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Amino Acid Compositions and Peptides in the Extracts of Some Corallinaceae Algae

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(Fig.1−3; Table 1−6)

Corallinaceae red algae, calcareous seaweeds, were reported by HAAS and HILL$^{1)}$ to contain relatively large amounts of peptides. They reported the occurrence of penta peptide of aspartic acid in the extractives of *Corallina officinalis*. Its minute structure, properties or metabolic roles in the alga however remained unexplored.

In the previous paper$^{2)}$, dealing with the amino acid compositions of 31 species of marine red algal extracts, we reported to have found a remarkable increase of some amino acids after hydrolysis in a specimen of *C. officinalis*, especially glutamic acid and aspartic acid. This phenomenon can not be explained by the hydrolysis of glutamine and asparagine only but rather points towards the possible presence of some peptides constituted from the increased moieties of glutamic acid, aspartic acid and some other amino acids.

To elucidate this phenomenon, we undertook a general survey of amino acid patterns in Corallinaceae algal extracts before and after acid hydrolysis. The present paper deals with amino acid compositions of 17 specimens of Corallinaceae algae and preliminarily with some properties of peptidyl fraction of *C. officinalis*.

EXPERIMENTALS AND RESULTS

Materials. The algal specimens used in this experiment are shown in Table 1. They were collected between 1978 and 1981 at the intertidal regions of Ibusuki, Kagoshima Prefecture; Kada, Wakayama City; Satamisaki and Hojo, Ehime Prefecture; Sanriku, Iwate Prefecture; Tomo and Onomichi, Hiroshima Prefecture. The materials from Kada, Hojo and Hiroshima were brought to our laboratory in the fresh state and put into ethanol as soon as possible after collection. Those from Kagoshima and Iwate were frozen in dry-ice, carried to the laboratory and treated with ethanol. The specimens from Satamisaki were briefly air-dried on the spot and treated in the same manner as above.

The amino acid composition of algal extracts. The fresh and frozen materials were kept in 3 volumes of ethanol for 1 week at room temperature on occasional stirring, respectively. The air-dried samples were extracted with 5 volumes of 80% aqueous ethanol at room temperature for 2 weeks. The obtained ethanolic extractives were concentrated under reduced pressure in order to remove ethanol and then defatted with diethylether. After removal of diethylether by evaporation, the resulting cleared solutions were made up to determined volumes and stored in a freezer until use, respectively. These solutions were used for the estimation of amino acids by using a Hitachi liquid chromatography 034 model and an amino acid analyzer 835 model, respectively.

An aliqout of each solution was hydrolyzed with 6 N hydrochloric acid in a sealed tube at 110°C for 20 hrs. After removal of the excess hydrochloric acid by evaporation, the residue was dissolved in appropriate buffer solutions and applied to amino acid analysis. These amino acid compositions are shown in Table 2, in which the concentration of each constituent is expressed as μmoles in 100 g of fresh or air-dried fronds according to the state of the sample materials, respectively. The figures shown in the parentheses are the increase of each amino acid after acid hydrolysis. The values expressed for taurine were calculated from the sum of the peaks appearing close to taurine as its equivalent.

Table 1. Specimens used as materials

No.	Scientific name	Locality	Date
1	*Amphiroa misakiensis*	Hojo, Ehime	May, 1979
2	*Amphiroa ephedraea*	Kada, Wakayama	June, 1980
3	"	Kada, Wakayama	June, 1981
4	*Amphiroa* sp.	Kada, Wakayama	June, 1981
5	*Corallina officinalis*	Ibusuki, Kagoshima	Mar., 1978
6	"	Sanriku, Iwate	June, 1979
7	"	Ibusuki, Kagoshima	Mar., 1981
8	*Corallina pilulifera*	Ibusuki, Kagoshima	May, 1979
9	"	Satamisaki, Ehime	May, 1979
10	"	Hojo, Ehime	May, 1980
11	"	Ibusuki, Kagoshima	Mar., 1981
12	"	Ibusuki, Kagoshima	May, 1981
13	*Corallina* sp.	Tomo, Hiroshima	Dec., 1980
14	*Colallina* sp.	Onomichi, Hiroshima	Feb., 1981
15	*Corallina* sp.	Kada, Wakayama	June, 1981
16	*Jania arborescens*	Kada, Wakayama	June, 1980
17	*Jania decussato-dichotoma*	Satamisaki, Ehime	May, 1980

