DISTRIBUTION OF GONGRINE AND GIGARTININE IN MARINE ALGAE

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(Received May 30, 1966)

In the previous publications^{1,2)}, ITO and HASHIMOTO reported on the occurrence of two guanylurea derivatives, named gongrine and gigartinine, in a red alga, *Gymnogongrus flabelliformis*. These substances were isolated and postulated to be γ -(guanylureido) butyric acid and L- α -amino- δ -(guanylureido) valeric acid, respectively.

The distribution of these guanylurea derivatives and free arginine was surveyed by paper chromatography, and the results are presented in this paper.

Experimental

Materials

Specimens were collected at the intertidal region of Hayama and Jōga-Shima, Kanagawa Prefecture in January, March and May 1965. The fresh seaweeds were roughly washed with water and air-dried. The dried materials were then powdered and preserved in a desiccator.

Preparation of the test solution for paper chromatography

Twenty grams of dried algal powder were extracted twice with a 100-ml portion of hot 75% ethanol and the extracts were concentrated in vacuum to 20 ml. After being decolorized with ether, the solution was passed through a column of Dowex 50 X-8 (10×2.0 cm, 50~100 mesh, H⁺). From the column washed with water the adsorbed fraction was eluted with 2N aqueous ammonia, until the ninhydrin test indicated the complete elution. The eluate freed from ammonia was made up to 2 ml with water, and subjected to paper chromatography.

Paper chromatography

By the ascending method, the extracts were run on Toyo-roshi No. 50 (2×40 cm) in a solvent, n-butanol-pyridine-acetic acid-water (4 : 1 : 1 : 2), and developed by the Sakaguchi reagent³⁾ consisting of 0.1% α -naphthol in N NaOH and 5% sodium hypochlorite solution. The R_f values for arginine, gongrine and gigartinine were 0.24, 0.70 and 0.32, respectively. Gongrine and gigartinine gave a specific orange color, clearly differing from the pink one given by arginine, and this facilitated characterization of these compounds.

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Results and Discussion

As summarized in Table 1, twenty-five species of algae were investigated. In green and brown algae any appreciable quantity of both gongrine and gigartinine is not detected, except one species of brown alga, *Colpomenia sinuosa*, which shows a doubtful spot of gigartinine. In red algae, gigartinine is widely distributed, whereas gongrine is limited to a few species. The former is found in a fairly high concentration in the following seven species, *Gelidium amansii*, *Grateloupia livida*, *Polyopes polyideoides*, *Carpopeltis flabellata*, *Hypnea japonica*, *Gracilaria textorii* and *Gymnogongrus flabelliformis*. The latter, on the other hand, is detected in *Grateloupia livida* collected in May, *Carpopeltis flabellata* in March and *Gracilaria textorii* in a

Table 1. Distribution in marine algae of the substances positive for Sakaguchi's reagent.

	Date of collection	Arginine	Gigartinine	Gongrine	R_f of unknown substances
Green algae:					
<i>Monostroma</i> sp.	Mar.	—	—	—	
<i>Enteromorpha prolifera</i>	Mar.	—	—	—	
<i>Codium adhaerens</i>	Mar.	+	—	—	
Brown algae:					
<i>Padina arborescens</i>	Mar.	—	—	—	
<i>Ishige okamurai</i>	Jan.	+	—	—	
<i>Colpomenia sinuosa</i>	Mar.	+	±	—	
<i>Hizikia fusiforme</i>	Jan.	++	—	—	
<i>Sargassum horneri</i>	Jan.	+	—	—	
<i>Sargassum ringgoldianum</i>	Jan.	++	—	—	
<i>Sargassum thunbergii</i>	Mar.	+	—	—	
Red algae:					
<i>Gelidium amansii</i>	Jan.	+	++	—	
<i>Grateloupia elliptica</i>	May	+	—	—	0.19
<i>Grateloupia livida</i>	Jan.	+	++	—	0.58
	May	+	++	+	
<i>Polyopes polyideoides</i>	Jan.	+	+++	—	
<i>Carpopeltis affinis</i>	Jan.	±	±	—	
<i>Carpopeltis flabellata</i>	Mar.	—	++	+	0.41
	May	±	±	—	
<i>Hypnea japonica</i>	Jan.	+	++	—	
<i>Gracilaria gigas</i>	Mar.	+	—	—	
<i>Gracilaria incurvata</i>	Mar.	—	—	—	
<i>Gracilaria textorii</i>	Jan.	+	+++	+	0.47
<i>Gymnogongrus flabelliformis</i>	May	+	++	+++	0.53
<i>Ahnfeltia concinna</i>	Jan.	—	—	—	
<i>Gigartina tenella</i>	Mar.	+	—	—	
<i>Chondrus ocellatus</i>	Mar.	—	—	—	
<i>Laurencia</i> sp.	Mar.	±	—	—	

small quantity respectively, and in *G. flabelliformis* at an exceptionally high level.

As for free arginine, the widespread distribution in marine algae have been recorded by many workers⁴⁻⁷⁾ and this fact is also recognized in the present work. Gigartinine, if present, seems to overwhelm arginine in quantity, from the observation that on paper chromatograms gigartinine appears much more distinctly than arginine, although the former is far less sensitive to Sakaguchi's reagent. The quantitative relation between these guanidino compounds will be discussed in detail in the next paper.

In this investigation, the existence of unidentified substances positive for Sakaguchi's reagent was detected in a few species of red algae. A substance of R_f 0.53, found in *G. flabelliformis*, has been recently isolated and identified as γ -guanidinobutyric acid, as will be reported in the near future.

Summary

By means of paper chromatography, the distribution of gongrine, gigartinine and arginine in the extractives of marine algae was investigated. In twenty-five species of marine algae examined, gongrine and gigartinine were found in four species and seven species of red algae, respectively. These guanylurea derivatives were not detected in green and brown algae except one species of brown alga which gave a doubtful spot of gigartinine.

Thanks are due to Mr. K. FUJIMOTO for his technical assistance.

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