

A New Record of the Marine Red Alga *Laurencia snackeyi* from Japan and its Chemotaxonomic Significance

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Abstract: The constitution of *Laurencia snackeyi* (Weber-van Bosse) Masuda (Ryukyu-sozo in Japanese) from three locations, Minna Island, Sesoko Island and Kayo Coast in Okinawa Prefecture, Japan, is reported. This species produced snyderane-type sesquiterpenes, palisadin A (1), palisadin B (2) and aplystatin (3) as characteristic metabolites. The species name of "*Laurencia luzonensis* Masuda", which has previously been reported in several papers, should be revised to *L. snackeyi*.

Keywords: *Laurencia snackeyi*; "*Laurencia luzonensis*"; Rhodomelaceae; chemotaxonomy; snyderane-type sesquiterpene. © 2019 ACG Publications. All rights reserved.

1. Plant Source

Laurencia snackeyi (Weber-van Bosse) Masuda was first described as *L. paniculata* J. Agardh f. *snackeyi* Weber-van Bosse (1923) on the basis of material from Semau Island near Timor, Indonesia. Although it had been recognized as *L. obtusa* (Hudson) Lamouroux var. *snackeyi* (Weber-van Bosse) Yamada (1931) for a long time, it was raised to the rank of species by Masuda [1].

2. Previous Studies

In Japan, *L. snackeyi* has first been found as an unrecorded *Laurencia* species during the field survey of Okinawan marine algae beginning 1991; for example, Bisezaki, Motobu (29th Mar. 1991, leg. M. Masuda and S. Kamura, SAP 094997~095000; 13th May 1991, leg. M. Masuda and S. Kamura, SAP 095001~095002; 27th Mar. 1997, leg. M. Masuda and T. Abe, SAP 095003), Henoko, Nago (16th

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May 1991, *leg.* M. Masuda, SAP 094991~094995; 26th Apr. 1993, *leg.* T. Abe, SAP 095040~095042), Kayo, Nago (25th Apr. 1993, *leg.* T. Abe, SAP 095034~SAP 095039) and Ginoza, Kunigami (8th Feb. 1992, *leg.* M. Masuda and S. Kamura, SAP 094985~SAP 094986). At that time these specimens were considered as a new species and tentatively named "*Laurencia luzonensis*" since the similar species was found in Luzon Island, Philippines. Then these specimens were identified as *L. snackeyi* (Weber-van Bosse) Masuda [1] and consequently the name of "*Laurencia luzonensis*" never saw the light of day. Until now *L. snackeyi* has yet been undescribed from Japanese waters [2]. This species grows on dead coral or limestone in the upper subtidal zone on reef flats and are widely distributed along the Okinawan coasts.

Okinawa is a subtropical island and situated in the southwesternmost side of Japan. The following Okinawan *Laurencia* spp. have been investigated to date; *L. brongniartii* [3,4], *L. intricata* [5], "*L. luzonensis*" [6-9], *L. majuscula* [10,11], *L. mariannensis* [11], *L. nidifica* [11,12], *L. venusta* [13], *L. yonaguniensis* [14-16] and two undescribed *Laurencia* species [17,18].

3. Present Study

We examined the chemical composition of *Laurencia snackeyi* collected from Okinawan waters. The three specimens of *L. snackeyi* were collected at Sesoko Island, Motobu (31st March 2014) (CMNH-BA-7550), Minna Island, Motobu (29th April 2014) (CMNH-BA-7547) and Kayo Coast, Nago (17th May 2014) (CMNH-BA-7548). The voucher specimens have been deposited in the Herbarium of the Coastal Branch of Natural History Museum and Institute, Chiba.