In the amino acid compositions before hydrolysis, alanine, glycine and taurine were relatively predominant in general, except in some specimens such as *C. pilulifera* (No. 8), where asparagine and glutamine were dominant. After hydrolysis, almost all kinds of amino acids present were found to increase considerably, especially aspartic acid and glutamic acid. Threonine, serine, proline, glycine, alanine, valine, isoleucine, leucine, lysine and arginine also increased in a considerable extent in these specimens. The total increase of amino acids after hydrolysis varied from 50 to 300 mol% in the present samples. As seen in some specimens such as *Amphiroa misakiensis, C. officinalis* and *C.*

Table 2. Amino acid composition of Corallinaceae red algae (μmoles/100 g).

	1 *Amphiroa misakiensis*	2 *Amphiroa ephedraea*	3 *Amphiroa ephedraea*	4 *Amphiroa* sp.	5 *Corallina officinalis*	6 *Corallina officinalis*	7 *Corallina officinalis*	8 *Corallina pilulifera*	9* *Corallina pilulifera*
Taurine	188 (10)	91	43 (23)	111 (4)	47	99	44	92 (26)	168 (63)
Aspartic acid	tr (120)	8 (167)	12 (26)	4 (31)	11 (473)	32 (119)	tr (53)	119 (893)	tr (158)
Threonine	52 (52)	- (24)	34	33 (4)	24 (67)	26	tr	68 (64)	101 (199)
Serine	22 (60)	5 (16)	5	10 (28)	29 (93)	23	tr (12)	103 (130)	39 (128)
Asparagine	tr	tr			tr			502	
Glutamine	tr	tr			tr			193	
Glutamic acid	42 (292)	60 (823)	19 (214)	32 (170)	36 (287)	37 (96)	14 (117)	135 (531)	91 (486)
Proline	47 (105)	50 (11)	13	16 (11)	tr (108)	69 (15)	tr (43)	28 (165)	127 (25)
Glycine	116 (181)	41 (91)	10 (65)	48 (69)	35 (187)	41 (96)	24 (38)	70 (328)	235 (253)
Alanine	202 (56)	344 (66)	86 (34)	143 (15)	205 (112)	109 (20)	59 (1)	220 (148)	209 (221)
Valine	181 (59)	58 (5)	43 (32)	74 (26)	67 (54)	24 (23)	29	91 (105)	283 (129)
Isoleucine	75 (42)	34 (5)	28 (19)	45 (9)	38 (61)	15 (20)	12 (4)	53 (84)	107 (100)
Leucine	19 (56)	19 (7)	tr (34)	27 (9)	33 (70)	20 (18)	tr (12)	68 (98)	- (176)
Tyrocine	tr (9)	11	tr	tr	tr (10)	tr (9)	-	tr (18)	tr
Phenylalanine	tr (21)	14	20 (9)	31 (2)	17 (18)	34 (8)	-	38 (35)	tr
Lysine	- (47)	tr(46)	7 (13)	5 (12)	7 (63)	17 (16)	- (19)	41 (83)	- (193)
Histidine	-	-	-	-	-	-	-	-	-
Arginine	- (18)	3 (10)	9 (7)	tr (15)	- (45)	11 (14)	tr (19)	31 (40)	- (49)
Baikiain	+	+	+	+	+	+	+	+	+
Ammonia	197 (382)	264 (273)	338 (782)	865 (442)	23 (336)	107 (113)	92 (320)	261 (561)	276 (607)
Total of estimated amino acids	944 (1128)	738 (1271)	329 (481)	579 (385)	549 (1648)	557 (454)	182 (318)	1852 (2748)	1360(2080)

*, Air-dried. tr, trace. +, detected. -, not detected.

