Japanese waters, we examined undescribed specimens collected from three different locations; Chinzei (Saga Prefecture), Hachijo-jima Island (Tokyo) and Miyake-jima Island (Tokyo). The Chinzei collection contained a new brominated C_{15} acetogenin (**1**), which was designated as chinzallene, and a new brominated diterpene (**2**) along with a known bromoallenic C_{15} acetogenin (**3**) (Suzuki et al., 1989). Diterpene (**2**) was also isolated from the Hachijo-jima collection that contained other new C_{15} acetogenins, whose structural elucidation is in progress. On the other hand, the Miyake-jima collection afforded known sesquiterpenes, 2,10-dibromo-3-chloro-α-chamigrene (**4**) (Howard and Fenical, 1975; Suzuki et al., 1979; Takahashi et al., 1999) and laurinterol (**5**) (Irie et al., 1970; Suzuki and Kurosawa, 1979), and another known bromoallenic C_{15} acetogenin (**6**) (Suzuki and Kurosawa, 1985). In this paper we report the isolation and structures of these halogenated compounds.

2. Results and discussion

Chinzallene (**1**), $[\alpha]_D^{21} + 184^\circ$ ($CHCl_3$), which was the major metabolite of the Chinzei sample, was obtained as colorless oil and analyzed for $C_{15}H_{18}Br_2O_3$ by its HR-EIMS. Its IR spectrum showed a characteristic band for a terminal bromoallene moiety at V_{max} $1960\ cm^{-1}$ and no bands for hydroxyl and carbonyl groups, suggesting that three oxygen atoms of **1** were

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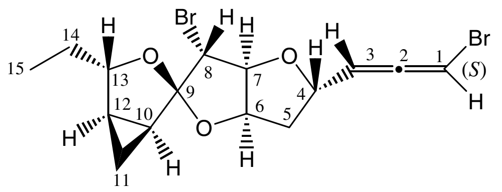
assumed to be involved in ether linkages. The presence of a terminal bromoallene moiety was also proven by typical signals in the ^{1}H and ^{13}C NMR spectra (Table 1) [δ_H 6.06 (1H, *dd*, $J = 5.9$, 1.5 Hz) and 5.37 (1H, *dd*, $J = 5.9$, 5.9 Hz); δ_C 201.9 (C), 101.1 (CH) and 73.6 (CH)]. The quaternary carbon at δ_C 116.5 in the ^{13}C NMR spectrum of **1** suggested the presence of an acetal moiety. Moreover, the NMR spectra indicated the presence of a 1,2-disubstituted cyclopropane ring [δ_H 0.76 (2H, *m*) and δ_C 8.3 (CH$_2$)].

Detailed analysis of the ^{1}H and ^{13}C NMR spectra, as well as HSQC and ^{1}H–^{1}H COSY spectra, showed the presence of partial structural units **1a**–**1d** in the molecule of chinzallene (**1**) (Fig. 1). In the partial structures, the substituents of bromine or oxygen atoms at C4, C6, C7, C8 and C13 were verified based upon the chemical shifts of the pertinent carbons at δ_C 76.5, 82.8, 90.6, 58.1 and 83.8, respectively. Since the C$_{15}$ cyclic ether acetogenins found in *Laurencia* are assumed to be derived from straight-chain C$_{15}$ precursors, laurediols



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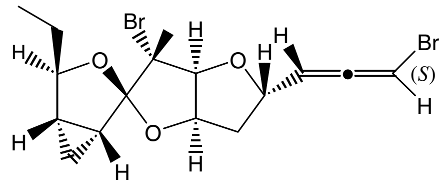

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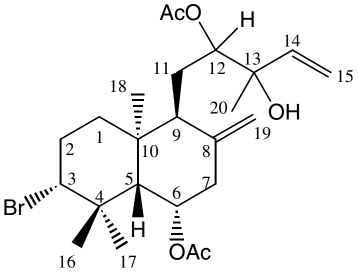

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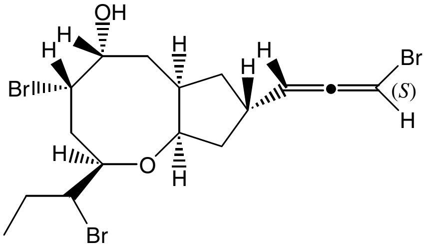

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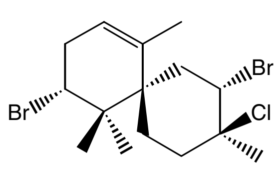

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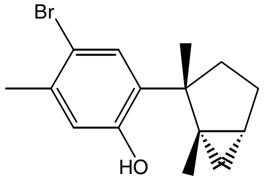

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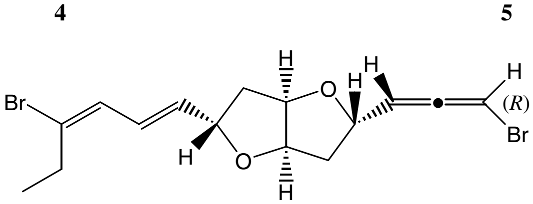

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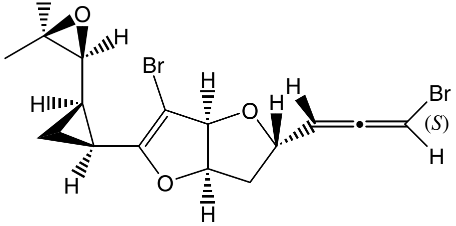

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