Short Paper

Isolation of L-Gigartinyl-L-gigartinine from Red Alga *Grateloupia livida*

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In our recent papers, we reported the isolations of two new ureido amino acids,¹⁾ several citrulline peptides,²⁾ and a unique cyclopropyl amino acid named carnosadine³⁾ from red algae *Grateloupia* C. Agardh genus. In the present work, a new basic peptide, L-gigartinyl-L-gigartinine (**1**), was isolated from red alga *Grateloupia livida* in which we had already found one of the new ureido amino acids, lividine (**2**).¹⁾

An aqueous extract of *Grateloupia livida* was subjected to a column chromatography as described in the previous paper¹⁾ and a strongly basic compound **1** was obtained in the same fraction containing lividine. Both compounds were separated by rechromatography on Amberlite IRCG-50 column (NH₄⁺ form). Lividine was first eluted with H₂O. The compound **1** was then eluted with 1 M NH₄OH, and rechromatographed on Amberlite IRCG-120 column (pyridine form). The successive elution with 0.2 M pyridine acetate (pH 4.4, 1.4 l) and 1 M pyridine acetate (pH 5.1, 0.5 l) buffers gave a pure substance **1** (27 mg from 260 g of dried alga), mp 195–197°C; [α]_D²⁰ +14° (c 0.58, H₂O). When the compound **1** was hydrolyzed with 6 M HCl for 24 h at 110°C in a sealed tube, gigartinine, citrulline, and ornithine were obtained in a ratio of 1.00:0.89:0.44. Acid hydrolysis of 2,4-dinitrophenyl (Dnp) derivative of the compound **1** produced both N^α-Dnp-gigartinine and gigartinine.

Based on the above results, the new basic compound

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Fig. 1. ¹H NMR spectra of gigartinine and the compound **1** in D₂O.

1 was assumed to be a peptide composed of gigartinine only. The number of gigartinine residue in the molecule was determined by comparison of ¹H NMR spectrum of the compound **1** with that of gigartinine (Fig. 1). As can be seen from Fig. 1, two α-CH signals were clearly observed in the spectrum of **1**. Thus, the structure of this new peptide was deduced to be gigartinylgigartinine.

The configurations of gigartinine at both N- and C-terminals were defined to be L-form in the following manner. N^α-Dnp-Gigartinine and gigartinine obtained by acid hydrolysis of Dnp derivative of the compound **1** were separated by preparative TLC and the latter was newly 2,4-dinitrophenylated. ORD spectrum of each N^α-Dnp-gigartinine thus obtained showed the same curve as that of authentic N^α-Dnp-L-gigartinine, respectively.

Gigartinine had been found in many species of red algae such as *Gymnogongrus flabelliformis*, *Carpopeltis flabellata*, *Grateloupia livida*, etc.^{4,5)} However, the occurrence of gigartinine dipeptide has not been known so far.

References

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