Continued

	10 *Corallina pilulifera*	11 *Corallina pilulifera*	12 *Corallina pilulifera*	13 *Corallina* sp.	14 *Corallina* sp.	15 *Corallina* sp.	16 *Jania arborescens*	17* *Jania decussato-dichotoma*
Taurine	162	34 (8)	36	110	113	252	115	420 (5)
Aspartic acid	34 (365)	6 (249)	34 (243)	30 (279)	11	65 (203)	tr (18)	9 (39)
Threonine	tr (48)	39 (21)	19 (33)	tr (12)	52	32 (22)	- (tr)	16 (17)
Serine	tr (13)	18 (74)	10 (60)	tr (41)	12	41 (93)	tr (15)	7 (29)
Asparagine	-	-			-	68	-	-
Glutamine	108	-		264	-	69	-	-
Glutamic acid	58 (317)	55 (274)	41 (130)	33 (342)	27 (5)	74 (345)	19 (129)	12 (51)
Proline	88 (24)	94 (301)	35 (36)	1 (29)	tr (35)	tr	tr (37)	25 (45)
Glycine	72 (143)	16 (156)	25 (92)	45 (53)	29 (1)	42 (99)	52 (49)	92 (111)
Alanine	104 (44)	18 (112)	34 (63)	35 (53)	63	244 (13)	159	5 (24)
Valine	33 (40)	50 (107)	25 (29)	19	33	75 (21)	45 (1)	13 (18)
Isoleucine	12 (30)	23 (40)	10 (26)	10 (2)	19	44 (19)	25 (3)	- (16)
Leucine	8 (39)	9 (45)	tr (45)	6 (4)	9	41 (29)	21 (6)	- (17)
Tyrocine	tr	-	tr	tr	-	tr	8	-
Phenylalanine	tr (20)	-	tr	7	13	tr	14	-
Lysine	-	6 (38)	tr (39)	18 (22)	- (20)	29 (27)	- (8)	- (16)
Histidine	tr (20)	-	-	-	-	-	-	-
Arginine	8 (38)	tr (36)	tr (11)	29 (40)	- (8)	46 (39)	- (tr)	- (12)
Baikiain	+	+	+	+	+	+		
Ammonia	229 (220)	283 (607)	153 (446)	42 (40)	35 (+)	467 (653)	54 (48)	579 (111)
Total of estimated amino acids	687 (1338)	368 (1461)	269 (816)	607 (824)	381 (78)	1122 (910)	458 (266)	599 (400)

pilulifera, the increase of aspartic acid and glutamic acid much surpassed the initial contents of asparagine and glutamine. This may suggest the presence of a relatively large amount of peptides containing glutamyl and aspartyl moieties in these algal extracts. In several specimens such as *C. pilulifera* (No. 5 and No. 6), taurine also increased considerably. This may indicate the presence of a substance which contains hydrolyzable taurine moiety.

In the amino acid analysis, a characteristic unidentified peak appeared partly overlapping the alanine peak. Its absorption at 440 nm was higher than that at 570 nm. This compound showed itself as being L-baikiain as described below. It was widely detected in the present Corallinaceae algal specimens, however its concentrations could not be evaluated definitely for reason of its duplicated elution position with alanine.

As for the protein amino acids, cystine and methionine were not found in these specimens, and histidine was detected in only one specimen of *C. pilulifera* (No. 10) after hydrolysis. Citrulline, gigartinine, methionine sulfoxide and citrullinylarginine, which were reported to show a relatively wide distribution in some red algae belonging to Gracilariaceae, Grateloupiaceae and Phyllophoraceae2), were not detected in these Corallinaceae specimens.

Separation procedure. To separate the constituents of the extracts, a sample of *C. officinalis* was treated as follows. Five hundred and seventy grams of fresh specimens collected at Kagoshima in May were used as material and their ethanolic extractives were prepared in the same manner as described above. The obtained clear solution was applied onto a column of Dowex 50X-8 (H^+ form) and separated into the adsorbed and passed parts. Passed fraction was next treated with Dowex 1X-8 (OH^- form) column. After rinsing the column with water, the adsorbed substances were eluted out with 4% acetic acid. Effluents positive to ninhydrin reaction were collected and concentrated to remove acetic acid.

Substances adsorbed by the Dowex 50X-8 column were eluted out with 2 N aqueous ammonia, and the ninhydrin positive fractions were collected. After removal of ammonia by evaporation, the residue was dissolved in water. The solution was applied onto a column of Dowex 1X-8 (acetate form) and its constituents were separated into the adsorbed acidic amino acids and the passed neutral and basic amino acids fractions. Adsorbed compounds were eluted out from the column with 0.5 M, 1 M and 2 M acetic acid in this order. Each 10 ml fraction was collected and checked by paper chromatography. The fraction passed through Dowex 1 (acetate form) column was also examined by paper chromatography.