The partially dried alga (133.3 g) collected at Kayo Coast was soaked in MeOH. The MeOH solution was concentrated *in vacuo*, and the residue was partitioned between EtOAc and H₂O. The EtOAc layer was then washed with water, dried over anhydrous Na₂SO₄ and evaporated to leave an oily substance (663 mg). The EtOAc-soluble extract (496 mg) was fractionated by Si-gel column chromatography with a step gradient (*n*-hexane and EtOAc) to give 5 fractions; 1st fr. [hexane–EtOAc (9:1), 254 mg], 2nd fr. [hexane–EtOAc (8:2), 68.0 mg], 3rd fr. [hexane–EtOAc (7:3), 102 mg], 4th fr. [hexane–EtOAc (1:1), 25.1 mg] and 5th fr. (EtOAc, 32.7 mg). A portion (40.0 mg) of the 1st fraction eluted with hexane–EtOAc (9:1) was separated by preparative TLC with toluene to give compounds palisadin A (**1**) (9.5 mg), palisadin B (**2**) (12.8 mg), luzonensol (**5**) (2.8 mg), 3,3-dimethyl-5-methylene-4-(3-methylpenta-2,4-dien-1-yl)cyclohex-1-ene (**6**) (0.8 mg), debromolaurinterol (**7**) (4.2 mg) and (-)- α -bromocuparene (**8**) (1.3 mg). A portion (25.0 mg) of the 2nd fraction eluted with hexane–EtOAc (8:2) was also subjected to preparative TLC with hexane–EtOAc (3:1) to afford aplysiastatin (**3**) (10.9 mg). In addition, a portion (30.3 mg) of the 3rd fraction eluted with hexane–EtOAc (7:3) was submitted to preparative TLC with hexane–EtOAc (2:1) to yield 12-hydroxypalisadin B (**4**) (13.3 mg).

The dried algae from Minna Island and Sesoko Island were treated as described above. The chemical investigation of the sample from Minna Island resulted in the isolation of same metabolites **1-7**. In addition, the sample from Sesoko Island also contained **1, 2, 3** and **5**.

The structures of the isolated compounds (Figure 1) were identified by comparison of their physical and spectral properties with those published; **1, 2** and **4** [19], **3** [20], **5** [7], **6** [21], **7** [22] and **8** [23,24].

4. Chemotaxonomic Significance

The Okinawan *Laurencia snackeyi* produced snyderane-type sesquiterpenes, palisadin A (**1**), palisadin B (**2**) and aplysiastatin (**3**) as characteristic metabolites, which are very similar to the case of the Malaysian *L. snackeyi* [1,25] (Table S1). Kuniyoshi *et al.* reported chemical constituents of "*Laurencia luzonensis* Masuda" collected from the Okinawan coasts, Kudaka Island, Nanjyo [6-8] and Sesoko Island, Motobu [9]. The sample from Sesoko Island also produced palisadin A (**1**), palisadin B (**2**), aplysiastatin (**3**) and luzonensol (**5**) as in the case of our sample (Table S1). As described in Section

2, the species name of "*Laurencia luzonensis* Masuda" is not a validly published name and should be revised to *L. snackeyi*.

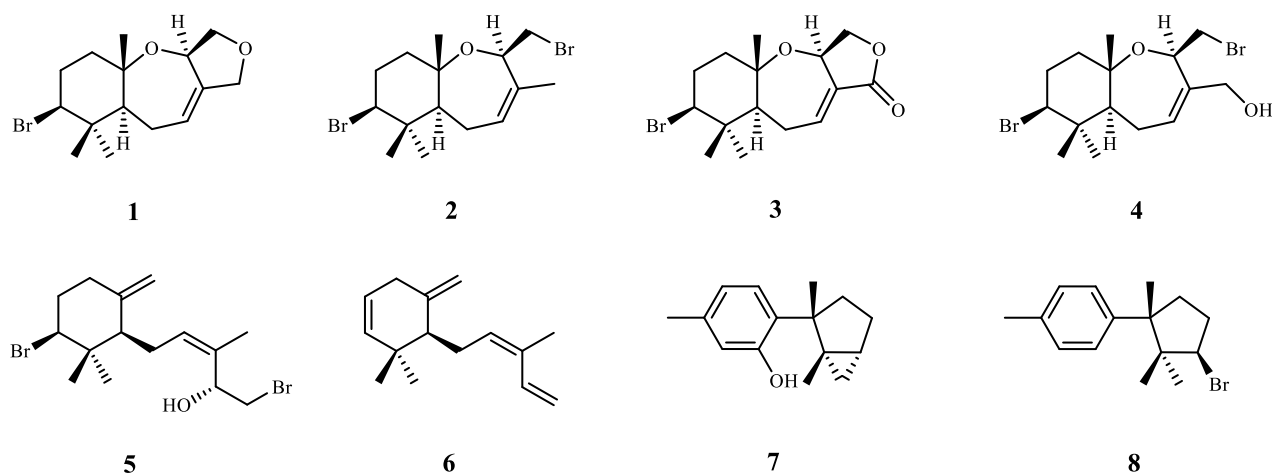


Figure 1. Chemical structures of compounds **1-8** isolated from *L. snackeyi*

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Supporting Information

Supporting Information accompanies this paper on <http://www.acgpubs.org/journal/records-of-natural-products>

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