Identification of L-baikiain. When the constituents of neutral and basic amino acids fractions were checked by paper chromatography, a distinct yellow spot differing from those of proline and hydroxyproline appeared with ninhydrin reaction. The Rf values in paper chromatography using mixtures of 1-butanol, acetic acid and water (4:1:2) and collidine, lutidine and water (2:2:1) as developping solvents were 0.42 and 0.90, respectively. This compound was isolated by preparative paper chromatography using the solvent system of 1-butanol, acetic acid and water and Toyoroshi No. 50 filter paper and recrystallized from aqueous ethanol. Yield 77 mg. Mp. 269°C (Lit.3) L-baikiain 274°C). This compound gave a yellow color with ninhydrin-isatin reagent, obviously different from the blue color of proline. After reduction with hydrogen gas on Pd-black in 3% acetic acid for 20 min., its color with ninhydrin changed from yellow into blue, showing that it afforded pipecolic acid. These properties indicated that this compound was baikiain[3]. The isolated specimen was identical with the authentic L-baikiain in paper chromatography and in the IR spectrum as shown in Fig. 1. L-Baikiain was confirmed to be eluted overlapping with alanine in the amino acid analysis. This imino acid was detected in 15 specimens of the 17 examined by an amino acid analyzer and/or thin layer chromatography.

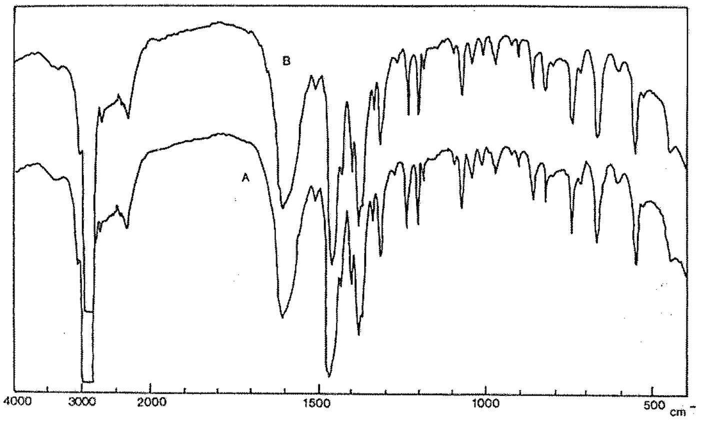

Fig. 1. IR spectra of isolated (A) and authentic (B) L-baikiain (Nujol).

Constituents of acidic amino acid fraction. In the elution of the acidic amino acid fraction of *C. officinalis* extracts on Dowex 1 (acetate form) column, glutamic acid appeared in the initial 0.5 M acetic acid eluted portion. And subsequently 3 ninhydrin positive spots appeared in overlapping, of which Rf values in paper chromatography using 1-butanol, acetic acid and water as solvent were 0.14, 0.45 and 0.57, abbreviated as A-1, A-2 and A-3 respectively. They were followed by aspartic acid as shown in Fig. 2.

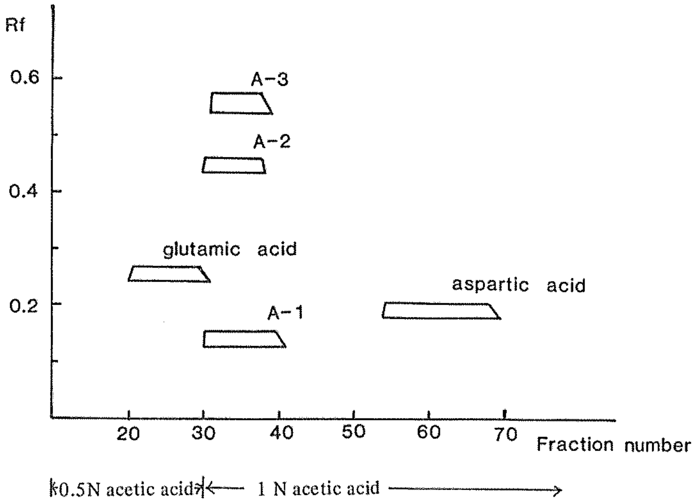

Fig. 2. Elution pattern of acidic amino acids and peptides on Dowex 1X-8 (acetate form) column. Examined by paper chromatography using a solvent system of 1-butanol, acetic acid and water (4:1:2) and ninhydrin reagent.

These unidentified substances (A-1, A-2 and A-3) were separated by preparative paper chromatography and their amino acid compositions and color yields with ninhydrin reaction after hydrolysis were examined. As shown in Table 3, it was suggested that A-1 substance mainly consisted of peptide containing glutamic acid and aspartic acid moieties in molar ratio of 5:1, A-2 of a dipeptide containing equimolar aspartic acid and valine, A-3 of a mixture of two dipeptides, one containing aspartic acid and isoleucine, the other aspartic acid and leucine, respectively.

Table 3. The molar ratio of amino acids in the hydrolysis products of A–1, A–2, and A–3 substance.

	A – 1 (Rf 0.14)	A – 2 (Rf 0.45)	A – 3 (Rf 0.57)
Aspartic acid	5.24	1.15	1.00
Threonine	tr	tr	-
Serine	0.16	tr	-
Glutamic acid	1.00	0.18	-
Glycine	tr	0.25	-
Alanine	tr	tr	-
Valine	-	1.00	-
Isoleucine	-	tr	0.53
Leucine	-	tr	0.46
Increase of ninhydrin color yield after hydrolysis	3.2	2.8	2.1

Occurrence of α-aspartylisoleucine and α-aspartylleucine. To isolate the above mentioned acidic peptides, another 3 kg of *C. officinalis* specimens collected at Ibusuki were treated in the same manner. As the A-3 substance was relatively abundant and the other two only existed in a very limitted quantity in this specimen, separation of former substance was tried out. After separation and purification by ion-exchange and paper chromatography, A-3 substance was obtained from aqueous ethanol as a white crystalline powder. Yield 75 mg. *Anal.* Found : C, 47.9; H, 7.3; N, 10.9%. Calcd. for $C_{10}H_{18}N_2O_5$: C, 48.8; H, 7.3; N, 11.4%. This specimen showed only one spot on paper and thin layer chromatography using mixtures of 1-butanol, acetic acid and water (4:1:2) and phenol and water (4:1) as developping solvents and showed also one spot on paper electrophoresis at pH of 3.45 and 6.6. It appeared as a single peak close to that of methionine in the amino acid analysis. However in the thin layer chromatography using a solvent system of *tert.*-amyl alcohol, acetic acid and water (15:1:15) and precoated Merck cellulose plate, it revealed very contiguously 2 spots at Rf values of 0.46 and 0.49. After acid hydrolysis, it furnished aspartic acid, isoleucine and leucine in a molar ratio of 1:0.5:0.5. Its DNP-derivative was prepared by the method of SANGER[4]. Hydrolysis products of the DNP-derivative in 6 N HCl at 105°C for 18 hrs were identified as DNP-aspartic acid, isoleucine and leucine by thin layer chromatography, of which Rf values are shown in Table 4.

Table 4. Rf values of DNP-peptide and its hydrolysis products in thin layer chromatography.

	A	B	C	D	E
DNP-peptide	0.21	0.12	-	-	-
Hydrolysate-I	0.10	0.08	-	-	-
DNP-aspartic acid	0.10	0.08	-	-	-
DNP-isoleucine	0.83	0.87	-	-	-
DNP-leucine	0.84	0.87	-	-	-
Hydrolysate-II	-	-	0.75	0.62	0.38, 0.42
Aspartic acid	-	-	0.35	0.20	0.11
Isoleucine	-	-	0.75	0.62	0.38
Leucine	-	-	0.76	0.62	0.42

A, chloroform-benzyl alcohol-acetic acid (70:30:3)
B, benzene-pyridine-acetic acid (80:20:2)
C, 1-butanol-acetic acid-water (4:1:2)
D, phenol-water (4:1).
E, *tert.*-amyl alcohol-acetic acid-water (15:1:15).

Hydrolysate-I DNP-fraction. Hydrolysate II amino acid fraction.

For comparison, α-aspartylisoleucine and β-aspartylisoleucine were synthesized according to the methods of IZUMIYA *et al.*[5] and SCHRÖDER *et al.*[6] as follows. α-Aspartylisoleucine : Carbobenzoxy-β-benzylaspartic acid prepared from aspartic acid, was coupled with isoleucine benzyl ester p-toluene sulfonate by DCC method[7]. The obtained peptide derivative was catalytically reduced with hydrogen gas on Pd-black. From aqueous ethanol, a white powder was obtained. β-Aspartylisoleucine : Carbobenzoxy aspartic acid α-p-nitrobenzyl ester DCHA salt prepared from carbobenzoxy aspartic acid, and isoleucine benzyl ester p-toluene sulfonate were coupled by the DCC method. The resulting peptide derivative was treated in the same manner as described above.

As shown in Table 5, Rf values and elution time in the amino acid analyzer of algal specimen and synthesized α-aspartylisoleucine showed satisfying agreements. IR spectra

Table 5. This layer chromatography and elution time on an amino acid analyzer of *C. officinalis* peptide, α-aspartylisoleucine and β-aspartylisoleucine.

	Rf values in TLC			Colors with ninhydrin	Elution time on an analyzer(min)
	A	B	C		
C. officinalis peptide	0.72	0.61	0.46, 0.49	purple	125
α-Aspartylisoleucine	0.72	0.61	0.46	purple	125
β-Aspartylisoleucine	0.66	0.61	0.42	grayish blue	70
Aspartic acid	0.38	0.20	0.11	purple	45
Isoleucine	0.75	0.62	0.38	purple	130
Leucine	0.76	0.62	0.42	purple	135

A, 1-butanol-acetic acid-water (4:1:2). B, phenol-water (4:1). C, *tert.*-amylalcohol-acetic acid-water (15:1:15) of algal and synthesized specimens were essentially in coincidence as shown in Fig. 3. The slight difference noticed may be due to the fact that the algal specimen is a mixture of two compounds with very similar structures. On the other hand, β-aspartylisoleucine revealed clearly different properties from algal peptides as shown. These results indicate that the obtained peptide specimen is a mixture of almost a same amount of α-aspartylisoleucine and α-aspartylleucine.

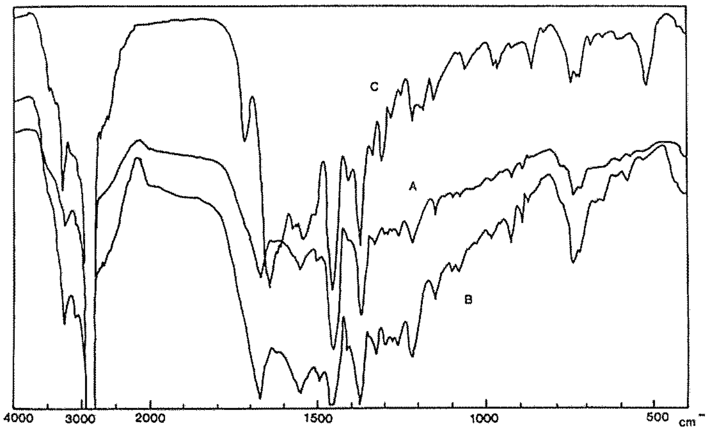

Fig. 3. IR spectra of *Corallina officinalis* peptide (A), synthesized α-aspartylisoleucine (B) and β-aspartylisoleucine (C) (Nujol).

Strongly acidic fraction. A strongly acidic portion of *C. officinalis* extracts, which passed through a column of Dowex 50 (H^+ form) and adsorbed to Dowex 1 (OH^- form), was separated by addition of methanol into precipitated and soluble fractions. Both fractions were dialyzable through a cellophane film. The methanolic soluble portion was constituted from 10 kinds of amino acids, in which aspartic acid and glutamic acid were predominant, as shown in Table 6. The precipitated portion contained aspartic acid and

Table 6. Composition of amino acids in the hydrolysate of strongly acidic, methanol soluble fraction (μmoles/1 mg N).

Amino acid	μmoles	Amino acid	μmoles
Aspartic acid	12.4	Methionine	tr
Threonine	1.5	Isoleucine	1.0
Serine	2.3	Leucine	1.0
Glutamic acid	7.0	Tyrosine	tr
Proline	1.4	Phenylalanine	tr
Glycine	2.4	Lysine	tr
Alanine	2.4	Arginine	tr
Valine	1.7	Ammonia	7.9

glutamic acid in a molar ratio of 9:1, and showed a ten folds increase of ninhydrin color yield after hydrolysis. These results seem to suggest that the methanolic soluble portion may contain a mixture of low molecular weight peptides and that the precipitated portion may be constituted by a deca peptide containing 9 aspartic acid and 1 glutamic acid moieties.

DISCUSSION

Amino acid patterns before and after hydrolysis in several species of Corallinaceae algal extracts were examined. Before the acid hydrolysis, alanine, glycine and taurine were predominant in general. Occurrence of L-baikiain in *C. officinalis* was confirmed and its wide distribution in the present specimens was observed. This imino acid was first isolated from the extracts of Rhodesian teak, *Baikiaia plurijuga* by KING *et al.*³⁾. Later, it was found in a legume, *Caesalpinia tinctoria* by WATSON and FOWDEN⁸⁾, and in marine red algae, such as Corallinaceae, Gracilariaceae species⁹⁾. This compound was reported to be detected usually in low concentration in a number of red seaweeds¹⁰⁾. Recently its wide distribution in Corallinaceae algae has been reported by MAEDA *et al.*¹¹⁾. The present results coincided with these reported issues.

A characteristic feature of amino acid patterns of these calcareous algal extracts was the remarkable increase of almost all kinds of amino acids present after hydrolysis. Furthermore augumentation of glutamic acid and aspartic acid was especially predominant. In total, these algal extracts showed increases of 50 to 300 mol % of amino acids after hydrolysis. This may indicate that a fairly large amount of peptides containing principally aspartic acid and glutamic acid and some other moieties, are present in these specimens. The compositions of these peptides seemed very complexed judging from the variety of the increased amino acids.

In the examination of peptidyl compounds in *C. officinalis*, some peptides mainly constituted from aspartic acid, glutamic acid and some other moieties were found to exist in their acidic fractions. Among them, the occurrence of α-aspartylisoleucine and α-aspartylleucine was confirmed, although these two compounds could not be isolated from each other. Yet these two compounds explained only in a small part the increase of amino acids after hydrolysis. Since penta peptide of aspartic acid had been separated from *C. officinalis* by HAAS and HILL¹⁾, five other peptides have been thus far isolated and characterized from algal extracts; eisenine from *Eisenia bicyclis* by OHIRA¹²⁾, fastigiatine from *Pelvetia fastigiata* by DECKKER *et al.*¹³⁾, L-arginyl-L-glutamine from *Cladophora* sp. by MAKISUMI¹⁴⁾, L-citrullinyl-L-arginine from *Grateloupia turuturu* by the present authors ¹⁵⁾ and β-aspartylglycine from *Ceramium rubrum* by SCUITO *et al.*¹⁶⁾. In addition, analipine from *Analipus japonicus* was obtained by TAKAGI et al.¹⁷⁾, although its structure and properties remain unspecified. From the present results, we may assume that a considerably large amount of peptides with a variety of amino acids moieties and molecular weights may usually exist in Corallinaceae algal extracts. Their physiological significance or situation in nitrogen pool may be an interesting problem.

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SUMMARY

Amino acid patterns before and after hydrolysis in several species of Corallinaceae algal extracts were examined by means of amino acid analyzers. Before hydrolysis, alanine, glycine and taurine were predominant in general. Occurrence of L-baikiain was also confirmed and its wide distribution in Corallinaceae algae was observed. These calcareous algal extracts showed a remarkable increase of amino acids after hydrolysis, especially aspartic acid and glutamic acid, suggesting the presence of a fairly large amount of peptides. In the examination of peptidyl compounds in *C. officinalis*, some acidic peptides mainly consisting of aspartic acid and glutamic acid were found to exist. Among them, occurrence of α-aspartylisoleucine and α-aspartylleucine was confirmed.

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数種サンゴモ科海藻エキスのアミノ酸組成とペプチッド

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6種17検体のサンゴモ科海藻エキスの加水分解前後のアミノ酸組成を調べた。その結果，加水分解前には一般にalanine, glycineおよびtaurineの含量が比較的高かった。またL-baikiainをサンゴモ（*Corallina officinalis*）より分離同定し，これがサンゴモ科の海藻に広く分布することを認めた。

加水分解後には全ての試料においてaspartic acidとglutamic acidを中心として著量のアミノ酸の増加が認められ，これら海藻エキス中にかなり多量のペプチッドの存在することが推定された。

サンゴモのエキスのペプチッド成分を検索した結果，酸性および強酸性区分中にaspartic acidとglutamic acidを主要な構成成分とするかなり多数のペプチッドの存在が認められた。これらのうちα–aspartylisoleucineとα–aspartylleucineの存在を確認した。